Nutrient Cycling

9

Nutrient cycling involves nutrient inputs to and outputs from ecosystems and the internal transfers of nutrients within ecosystems. This chapter describes these nutrient dynamics.

Introduction

Human impacts on nutrient cycles have fundamentally altered the regulation of ecosystem processes. Rates of cycling of carbon (see Chaps. 5– 7) and water (see Chap. 4) are ultimately regulated by energy and the availability of a few chemical resources, so changes in availability of these resources fundamentally alter all ecosystem processes. The combustion of fossil fuels has released large quantities of nitrogen and sulfur oxides to the atmosphere and increased their inputs to ecosystems (see Chap. 14). Fertilizer use and the cultivation of nitrogen-fixing crops have further increased the fluxes of nitrogen in agricultural and downstream aquatic ecosystems (Galloway et al. 1995; Vitousek et al. 1997a; Gruber and Galloway 2008). Together these human impacts have doubled the natural background rate of nitrogen inputs to the biosphere and quadrupled the rate of phosphorus inputs (Falkowski et al. 2000). The resulting increases in plant production may be large enough to affect the global carbon cycle. Human disturbances such as forest conversion, harvest, and fire increase the proportion of the nutrient pool that is available and therefore vulnerable to loss. Some of these losses occur by leaching of dissolved elements to groundwater, causing a depletion of soil cations, an increase in soil acidity, and increases in nutrient inputs to aquatic ecosystems. Gaseous losses of nitrogen influence the chemical and radiative properties of the atmosphere, causing air pollution and enhancing the greenhouse effect (see Chap. 2). Changes in the cycling of nutrients therefore dramatically affect the interactions among ecosystems (see Chap. 13) as well as the carbon cycle and climate of Earth.

A Focal Point

Nutrient runoff from freshwater systems to the ocean has created or intensified dead zones in two-thirds of the world's estuaries. Agriculturally derived nutrients delivered to estuaries and coastal zones stimulate production and rain of dead organic matter to depth. This depletes oxygen, leading to extensive death of fish, shrimp, and other invertebrates (Fig. 9.1). How can these effects be reduced by more careful management of nutrient sources in agricultural lands and cities? How can fertilizer applications be matched with crop nutrient demands to reduce fertilizer requirements and reduce offsite impacts of pollution? What is the fate of excess nutrients delivered to the coastal zone? Understanding controls on nutrient fluxes in ecosystems provides insights that can help answer these important management questions.

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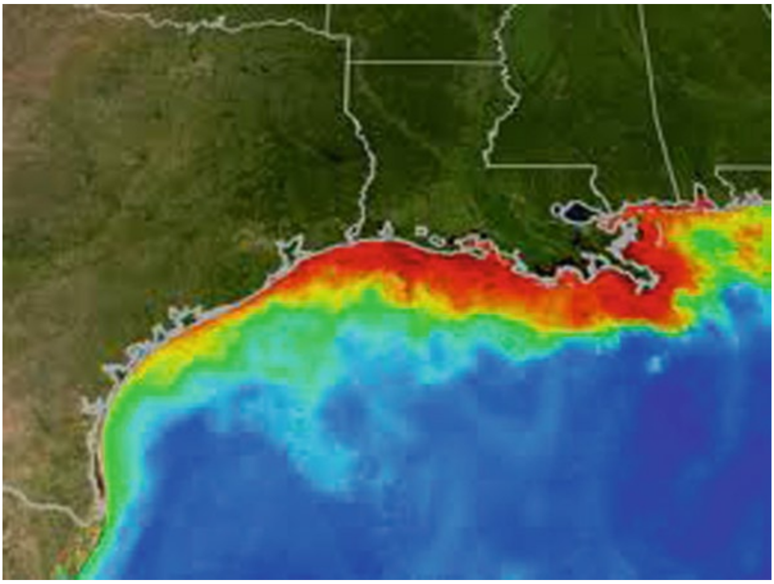


Fig. 9.1 Dead zone in the Gulf of Mexico, magnified by nutrient inputs from agricultural runoff from the Mississippi river drainage. Reds and oranges represent high concentrations of phytoplankton and sediments (http://www.nasa.gov/vision/earth/environment/dead_zone.html)

Overview of Nutrient Cycling

Nutrient cycling involves the entry of nutrients to ecosystems, their internal transfers among plants, microbes, consumers, and the environment, and their loss from ecosystems. Some elements, for example, nitrogen, may move either by water or air, while others, for example, phosphorus, lack a significant gaseous phase and generally move only downhill in aqueous solution or as dust particles in the atmosphere. Nutrients become available to ecosystems through lateral transport, the chemical weathering of rocks, the biological fixation of atmospheric nitrogen, and the deposition of nutrients from the atmosphere in rain, wind-blown particles, or gases. Anthropogenic fertilization is an additional nutrient input in managed ecosystems. Internal cycling processes include the interconversion of organic and inorganic forms, chemical reactions that change elements from one ionic form to another, biological absorption by plants and microbes, and exchange of nutrients on surfaces within the soil matrix. Nutrients are lost from ecosystems by leaching, trace gas emission, wind and water erosion, fire, outflow, burial, and the removal of materials in harvest.

Most of the nitrogen and phosphorus required for plant growth in unmanaged ecosystems is supplied by the decomposition of past primary production, including plant litter and soil organic matter (SOM) in terrestrial environments and mineralization of organic matter in the water column or sediments of aquatic ecosystems. Inputs and outputs to or from these ecosystems are a small fraction of the quantity of nutrients that cycle internally, producing relatively **closed systems** with conservative nutrient cycles. Human activities tend to increase inputs and outputs relative to the internal transfers and make the element cycles more open.

We have already described the cycling of nutrients through plants (see Chap. 8). In this chapter, we focus on the nutrient inputs and losses from ecosystems and on the processes within ecosystems that regenerate available nutrients from dead organic matter.

Marine Nutrient Cycling

Large-Scale Nutrient Cycles

Pelagic nutrient cycling in the open ocean is closely coupled to the flow of carbon. The extremely small size of marine primary producers (submicroscopic algal cells and photosynthetic bacteria) dictates that the processes of photosynthesis, nutrient absorption, growth, and reproduction are tightly integrated at the cellular level. We have therefore already described many of the basic features of pelagic nutrient cycling in the context of plant carbon and nutrient absorption (see Chaps. 5 and 8) and growth (see Chap. 6). Key features of pelagic nutrient cycling through phytoplankton include:

- Large-scale patterns of nutrient availability to phytoplankton in the surface ocean depend on the balance of three processes (see Chaps. 6 and 8): (1) Stratification driven by surface heating restricts nutrient delivery from deep water to the surface. (2) Wind-driven mixing disrupts stratification and deepens the mixed layer, increasing nutrient supply but reducing average light availability through the mixed layer. (3) Upwelling supplements nutrient supply and keeps phytoplankton in shallow well-lighted surface waters, supporting high gross primary production (GPP) and NPP.
- Primary production in the open ocean is generally limited in the short term by both nitrogen and phosphorus, with production usually responding most strongly to nitrogen over seasonal-to-annual cycles and to phosphorus or micronutrients over the long term (see Chap. 8).
- Grazing accounts for most of the nutrient return from phytoplankton to the environment (see Chaps. 8 and 10).
- Sedimentation of zooplankton feces and phytoplankton causes a continuous nutrient loss from the pelagic zone that is replenished by nitrogen fixation, upwelling, and mixing (see Chap. 7).

Nitrogen is mineralized (converted from organic nitrogen to ammonium) by several processes in the ocean. Grazers and their predators excrete nitrogen when they breakdown nitrogenous compounds to meet their energetic demands for growth and movement or maintain element **stoichiometry** (nutrient balance), just like protozoans in the rhizosphere (see Chaps. 8 and 10). Grazing is a more prominent pathway of nutrient mineralization in the ocean than on land because of the high proportion of phytoplankton biomass that is grazed rather than dying and decomposing (see Chap. 7). In addition, decomposer bacteria excrete ammonium when their growth is energy-limited. Much of this bacterial nitrogen mineralization occurs on particles to which algae and cyanobacteria are also attached or in micro-patches of high nutrient concentration (Stocker et al. 2008), facilitating efficient recycling of ammonium back to primary producers. This **regenerated production** based on ammonium that is produced within the water column contributes to tight nutrient recycling in the pelagic zone (Dugdale and Goering 1967).

Those dead cells and fecal pellets that sink beneath the pycnocline continue to decompose and mineralize nitrogen. Due to the absence of phytoplankton in these deep dark waters, much of the resulting ammonium is absorbed by nitrifying bacteria that use it as an energy source, releasing nitrate as a waste product (the process of **nitrification**). Thus deep waters tend to have a higher nitrate-to-ammonium ratio than surface waters. In the open ocean, most organic carbon and nitrogen are mineralized in the water column before reaching the sediments (Mann and Lazier 2006). Rates of organic matter inputs and decomposition in the sediments are therefore relatively low, causing sediments to remain relatively well oxygenated. These aerobic conditions favor nitrification (an aerobic process of nitrate release) rather than **denitrification** (anaerobic release of nitrogen trace gases).

In the coastal zone, by contrast, greater productivity and shallower water allow more organic matter to reach the sediments, where it is decomposed or buried. Decomposition of this organic matter in deep water and sediments consumes some or all of the available oxygen, creating an anaerobic environment where sulfate-reducing and denitrifying bacteria use dead organic matter as an energy source and sulfate or nitrate, respectively, as an electron acceptor, producing hydrogen sulfide or nitrogen trace gases (N_2O and N_2) as waste products (see Chap. 3). The gaseous release of N_2O and N_2 by denitrification depletes ocean waters of nitrogen relative to other nutrients such as phosphorus, contributing to the frequent occurrence of nitrogen limitation in coastal waters. Sulfate reduction, however, usually accounts for most of the anaerobic decomposition in coastal sediments (Howarth 1984).

Estuaries

Horizontal flows of water and nutrients govern the nutrient cycling and productivity of estuaries. **Estuaries**, where rivers enter the ocean, are interfaces between fresh and saline water. Estuaries tend to become stratified by the inflow of low-density fresh water from rivers. This water **entrains** (carries with it) surface ocean water as it flows from the river mouth out into the coastal ocean. Phosphorus-rich bottom water that has been depleted of nitrogen by denitrification flows up bay to replace this surface water. The extent of mixing of phosphorus-rich bottom water with surface water depends primarily on tidal mixing, which is greatest in long or shallow estuaries, and on surface turbulence caused by river discharge, winds, and storms. The Chesapeake Bay, for example, receives about 25% of its phosphorus from the coastal ocean but most of its nitrogen from rivers (Nixon et al. 1996). The balance between stratification and turbulence favors much more mixing in estuaries than in the open ocean, creating an environment that supports very high productivity (Mann and Lazier 2006). Productivity is particularly high at “fronts” between relatively well-mixed estuarine water and deeper, more stratified zones of the coastal ocean. Plumes of estuarine water spread the influence of estuarine mixing well beyond the bay where the river enters the ocean.

Estuaries receive most of their nutrients from the land, an input that has increased substantially in the last century. Outflows of nitrate and phosphate from the Mississippi River doubled in the last half of the twentieth century (Lohrenz et al. 1999), and nitrate movement to the North Atlantic Ocean from major rivers has increased 6–20-fold in the past century (Howarth et al. 1996a). Two-thirds of the estuaries in the U.S. are degraded by nutrient pollution (Howarth et al. 2011). This pollution by rivers reflects increased inputs of fertilizer, atmospheric nitrogen deposition, nitrogen fixation by crops, and food imports (see Chap. 14). The nutrients support extremely high productivity in the estuary and generate large quantities of organic matter that sinks to depth. The resulting stimulation of bacterial activity depletes oxygen in the lower 20 m of the water column, especially in summer. This creates zones of **hypoxia** (low oxygen) and **anoxia** (zero oxygen) thousands of square kilometers in area (Fig. 9.1; Rabalais et al. 2002; Díaz and Rosenberg 2008). Anoxia in these **dead zones** kills benthic organisms and bottom-feeding shrimp and fish and dramatically alters nutrient cycling at the sediment–water interface (Howarth et al. 2011). A combination of increasing land-use change, intensification of agriculture, and warming ocean temperatures has increased the frequency and extent of dead zones in the world’s estuaries and coastal waters, threatening many of Earth’s most productive fisheries. In addition, dead zones have created a new climate feedback, in which climate warming intensifies stratification that augments the low-oxygen, high-nitrate conditions that favor denitrification and the production of N_2O, a powerful greenhouse gas that contributes to warming climate (Mann and Lazier 2006; Stramma et al. 2008; Codispoti 2010). This exemplifies the unintended global consequences of massive human modification of the global nitrogen cycle (see Chap. 14).

Construction of dams and reservoirs has modified the flow regime of estuaries. Reservoirs accumulate water at times of peak flows and release the water in dry seasons to meet demands for agriculture, hydropower, and other human uses (Carpenter and Biggs 2009). This reduces peak inputs to estuaries that drive mixing and support spring blooms of productivity. This homogenization of flow regime is counterbalanced by levees that prevent floodwaters from spreading over the floodplain and increase peak discharges to estuaries during floods. Surface evaporation from reservoirs and water withdrawals for agriculture reduce discharge and mixing at other times of year. The life history of many fish is linked to the predictable seasonality of estuarine flows and blooms and is often disrupted when dams alter the seasonal flow regime of rivers. Reservoirs also retain substantial amounts of nitrogen and especially phosphorus in sediments (Friedl and Wüest 2002).

Coastal Currents

Upwelling drives the high productivity of coastal currents. There are broad areas of the ocean, especially on the western edges of continents, where surface waters move away from the coast toward the open ocean and are replaced by deep waters that move toward the coast (see Chap. 2). This circulation moves deep nutrient-rich waters to the surface and buoys phytoplankton up to the surface, where light availability is high. Many factors influence the location and strength of coastal upwelling. The strength of offshore winds, for example, is generally strongest during La Niña conditions, and the stability of the surface layer that counterbalances upwelling is generally strongest during summer.

In coastal areas unaffected by upwelling, diurnal tidal fluctuations generate turbulence that mixes deep nutrients upward. The mixing front brings together a low-salinity coastal water mass that is stratified enough to keep phytoplankton in a well-lighted surface zone and a more saline deep-water mass that provides nutrients. The relatively stable location of this front and regular diurnal cycles of tidal mixing provide the conditions that sustain high plankton productivity and support large populations of fish, sea birds, and marine mammals (Mann and Lazier 2006). Upwelling and tidal mixing generate complex temporal and spatial patterns of coastal productivity and trophic dynamics that are often linked to long archeological records of human use.

Lake Nutrient Cycling

As in the ocean, active absorption of nitrogen and phosphorus by phytoplankton often maintains extremely low nutrient concentrations in surface waters of unpolluted lakes. Also, as in the open ocean, nutrient delivery from more nutrient-rich deep waters is minimized by thermal stratification that is occasionally disrupted by mixing events. The isolation of surface waters from nutrient supplies in sediments, however, is less extreme in lakes than in the open ocean for several reasons. (1) The small size of most lakes and ponds fosters tight coupling between primary production (much of which is rooted vascular plants or benthic algae) and resupply of nutrients from sediments. The centers of large lakes have surface waters that are less well coupled to sediments, and the open ocean is extremely disconnected from its sediments. (2) Stratification in lakes reflects only a thermal gradient, whereas the ocean thermocline is reinforced by a salinity gradient, making it more difficult for nutrients to mix to the surface. Storms are therefore more effective in mixing nutrients from depth to the surface in lakes than in the ocean. (3) Finally, due to expected scaling relationships of edges to volume, smaller lakes are more exposed to their surroundings than is the open ocean. Streams and the atmosphere are therefore additional nutrient sources that range from being unimportant to dominant influences in the annual nutrient budgets of lakes.

Nutrient mineralization in lakes has both similarities and differences to that in the ocean. In both lakes and the ocean, grazing and bacterial mineralization on particles of dead organic water recirculates nutrients rapidly within the water column. Dead cells and the feces of zooplankton reach the sediments more readily in lakes than in the ocean because organic matter has only a short distance to travel before reaching the bottom. Although lakes, ponds, and reservoirs cover a very small fraction of Earth's surface (Downing et al. 2006), they are globally important locations for carbon burial (Dean and Gorham 1998). Rates and pathways of nutrient mineralization in sediments

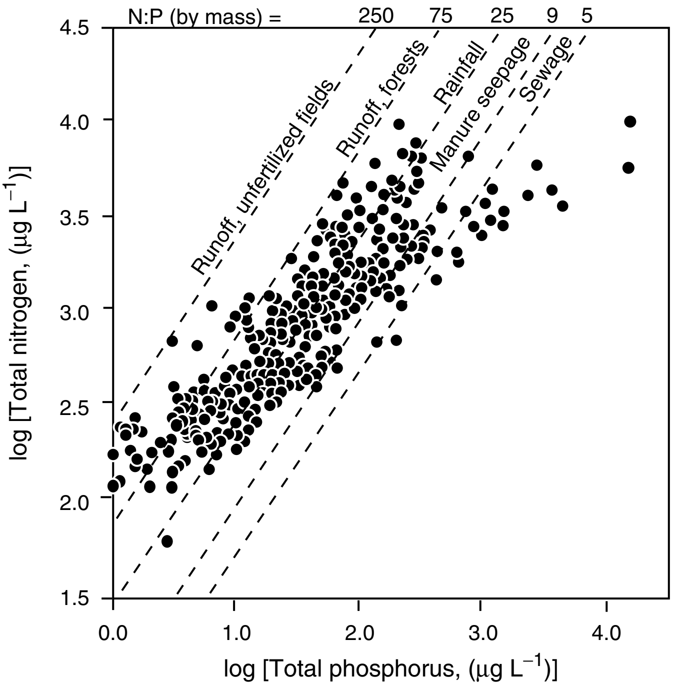


Fig. 9.2 Relationship between average summer total nitrogen and phosphorus concentrations in surface waters of the world's lakes. Pollution causes greater enrichment of phosphorus than of nitrogen. Redrawn from Downing and McCauley (1992)

differ strikingly between lakes and the ocean. In unpolluted lakes, phosphorus binds tightly to clay and silt particles in the sediments. In contrast, phosphorus is desorbed from ocean sediments due to competition with sulfate and other anions for exchange sites (Howarth et al. 2011). In addition, nitrogen is depleted by denitrification in anaerobic sediments of estuaries and coastal waters, and phosphorus is resupplied to surface waters, leading to a relatively phosphorus-rich environment.

