The biogeochemistries of nitrogen and sulfur have much in common. Both are essential nutrients found primarily in organic forms in soils. Both move in soils and plants mostly in the form of anions. Both undergo oxidation and reduction to form gases, and both are responsible for serious environmental problems. This chapter explores the stories of these two elements, starting with nitrogen.\(^1\)

More money and effort are spent on the management of nitrogen than on any other nutrient element, and for good reason. Deficiencies or excesses of nitrogen have major impacts on the health and productivity of the world’s ecosystems. Were it not for the biological fixation of nitrogen from the atmosphere by certain soil microbes, and for the recycling back to the soil of much of the nitrogen taken up by the vegetation, deficiencies of nitrogen would be ubiquitous, and most ecosystems would grind to a halt. Where humans harvest food from the land, these cycles have been disrupted. Yellowish leaves of nitrogen-starved crops forebode hunger or financial ruin for people in all corners of the globe. Nitrogen fertilizer is an expensive but often necessary input in agricultural systems. Its manufacture accounts for a large part of the fossil fuel energy used by the agricultural sector. The quest for protein—which contains about one-sixth nitrogen—by billions of humans is fueling demand for nitrogen fertilizer and transforming both global agriculture and the global N cycle.

Nitrogen excesses are now nearly as common as deficiencies and can adversely affect both human and ecosystem health. Nitrogen leaking from overly enriched soils can lead to nitrate pollution of groundwater, making it unfit for human or animal consumption. In addition, the movement of soluble nitrogen compounds from soils to aquatic systems can disrupt the balance of those systems, leading to algae blooms, declining levels of dissolved oxygen, and subsequent death of fish and other aquatic species. Yet another way in which nitrogen links soils to the wider environment is the ozone-destroying and climate-forcing action of nitrous oxide gas generated in soils. Clearly, soil processes are central to the global nitrogen cycle. The ecological, financial, and environmental stakes for the management of soil nitrogen are very high, indeed.

\(^1\)For a review of nitrogen in agriculture, with special emphasis on environmental and human health impacts, see Addiscott (2005). For how nitrogen interacts with Earth’s ecosystems, see Gruber and Galloway (2008). For current and future global nitrogen cycle processes under climate change, see Fowler et al. (2015).
13.1 INFLUENCE OF NITROGEN ON PLANT GROWTH AND DEVELOPMENT

Roles in the Plant. Healthy plant foliage generally contains 2.0–4.0% nitrogen, depending on plant species and age of the leaves. Nitrogen is an integral component of many essential plant compounds. It is a major part of all amino acids, the building blocks of all proteins—including the enzymes, which control virtually all biological processes. Other critical nitrogenous plant components include the nucleic acids, in which hereditary control is vested, and chlorophyll, which is at the heart of photosynthesis. Nitrogen is also essential for carbohydrate use within plants. A good supply of nitrogen stimulates root growth and development, as well as the uptake of other nutrients.

Plants respond quickly to increased availability of nitrogen, their leaves turning deep green in color. Nitrogen increases the plumpness of cereal grains, the protein content of both seeds and foliage, and the succulence of leaves, stems and tubers. It can dramatically stimulate plant productivity, whether measured in tons of grain, volume of lumber, carrying capacity of pasture, or thickness of lawn.

Deficiency. Plants deficient in nitrogen tend to exhibit chlorosis (yellowish or pale green leaf colors), a stunted appearance, and thin, spindly stems (Figure 13.1). In nitrogen-deficient plants, the protein content is low and the sugar content is usually high, because carbon compounds normally destined to build proteins cannot do so without sufficient nitrogen. Nitrogen is quite mobile (easily translocated) within the plant. When plant uptake is inadequate, nitrogenous compounds in the oldest leaves are broken down and the nitrogen transferred to the newest foliage, causing the older leaves to show pronounced chlorosis. The older leaves of nitrogen-starved plants are therefore the first to turn yellowish, typically becoming prematurely senescent and dropping off (Figures 13.1a,b). Nitrogen-deficient plants often have a low shoot-to-root ratio, and they mature more quickly than healthy plants. The negative effects of nitrogen deficiency on plant size and vigor are often dramatic (Figure 13.1a).

Oversupply. When too much nitrogen is available, excessive vegetative growth occurs; the cells of the plant stems become enlarged but relatively weak, and the top-heavy plants are prone to falling over (lodging) with heavy rain or wind (Figure 13.1d). High nitrogen applications may delay plant maturity and cause the plants to be more susceptible to disease (particularly fungal disease) and to insect pests. These problems are especially noticeable if other nutrients, such as potassium, are in relatively low supply.