Even among lakes, there is tremendous diversity in nutrient dynamics that reflect differences in origin and watershed geology, human impact on watersheds, and current biota. Lakes make up about 3% of the global terrestrial land surface. Most lakes and ponds are small and have closer contact with terrestrial ecosystems than the large lakes that have been most intensively studied. Ponds and small lakes <1 km^2 in area, for example, may account for about 40% of global lake area (Downing et al. 2006). Glacial lakes, which account for about half of the remaining lake area, exhibit a wide range of depths and sizes. Other important lake types include large deep tectonic lakes such as Lake Baikal and the African rift lakes and small shallow riverine lakes such as oxbows (Kalff 2002).

Deep lakes do not mix seasonally, especially in the tropics where there is little seasonal temperature variation. Deep lakes also have anoxic hypolimnia, where much of the nitrogen reaching the sediments is denitrified and returned to the atmosphere. At the opposite extreme, shallow lakes often have an extensive littoral zone dominated by vascular plants with high productivity, rapid rates of nutrient cycling, and tight coupling between plant production and sediment resupply of nutrients. Nutrient addition from agricultural runoff and sewage has substantially increased the nutrient content of many lakes, changing them from clear blue to a turbid green color (see Fig. 8.2; Carpenter and Biggs 2009). In general, oligotrophic lakes tend to have high N:P ratios, suggesting phosphorus limitation, and N:P ratio in the water decreases in more nutrient-rich lakes (Fig. 9.2).

Water residence time (the time required to replace the water volume of a system) influences many ecosystem properties of aquatic ecosystems (Kalff 2002). The open ocean has a longer water residence time, and estuaries have shorter

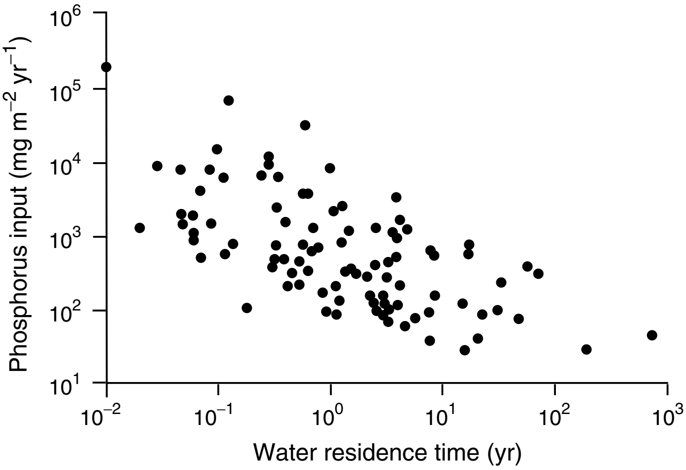


Fig. 9.3 Log–log relationship between water residence time and phosphorus input to moist-temperate lakes. Redrawn from Kalff (2002)

residence times than most lakes. Among lakes, water residence time tends to be long in lakes that are deep (e.g., hundreds to thousands of years in tectonic rift lakes), have small watersheds (e.g., lakes that are high in a drainage basin), or low river-input rates. These lakes are dominated by internal recycling processes, have small inputs of organic carbon and nutrients, support relatively low productivity and rates of nutrient cycling, and are vulnerable to the direct impacts of atmospheric deposition on the lake. Lakes that flush more rapidly (water residence times less than a decade) are particularly vulnerable to pollution from land-use change within the watershed (Fig. 9.3). Pollution that exceeds the capacity of sediments to sequester phosphorus, for example, can cause the sediments to switch from being a sink to a source of phosphorus, at which point it becomes very difficult to control phytoplankton production and maintain water clarity (see Fig. 12.6; Carpenter 2003).

Stream Nutrient Cycling

Carbon and nutrients spiral down streams and rivers and the groundwater beneath them. Streams are not passive channels that carry materials from land to the ocean but process much of the material that enters them (Cole et al. 2007; Mulholland et al. 2008). The strong horizontal flow of water in streams and rivers carries the resulting products downstream, where they are repeatedly reprocessed in successive stream sections (Fisher et al. 1998). This leads to open patterns of nutrient cycling, in which the lateral transfers are much larger than the internal recycling (Giller and Malmqvist 1998). Stream productivity therefore depends on regular subsidies from the surrounding terrestrial matrix and is quite sensitive to changes in these inputs that result from pollution or land-use change (Mulholland et al. 2008). The **spiraling length** of a stream is the average horizontal distance between successive uptake events. It depends on the **turnover length** (the downstream distance moved while an element is in organic form) and the **uptake length** (the average distance that an atom moves from the time it is released until it is absorbed again). A representative spiraling length of a woodland stream is about 200 m. Of this distance, about 10% occurs as microorganisms flow downstream attached to CPOM and FPOM, 1% as consumers move downstream, and the remaining 89% after release of the nutrient by mineralization (Giller and Malmqvist 1998). A unit of nutrient therefore spends most of its time with relatively little movement, but moves rapidly once it is mineralized and soluble in the water. Spiraling is therefore not a gradual process but occurs in pulses. The patterns of **drift** of stream invertebrates are consistent with these generalizations. Invertebrates drift downstream when they are dislodged from substrates or disperse. Drift is

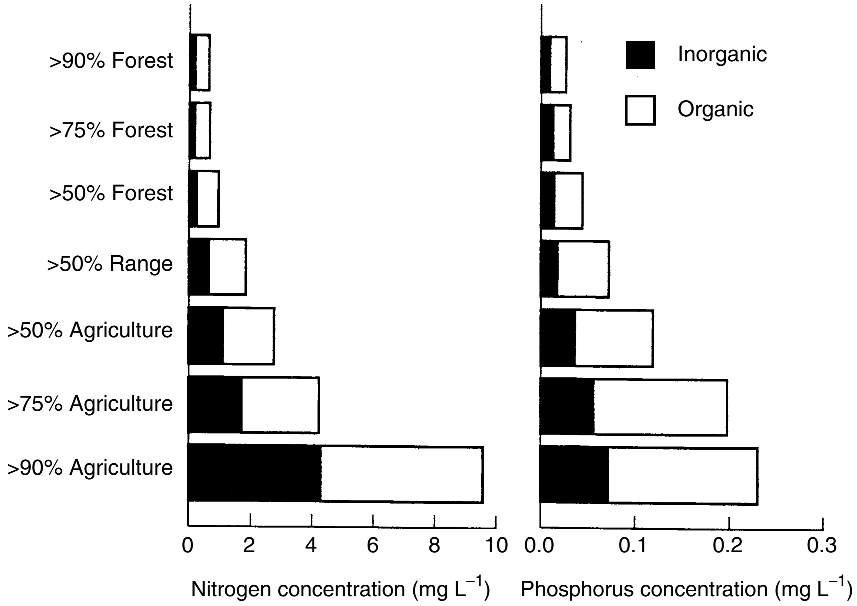


Fig. 9.4 Concentrations of organic and inorganic nitrogen and phosphorus in 928 relatively unpolluted U.S. streams in watersheds with varying degrees of conversion from forest to agriculture. Redrawn from Allan and Castillo (2007)

an important food source for fish but represents only about 0.01% of the invertebrate biomass in a stream at any point in time. In other words, stream invertebrates are so strongly attached to their substrates that carbon and nutrients spiral downstream primarily in the dissolved phase.

Headwater streams less than 10-m wide are particularly important in nutrient processing because they are the immediate recipient of most terrestrial inputs and account for up to 85% of the stream length within most drainage networks (Peterson et al. 2001). Small streams cycle nitrogen efficiently (have shorter uptake lengths) because their shallow depths and high surface–volume ratios enhance nitrogen absorption by algae and bacteria that are attached to rocks and sediments. Large rivers are also important, but for different reasons. Their relatively low velocities, long stream reaches, and high nitrate concentrations allow large quantities of nitrate to be absorbed (Wolheim et al. 2006; Mulholland et al. 2008). Uptake lengths for ammonium range from 10 to 1,000 m and increase exponentially with increases in stream discharge (Peterson et al. 2001).

In unpolluted rivers, a large proportion of the dissolved nitrogen is organic, and nitrate constitutes the bulk of the inorganic nitrogen (Allan and Castillo 2007). Nitrogen fixation by cyanobacteria supplements terrestrial nitrogen inputs in those streams (e.g., desert streams) that are nitrogen-limited and have enough light to support nitrogen fixation (Grimm and Petrone 1997). Land-use change and agricultural intensification increase both the quantity of dissolved nitrogen and phosphorus entering streams and the proportion of it that is inorganic (Fig. 9.4; Seitzinger et al. 2005). Of the nitrogen that enters polluted rivers, 60–75% is denitrified, particularly in the hyporheic zone. In contrast, phosphorus tends to be trapped in sediments, especially in reservoirs, or be transported to the ocean. The N:P ratio of water entering the ocean is typically much lower than that which enters the river (Howarth et al. 1996a).

Nitrogen Inputs to Terrestrial Ecosystems

Biological nitrogen fixation is the main pathway by which new nitrogen enters unpolluted terrestrial ecosystems. Only nitrogen-fixing bacteria

Table 9.1 Organisms and associations involved in di-nitrogen fixation

Type of association[a]	Key characteristics	Representative genera
Heterotrophic N fixers		Bacteria
Associative		
Nodulated (symbiotic)	Legume	*Rhizobium*
	Nonlegume woody plants	*Frankia*
Non-nodulated	Rhizosphere	*Azotobacter, Bacillus*
	Phyllosphere	*Klebsiella*
Free-living	Aerobic	*Azotobacter, Rhizobium*
	Facultative aerobic	*Bacillus*
	Anaerobic	*Clostridium*
Phototrophic N fixers		Cyanobacteria
Associative	Lichens	*Nostoc, Calothrix*
	Liverworts (*Marchantia*)	*Nostoc*
	Mosses	*Holosiphon*
	Gymnosperms (*Cycas*)	*Nostoc*
	Water fern (*Azolla*)	*Nostoc*
Free-living	Cyanobacteria	*Nostoc, Anabaena*
	Purple non-sulfur bacteria	*Rhodospirillium*
	Sulfur bacteria	*Chromarium*

[a] Nitrogen-fixing microbes are heterotrophic bacteria, if they get their organic carbon from the environment. They are phototrophic bluegreen algae, if they produce it themselves through photosynthesis. Some forms of both microbial groups are typically associated with plants, whereas others are free living. Note that the same microbial genus can have both associative and free-living forms

Data from Paul and Clark (1996)

have the capacity to break the triple bonds of N_2 and reduce it to ammonium (NH_4^+), which supports their own growth. Nitrogen fixed by nitrogen-fixing plants becomes available to other plants in the community primarily through the production and decomposition of nitrogen-rich litter.

Biological Nitrogen Fixation

The characteristics of nitrogenase, the enzyme that catalyzes the reduction of N_2 to NH_4^+, dictate much of the biology of nitrogen fixation. The reduction of N_2 catalyzed by nitrogenase has a high energy requirement and therefore occurs only where the bacterium has an abundant carbohydrate supply and adequate phosphorus. The enzyme is denatured in the presence of oxygen, so organisms must protect the enzyme from contact with oxygen. Finally, temperature often constrains the carbon supply and activity of nitrogenase enzymes, so nitrogen fixation is most prominent in tropical environments and constrained at high latitudes (Houlton et al. 2008).

Groups of Nitrogen Fixers

Nitrogen-fixing bacteria in symbiotic association with plants have the highest rates of nitrogen fixation. This occurs because plants can provide the abundant carbohydrates needed to meet the high energy demand of nitrogen fixation. The most common symbiotic nitrogen fixers are *Rhizobium* species associated with legumes (soybeans, peas, etc.) and *Frankia* species (actinomycete bacteria) associated with alder, *Ceanothus*, and other nonlegume woody species (Table 9.1). These plant-associated symbiotic nitrogen-fixing bacteria usually reside in root nodules, where the nitrogenase enzyme is protected from oxygen. Legumes, for example, have leghemoglobin, an oxygen-binding pigment similar to the hemoglobin that transports oxygen in the bloodstream of vertebrate animals. Nitrogen-fixing bacteria in nodules are heterotrophic and depend on carbohydrates from plants to meet the energy requirements of nitrogen fixation. The energetic requirement for nitrogen fixation can be about 25% of GPP under laboratory conditions, two to four times higher than the cost of absorbing inorganic nitrogen from soils (Lambers et al. 2008). The relative costs of nitrogen fixation and nitrogen absorption under field conditions are more difficult to estimate because of the uncertain costs of mycorrhizal association, nitrate reduction, and root exudation. When inorganic nitrogen is naturally abundant or is added to soils, nitrogen-fixing plants generally reduce their capacity for nitrogen fixation and absorb nitrogen from the soil. Phosphorus availability often limits the growth of nitrogen-fixing plants. Moreover, high phosphatase activities in soils associated with nitrogen fixers often supplement supplies of inorganic phosphorus to nitrogen fixers (Houlton et al. 2008).

Free-living heterotrophic nitrogen-fixing bacteria typically have the lowest rates of nitrogen fixation. These bacteria get their organic carbon from the environment and are most active in soils or sediments that have high concentrations of organic matter to provide the carbon substrate that fuels nitrogen reduction (Table 9.1). Other heterotrophic nitrogen fixers occur in the rhizosphere and depend on root exudation and root turnover for their carbon supply. Nitrogen fixers in the anaerobic hindguts of termites provide an important nitrogen source that facilitates the decomposition of wood in the tropics (Yamada et al. 2006). Aerobic heterotrophs have various mechanisms that reduce oxygen concentration in the vicinity of nitrogenase, including high rates of bacterial respiration that depletes oxygen around the bacterial cells or production of slime that reduces oxygen diffusion to the enzyme.

Many free-living nitrogen-fixing **phototrophs** produce their own organic carbon by photosynthesis. These include cyanobacteria (bluegreen bacteria) that occur in aquatic systems and on the surface of many soils. Many phototrophs have specialized non-photosynthetic cells called **heterocysts** that protect nitrogenase from denaturation by the oxygen produced during photosynthesis in adjacent photosynthetic cells.

There are also associative (symbiotic) nitrogen-fixing phototrophs. For example, nitrogen-fixing lichens are composed of green algae or cyanobacteria as the photosynthetic symbiont, cyanobacteria that fix nitrogen, and fungi that provide physical protection. These lichens provide an important nitrogen input in many early successional ecosystems. The small freshwater fern *Azolla* and cyanobacteria such as *Nostoc* form a phototrophic association that is common in rice paddies and tropical aquatic systems.

Legumes and other symbiotic nitrogen fixers have the highest rates of nitrogen fixation, often 5–20 g m^{-2} $year^{-1}$. Phototrophic symbionts such as *Nostoc* in association with *Azolla* in rice paddies may fix 10 g m^{-2} $year^{-1}$. When *Nostoc* is a free-living phototroph, it typically fixes about 2.5 g m^{-2} $year^{-1}$. In contrast, free-living heterotrophs fix only 0.1–0.5 g m^{-2} $year^{-1}$, a quantity similar to the input from nitrogen deposition in unpolluted environments.

Causes of Variation in Nitrogen Fixation

Biotic and abiotic constraints on nitrogen fixation lead to nitrogen limitation or co-limitation in many ecosystems. The rate of nitrogen fixation varies widely among ecosystems, in part reflecting the types of nitrogen fixers that are present. Even within a single type of nitrogen-fixing system, however, nitrogen fixation rates vary widely. What causes this variation? If nitrogen limits growth in many ecosystems, why does nitrogen fixation not occur almost everywhere? One would expect nitrogen fixers to have a competitive advantage over other plants and microbes that cannot fix their own nitrogen. Why don't nitrogen fixers respond to nitrogen limitation by fixing nitrogen until nitrogen is no longer limiting in the ecosystem? Several factors constrain nitrogen fixation, thereby maintaining nitrogen limitation or co-limitation in many ecosystems (Vitousek and Howarth 1991; Vitousek and Field 1999; Vitousek et al. 2002; Houlton et al. 2008; Hedin et al. 2009).

Energy availability constrains nitrogen fixation rates in closed-canopy ecosystems. The cost of nitrogen fixation (3–6 g carbon g^{-1} N, not including the cost of nodule production) by symbiotic and autotrophic nitrogen fixers is high relative to that of absorbing ammonium or nitrate. Nitrogen fixation is therefore largely restricted to high-light environments where light is less limiting than nitrogen. As canopies close during succession, energy becomes limiting to the establishment of nitrogen-fixing plants. These plants could fix nitrogen if they were in the canopy, but the cost of nitrogen fixation makes it difficult for them to grow through shade to the canopy. Leguminous trees are common in tropical forests and savannas. In savannas, where fires cause large nitrogen losses, leguminous trees are heavily nodulated and fix substantial quantities of nitrogen (Högberg and Alexander 1995). Leguminous trees in tropical forests are less extensively nodulated, but their nitrogen-rich lifestyle is accommodated by the high nitrogen availability of these ecosystems (Vitousek et al. 2002). Here they contribute modestly to annual nitrogen inputs but are important to the long-term nitrogen economy of forests (Pons et al. 2006; Hedin et al. 2009). Nitrogen fixation in aquatic systems is most common in shallow waters or waters with low turbidity where light reaches benthic cyanobacterial mats. When phosphorus availability is adequate, these mats have high fixation rates.

Non-symbiotic heterotrophic nitrogen-fixing bacteria are also limited by the availability of labile organic carbon. When available carbon is scarce, there is no benefit to heterotrophic nitrogen fixation. Decaying wood, which has low nitrogen and high levels of organic carbon, often has substantial rates of heterotrophic nitrogen fixation, including that which occurs in the guts of tropical termites (Yamada et al. 2006). Heterotrophic nitrogen fixation also occurs in anaerobic sediments, but the gaseous loss of nitrogen by **denitrification**, that is, the conversion of nitrate to gaseous forms, usually exceeds the gains from nitrogen fixation.

Nitrogen fixation in many ecosystems is limited by the availability of other nutrients, such as phosphorus. Due to their ready access to nitrogen, the growth of nitrogen-fixing plants is often limited by other nutrients, particularly by phosphorus, which co-limits or secondarily limits plant production in most ecosystems (Elser et al. 2007). Nitrogen fixers often have a nutrient-rich stoichiometry; they use large amounts of phosphorus as well as nitrogen. The growth of nitrogen fixers therefore often becomes phosphorus-limited before that of other plants. Other elements that can limit nitrogen fixation include molybdenum, iron, and sulfur, which are essential co-factors of nitrogenase (Barron et al. 2009). Molybdenum, for example, often limits nitrogen fixation on highly weathered soils of Australian pastures and lowland tropical forests. Nitrogen fixers may be limited by iron in marine ecosystems, as discussed earlier. Phosphorus, iron, sulfur, or molybdenum may, in these cases, be the ultimate "master element" that limits production, even though nitrogen is the factor to which primary production responds most strongly in short-term experiments.

Consumption of nitrogen-fixing organisms often constrains their capacity to support continuously high nitrogen fixation rates. The high protein content typical of nitrogen fixers enhances their palatability to many herbivores, although nitrogen-based defenses such as alkaloids, which occur in many nitrogen-fixing plants, deter generalist herbivores (see Chap. 10). The resulting intense herbivory on many nitrogen-fixing plants reduces their capacity to compete with other plants, constraining their abundance and nitrogen inputs to the ecosystem (Vitousek and Field 1999; Vitousek et al. 2002). Areas from which grazers are excluded often have more nitrogen-fixing plants and greater nitrogen inputs to the ecosystem and ultimately more productivity and biomass (Ritchie et al. 1998).

Nitrogen Deposition

Nitrogen is deposited in ecosystems in particulate, dissolved, and gaseous forms. All ecosystems receive nitrogen inputs from atmospheric deposition. These inputs are smallest, often 0.1–0.5 g m^{-2} $year^{-1}$, in ecosystems downwind from pollution-free open-ocean waters (Hedin et al. 1995). Nitrogen inputs to coastal ecosystems derive primarily from organic particulates and nitrate (NO_3^-) in sea-spray evaporites and from ammonia (NH_3) volatilized from seawater. In inland areas, nitrogen derives from the volatilization of NH_3 from soils and vegetation and from dust produced by wind erosion of deserts, unplanted agricultural fields, and other sparsely vegetated ecosystems. Lightning also fixes nitrogen that ultimately contributes to atmospheric deposition.

Human activities are now the major source of nitrogen deposited in many areas of the world (Vitousek et al. 1997a; Gruber and Galloway 2008). The application of urea or ammonia fertilizer leads to volatilization of NH_3, which is then converted to NH_4^+ in the atmosphere and deposited in rainfall. Domestic animal husbandry has also substantially increased emissions of NH_3 to the atmosphere. The emission of nitric oxides (NO and NO_2, together known as NO_x) from fossil fuel combustion, biomass burning, and volatilization from fertilized agricultural systems has dwarfed natural sources at the global scale: 80% of all NO_x flux is anthropogenic (Delmas et al. 1997). Nitrogen derived from these sources can be transported long distances downwind from industrial or agricultural areas before being deposited. "Arctic haze" over the Arctic Ocean and Canadian High Arctic islands, for example, derives primarily from pollutants produced in China and Eastern Europe. Inputs of anthropogenic sources of nitrogen to ecosystems can be quite large, for example 1–2 g m^{-2} $year^{-1}$ in the northeastern U.S. or 5–10 g m^{-2} $year^{-1}$ in northern China, 10–100-fold greater than background levels of nitrogen deposition. The highest rates are similar to the amounts annually absorbed by vegetation and cycled through litterfall (see Chap. 8). Most ecosystems have a substantial capacity to store added nitrogen in soils and vegetation. Once these reservoirs become **nitrogen saturated**, however, nitrogen losses to the atmosphere and groundwater can be substantial. The nitrogen cycle in some polluted ecosystems has changed from being >90% closed (see Table 8.2) to being almost as open as the carbon cycle, in which the amount of nitrogen or carbon annually cycled by vegetation is similar to the amount that is annually gained and lost from the ecosystem. Agricultural systems are often nitrogen-saturated and release substantial quantities of nitrogen to aquifers and aquatic ecosystems; we discuss nutrient cycling in agricultural systems in more detail later. Most forests, in contrast, increase their carbon sequestration in response to nitrogen deposition, indicating that these forests are not yet nitrogen-saturated (Magnani et al. 2007). The role of nitrogen deposition on carbon sequestration at the global scale, however, appears to be modest, suggesting that anthropogenic nitrogen inputs are unlikely to "solve the climate problem" by enhancing carbon sequestration (Gruber and Galloway 2008).

Climate and ecosystem structure determine the processes by which nitrogen is deposited in ecosystems. Deposition occurs by three processes. (1) Wet deposition delivers nutrients dissolved in precipitation. (2) Dry deposition delivers compounds as dust or aerosols by sedimentation (vertical deposition) or impaction (horizontal deposition or direct absorption of gases such as HNO_3 vapor). (3) Cloud-water deposition delivers nutrients in water droplets onto plant surfaces immersed in fog. Although data are most available for wet deposition because it is most easily measured, wet and dry deposition are often equally important sources of nitrogen inputs (Fig. 9.5). Wet deposition of nitrogen is typically greater in wet than in dry ecosystems. Dry deposition of nitrogen, however, shows no clear correlation with climate, although arid ecosystems receive a larger *proportion* of their nitrogen inputs by dry deposition. Cloud water deposition is greatest on cloud-covered mountaintops and areas of coastal fog. The relative importance of wet, dry, and cloud-water deposition also depends on ecosystem structure. Conifer canopies, for example, tend to collect more dry deposition and cloud-water deposition than do deciduous canopies because of their greater leaf surface area. Their rough canopies also cause moisture-laden air to penetrate more deeply within the forest canopy and therefore to contact more leaf surfaces (see Chap. 4).

The form of nitrogen deposition determines its ecosystem consequences. NO_3^- and NH_4^+ are immediately available for biological absorption by plants and microbes, whereas some organic nitrogen must first be mineralized. Nitrate inputs as nitric acid (and ammonium inputs, if followed by **nitrification**, the conversion of ammonium to nitrate) acidify the soil when nitrate accompanied by base cations leaches from the ecosystem. Organic nitrogen compounds make up about a third of the total nitrogen deposition, but their

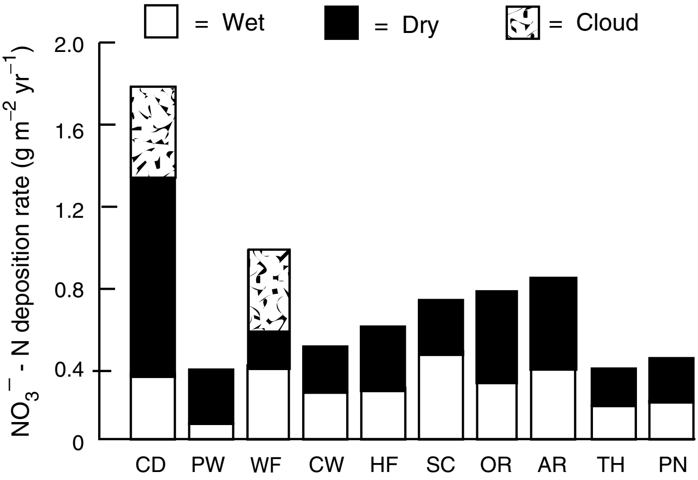


Fig. 9.5 Wet, dry, and cloud-water deposition of nitrogen in a variety of ecosystems. These ecosystems are (from high to low elevation): Clingman's Dome NC (CD), Pawnee CO (PW), Whiteface Mountain NY (WF), Coweta NC (CW), Huntington Forest NY (HF), State College PA (SC), Oak Ridge TN (OR), Argonne IL (AR), Thompson WA (TH), and Panola GA (PN). Data from Lovett (1994)

chemical nature varies among ecosystems (Neff et al. 2002). In coastal areas, for example, organic nitrogen is deposited primarily as marine-derived reduced compounds such as amines. In inland areas affected by air pollution, most organic nitrogen enters as oxidized organic nitrogen compounds that result from the reaction of organic compounds with NO_x in the atmosphere.

Weathering of sedimentary rocks may contribute to the nitrogen budgets of some ecosystems. Sedimentary rocks, which make up 75% of the exposed rocks on Earth's surface, sometimes contain substantial nitrogen. In some watersheds underlain by high-nitrogen sedimentary rocks, rock weathering contributes significant nitrogen inputs to ecosystems (Holloway et al. 1998; Thompson et al. 2001). In most ecosystems, however, rock weathering is thought to provide only a small nitrogen input to ecosystems.

Internal Cycling of Nitrogen

Overview of Mineralization

In natural ecosystems, most nitrogen absorbed by plants becomes available through the decomposition of organic matter. In most ecosystems, most (> 99%) soil nitrogen is contained in dead organic matter derived from plants, animals, and microbes. As microbes break down this dead organic matter during decomposition (see Chap. 7), the nitrogen is released as **dissolved organic nitrogen** (DON) through the action of exoenzymes (Fig. 9.6). Plants and mycorrhizal fungi absorb some DON, using it to support plant growth. Decomposer microbes also absorb DON, using it to support their nitrogen or their carbon requirements for growth. When DON is insufficient to meet the microbial nitrogen requirement, microbes absorb additional inorganic nitrogen, primarily as NH_4^+, from the soil solution (Vitousek and Matson 1988; Fenn et al. 1998). **Immobilization** is the removal of inorganic nitrogen from the available pool by microbial absorption and chemical fixation. Microbial growth is often carbon-limited. Under these circumstances, microbes break down DON, use the carbon skeleton to support their energy requirements for growth and maintenance, and secrete NH_4^+ into the soil. This process is termed **nitrogen mineralization** or **ammonification** because ammonium is the immediate product of this process. In some ecosystems, some or all NH_4^+ is converted to nitrite (NO_2^-) and then to nitrate (NO_3^-), the process of **nitrification**.

Production and Fate of Dissolved Organic Nitrogen

The conversion from insoluble organic nitrogen to dissolved organic nitrogen (DON) makes nitrogen available to plants and microbes (Fig. 9.6). The large pool of particulate organic nitrogen in soils, relative to the sizes of

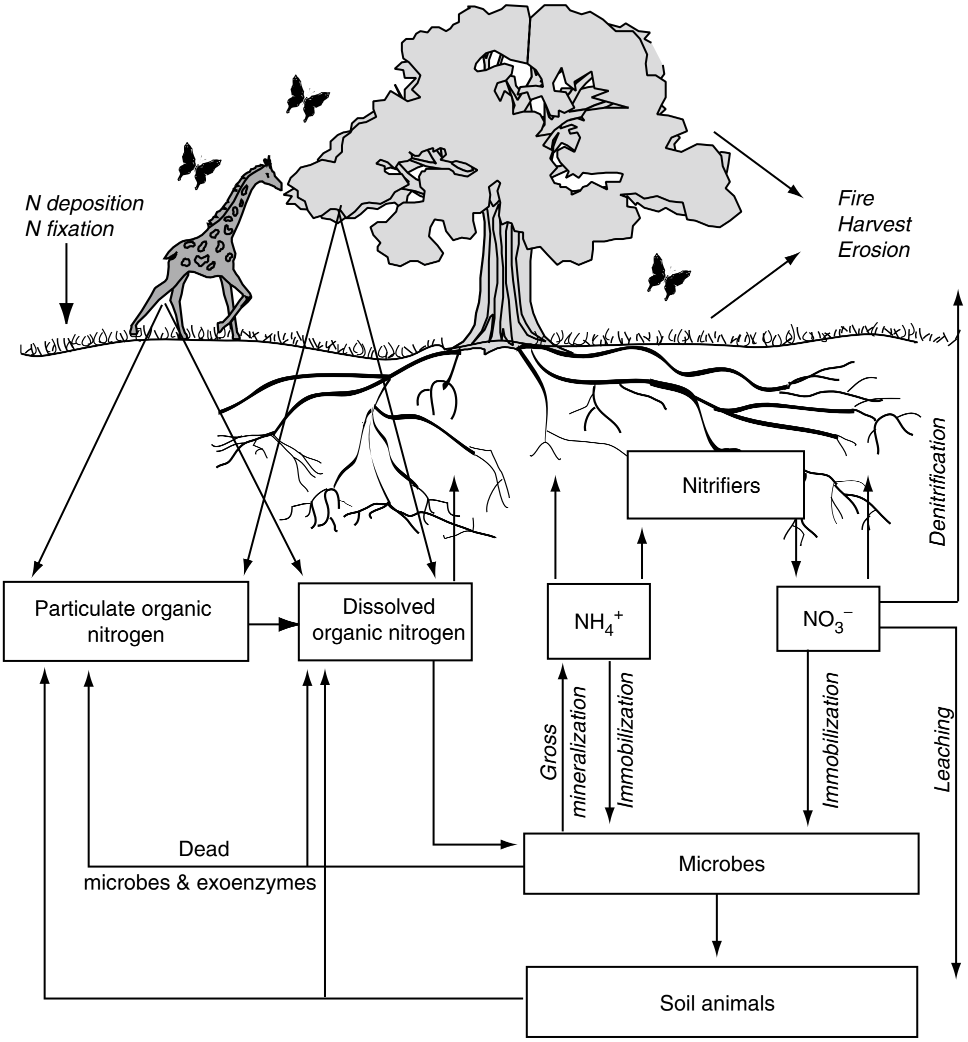
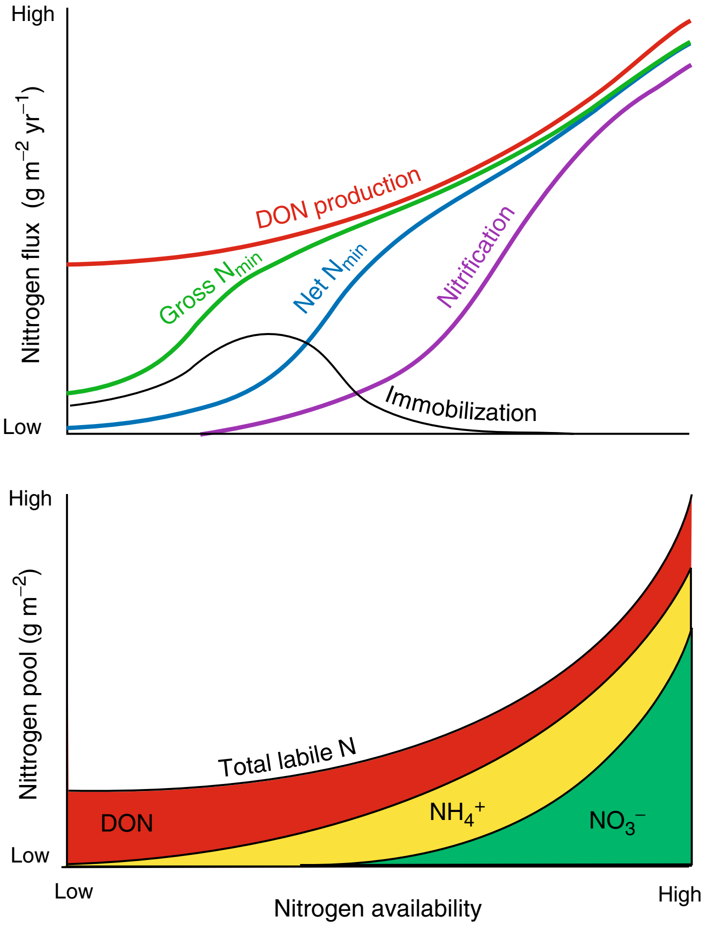


Fig. 9.6 Simplified diagram of the terrestrial nitrogen cycle. Both plants and microbes take up dissolved organic nitrogen (DON), NH_4^+, and NO_3^- and release particulate organic nitrogen (as dead organic matter) and DON. Microbes also release ammonium when they absorb more nitrogen than they require for growth. Nitrifiers are a specialized microbial group that either converts ammonium to nitrite or nitrite to nitrate. Nitrogen is consumed by animals when they eat plants or soil microbes and is returned to the soil as particulate organic nitrogen and DON. Nitrogen is lost from the ecosystem by denitrification, leaching, erosion, harvest, or fire. Nitrogen enters the ecosystem through nitrogen deposition or nitrogen fixation

inorganic pools suggests that this initial step in nitrogen mineralization is the rate-limiting step. All of the organic nitrogen that is eventually mineralized to NH_4^+ or NO_3^- must first be converted to soluble organic forms that can be absorbed by microbes and mineralized (Fig. 9.7). The flux through the DON pool is therefore large, relative to other nitrogen fluxes, even in ecosystems where its concentration is low (Schimel and Bennett 2004). The breakdown of particulate organic nitrogen is carried out in parallel with the breakdown and use of particulate organic carbon and is therefore controlled by the same organisms and factors that control decomposition (see Fig. 7.15). These controls include the quantity and chemical nature of the substrate, the

Fig. 9.7 Effect of nitrogen availability on the pools and fluxes of major forms of available nitrogen (dissolved organic nitrogen [DON], ammonium, and nitrate)



environmental factors regulating the activity of soil microbes and animals, and the composition of the microbial community (see Chap. 7; Booth et al. 2005).