An oversupply of nitrogen degrades crop quality, resulting in undesirable color and flavor of fruits and low sugar and vitamin levels of certain vegetables and root crops. Flower production in ornamentals is reduced in favor of abundant foliage. An oversupply can also cause the buildup of nitrogen in the form of nitrates that are harmful to livestock in the case of forage and to babies in the case of leafy vegetables. Growth-inhibiting environmental conditions (e.g., drought; dark, cloudy days; or cool temperatures) can exacerbate the accumulation of nitrate in tissues because plant conversion of nitrate into protein is slowed. The leaching of excess nitrogen from the soil is a major water pollution problem particularly degrading to groundwater and downstream estuaries (see Sections 13.14 and 16.2).

Forms of Nitrogen Taken up by Plants. Plant roots take up nitrogen from the soil principally as dissolved nitrate (NO$_3^-$) and ammonium (NH$_4^+$) ions. Although certain plants grow best when provided mainly with one or the other of these forms, a relatively equal mixture of the two ions gives the best results with most plants. As explained in Chapter 9 (see Sections 9.1 and 9.5 and Figure 9.14), uptake of ammonium markedly lowers the pH of the rhizosphere soil while uptake of nitrate tends to have the opposite effect. These pH changes, in turn, influence the uptake of other ions such as phosphates and micronutrients. In addition to NO$_3^-$ and NH$_4^+$ ions, nitrite ions (NO$_2^-$) can also be taken up, but fortunately only trace quantities of this toxic ion usually occur in field soils.

Although NO$_3^-$ and NH$_4^+$ ions are the dominant forms of N taken up by plants in many systems, numerous plants have been shown to also take up low molecular weight dissolved organic compounds (mainly soluble proteins, amino acids, and urea). Generally, when soluble
organic and inorganic N sources are both present in equal amounts, the plant uptake of organic N is an order of magnitude smaller than the uptake of mineral N. However, there is much variation, even within a family of plants. For example, among the Gramineae, sorghum and rice seem to efficiently take up soluble protein N, while corn and millet do not. Also, some evidence suggests that if grown with soil solutions relatively high in organic N and low in inorganic N, some plant species may become conditioned to utilize organic N more effectively. The direct uptake of soluble organic N is of particular significance in natural grasslands and forests.

13.2 DISTRIBUTION OF NITROGEN AND THE NITROGEN CYCLE

Most of Earth’s nitrogen is either in the atmosphere (about 4,000 Eg = exagrams = $10^{18}$ g) or in crustal rocks (about 2,000 Eg). We will not consider here the vast pool of N contained in igneous rocks deep in the planet’s crust, where it is effectively out of contact with the atmosphere.

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2To read about the evolution of Earth’s nitrogen cycle, its disruption during the past century by industrial agriculture, and its inevitable microbial rebalancing, with or without human adaptation, see Canfield et al. (2010).
biosphere. The air above each hectare of the Earth’s surface contains some 75,000 Mg of nitrogen. The atmosphere, which is 78% gaseous nitrogen (N₂), would appear to be a virtually limitless reservoir of this element. However, the very stable triple bond between two nitrogen atoms (N≡N) makes this gas extremely inert and not directly usable by plants or animals. Little nitrogen would be found in soils and little vegetation would grow in terrestrial ecosystems around the world were it not for certain natural processes (principally nitrogen fixation by microbes and lightning) that can break this triple bond and form reactive nitrogen (see Section 13.10). In reactive nitrogen compounds the N is usually bonded to hydrogen, oxygen, or carbon (e.g., NH₄⁺, NO₃⁻, N₂O, and amino acids, R—C—NH₂) making it easily used in a variety of biological and chemical reactions.

Much of the reactive N is mobile and large amounts move between the atmosphere, the land, and the oceans (Figure 13.2). Nitrogen moves from the atmospheric N≡N pool to the terrestrial and marine reactive N pools mainly by various categories of nitrogen fixation (Section 13.9). Burning of fossil fuels also adds reactive N, initially mainly to the land. Nitrogen is transferred from land to water and eventually to the oceans principally by leaching of nitrates and dissolved organic nitrogen (DON) and by atmospheric deposition. Finally, the cycle is brought full circle with the transfer of reactive nitrogen from land and water back to the atmosphere as N≡N and other nitrogen-containing gases, principally by certain microbial processes termed denitrification (see Section 13.8 and 13.9).