Most nitrogen in dead organic matter is contained in complex polymers such as proteins, nucleic acids, and chitin (from fungal cell walls and insect exoskeletons) that are too large to pass through microbial membranes. Microbes must therefore secrete exoenzymes such as proteases, ribonucleases, and chitinases to break down the large polymers into small water-soluble subunits such as amino acids and nucleotides that can be absorbed by microbial cells. Urease is an exoenzyme that breaks down urea from animal urine or fertilizer into CO_2 and NH_3. The microbial enzymes are themselves subject to attack by microbial proteases, so microbes must continually invest nitrogen in exoenzymes to acquire nitrogen from their environment, a potentially costly process. Exoenzymes often bind to soil minerals and organic matter. This can inactivate the enzyme, if the shape of the active site is altered, or can protect the enzyme against attack from other exoenzymes, lengthening the time that the enzyme remains active in the soil (see Chap. 7). Proteases are produced by mycorrhizal and saprophytic fungi and by bacteria.

Plants, mycorrhizal fungi, or decomposer microbes all absorb DON. This is an important source of both nitrogen and carbon for soil microbes. Plants that absorb DON directly or through their mycorrhizal fungi require no mineralization to acquire this nitrogen. This direct absorption of organic nitrogen by plants occurs in most ecosystems (Read 1991; Kielland 1994; Näsholm et al.

1998; Lipson et al. 1999; Raab et al. 1999) and can meet a significant proportion of the plant nitrogen requirement (see Chap. 8; Lipson et al. 2001), particularly in nitrogen-limited ecosystems. Even crop plants absorb and use DON.

DON is a chemically complex mixture of compounds, only a few percent of which consists of amino acids and other labile forms of nitrogen. Most soils exhibit a similar balance of amino acids (Sowden et al. 1977). The labile DON that is absorbed by microbial cells can be incorporated directly into microbial proteins and nucleic acids. These and other DON compounds can also be metabolized to provide carbon or nitrogen to support microbial growth and maintenance. DON can also be adsorbed onto the soil exchange complex, incorporated into humus, or leached from the ecosystem in groundwater. Amino acids have both positively and negatively charged groups (NH_2^+ and COO^-, respectively). Small neutrally charged amino acids, such as glycine, are most mobile in soils and are therefore most readily absorbed by both plants and microbes (Kielland 1994).

Production and Fate of Ammonium

The net absorption or release of ammonium by microbes depends on their carbon status. When microbial growth is carbon-limited, microbes use the carbon from DON to support growth and respiration and secrete NH_4^+ as a waste product into the soil solution. This process of ammonification is the mechanism by which DON is mineralized to ammonium in soils. Other nitrogen-limited microbes may absorb, or **immobilize**, some of this ammonium and use it for growth. For example, the nitrogen mineralized in nitrogen-rich microsites may diffuse to adjacent nitrogen-limiting microsites, where it is absorbed by plants or other microbes (Schimel and Bennett 2004). Because of this fine-scale heterogeneity in soil nitrogen availability, a given unit of nitrogen can cycle between microbial release and absorption many times before it is absorbed by plants or undergoes some other fate. **Gross mineralization** is the *total* amount of nitrogen released via mineralization (regardless of whether it is subsequently immobilized or not). Its rate depends primarily on the quantity of microbial food (soil organic matter) and microbial biomass in the soil (Booth et al. 2005). **Net mineralization** is the *net* accumulation of inorganic nitrogen (ammonium plus nitrate) in the soil solution over a given time interval. Net mineralization occurs when microbial growth is limited more strongly by carbon than by nitrogen, whereas net immobilization occurs when microbial growth is nitrogen-limited (Schimel and Bennett 2004). Net mineralization of nitrogen is rapid when either biological processes such as grazing by microbivores or abiotic processes such as freeze–thaw and wet–dry cycles cause a crash of decomposer populations. In either case, surviving microbes have access to large quantities of nutrient-rich tissues.

The form of labile nitrogen that is most available to plants depends primarily on the relative abundance of microsites where microbial growth is nitrogen-limited (immobilization > mineralization) or carbon-limited (nitrogen mineralization > immobilization). In extremely nitrogen-limited soils, such as arctic and alpine tundra and boreal forest, where immobilization predominates, DON produced by exoenzymes of both mycorrhizal and saprophytic microbes is the predominant N form available in the soil and accounts for most nitrogen absorbed by plants. As nitrogen availability increases, so does the proportion of nitrogen-mineralizing microsites, and ammonium diffusing from these microsites becomes available to plants and to microbes (Schimel and Bennett 2004). In addition, nitrifying bacteria, which use ammonium as an energy source, convert increasing proportions of ammonium to nitrate, as ammonium availability increases. In summary, as nitrogen availability increases, microbial growth shifts from nitrogen to carbon limitation; an increasing proportion of the DON absorbed by microbes supports energy demands for growth, with excess nitrogen excreted as ammonium; and nitrifying bacteria use much of the available ammonium as an energy source to support their growth, so nitrification becomes the predominant process.

Net nitrogen mineralization is an excellent measure of the nitrogen supply to plants in ecosystems with high nitrogen availability, where

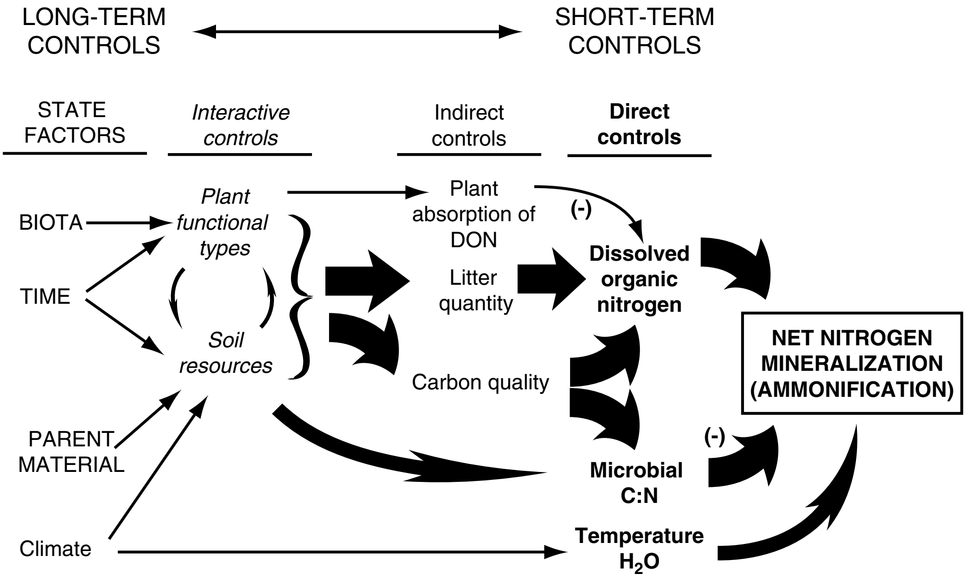


Fig. 9.8 The major factors governing temporal and spatial variation in ammonification (net nitrogen mineralization) in soils. These controls range from the proximate control over nitrogen mineralization (the concentration of dissolved organic nitrogen, physical environment, and microbial C:N ratio) to the state factors and interactive controls that ultimately determine the differences among ecosystems in mineralization rates. The influence of one factor on another is positive unless otherwise indicated (–), and the thickness of the arrows indicates the strength of the direct and indirect effects

microbial growth is primarily carbon-limited, and microbes use DON as a carbon source and excrete the excess nitrogen as ammonium. Under these circumstances, there is little competition for nitrogen between plants and soil microbes. The annual net mineralization in the deciduous forests of eastern North America, for example, approximately equals nitrogen absorption by vegetation (Nadelhoffer et al. 1992). In less fertile ecosystems, such as arctic tundra, plants actively absorb DON, and net nitrogen mineralization rate underestimates the amount of nitrogen that is annually acquired by plants (Nadelhoffer et al. 1992; Schimel and Bennett 2004).

Nitrogen mineralization rate is controlled by the availability of DON and inorganic nitrogen, the activity of soil microbes, and their relative demands for carbon and nitrogen. The quantity and quality of organic matter that enter the soil are the major determinants of the substrate available for both decomposition (see Fig. 7.15) and nitrogen mineralization (Fig. 9.8), so the ecological controls over these inputs govern the rates of both decomposition and nitrogen mineralization (Booth et al. 2005).

Nitrogen mineralization rate responds to two dimensions of substrate quality: (1) carbon quality, which governs the breakdown of dead organic matter to soluble forms (see Chap. 7), and (2) C:N ratio which determines the balance between carbon and nitrogen limitation of microbial growth. The C:N ratio in microbial biomass is about 10:1 (Cleveland and Liptzin 2007). As microbes break down organic matter, they incorporate about 40% of the carbon from their substrates into microbial biomass and return the remaining 60% of the carbon to the atmosphere as CO_2 through respiration. With this 40% growth efficiency, microbes require substrates with a C:N ratio of about 25:1 to meet their nitrogen requirement (Box 9.1). At higher C:N ratios, microbes import nitrogen to meet their growth requirements, and at lower C:N ratios nitrogen exceeds microbial growth requirements and is excreted into the litter and soil. In practice, microbes vary in their C:N ratio (5–10 in bacteria

Box 9.1 Estimation of Critical C:N Ratio for Net Nitrogen Mineralization

The critical C:N ratio that marks the dividing line between net nitrogen mineralization and net nitrogen absorption by microbes can be calculated from the growth efficiency of microbial populations and the C:N ratios of the microbial biomass and their substrate. Assume, for example, that the microbial biomass has a growth efficiency of 40% and a C:N ratio of 10:1. If the microbes break down 100 units of carbon, they will incorporate 40 units of carbon into microbial biomass and respire 60 units of carbon as CO_2. The 40 units of microbial carbon require 4 units of nitrogen to produce a microbial C:N ratio of 10:1 (= 40:4). If the 100 units of original substrate are to supply all of this nitrogen, the initial C:N ratio must have been 25:1 (= 100:4). At higher C:N ratios, microbes must absorb additional inorganic nitrogen from the soil to meet their growth demands. At lower C:N ratios, microbes excrete excess nitrogen into the soil.

and 8–15 in fungi; Paul and Clark 1996), although it is not clear that this translates into any systematic variation in growth efficiency (Thiet et al. 2006). All microbes convert substrates into biomass less efficiently when carbon or nutrient substrates limit their growth, in stressful environments (greater maintenance respiration) or when confronted with more recalcitrant substrates (greater maintenance respiration and more exoenzymes required; Thiet et al. 2006; Manzoni et al. 2008). Nonetheless, 25:1 is often considered the critical C:N ratio above which there is no net nitrogen release from decomposing organic matter. C:N ratio is typically highest in fresh litter, especially woody litter, and declines with time, approaching a C:N ratio of 14 in soil of relatively undisturbed ecosystems and a C:N ratio of 10 in agricultural systems (Stevenson 1994; Cleveland and Liptzin 2007; Fierer et al. 2009a). Thus there is a shift from immobilization (or mineralization, depending on initial C:N ratio) in fresh litter to mineralization as litter is decomposed. Note that, although C:N ratio only indirectly affects decomposition, reflecting its correlation with substrate carbon quality (see Chap. 7), it has a clear mechanistic effect on the net immobilization or mineralization of nitrogen.

There appears to be a universal relationship between litter C:N ratio and nitrogen mineralization or immobilization that depends on substrate quality but is independent of climate (Parton et al. 2007; Manzoni et al. 2008). Climate simply influences the rate at which mineralization or immobilization of nitrogen occurs. Favorable environmental conditions often promote nitrogen immobilization in recent or woody litter with a high C:N ratio but promote mineralization in later stages of decomposition or in long-term studies, where C:N ratio is likely to be lower. Long-term laboratory incubations, for example, show a generally positive effect of temperature on net nitrogen mineralization under favorable moisture conditions. This occurs because temperature stimulates maintenance respiration more strongly than microbial growth, leading to carbon limitation to microbial growth at warm temperatures and excretion of ammonium. In addition, both warm temperatures and microbial production promote predation by soil animals, causing greater microbial turnover and excretion of nitrogen into the soil. Moisture effects are more complex, with nitrogen mineralization generally increasing with soil moisture up to a threshold, above which high moisture restricts oxygen diffusion, microbial activity, and net nitrogen mineralization (Stanford and Epstein 1974). Due to their more favorable soil temperature and moisture and other factors, recently deforested areas typically have higher rates of net nitrogen mineralization than do undisturbed forests (Matson and Vitousek 1981). Across a moisture gradient in the Central Great Plains of the U.S., however, high moisture retarded decomposition and nitrogen mineralization, so the large plant nitrogen pools at the wet end of the gradient reflected greater nitrogen retention by plants and ecosystems rather than a moisture stimulation of nitrogen mineralization (McCulley et al. 2009). Clearly, predictions of environmental effects on nitrogen mineralization require attention to multiple plant and microbial processes, including microbial growth, respiration, and substrate-determined balance between immobilization and mineralization.

The ammonium produced by nitrogen mineralization has several potential fates. In addition to being absorbed by plants or microbes, ammonium readily adsorbs to the negatively charged surfaces of soil minerals and organic matter (see Chap. 3), reducing the concentration of NH_4^+ in the soil solution (often less than 1 ppm). Plant and microbial absorption of NH_4^+ depletes its concentration in the soil solution. This shifts the equilibrium between dissolved and exchangeable pools, causing adsorbed ions to go back into solution from the exchange complex. The cation exchange complex thus serves as a storage reservoir of readily available NH_4^+ and other cations. NH_4^+ can also be fixed in the interlayer portions of certain aluminosilicate clays or complexed with stabilized soil organic matter, which reduces its availability to plants and microbes as long as the organic mineral complex remains intact. Finally, NH_4^+ can be oxidized, mainly by bacteria, to NO_2^- and NO_3^- or converted to ammonia gas (NH_3), and lost to the atmosphere, as described in the next sections.

Production and Fate of Nitrate

Nitrification is the process by which NH_4^+ is oxidized to NO_2^- and subsequently to NO_3^-. Unlike ammonification, which is carried out by a broad suite of decomposers, most nitrification is carried out by a restricted group of **nitrifying bacteria**. There are two general classes of nitrifiers. **Autotrophic nitrifiers** use the energy yield from NH_4^+ oxidation to fix carbon that supports their growth and maintenance, analogous to the use by plants of solar energy to fix carbon via photosynthesis. **Heterotrophic nitrifiers** gain their energy from breakdown of organic matter.

Autotrophic nitrifiers include two groups, one that converts ammonium to nitrite, for example *Nitrosolobus* and other "Nitroso-" genera, and another that converts nitrite to nitrate, for example *Nitrobacter* and other "Nitro-" genera. These autotrophic nitrifiers are obligate aerobes that synthesize structural and metabolic carbon compounds by reducing CO_2 using energy from NH_4^+ or NO_2^- oxidation to drive CO_2 fixation. In most systems, these two groups occur together, so NO_2^- typically does not accumulate in soils. NO_2^- is most likely to accumulate in dry forest and savanna ecosystems during the dry season, when the activity of *Nitrobacter* is restricted, and in some fertilized ecosystems, where nitrogen inputs are high relative to plant and microbial demands.

Although autotrophic nitrification predominates in many ecosystems, heterotrophic nitrification can be important in ecosystems with low nitrogen availability or acidic soils. Many heterotrophic fungi and bacteria, including actinomycetes, produce NO_2^- or NO_3^- from NH_4^+. Some also use organic nitrogen in the process. Because heterotrophs obtain their energy from organic materials, it is not clear what advantage they gain from the oxidation of NH_4^+ to NO_3^-.