Most of the nitrogen in terrestrial systems is found in the soil, with A horizons normally ranging from 0.02 to 0.5% N by weight. A value of about 0.15% N would be representative for cultivated soils. A hectare of such a soil would contain about 3.5 Mg nitrogen in the A horizon and perhaps an additional 3.5 Mg in the deeper layers. In forests, the litter layer (O horizons) might contain 1–2 Mg of nitrogen in addition to that in the mineral soil. Thus, soils contain 10–20 times as much nitrogen as does the standing vegetation (including roots) of either forested or cultivated areas.

Most soil nitrogen is present as part of organic molecules, therefore, the distribution of soil nitrogen closely parallels that of soil organic matter (SOM), which typically contains about 5% nitrogen (see Sections 12.3 and 12.10).

Except where large amounts of chemical fertilizers have been applied, inorganic (i.e., mineral) nitrogen seldom accounts for more than 1–2% of the total nitrogen in the soil. Unlike the bulk of organic nitrogen, most mineral forms of nitrogen are quite soluble in water and may be easily lost from soils through leaching and volatilization.

---

Figure 13.2 The movement of nitrogen between Earth’s atmosphere (mainly N≡N), land masses (terrestrial ecosystems), and oceans (marine ecosystems). The arrows are labeled with the general processes they represent and the numbers in each arrow indicate the estimated global annual nitrogen flux in Tg/yr (teragrams or 10¹² g per year) via each process. The three main anthropogenic processes are labeled in yellow. (Redrawn and recalculated from data in Canfield et al. (2010).)

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¹The weathering of certain N-rich sedimentary rocks at the Earth’s surface may, however, contribute significant amounts of N to both forest tree nutrition and N loading to rivers in drainage water (Morford et al., 2011).
The Nitrogen Cycle

The nitrogen cycle has long been the subject of intense scientific investigation, because understanding the translocations and transformations of this element is fundamental to solving many environmental, agricultural, and natural resource–related problems. As an atom of nitrogen moves through the nitrogen cycle it appears in many different chemical forms. Each form has its own properties, behaviors, and consequences for the ecosystem. This cycle explains why vegetation (and, indirectly, animals) can continue to remove nitrogen from a soil for centuries without depleting the soil of this essential nutrient. The biosphere does not run out of nitrogen (or other nutrient elements) because it uses the same atoms over and over again. This cycling of N is highly visible in Figure 11.31, which shows a dark green circle of grass plants that have responded to the fungal release of N from the residues of previous grass growth.

The principal pools and forms of nitrogen, and the processes by which they interact in the cycle, are illustrated in Figure 13.3. This figure deserves careful study; we will refer to it frequently as we discuss each of the major processes of the nitrogen cycle.

Ammonium (NH\(_4^+\)) and nitrate (NO\(_3^-\)) are two critical forms of inorganic nitrogen which are subject to various fates in the N cycle (see the arrows leaving the nitrate and ammonium boxes in Figure 13.3). In addition to its possible loss by erosion and runoff, the N in NH\(_4^+\) can be subject to at least six fates: (1) immobilization by microorganisms; (2) removal by plant uptake; (3) anaerobic oxidation of NH\(_4^+\) in conjunction with nitrite (NO\(_2^-\)) to produce N\(_2\)O gas; (4) volatilization after being transformed into ammonia gas; (5) nitrification—the microbial oxidation of ammonium to nitrite and subsequently to nitrate; and (6) fixation or strong sorption in the interlayers of certain 2:1 clay minerals.

Similarly, in addition to loss by erosion and runoff, the N in NO\(_3^-\) is subject to six possible fates (note that some of these fates are shared with the N in NH\(_4^+\)): (1) immobilization by microorganisms; (2) removal by plant uptake; (3) microbial reduction to NO\(_2^-\) followed by conversion, along with ammonium, by anammox to N\(_2\)O gas; (4) denitrification—microbial reduction forming N\(_2\) and other nitrogen-containing gases which are lost to the atmosphere; (5) dissimilatory reduction by microbes to ammonium; and (6) loss to groundwater by leaching in drainage water. We will discuss these N transformations in subsequent sections of this chapter.