Nitrification has multiple effects on ecosystem processes. The oxidation of NH_4^+ to NO_2^- in the first step of nitrification produces two moles of H^+ for each mole of NH_4^+ consumed and therefore tends to acidify soils. The monooxygenase that catalyzes this step has a broad substrate specificity and also oxidizes many chlorinated hydrocarbons, suggesting a role of nitrifiers in the breakdown of pesticide residues. Finally, nitric oxide (NO) and nitrous oxide (N_2O), which are produced during nitrification (Fig. 9.9), are gases that have important effects on atmospheric chemistry.

The availability of NH_4^+ is the most important direct determinant of nitrification rate (Fig. 9.10; Robertson 1989; Booth et al. 2005). The NH_4^+ concentration must be high enough, at least in some soil microsites, to allow nitrifiers to compete with other soil microbes. This is particularly important for autotrophic nitrifiers, which

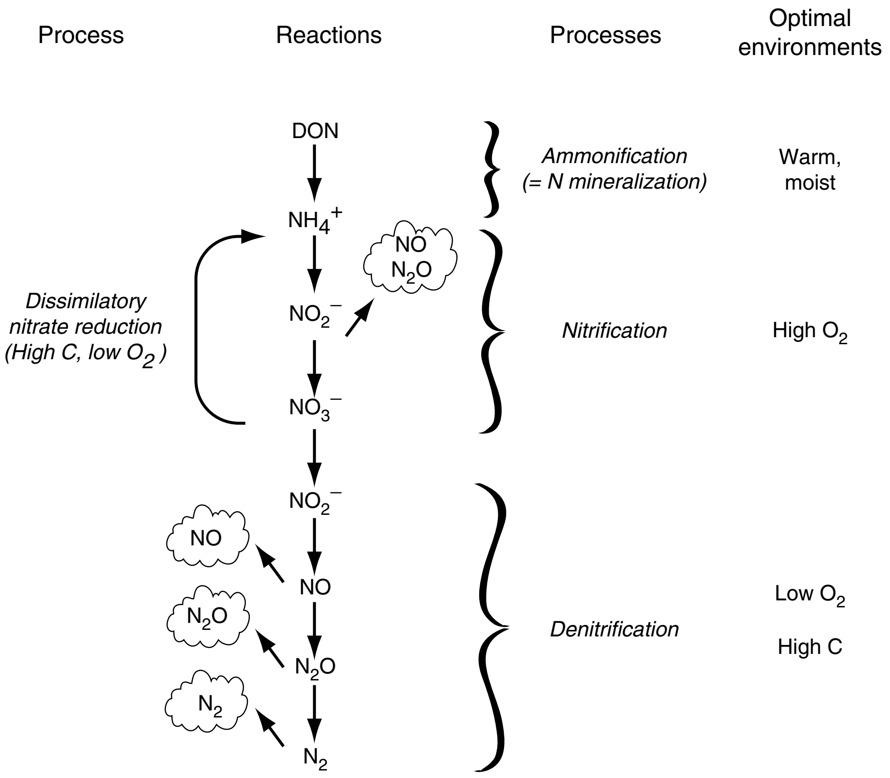


Fig. 9.9 Pathways of autotrophic nitrification and of denitrification and the nitrogen trace gases emitted by these pathways (Firestone and Davidson 1989)

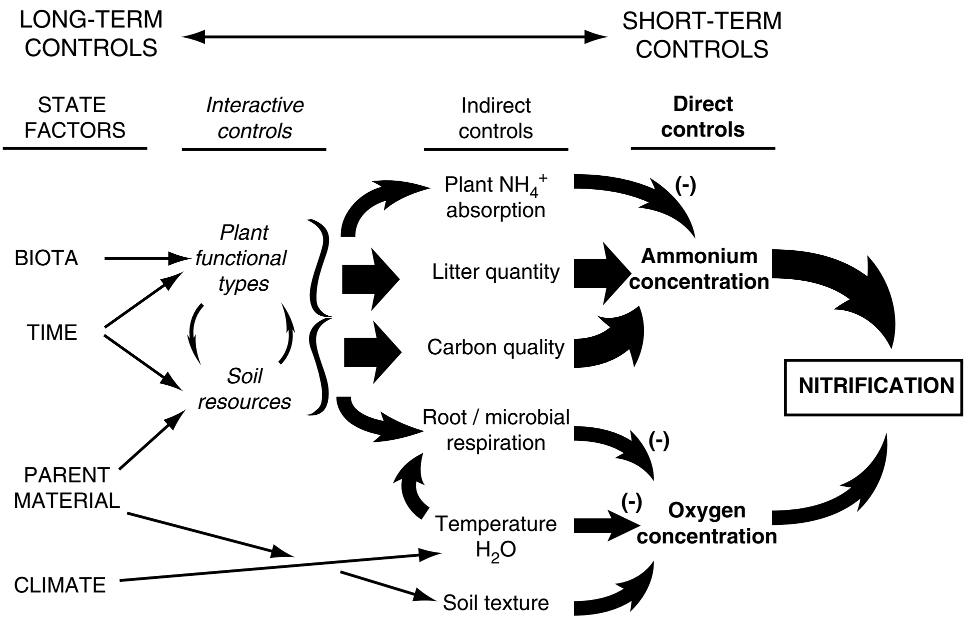


Fig. 9.10 The major factors governing temporal and spatial variation in nitrification in soils (Robertson 1989). These controls range from concentrations of reactants that directly control nitrification to the interactive controls such as climate and disturbance regime that are the ultimate determinants of nitrification rate. The influence of one factor on another is positive unless otherwise indicated (–), and the thickness of the arrows indicates the strength of the direct and indirect effects

rely on NH_4^+ as their sole energy source. NH_4^+ supply, in turn, is regulated by the effects of substrate quality and environment on ammonification rate, as described earlier (Fig. 9.8). Fertilizer inputs and ammonium deposition are additional sources of ammonium to many ecosystems. Conversely, plant roots lower NH_4^+ concentration in the soil solution, thereby competing with nitrifiers for NH_4^+. Productive ecosystems generally have high nitrification rates because high mineralization rates provide abundant ammonium as a substrate for nitrification (Booth et al. 2005). The resulting nitrate is, however, relatively mobile (see Chap. 3) and is often rapidly absorbed by plants or denitrified, so soil nitrate *concentrations* are not necessarily a good indicator of nitrification rate.

Nitrifier populations are often too small in infertile soils to support significant nitrification. When ammonium substrate becomes available (e.g., through additions of nitrogen, or increases in mineralization rates), nitrifier populations and nitrification rates can increase. The response can be rapid in some soils but show a long delay in others (Vitousek et al. 1982). Secondary metabolites, such as tannins, have been hypothesized to inhibit nitrification in some ecosystems, including those in late succession (Rice 1979), but the decline in nitrification in late succession is generally best explained by a decline in ammonium supply rather than through phenolic toxicity to nitrifiers (Pastor et al. 1984; Schimel et al. 1996). Limitation of nitrifier activity by other resources is another possible cause of slow or delayed nitrification. In most cases, however, the availability of ammonium ultimately governs nitrification rate through its effects on both the population density and activity of nitrifying bacteria.

Oxygen is an important additional factor controlling nitrification because most nitrifiers require oxygen as an electron acceptor for the oxidation of NH_4^+. Oxygen availability, in turn, is influenced by many factors, including soil moisture, soil texture, soil structure, and respiration by microbes and roots (Fig. 9.10; see Chap. 3).

Nitrifier activity is sensitive to temperature. It does, however, continue at low rates at low temperatures, so over a long winter season, substantial nitrification can occur, particularly in nitrogen-rich agricultural soils. Nitrification rates are slow in dry soils primarily because thin water films restrict NH_4^+ diffusion to nitrifiers (Stark and Firestone 1995). Under extremely dry conditions, low water potential further restricts the activity of nitrifiers. The importance of acidity in regulating nitrification rates is uncertain. In laboratory cultures of agricultural soils, maximum nitrification rates occur between pH 6.6 and 8.0 and are negligible below pH 4.5 (Paul and Clark 1996). Many natural ecosystems with acidic soils, however, have substantial nitrification rates, even at pH 4 (Stark and Hart 1997; Booth et al. 2005).

The fraction of mineralized nitrogen that is oxidized to nitrate varies widely among ecosystems. In many unpolluted temperate coniferous and deciduous systems, nitrification is only a small proportion of net mineralization (e.g., 0–4%) because plants and decomposer organisms compete with nitrifiers for ammonium. Nitrogen deposition can increase the fraction of mineralized nitrogen that is nitrified to 23% (McNulty et al. 1990). In tropical forests, in contrast, net nitrification is typically nearly 100% of net mineralization, even in sites with low rates of net mineralization and without inputs of additional nitrogen (Fig. 9.11; Vitousek and Matson 1988). In tropical ecosystems, plant and microbial growth are often limited by nutrients other than nitrogen, and their demand for nitrogen is low, so nitrifiers have ready access to NH_4^+.

The potential fates of nitrate are absorption by plants and microbes, exchange on anion exchange sites, or loss from ecosystems via denitrification or leaching. Nitrate is relatively mobile in soil solutions because it is negatively charged and does not bind to cation exchange sites. It therefore moves readily to plant roots by mass flow or diffusion (see Chap. 8) or can be leached from the soil. Some microbes also absorb nitrate and reduce it to ammonium through **dissimilatory nitrate reduction**, that is, nitrate reduction that does not involve assimilation (immobilization) by microbes (Fig. 9.9). This process is energetically expensive and occurs primarily when microbes are exposed to abundant nitrate and labile carbon under anaerobic conditions, as in tropical wet forests (Silver et al. 2001). Since this combination of conditions also facilitates

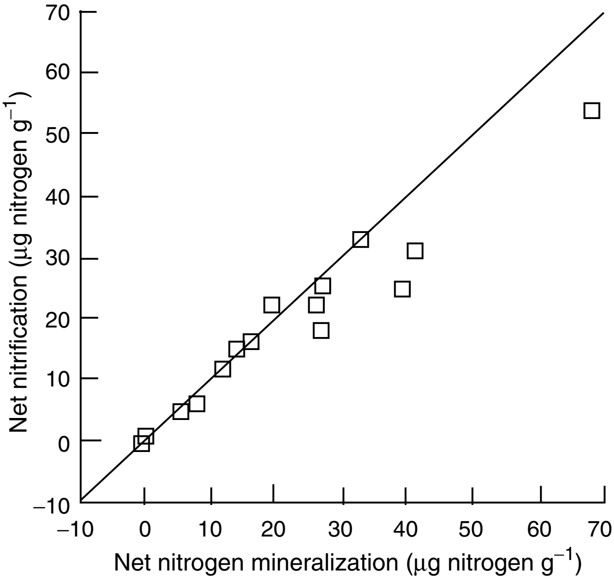


Fig. 9.11 The relationship between net nitrogen mineralization and net nitrification (g nitrogen g^{-1} of dry soil for a 10-day incubation) across a range of tropical forest ecosystems (Vitousek and Matson 1984). Nearly all nitrogen that is mineralized in these systems is immediately nitrified. In contrast, nitrification is often less than 25% of net mineralization in temperate ecosystems

denitrification, as described later, dissimilatory nitrate reduction can be an important mechanism of nitrogen retention in wet environments. The low nitrate concentrations observed in many acidic conifer forest soils reflect a combination of low nitrification rates and nitrate absorption by soil microbes and plants (Stark and Hart 1997).

Although NO_3^- is more mobile than most cations, it can be held on exchange sites of soils with a high anion exchange capacity (see Chap. 3). Soils with enough anion exchange capacity can prevent leaching losses of nitrate after disturbance (Matson et al. 1987). In most soils, the strength of the anion adsorption is $PO_4^{3-}>SO_4^{3-}>Cl^->NO_3^-$, so NO_3^- is desorbed and leached relatively easily.

Temporal and Spatial Variability

Fine-scale ecological controls cause large temporal and spatial variability in nitrogen cycling. Nitrogen transformation rates in soils are notoriously variable, with rates often differing by an order of magnitude between adjacent soil samples or sampling dates (Robertson et al. 1997; Schimel and Bennett 2004; Fierer et al. 2009a). This variability reflects the fine temporal and spatial scales over which controlling factors vary. Anaerobic conditions that support denitrification (see below) in the interiors of soil aggregates, for example, can occur within a millimeter of aerobic soil pores. Fine roots create rhizospheres with high carbon and low soluble nitrogen concentrations adjacent to bulk soil, where carbon-limited soil microbes mineralize organic nitrogen to meet their energy demands. In densely rooted microsites, plants deplete concentrations of NH_4^+ below levels that can sustain nitrification, whereas nitrification can be substantial in adjacent root-free microsites. The impacts of this fine-scale spatial heterogeneity on nitrogen cycling are difficult to study, so we know only qualitatively of their importance (Schimel and Bennett 2004).

Temporal variability in environment and extreme events have a strong influence on nitrogen mineralization. Drying–wetting events and freeze–thaw events, for example, burst many microbial cells and release pulses of nutrients. For this reason, the first rains after a long dry season often causes a pulse of nitrification and nitrate leaching (Davidson et al. 1993). The spring runoff after snowmelt in northern or mountain ecosystems also often carries with it a pulse of nutrient loss to streams because of both freeze–thaw events and the absence of plant absorption of nitrogen during winter. Ninety percent of the annual nitrogen input to Toolik Lake in arctic Alaska, for example, occurs in the first 10 days of snowmelt (Whalen and Cornwell 1985).

The seasonality of nitrogen mineralization often differs from the seasonality of plant nitrogen absorption. In those ecosystems where plants are dormant for part of the year, soil microbes continue to mineralize nitrogen during the dormant season. This temporal asynchrony between microbial activity and plant absorption leads to an accumulation of available nitrogen during the season of plant dormancy that plants use when they become active. In temperate forests, for example, mineralization during winter (even beneath a snowpack) creates a substantial pool of available nitrogen that is not absorbed by plants until the following spring. This asynchrony is particularly important in low-nutrient environments, where microbes may immobilize nitrogen during the season of most active plant growth, effectively competing with plants for nitrogen (Jaeger et al. 1999). In soils that freeze or dry, the death of microbial cells provides additional labile substrates that support net mineralization by the remaining microbes when conditions again become suitable for microbial activity.

Pathways of Nitrogen Loss

Gaseous Losses of Nitrogen

Ammonia volatilization, nitrification, and denitrification are the major avenues of gaseous nitrogen loss from ecosystems. These processes release nitrogen as ammonia gas, nitrous oxide, nitric oxide, and di-nitrogen. Gas fluxes are controlled by the rates of soil processes and by soil and environmental characteristics that regulate diffusion rates through soils. Once in the atmosphere, these gases can be chemically modified and deposited downwind.

Ecological Controls

Ammonia gas (NH_3) can be emitted from soils and senescing leaves. In soils, it is emitted as a consequence of the pH-dependent equilibrium between NH_4^+ and NH_3. At pH values greater than 7, a significant fraction of NH_4^+ is converted to NH_3 gas.

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \qquad (9.1)$$

Ammonia then diffuses from the soil to the atmosphere. This diffusion is most rapid in coarse dry soils with large air spaces. In dense canopies, some of the NH_3 emitted from soils is absorbed by plant leaves and incorporated into amino acids.

NH_3 flux is low from most ecosystems because NH_4^+ is maintained at low concentrations by plant and microbial absorption and by binding to the soil exchange complex. NH_3 fluxes are substantial, however, in ecosystems where NH_4^+ accumulates due to large nitrogen inputs. In grazed ecosystems, for example, urine patches dominate the aerial flux of NH_3. Agricultural fields that are fertilized with ammonium-based fertilizers or urea often lose 20–30% of the added nitrogen as NH_3, especially if fertilizers are placed on the surface. Nitrogen-rich basic soils are particularly prone to NH_3 volatilization because of the pH effect on the equilibrium between NH_4^+ and NH_3. Leaves also emit NH_3 during senescence, when nitrogen-containing compounds are broken down for transport to storage organs. Fertilization and domestic animal husbandry have substantially increased the flux of NH_3 to the atmosphere (see Chap. 14).

The production of NO and N_2O during nitrification depends primarily on the rate of nitrification. The conversion of NH_4^+ to NO_3^- by nitrification produces some NO and N_2O as by-products (Fig. 9.9), typically at a NO to N_2O ratio of 10–20. The quantities of NO and N_2O released during nitrification are correlated with the total flux through the nitrification pathway, suggesting that nitrification acts like a leaky pipe (Firestone and Davidson 1989), in which a small proportion (perhaps 0.1–10%) of the nitrogen "leaks out" as trace gases during nitrification.