13.3 IMMOBILIZATION AND MINERALIZATION

Most (95–99%) soil nitrogen exists in large organic molecules that protect it from loss but also leave it unavailable for uptake by plant roots. Microbial decomposition breaks these large, insoluble N-containing organic molecules into smaller and smaller units with the eventual production of simple amino compounds, or amine groups (R—NH\(_3^+\)). Then the amine groups are hydrolyzed, and the nitrogen is released as ammonium ions (NH\(_4^+\)), which can be oxidized to the nitrate form. The enzymes that bring about this process are produced mainly by microorganisms (but some are produced by plant roots and soil animals) and include hydrolases and deaminases that break C—H and C—NH\(_2\) bonds. The enzymes may carry out the reactions inside microbial cells, but most often they are excreted by the microbes and work extracellularly in the soil solution or while adsorbed to colloidal surfaces. This enzymatic process termed mineralization (Figure 13.3) may be indicated as follows, using an amino compound (R—NH\(_2\)) as an example of the organic nitrogen source:

\[
\text{R—NH}_2 \xrightarrow{\text{ Mineralization }} \text{NH}_4^+ + \text{OH}^- + \text{R—OH} \xrightarrow{\text{ Immobilization }} \text{NH}_4^+ + \text{OH}^- + \frac{1}{2}\text{O}_2 \quad \text{energy} + \text{NO}_2^- \xrightarrow{\text{ energy}} \text{NO}_3^-
\]

(13.1)

Amino acids such as lysine (CH\(_2\)NH\(_2\)COOH) and alanine (CH\(_3\)CHNH\(_2\)COOH) are examples of these simpler compounds. The R in the generalized formula represents the part of the organic molecule with which the amino group (NH\(_3^+\)) is associated. For example, for lysine, the R is CH\(_2\)COOH.
Many studies have shown that about 1.5–3.5% of the organic nitrogen in A horizon soil mineralizes annually. In most soils, this rate of mineralization provides sufficient mineral nitrogen for normal growth of natural vegetation; in soils with relative high levels of organic matter, mineralization may provide enough mineral N for good crop yields, as well. Furthermore, isotope tracer studies of farm soils that have been amended with synthetic nitrogen...
fertilizers show that mineralized soil nitrogen constitutes a major part of the nitrogen taken up by crops. If the organic matter content of a soil is known, one can make a rough estimate of the amount of nitrogen likely to be mineralized during a typical growing season (Box 13.1).

The opposite of mineralization is immobilization, the conversion of inorganic nitrogen ions (NO$_3^-$ and NH$_4^+$) into organic forms (see Eq. (13.1) and Figure 13.3). Immobilization can take place by both biological and nonbiological (abiotic) processes. The latter probably involves chemical reactions with high C/N ratio organic matter and can be quite important in forested soils (Figure 13.4).

Most nitrogen immobilization occurs biologically when microorganisms decomposing organic residues require more nitrogen than they can obtain from the residues they are metabolizing. The microorganisms then scavenge NO$_3^-$ and NH$_4^+$ ions from the soil solution to incorporate into such cellular components as proteins, leaving the soil solution essentially devoid of mineral N. When the organisms die, some of the organic nitrogen in their cells may be converted into forms that make up the SOM, and some may be released as NO$_3^-$ and NH$_4^+$ ions. Mineralization and immobilization occur simultaneously in the soil; whether the net effect is an increase or a decrease in the mineral nitrogen supply depends primarily on the ratio of carbon to nitrogen in the organic residues undergoing decomposition (see Section 12.3).

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**BOX 13.1**

**CALCULATION OF NITROGEN MINERALIZATION**

If the organic matter content of a soil, management practices, climate, and soil texture are known, it is possible to make a rough estimate of the amount of N likely to be mineralized each year. The following equation may be used:

$$\text{kg N mineralized/ha 15 cm deep} = \left( \frac{A \text{ kg SOM}}{100 \text{ kg soil}} \right) \left( \frac{B \text{ kg soil}}{15 \text{ cm deep}} \right)$$

where

- $A =$ The amount of SOM in the upper 15 cm of soil, given in kg SOM per 100 kg soil (this is same value as the % SOM as is often reported by test labs). This value may range from close to zero to over 75% (in a Histosol) (see Section 3.9). Values between 0.5 and 5% are most common. Use a value of 2.5% (2.5 kg SOM/100 kg soil) for the example shown below.

- $B =$ For the weight of soil per hectare to the depth of 15 cm, $2 \times 10^6$ kg/ha is a reasonable estimate. See Section 4.7 to calculate the weight of such a soil layer if bulk density of a soil is known. In some soils it may be important to also consider deeper layers. Use $2 \times 10^6$ kg soil/ha 15 cm deep in the example shown below.