The reduction of nitrate or nitrite to gaseous nitrogen by denitrification occurs under conditions of high nitrate and low oxygen. Many types of bacteria contribute to biological denitrification. They use NO_3^- or NO_2^- as an electron acceptor to oxidize organic carbon for energy when oxygen concentration is low. Most denitrifiers are facultative anaerobes and use oxygen rather than NO_3^-, when oxygen is available. In addition to biological denitrification, **chemodenitrification** converts NO_2^- (nitrite) abiotically to nitric oxide gas (NO) where NO_2^- accumulates

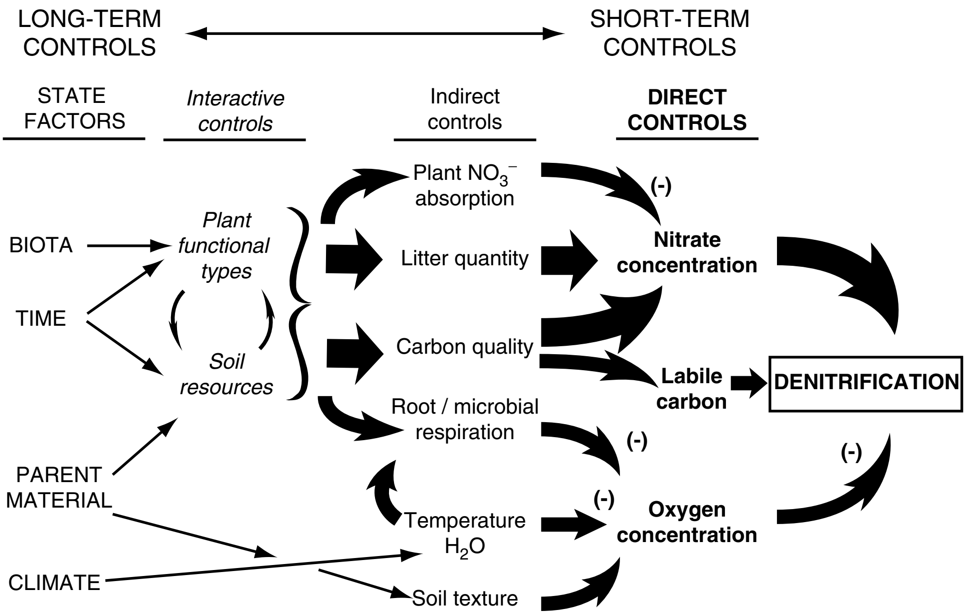


Fig. 9.12 The major factors governing temporal and spatial variation denitrification in soils. These controls range from concentrations of substrates that directly control nitrification to the interactive controls such as climate and disturbance regime that are the ultimate determinants of denitrification rate. The influence of one factor on another is positive unless otherwise indicated (–), and the thickness of the arrows indicates the strength of the direct and indirect effects

in the soil at low pH. Chemodenitrification is typically much less important than biological denitrification.

The sequence of NO_3^- reduction is: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$, with the last three products, particularly N_2O and N_2, being released as gases to the atmosphere (Fig. 9.9). Most denitrifiers have the enzymatic potential to carry out the entire reductive sequence, but produce variable proportions of N_2O and N_2, depending in part on the relative availability of oxidant (NO_3^-) versus reductant (organic carbon). When NO_3^- is relatively more abundant than labile organic carbon, the reaction goes only partially to completion, and relatively more N_2O than N_2 is produced. Other factors that favor N_2O over N_2 production include low pH, low temperature, and high oxygen. Although NO is often released during denitrification in laboratory incubations, there is seldom a net release in nature because its diffusion to the air is impeded by water-filled pore spaces. Some of the NO that is produced serves as a substrate for further reduction to N_2O or N_2 by denitrifying bacteria.

The three conditions required for significant denitrification are low oxygen, high nitrate concentration, and a supply of organic carbon (Fig. 9.12; Del Grosso et al. 2000). In most non-flooded soils, oxygen and nitrate availabilities exert the strongest control over denitrification. Oxygen supply is reduced by high soil water content, which impedes the diffusion of oxygen through soil pores. Soil moisture, in turn, is controlled by other environmental factors such as slope position, soil texture, and the balance between precipitation and evapotranspiration. Soil oxygen concentration is also sensitive to its rate of consumption by soil microbes and roots. It is consumed most quickly in warm, moist environments.

The second major control over denitrification is an adequate supply of the substrate NO_3^-. Because nitrification is primarily an *aerobic* process, the low-oxygen conditions that favor denitrification often limit NO_3^- supply. Some wetlands, for example, have low denitrification rates despite their saturated soils and large quantities of organic matter due to low availability of nitrate. Wetlands support high denitrification rates only if (1) they receive NO_3^- from outside the system (lateral transfer), (2) they have an aerobic zone above an anaerobic zone (vertical transfer), as in partially drained wetlands, or (3) go through cycles of flooding and drainage (temporal separation) as in many rice paddies. At a finer scale, denitrification can occur within soil aggregates or other anaerobic microsites (e.g., pieces of soil organic matter) in moderately well-drained soils due to fine-scale heterogeneity in soil oxygen concentration and nitrification rate.

Finally, the availability of organic carbon substrates can limit denitrification because the process is carried out primarily by heterotrophic bacteria. Long-term cultivation of agricultural soils, for example, can reduce soil organic matter concentrations enough to limit denitrification. Denitrification, as estimated from major components of the global nitrogen budget (Box 9.2), is quantitatively important, accounting for about a third of the nitrogen loss from the unmanaged terrestrial biosphere (Houlton and Bai 2009).

Box 9.2 Nitrogen Isotopes

Joseph M. Craine

The two isotopic forms of nitrogen (^{14}N and ^{15}N) differ in their number of neutrons but have the same number of protons. As with carbon isotopes (see Box 5.1), the ∂ notation represents the ratio of ^{15}N to ^{14}N relative to an atmospheric standard. Like carbon, the additional atomic mass causes the heavier isotope to react more slowly in some reactions. For the nitrogen cycle, three steps strongly discriminate against molecules that have the heavier isotope (Fig. 9.13). The first is nitrification, which leaves NH_4^+ enriched and NO_3^- depleted in the heavier isotope whenever only a portion of the NH_4^+ pool is nitrified. Second, gaseous nitrogen loss discriminates strongly, whether it is NH_3 volatilization, losses during nitrification, or denitrification, just as the evaporation of water discriminates against the heavier isotopes of hydrogen and oxygen (see Box 4.2). Lastly, the transfer of nitrogen from mycorrhizal fungi to plants leaves the fungi relatively enriched in nitrogen and the plants depleted in ^{15}N.

The changes in the isotopic composition of the different forms of nitrogen in different ecosystems have little functional significance, but the isotopic differences among plants provide key insights into the functioning of plants and the workings of the nitrogen cycle. The differences in $\partial^{15}N$ among plants in the same ecosystem can be used to infer the relative dependence on NH_4^+ vs. NO_3^-. All else being equal, plants that absorb more NH_4^+ are enriched relative to plants that absorb more NO_3^- because of fractionation during nitrification. At the stand level, the relative dependence of different plants on different forms of nitrogen cancel each other out, and stand-level ^{15}N signatures can be used as an index of nitrogen availability. When nitrogen availability is low, nitrogen tends to cycle as organic nitrogen, and plants rely more on mycorrhizal fungi and are relatively depleted in ^{15}N. As nitrogen availability increases, mineralization and inorganic nitrogen pools increase, leading to greater gaseous nitrogen loss and leaving behind enriched forms of nitrogen for plants. Under these conditions, plants also rely less on mycorrhizal fungi for nitrogen. Together, the enrichment of nitrogen pools and the decreasing reliance on mycorrhizal fungi leads to increases in plant $\partial^{15}N$ with increasing nitrogen availability, when ecosystems are compared.

At global scales, non-mycorrhizal plants with high nitrogen concentrations that occupy hot–dry ecosystems have the highest $\partial^{15}N$, while ectomycorrhizal plants from cold–wet ecosystems have the lowest $\partial^{15}N$. These patterns are also reflected in soil $\partial^{15}N$ as plant organic matter is returned to the soil and incorporated into soil organic matter. Besides understanding modern patterns of nitrogen availability, the signature of $\partial^{15}N$ remains in plant wood over time and therefore can be used to reconstruct past changes in ecosystem N availability.

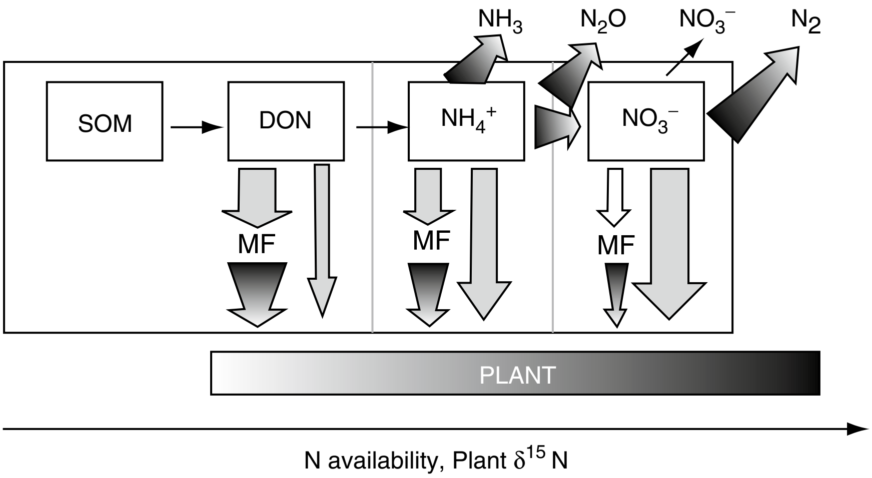


Fig. 9.13 Effect of isotopic fractionation on the ∂^{15}N of ecosystems. As nitrogen availability increases, plants shift from tapping predominantly dissolved organic nitrogen (DON) to ammonium to nitrate, while relying less on mycorrhizal fungi (MF). The width of each arrow indicates the relative contribution of mycorrhizal transfers and direct absorption by roots to total plant absorption. Steps that discriminate against ^{15}N are shown with shaded arrows, leading to a product that is less enriched in ^{15}N (lighter in color) and a substrate that is more enriched in ^{15}N (darker in color). Gaseous nitrogen loss leads to a progressive enrichment of soil available nitrogen from DON to NH_4^+ to NO_3^-. Plants tap progressively more enriched pools as nitrogen availability increases, causing plant ∂^{15}N to be a useful indicator of nitrogen availability when comparing ecosystems

Fires also account for large gaseous losses of nitrogen. The amount and forms of nitrogen volatilized during fire depend on the temperature of the fire. Fires with active flames produce considerable turbulence, are well supplied with oxygen, and release nitrogen primarily as NO_x. Smoldering fires release nitrogen in more reduced forms, such as ammonia (Goode et al. 2000). About a third of the nitrogen is emitted as N_2. Severe stand-replacing fires can cause loss of most of the ecosystem nitrogen, which is gradually replaced during post-fire succession (see Chap. 12). In cooler ground fires, less organic matter is combusted, and less nitrogen is lost. Fire suppression in some areas and biomass burning in others have altered the natural patterns of nitrogen cycling in many ecosystems.

Atmospheric Roles of Nitrogen Gases

The four nitrogen gases have different roles and consequences for the atmosphere. NH_3 that enters the atmosphere reacts with acids and thus neutralizes atmospheric acidity.

$$NH_3 + H_2SO_4 \leftrightarrow (NH_4)_2SO_4 \qquad (9.2)$$

With this reaction, NH_3 is converted back to NH_4^+, which can be deposited downwind on the surface of dry particles or as NH_4^+ dissolved in precipitation. Ammonia volatilization and deposition transfer nitrogen from one ecosystem to another. Ammonia gas itself also can be taken up through the stomates of plant leaves. Indeed, plants typically have an ammonia compensation point, analogous to their CO_2 compensation point for photosynthesis (see Chap. 5).

In the atmosphere, the nitrogen oxides (NO and NO_2, together known as NO_x) are in equilibrium with one another due to their rapid interconversion. NO_x is very reactive, and its concentration regulates several important atmospheric chemical reactions. High NO_x concentrations, for example, direct the oxidation of carbon monoxide, methane, and non-methane hydrocarbons into reactions that produce tropospheric ozone (O_3), an important component of photochemical smog in urban, industrial, and agricultural areas.

$$CO + 2O_2 \leftrightarrow CO_2 + O_3 \qquad (9.3)$$

At low NO_x concentrations, the oxidation of CO consumes O_3.

$$CO + O_3 \leftrightarrow CO_2 + O_2 \qquad (9.4)$$

In addition to its role as a catalyst that alters atmospheric chemistry and generates pollution, NO_x can be transported long distances and alter the functioning of ecosystems downwind. In the form of nitric acid, it is a principal component of acid deposition and adds both available nitrogen and acidity to the soil. In its gaseous NO_2 or HNO_3 forms, it can be absorbed through the stomata of leaves and be used in metabolism (see Chap. 5). It can also be deposited in particulate form, another type of inadvertent fertilization.

In contrast to the highly reactive NO_x, nitrous oxide (N_2O) has an atmospheric lifetime of 150 years and is not chemically reactive in troposphere. The low reactivity of N_2O contributes to a different environmental problem. N_2O is a greenhouse gas that is more than 200 times more efficient per molecule than is CO_2 in absorbing infrared radiation (see Chap. 2). In addition, N_2O in the stratosphere reacts with excited oxygen in presence of ultraviolet radiation to produce NO, which catalyzes the destruction of stratospheric ozone (O_3).

Given that the atmosphere is already 78% N_2, N_2 emissions to the atmosphere via denitrification have no significant atmospheric effects, although these losses may influence ecosystem nitrogen pools. Atmospheric N_2 has a turnover time of thousands of years.

Solution Losses

Nitrogen is lost by leaching as dissolved organic nitrogen from all ecosystems and as nitrate from nitrate-rich ecosystems. Undisturbed and unpolluted ecosystems lose relatively little nitrogen, primarily in the form of dissolved organic nitrogen (Hedin et al. 1995; Perakis and Hedin 2002). Although nitrate is also highly mobile in soils, plants and microbes absorb much of the nitrate before it leaches below the rooting zone of many ecosystems. Disturbance, however, often augments nitrate leaching from ecosystems by creating environmental conditions that stimulate nitrogen mineralization and by reducing the biomass of vegetation available to absorb nutrients (see Chap. 8). At the Hubbard Brook Forest in the northeastern U.S., for example, experimental removal of all vegetation caused large losses of nitrate, calcium, and potassium to the groundwater and streams (Fig. 9.14; Bormann and Likens 1979). Once vegetation began to regrow, however, the accumulating plant biomass absorbed most of the mineralized nutrients, and stream nutrient concentrations returned to their pre-harvest levels. Nitrate leaching also occurs when additions of fertilizer nitrogen or nitrogen deposition exceed plant and microbial nitrogen demands. Nitrate leaching can therefore be an indicator of **nitrogen saturation**, the changes that occur in ecosystem functioning when anthropogenic nitrogen additions relieve nitrogen limitation to plants and microbes (Aber et al. 1998; Driscoll et al. 2001). In general, the proportional increase in nitrogen losses via leaching and denitrification are larger than the increases in nitrogen pools retained within the ecosystem (Lu et al. 2010). In other words, nitrogen addition makes ecosystems more leaky.

Nitrate loss to groundwater can have important consequences for human health and for the ecological integrity of aquatic ecosystems. Under reducing conditions, nitrate is converted to nitrite, which can reduce the capacity of hemoglobin in animals to transport oxygen, producing anemia, especially in infants. Groundwater in areas of intensive agriculture often has nitrate concentrations that exceed public health standards.

Nitrogen leached from terrestrial ecosystems moves in groundwater to lakes and rivers, and is subsequently lost to the atmosphere through denitrification or transported to the ocean, as discussed earlier.

Solutions that move through the soil must maintain a balanced charge, with negatively charged ions like nitrate balanced by cations or protons. Therefore, every nitrate ion that leaches from soil carries with it a cation such as calcium,

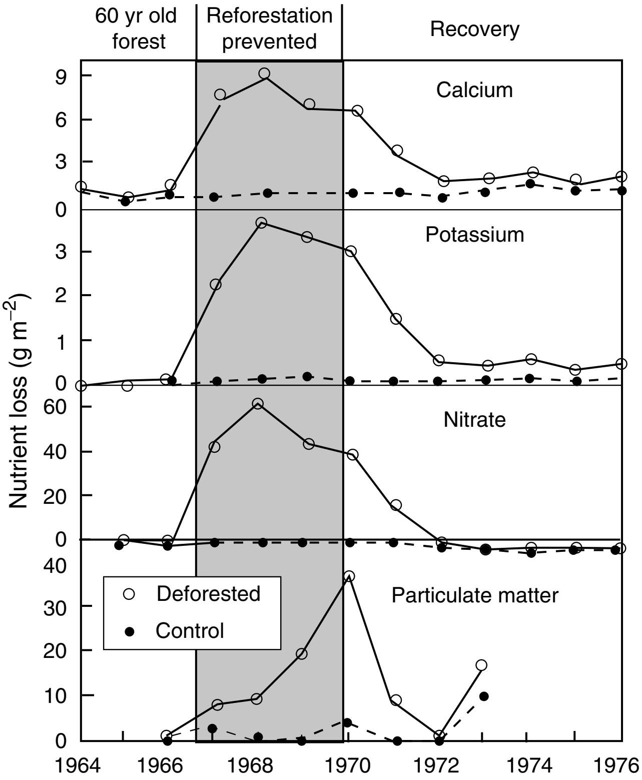


Fig. 9.14 Losses of calcium, potassium, nitrate, and particulate organic matter in stream water before and after deforestation of an experimental watershed at Hubbard Brook in the northeastern U.S. The shaded area shows the time interval during which vegetation was absent due to cutting of trees and herbicide application. Redrawn from Bormann and Likens (1979)

potassium, and ammonium to maintain charge balance. When cation loss by leaching exceeds the rate of cation supply by weathering plus deposition, the net loss of cations can lead to cation deficiency (Driscoll et al. 2001). After these nutrient cations are depleted, nitrate takes with it H^+ or Al^{3+}, which are deleterious to downstream ecosystems. Nitrification also generates acidity:

$$2NH_4^+ + 3O_2 \leftrightarrow 2NO_2^- + H_2O + H^+ \qquad (9.5)$$

The hydrogen ion released in this reaction exchanges with other ions on cation exchange sites in the soil, making these cations more vulnerable to leaching loss.