- $C =$ The amount of nitrogen in the SOM (see Section 12.3). Use the typical figure of 5 kg N/100 kg SOM in the example shown below.

- $D =$ The amount of SOM likely to be mineralized in one year for a given soil. This figure depends upon the soil texture, climate, and management practices. Values of around 2% are typical for a fine-textured soil, while values of around 3.5% are typical for coarse-textured soils. Slightly higher values are typical in warm climates; slightly lower values are typical in cool climates. Assume a value of 2.5 kg SOM mineralized/100 kg SOM for the example shown below.

The amount of nitrogen likely to be released by mineralization during a typical growing season may be calculated by substituting the example values given above:

$$\text{kg N mineralized/ha 15 cm deep} = \left( \frac{2.5 \text{ kg SOM}}{100 \text{ kg soil}} \right) \left( \frac{2 \times 10^6 \text{ kg soil}}{15 \text{ cm deep}} \right)$$

$$\text{kg N mineralized/ha 15 cm deep} = \left( \frac{5 \text{ kg N}}{100 \text{ kg SOM}} \right) \left( \frac{2.5 \text{ kg SOM mineralized}}{100 \text{ kg SOM}} \right)$$

$$\text{kg N mineralized/ha} = \left( \frac{2.5}{100} \right) \left( \frac{2 \times 10^6}{15} \right) \left( \frac{5}{100} \right)$$

$$\text{kg N mineralized/ha} = 62.5 \text{ kg N/ha}$$

Most nitrogen mineralization occurs during the growing season when the soil is relatively moist and warm. Contributions from the deeper layers of this soil might be expected to bring total nitrogen mineralized in the root zone of this soil during a growing season to over 120 kg N/ha.

These calculations estimate the nitrogen mineralized annually from a soil that has not had large amounts of organic residues added to it. Animal manures, legume residues, or other nitrogen-rich organic soil amendments would mineralize much more rapidly than the native SOM and thus would substantially increase the amount of nitrogen available in the soil.
13.4 DISSOLVED ORGANIC NITROGEN

Until recently, most studies of nitrogen uptake and leaching focused exclusively on mineral N, especially nitrate. However, modern analytical tools have now shown conclusively that plant uptake and leaching losses in both natural and agroecosystems involved nitrogen-containing organic compounds. These compounds either actually exist dissolved in the soil solution (DON) or can be easily extracted out of soil samples using simple salt solutions (SON). Thus the DON is a portion of the SON (Figure 13.5). The DON generally accounts for between 0.1 and 3% of the total N in soils, a pool size similar to that of mineral nitrogen ($NH_4^+$ and $NO_3^-$). In fact, where organic manures have been applied to arable soils or where animal urine is applied to grassland, DON contents are often considerably higher than those of mineral nitrogen. The nitrogen mobilized from the litter of some forest species may have DON:inorganic N ratios of 10:1 or higher.

**Plant Uptake of DON.** In nitrogen-limited ecosystems, such as those in strongly acidic and infertile soils (including some organic soils), DON may be the primary source of absorbed nitrogen. This helps explain the fact that plant growth, particularly of some forest species, is considerably greater than one would expect based on the limited supply of inorganic nitrogen at any one time. Low molecular weight compounds in the DON, such as amino acids, may be taken up directly by plant roots, or they may be assimilated through mycorrhizal associations.

**Figure 13.5** Soluble organic nitrogen (SON) is comprised of compounds that can be easily dissolved in water or mild salt solutions. It is a small portion of the total organic N. The SON is potentially subject to leaching loss and—in the case of the smaller soluble molecules—to absorption by plant roots. The measured size of the SON pool depends on the particular lab method used to extract it from the soil. The portion of the SON that is actually dissolved in the soil solution at a given time is termed the dissolved organic nitrogen (DON). Thus the DON measured in soil solution or leachates in the field is part of a larger pool of SON which can be measured by lab extraction, and which in turn comprises a few percent of the total organic nitrogen in a soil. (Diagram courtesy of R. Weil.)
Most root uptake of nitrogen from DON occurs, however, after the readily decomposable organic N compounds are mineralized to NH$_4^+$ and NO$_3^-$ ions.

**Microbial Utilization.** Low molecular weight DON compounds can be transported into microbial cells for direct assimilation. Once inside the microbial cell, enzymes decompose these DON compounds, and the N is used to make proteins and other components needed by the microbe. If the N from the DON exceeds the immediate need in the cell, the excess will be released back into the soil solution (mineralization). Microbial uptake of both DON and mineral N take place concurrently in soils, giving rise in some soils to direct competition between plants and microbes for both forms of nitrogen.