Erosional Losses

Erosion is a natural pathway of nitrogen loss that often increases dramatically after land-use changes. As with leaching, erosional losses of nitrogen include both organic and inorganic forms, although organic forms associated with soil aggregates and particles are the most important erosional fluxes.

Other Element Cycles

Differences among elements in source (rocks or atmosphere), chemical properties, and plant demand lead to predictable patterns and rates of element cycling. Because most plants have similar stoichiometric ratios of elements (see Chap. 8), there are broad similarities in the patterns of cycling of all essential elements that cycle through ecosystems (Sterner and Elser 2002). This stoichiometry creates a functional linkage, as these elements cycle through vegetation, just as observed in aquatic ecosystems. Productive ecosystems, for example, cycle larger quantities of all essential nutrients through vegetation than do less productive ecosystems. Despite these broad similarities among element cycles, there are important differences in cycling patterns among both elements and ecosystems that depend on the source (rocks or atmosphere), chemical properties, and quantities of different elements required by vegetation. The abiotic processes that provide elements to ecosystems (especially weathering and atmospheric deposition) generally have very different element ratios than those that govern cycling through organisms, and this interplay of biological and geological stoichiometries adds richness and complexity to our analysis of element cycling in terrestrial ecosystems.

Ecosystems differ substantially in the availability of various rock-derived nutrients, depending on parent material and the erosional and weathering history of the site. Limestone, for example, which is derived from marine sediments, often contains substantial phosphorus and is less likely to give rise to phosphorus-limited ecosystems than rocks containing less phosphorus. In contrast, the availability of atmospherically derived nutrients like nitrogen depends strongly on the biological interactions among organisms. The tightness of element cycling within ecosystems also depends on both their solubility in water and the quantities required by vegetation. Chloride, for example, which is highly soluble and required in small quantities by vegetation, has a much more open cycle than do sparingly soluble essential macronutrients like phosphorus.

Beyond these broad generalities, however, the specific properties of elements and their use by organisms generate important differences among elemental cycles. We briefly sketch the major features of the cycling of macronutrients that most often limit the productivity of ecosystems (nitrogen, phosphorus, and potassium) and give examples of macronutrients that less frequently limit productivity (calcium and sulfur), micronutrients that are required in very small quantities (chloride), and elements that are not required and are potentially toxic to organisms (lead).

Phosphorus

Phosphorus is the nutrient whose cycling through vegetation is most tightly coupled to nitrogen. These two nutrients are usually least available in the soil solution relative to annual plant requirement (see Table 8.3) and therefore most often limit or co-limit plant productivity (Elser et al. 2007). Nitrogen and phosphorus are essential components of the energetic engines of plant production (photosynthesis and respiration). It is therefore not surprising that there are many similarities in their patterns of cycling through vegetation. Mycorrhizal fungi play an important role in the absorption of both nutrients by breaking down nitrogen- and phosphorus-containing particulate organic compounds and transporting the nutrients to plant roots more rapidly than would occur by diffusion. Ectomycorrhizae typical of temperate and high-latitude forests are particularly important in nitrogen acquisition, and arbuscular mycorrhizae typical of grasslands and tropical forests are particularly important in phosphorus acquisition. Plants allocate both nutrients preferentially to metabolically active, resource-acquiring tissues (leaves and fine roots), creating an amplifying (positive) feedback that enhances the capacity of plants to capture additional resources. About half of leaf nitrogen and phosphorus are resorbed from leaves during senescence.

Although these common features link the nitrogen and phosphorus cycles, some processes strengthen this coupling, and others tend to disrupt it (Chapin and Eviner 2004). Within organisms, this coupling is strengthened by ion-specific nutrient absorption adjustments that up-regulate nitrate and ammonium absorption in nitrogen-limited plants and up-regulate phosphate absorption in phosphorus-limited plants (see Table 8.5). Thus plants and the detritus that they produce tend to cycle nitrogen and phosphorus in a ratio that is favorable for plant growth (N:P molar ratio of about 28; Sterner and Elser 2002; McGroddy et al. 2004), although this ratio is quite variable within and among ecosystems (Sterner and Elser 2002; Townsend et al. 2007). At the ecosystem scale over years to decades, nitrogen fixation tends to add nitrogen to nitrogen-limited ecosystems, and denitrification and nitrate leaching tend to remove nitrogen in anaerobic microsites of ecosystems where available nitrogen accumulates in excess of plant and microbial requirements. These fluxes are quantitatively large and strongly influence the nitrogen concentration and its isotopic composition at global scales (Houlton and Bai 2009). These processes strengthen the coupling between nitrogen and phosphorus cycles and generate N:P ratios that are favorable for plants and microbes.

There is also a relatively consistent ratio of nitrogen to organic phosphorus in soils (13.1 ± 0.8) and microbial biomass (6.9 ± 0.4, geometric mean ± SE) across terrestrial ecosystems (Fig. 9.15; Cleveland and Liptzin 2007). As in the ocean and fresh waters (Sterner and Elser 2002), variation in phosphorus concentration accounts for much of the variation in N:P ratios among ecosystems. Microbial N:P ratio, for example, is higher in forests than in grasslands, due to lower microbial P concentrations in forests (Cleveland and Liptzin 2007).

The higher N:P ratio of plants (28:1) than of microbes (7:1) may reflect differences in their biology. Microbes have a higher growth potential than plants, given the need to respond rapidly in a highly variable soil environment. This should require high phosphorus concentrations (low N:P ratio) to support rapid protein synthesis (Sterner and Elser 2002). Plants, in contrast, have a high nitrogen requirement (high N:P ratio) for photosynthesis (half of the nitrogen in leaves). The differences in observed N:P ratios (McGroddy et al. 2004; Cleveland and Liptzin 2007) therefore make sense. We expect plants to be relatively nitrogen-limited and microbes to be relatively phosphorus-limited in the same environment. Each group should adjust nutrient acquisition and release to meet their requirements and should return dead organic matter with an N:P ratio characteristic of their biomass. Through these processes, we expect soil to have an N:P ratio intermediate between that of plants and microbes, as is observed (Cleveland and Liptzin 2007).

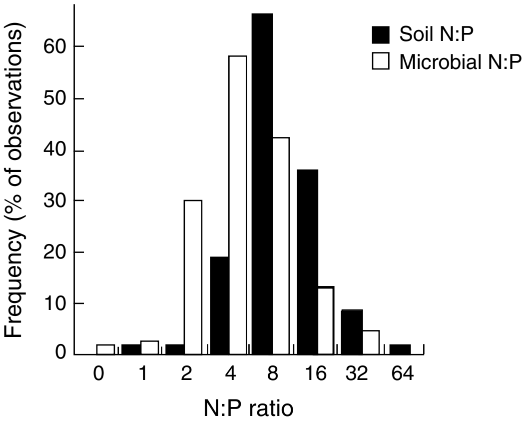


Fig. 9.15 Frequency distribution of N:P ratios in soils and microbial biomass on a $\log_2$ scale. Redrawn from Cleveland and Liptzin (2007)

Differences in the chemistry of nitrogen and phosphorus weaken the coupling of their cycles, particularly over long time scales (decades to millennia; Chapin and Eviner 2004). The two elements enter ecosystems through radically different pathways, nitrogen from a constantly available atmosphere pool through nitrogen fixation and phosphorus from the weathering of primary minerals that become depleted by weathering over millions of years (see Fig. 3.5). On young landscapes, for example, weathering of phosphorus-containing apatite by the carbonic acid generated from soil respiration releases phosphorus in available forms at a time when nitrogen often is in short supply (Eq. 9.6).

$$Ca_5(PO_4)_3 + 4H_2CO_3 \leftrightarrow 5Ca^{2+} + 3HPO_4{}^{2-} + 4HCO_3{}^{-} + H_2O \qquad (9.6)$$

This weathering source of phosphorus can be depleted over time, however, especially in wet areas outside the influence of glacial–interglacial cycles, and where geological uplift and erosion are slow. Once it is depleted, there is little or no internal source of phosphorus, and phosphorus inputs are derived primarily from the transport of dust from agricultural or arid areas upwind. Accordingly, the supply of nitrogen vs. phosphorus is decoupled at the ecosystem scale, and ecosystems on ancient soils are more likely to be constrained by phosphorus than by nitrogen (Vitousek 2004).

Microbial processing of dead organic matter can weaken the coupling of phosphorus and nitrogen cycles. Phosphorus turnover is somewhat less tightly linked to decomposition than is nitrogen because the ester linkages that bind phosphorus to carbon (C-O-P) can be cleaved enzymatically without breaking down the carbon skeleton. Nitrogen, in contrast, is more closely coupled to carbon; it is directly bonded to the carbon skeletons of organic matter (C-N) and is generally released by breaking the carbon skeleton into amino acids and other dissolved organic nitrogen-containing compounds. The decomposition process fragments organic matter and exposes the C-O-P bonds to enzymatic attack. Low soil phosphorus availability and high nitrogen availability induces plants and microbes to invest nitrogen in enzymes to acquire phosphorus (Olander and Vitousek 2000). Plant roots and their mycorrhizal associates, particularly arbuscular mycorrhizae, produce phosphatases that cleave ester bonds in organic matter to release phosphate (PO_4^{3-}). Phosphorus therefore cycles quite tightly between organic matter and plant roots in many ecosystems. In tropical forests, for example, mats of mycorrhizal roots in the litter layer produce phosphatases that cleave phosphate from organic matter. Mycorrhizal roots directly absorb much of this phosphate before it interacts with the mineral phase of the soil. Plant and microbial phosphatases are induced by low soil phosphate, as long as there is enough nitrogen to produce these nitrogen-rich enzymes. This contrasts with protease, whose activity correlates more strongly with microbial activity than with concentrations of soil organic nitrogen.

Microbial biomass often accounts for 20–30% of the organic phosphorus in soils (Smith and Paul 1990; Jonasson et al. 1999), much larger than the proportion of microbial carbon (about 2%) or nitrogen (about 4%). Microbial biomass is therefore an important reservoir of potentially available phosphorus, particularly in ecosystems with highly basic or acidic soils that strongly bind phosphorus to mineral surfaces. Microbial phosphorus is potentially more available than inorganic phosphate because it is protected from reactions with the mineral phase of soils, as described later. Although C:N ratios are often considered critical for understanding ecosystem nutrient cycling, C:P ratios of dead organic matter can also be critical in controlling the balance between phosphorus mineralization and immobilization and therefore the supply of phosphorus to plants.

Chemical reactions with soil minerals play a key role in controlling phosphorus availability in soils. Unlike nitrogen, phosphorus undergoes no oxidation–reduction reactions in soils and has no important gas phases. In addition, many of the reactions that control phosphorus availability are geochemical rather than biological in nature. Phosphate (PO_4^{3-}) is the main form of available inorganic phosphorus in soils. Phosphate is initially electrostatically attracted to positively charged sites on minerals through anion exchange. Once there, phosphate can become increasingly tightly bound (and correspondingly unavailable to plants) as it forms one or two covalent bonds with the metals on the mineral surface. Phosphorus can also bind with soluble minerals (especially iron oxides) to form insoluble precipitates. These precipitation reactions help to explain why highly weathered tropical soils (oxisols and ultisols) have extremely low phosphorus availability and why the growth of forests on those soils is often phosphorus-limited (see Chap. 3). The silicate clay minerals that dominate temperate soils fix phosphate to a lesser extent than do the oxides of tropical oxisols.

Phosphate availability is quite sensitive to pH. At low pH, iron, aluminum, and manganese are quite soluble and react with phosphate to form insoluble compounds:

$$\underbrace{Al^{3+} + H_2PO_4^{-} + 2H_2O}_{\text{soluble}} \leftrightarrow 2H^{+} + \underbrace{Al(OH)_2H_2PO_4}_{\text{insoluble}} \tag{9.7}$$

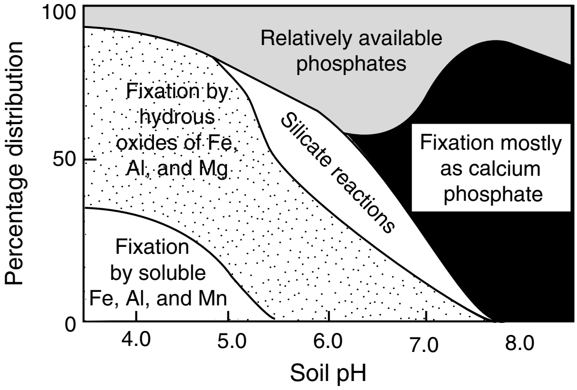


Fig. 9.16 Effect of pH on the major forms of phosphorus present in soils. The low solubility of phosphorus compounds at low and high pH result in a relatively narrow window of phosphate availability near pH 6.5. Redrawn from Brady and Weil (2001)

In soils with high concentrations of exchangeable calcium and $CaCO_3$, which typically occur at high pH, calcium phosphate precipitates, reducing phosphate availability in solution:

$$\underset{\text{soluble}}{Ca(H_2PO_4)_2} + 2Ca^{++} \leftrightarrow \underset{\text{insoluble}}{Ca_3(PO_4)_2} + 4H^+ \qquad (9.8)$$

Precipitation of calcium phosphate is one of the main reasons that phosphate fertilizer rapidly becomes unavailable in calcium-rich temperate agricultural ecosystems. Due to the precipitation reactions that occur at high and low pH, phosphorus is most available in a narrow range around pH 6.5 (Fig. 9.16).

Organic compounds in the soil also regulate, both directly and indirectly, phosphorus binding and availability. Charged organic compounds, for example, can compete with phosphate ions for binding sites on the surfaces of oxides or can chelate metals and prevent their reaction with phosphate. Both processes increase phosphate availability in mineral soils. On the other hand, organic compounds form complexes with iron, aluminum, and phosphate that protect these compounds from enzymatic attack. In tropical allophane soils, these complexes constitute a major sink for phosphorus.

Much of the phosphorus that precipitates as iron, aluminum, and calcium compounds is essentially unavailable to plants and is referred to as **occluded phosphorus**. During soil development, primary minerals gradually disappear as a result of weathering and erosional loss. The mass of phosphate in soils tends to shift from mineral, organic, and non-occluded forms to occluded and organically bound forms, causing a shift from nitrogen to phosphorus limitation in ecosystems over long time scales (see Fig. 3.5; Crews et al. 1995).

The tight binding of phosphate to organic matter or to soil minerals in most soils causes 90% of the phosphorus loss to occur through surface runoff and erosion of particulate phosphorus rather than through leaching of soluble phosphate to groundwater (Tiessen 1995). Two-thirds of the dissolved phosphorus that enters groundwater is organic and therefore less reactive with soil minerals.

Sulfur

Sulfur cycling is tightly coupled to cycling of nitrogen and phosphorus in unpolluted ecosystems, but sulfur pollution uncouples element cycles by enhancing cation loss. Sulfur cycling in unpolluted ecosystems is tightly coupled to the cycling of nitrogen and phosphorus because sulfur is an essential component of proteins and therefore, like nitrogen and phosphorus, is needed to produce metabolically active tissues such as leaves and fine roots. The control over sulfur mineralization from dead organic matter is intermediate between that of nitrogen and phosphorus because sulfur occurs in both carbon-bonded and ester-bonded forms. The ester-bonded forms are sulfur-storage compounds produced by plants under conditions of high sulfur availability. Under sulfur-limiting conditions, plants produce mainly carbon-bonded forms of sulfur, so its mineralization is determined by the carbon demand of microbes, just as with nitrogen (McGill and Cole 1981). Under high-sulfur conditions, however, microbes preferentially mineralize ester-bonded forms of sulfur at a rate that depends on sulfur demand by plants and microbes, just as phosphorus mineralization depends on phosphorus demands of plants and microbes (Chapin and Eviner 2004). Because it is a component of most enzymes, including the nitrogenase of nitrogen fixers, sulfur availability in highly weathered soils of unpolluted areas can limit nitrogen inputs to ecosystems and therefore plant production and nutrient turnover.

Like nitrogen, inorganic sulfur undergoes oxidation–reduction reactions and is therefore sensitive to oxygen availability in the environment. In anaerobic soils, sulfate acts as an electron acceptor that allows microbes to metabolize organic carbon for energy, with hydrogen sulfide being produced as a by-product. In aerobic environments, however, reduced sulfur can be an important energy source for bacteria. The high productivity of deep-sea vents, for example, is based entirely on the oxidation of H_2S from the vents.

Rock weathering, which, together with atmospheric deposition of marine aerosols, is the primary natural source of sulfur in most ecosystems, is increasingly supplemented by atmospheric inputs in the form of acid rain. Combustion of fossil fuels produces gaseous SO_2, which dissolves in cloud droplets to produce H_2SO_4, a strong acid that is a major component of acid rain. As sulfate leaches from soils of ecosystems exposed to acid rain, it carries with it cations such as potassium and magnesium, depleting available pools within the soil and making vegetation demands for these cations increasingly dependent on weathering inputs. In other words, it reduces the tightness of cation recycling in ecosystems. Sulfur compounds in the atmosphere also play critical roles as aerosols, which increase the albedo of the atmosphere and therefore cause climatic cooling (see Chap. 2).

Essential Cations

Rock weathering and atmospheric inputs are the primary inputs of potassium, calcium, and magnesium, the cations required in largest amounts by plants. As with nitrogen, phosphorus, and sulfur, the quantities of these cations cycling in ecosystems from soils to plants and back to soils are much larger than are annual inputs to and losses from ecosystems. Unlike those elements, however, many soils contain a relatively large exchangeably bound pool of cations, whose availability in the soil solution is largely governed by exchange reactions. Their supply depends on the cation exchange capacity of the soil and its base saturation (see Chap. 3), which, in turn, are influenced by parent material and weathering characteristics. Calcium is an important structural component of plant and fungal cell walls. Its release and cycling therefore depends on decomposition in a way somewhat similar to that of nitrogen and phosphorus (Fig. 9.17). Potassium, on the other hand, occurs primarily in cell cytoplasm and is released through the leaching action of water moving through live and dead organic material. Magnesium is intermediate between calcium and potassium in its cycling characteristics. Potassium limits plant production in some ecosystems, but calcium concentration in the soil solution of most ecosystems is so high that it is actively excluded by plant cells during the absorption process (see Chap. 8). Availability of calcium and other cations may be low enough to limit plant production on some old, highly weathered tropical soils.

These cations have no gaseous phase, but atmospheric transfers of these elements (and of essential micronutrients) in dust can be an important pathway of loss by wind erosion from deserts and agricultural areas and an important input to the open ocean and to ecosystems on highly weathered parent materials. Cations can also be lost via leaching. Nitrate, sulfate, and other anions that are leached from ecosystems must be accompanied by cations to maintain electrical neutrality. Intensively fertilized agricultural fields, for example, are prone to cation leaching loss.

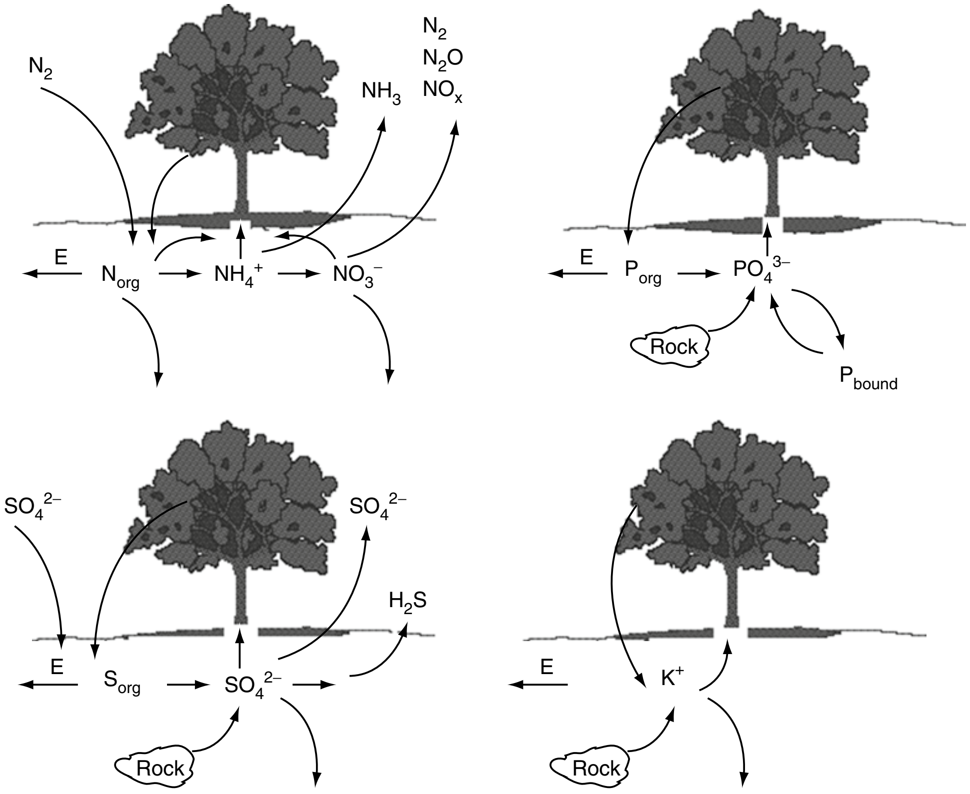


Fig. 9.17 Comparison of natural element cycles with respect to the relative importance of internal recycling, inputs, and outputs. Inputs of nitrogen come primarily from the atmosphere, whereas inputs of phosphorus and potassium come primarily from rocks. Sulfur comes from both the atmosphere and rocks. Over long time scales, atmospheric inputs of all elements can be important. Element losses occur through downward leaching, erosion (E), and, in the case of nitrogen and sulfur, gaseous loss

The declines in forest production observed in Europe and the eastern U.S. in response to acid rain are at least partly a consequence of calcium and magnesium deficiencies induced by cation leaching (Schulze 1989; Aber et al. 1998; Driscoll et al. 2001).

Why does phosphorus rather than rock-derived cations most often limit biological processes in highly weathered sites? The major cations, especially calcium, are absorbed by organisms in much larger quantities than is phosphorus and are more readily leached from soils. In Hawai'i, rock-derived calcium, magnesium, and potassium virtually disappear within 100,000 years but do not limit forest production anywhere on the sequence (Vitousek and Farrington 1997; Vitousek 2004). Atmospheric inputs of cations prevent these elements from becoming limiting in Hawai'i, and likely in many other places. Marine-derived aerosols containing calcium, magnesium, and potassium are deposited on forests in Hawai'i through rain and cloud droplets. Phosphorus concentrations in marine aerosols are low, however, because high phosphorus demands by marine organisms maintain a low concentration in surface waters. The atmospheric inputs of calcium are 10-fold less than weathering inputs in young sites, but are nearly a 100-fold greater than weathering inputs in older sites (Vitousek 2004). In continental interiors, dust from semi-arid and other sparsely vegetated areas is a major source of cations. Even in Hawai'i, dust from Asia, over 6,000 km away, is an important input of phosphorus, especially during glacial times, when vegetation cover was sparse and wind speeds were high (Box 9.3; Chadwick et al. 1999). In situ weathering of parent material is therefore not always the dominant input of minerals to ecosystems.

Box 9.3 Geochemical Tracers to Identify Source of Inputs to Ecosystems

Geochemical tracers have been used to identify dust and determine its rate of input to the Hawaiian Islands. Hawaiian rocks are derived from Earth's mantle, whereas Asian dust comes from the crust. These two sources differ in the ratio of two isotopes of neodynium, in the ratio of europium to other lanthanide elements, and in the ratio of thorium to halfnium. All of these elements are relatively immobile in soils, so changes over time in the isotopic or elemental ratios can be used to calculate time-integrated inputs of Asian dust. Knowing the phosphorus content of the dust, it is then possible to calculate phosphorus inputs by this pathway. Atmospheric inputs of phosphorus are much lower than weathering for the first million years or more of soil development. However, by four million years, rock-derived phosphorus has nearly disappeared, and Asian dust provides most of the phosphorus input to the soil. The biological availability of phosphorus is low in old sites, but it would be much lower were it not for inputs of Asian dust, most of it transported more than 10,000 years ago (Chadwick et al. 1999).

Micronutrients and Nonessential Elements

The cycling of micronutrients and nonessential elements is dominated by the balance between inputs from weathering, precipitation and dust, and outputs in leaching. Vegetation plays relatively little role in the balance between inputs and outputs of elements that are required in small quantities (e.g., chloride) or are not required by organisms (e.g., mercury and lead). Consequently, *external* cycling of elements (ecosystem inputs and outputs) dominates the cycling of nonessential elements, whereas *internal* cycling through vegetation dominates the cycling of essential elements (at least on annual to decadal time scales). The cycling of nonessential elements is therefore not strongly affected by successional changes in vegetation activity, whereas the losses of essential elements decline dramatically during early succession when organic matter and associated nutrients are accumulating in plant and microbial biomass (see Fig. 12.18; Vitousek and Reiners 1975).

Nitrogen and Phosphorus Cycling in Agricultural Systems

Intensive agricultural systems represent an endpoint in terrestrial nutrient cycling and an especially important one for human well-being as well as for their effects on surrounding ecosystems. Harvested crops remove nitrogen, phosphorus, and other nutrients from agricultural soils, and the higher yielding the agricultural system, the greater the removals of essential nutrients. Sustaining agricultural production requires replacing those nutrients, either through biological processes like nitrogen fixation or through the addition of mineral fertilizer or off-site plant or animal wastes to fields. These inputs are a dominant feature of agricultural nutrient cycles (Robertson and Vitousek 2009).

Globally, fertilizer is the major pathway of nutrient addition. These inputs have helped to keep world crop productivity ahead of human population growth. However, environmental costs of nutrient pollution from agriculture have been substantial, including the degradation of downstream water quality and eutrophication of coastal marine ecosystems (Fig. 9.1), the deposition of agriculturally derived nitrogen on downwind terrestrial ecosystems, the development of photochemical smog, and rising global concentrations of the powerful greenhouse gas nitrous oxide.

The fundamental challenge of nutrient management in grain crops in particular is easy to state, but hard to solve. The most economical way to add large quantities of nutrients is a single application of nitrogen-and phosphorus-rich fertilizer once during the cropping cycle, often near planting. At this time, the supply of available nitrogen and phosphorus is much greater than potential plant demand, and much of the fertilizer can be lost to the environment. Alternatively, additions of organically bound nutrients break down more slowly, so supply is less likely to radically exceed demand during the plant-growing season. However, typically they continue to break down during times that annual crops are inactive – after harvest and before planting in subsequent years, so again there are substantial time periods when supply exceeds demand, and high rates of nutrient loss are likely to occur. In contrast, nutrient supply (mainly through decomposition and mineralization) is more closely synchronized with plant nutrient demand in natural systems with perennial plants, and the microbial immobilization of nutrients that often are in short supply further serves to retain essential nutrients. The challenge, then, is to use agricultural practices and biological processes to increase the synchrony of nutrient supply and demand within intensive agricultural systems and to manage the fate of any nutrients that are lost, so they leave in environmentally benign forms (such as N_2) or are recaptured in riparian buffer strips or wetlands.

Crop yields and rates of nutrient input differ markedly among agricultural systems, as do the scientific and policy challenges that must be solved if we are to reduce the environmental footprint of intensive agriculture. The largest differences are associated with different levels of economic development (Vitousek et al. 2009b). In the poorest countries, rates of nitrogen and phosphorus application are less than those removed annually in harvested products – a deficit that contributes to continuing food insecurity in poor countries. These agricultural systems can persist only by drawing down the nutrient capital of soils, thereby decreasing their fertility and over time driving a cycle of degradation. In contrast, many rapidly developing economies have greatly increased both fertilizer applications and agricultural yields in recent decades. The transformation is particularly striking in China, where policy-driven increases in fertilizer use contributed to rising crop yields as China strived for food security. Nutrient additions to many fields far exceed those in the U.S. and Northern Europe, with rates of nitrogen and phosphorus application approaching 700 and 100 kg ha^{-1} $year^{-1}$ (70 and 10 g m^{-2} $year^{-1}$), respectively. These applications are much greater than the requirements of even the highest-yielding crops, and much of the excess fertilizer is lost to the environment, degrading both air and water quality (Ju et al. 2009). At one time, agricultural production in northwestern Europe followed a similar path. After World War II, national and later European Community policies to boost food security caused many areas to reach nitrogen and phosphorus surpluses within integrated crop/animal production systems as large and damaging as those now observed in China. Since the 1980s, however, increasingly stringent national and European Union regulations and policies have reduced nutrient surpluses. Despite these steps toward nutrient balance, however, agriculturally derived pollution remains substantial in both the air and water of northwestern Europe (Billen et al. 2007; Erisman et al. 2008).

The human costs of inadequate nutrient inputs in the poorest countries are substantial, and research, and policies that address those nutrient deficits can provide substantial human benefits (Sanchez 2010). In contrast, the excessive use of fertilizers in many rapidly developing economies has substantial human and environmental costs and provides equally substantial scientific challenges. In China, research in agricultural biogeochemistry has focused on developing cropping systems in which the supply of nutrients (via fertilizer or other nutrient inputs) is matched as closely as possible in time and space to the demands of growing crops. For example, Ju et al. (2009) demonstrated experimentally that with such practices, additions of nitrogen fertilizer could be cut in half without loss of yield or grain quality, thereby reducing nitrogen losses by >50%. Matson et al. (1998) described a similar solution to excessive fertilizer application to intensive wheat systems in Mexico. In these situations, reducing nutrient inputs, while maintaining or increasing yields, is beneficial agronomically, economically, and environmentally.

Experience in North America and Europe suggests that, even with reduced nutrient inputs, intensive agriculture will cause substantial fluxes of nutrients to downwind and downstream ecosystems. Reducing these losses will require additional efforts. Some practices that can contribute to reducing nutrient losses from agriculture are available now, such as additional technologies for placing or timing nutrient supply to crop needs, modifications to livestock diets, and the preservation or restoration of riparian vegetation strips (Cherry et al. 2008). Bolder efforts to redesign agriculture (e.g., by incorporating perennials into cropping systems) may also be needed. Overall, agricultural systems represent fertile ground for research that is based in and contributes to our fundamental understanding of nutrient cycling and that also contributes to human well-being and environmental quality.

Summary

Nutrients enter ecosystems through inflow from upstream (in aquatic systems), chemical weathering of rocks, the biological fixation of atmospheric nitrogen, and the deposition of nutrients from the atmosphere in rain, windblown particles, or gases. Human activities have greatly increased these inputs, particularly of nitrogen and sulfur, through combustion of fossil fuels, addition of fertilizers, and planting of nitrogen-fixing crops. Unlike carbon, the internal recycling of essential plant nutrients is much larger than the annual inputs and losses from the ecosystem, producing relatively closed nutrient cycles.

Most nutrients that are essential to plant production become available to plants through microbial release of elements from dead organic matter during decomposition. Microbial exoenzymes break down the large polymers in particulate dead organic matter into soluble compounds and ions that can be absorbed by microbes or plant roots. The net mineralization of nutrients depends on the balance between the microbial immobilization of nutrients to support microbial growth and the excretion of nutrients that exceed microbial growth requirements. The first product of nitrogen mineralization is ammonium. Ammonium can be converted to nitrate by autotrophic nitrifiers that use ammonium as a source of reducing power or by heterotrophic nitrifiers. Both plants and microbes use dissolved organic nitrogen, ammonium, and nitrate in varying proportions as nitrogen sources, when their growth is nitrogen-limited. Soil minerals and organic matter also influence nutrient availability to plants and microbes through exchange reactions (primarily with soil cations, except in some tropical soils that have a substantial anion exchange capacity), the precipitation of phosphorus with soil minerals, and the incorporation of nitrogen into humus.

Nutrients are lost from ecosystems through the leaching of elements out of the ecosystem in solution, emissions of gases, loss of nutrients adsorbed on soil particles in wind or water erosion, and the removal of materials in harvest. Human activities, as with nutrient inputs, often increase nutrient losses from terrestrial ecosystems.

The productivity of most rivers and streams is also co-limited by nitrogen and phosphorus. Nutrients spiral down rivers as they are mineralized from decomposing litter in one stream segment and absorbed by phytoplankton downstream. Nutrients spend 90% of their time in stream organisms attached in place, and 90% of their horizontal distance traveled in the dissolved phase between release from organisms in one place and subsequent absorption by another organism downstream.

Review Questions

1. What are the relative magnitudes of atmospheric inputs and mineralization from dead organic matter in supplying the annual nitrogen absorption by vegetation?
2. If Earth is bathed in di-nitrogen gas, why is the productivity of so many ecosystems limited by availability of nitrogen? What is biological nitrogen fixation? What factors influence the times and places where it occurs?
3. What are the mechanisms by which nitrogen moves from the atmosphere into terrestrial ecosystems?

4. What are the major steps in the mineralization of litter nitrogen to inorganic forms? What microbial processes mediate each step and what are the products of each step? Which of these processes are extracellular and which are intracellular?
5. What ecological factors account for differences among ecosystems in annual net nitrogen mineralization? How does each of these factors influence microbial activity?
6. What determines the balance between nitrogen mineralization and nitrogen immobilization in soils?
7. What factors determine the balance between plant absorption and microbial absorption of dissolved organic and inorganic nitrogen in soils?
8. How do ammonium and nitrate differ in mobility in the soil? Why? How does this influence plant absorption and susceptibility to leaching loss?
9. What is denitrification and what regulates it? What are the gases that can be produced, and what are their roles in the atmosphere?
10. What is the main mechanism by which phosphorus enters ecosystems?
11. What factors control availability of phosphorus for plant absorption? Why is phosphorus availability low in many tropical soils?
12. Why are mycorrhizae so important for plant acquisition of phosphorus?
13. What is the main pathway of phosphorus loss from terrestrial ecosystems?

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