**Leaching Potential of DON.** Dissolved organic nitrogen is also a significant component of the N lost by leaching. For example, DON may comprise nearly all the N leached from some pristine forests and typically 30–60% of that leached from dairy farms and beef feedlots. In fact, DON comprises about 25% of the N carried by the Mississippi River into the Gulf of Mexico. Thus, DON likely contributes to the environmental problems downstream and should be studied along with nitrate N to understand and solve nitrogen-pollution problems.

**Chemical Makeup of DON.** The chemical constituents of DON are believed to originate from microbial and root exudates and litter leachates, as well as hydrolyzed insoluble organic matter. We know that some of the compounds are hydrophilic and that others are hydrophobic. This suggests some may be able to interact with inorganic colloids, but others would react primarily with SOM. About a third of the DON is in the form of amino compounds such as amino sugars and amino acids. However, more research is needed to further ascertain the compounds that make up DON and the role they play in soil and related ecosystems.

### 13.5 Ammonium Fixation by Clay Minerals

Like other positively charged ions, ammonium ions are attracted to the negatively charged surfaces of clay and humus, where they are held in exchangeable form, available for plant uptake, but partially protected from leaching (see Section 8.7). However, because of its particular size, the ammonium ion (as well as the similarly sized potassium ion) can become entrapped or fixed within cavities in the crystal structure of certain 2:1-type clay minerals. Vermiculite has the greatest capacity for such ammonium (and potassium) fixation, followed by fine-grained micas and some smectites (see Figures 8.16 and 14.43 and 14.44). Ammonium and potassium ions fixed in the rigid part of a crystal structure are held in a nonexchangeable form, from which they are released only slowly. This use of the term *fixation* should not be confused with its use regarding biological nitrogen fixation, a process by which inert atmospheric N$_2$ gas is fixed in reactive, plant available forms (see Section 13.10).

Ammonium fixation by clay minerals is generally greater in subsoil than in topsoil, due to the higher clay content of subsoils (Table 13.1). In soils with considerable 2:1 clay content, interlayer-fixed NH$_4^+$ typically accounts for 5–10% of the total nitrogen in the surface soil and up to 20–40% of the nitrogen in the subsoil. In highly weathered soils, on the other hand, ammonium fixation is minor because little 2:1 clay is present. In some forest soils, about half the nitrogen in the O and A horizons is immobilized by either ammonium fixation or chemical reactions with humus. While ammonium fixation may be considered an advantage because it provides a means of conserving nitrogen, the rate of release of the fixed ammonium is often too slow to be of much practical value in fulfilling the needs of fast-growing annual plants.

### 13.6 Ammonia Volatilization

Ammonia gas (NH$_3$) can be produced from the breakdown of plant residues, animal excrement, and from such fertilizers as anhydrous ammonia and urea. This gas may diffuse into the atmosphere, resulting in a loss of valuable nitrogen from the soil and environmentally
detrimental increases on nitrogen deposition from the atmosphere (see Section 13.1.2). The ammonia gas is in equilibrium with ammonium ions according to the following reversible reaction:

\[
\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3 \uparrow
\]  

(13.3)

From Reaction (13.3) we can draw two conclusions. First, ammonia volatilization will be more pronounced at high pH levels (i.e., OH\(^-\) ions drive the reaction to the right); second, ammonia gas–producing amendments or the addition of water will drive the reaction to the left, raising the pH of the solution in which they are dissolved.

Soil colloids, both clay and humus, adsorb ammonia gas, so ammonia losses are greatest where low quantities of these colloids are present or where the ammonia is not in close contact with the soil. For these reasons, ammonia losses can be quite large from sandy soils and from alkaline or calcareous soils, especially when the ammonia-producing materials are left at or near the soil surface and when the soil is drying out. High temperatures, as often occur on the surface of the soil, also favor the volatilization of ammonia (Figure 13.6).

Incorporation of manure and fertilizers into the top few centimeters of soil can reduce ammonia losses by 25–75% from those that occur when the materials are left on the soil surface. In natural grasslands and pastures, incorporation of animal wastes by earthworms and dung beetles is critical in maintaining a favorable nitrogen balance and a high animal-carrying capacity in these ecosystems (see Section 11.2). A well-timed application of irrigation water can greatly reduce the loss of NH\(_3\) gas from surface-applied fertilizers (Figure 13.7).

**Table 13.1**
**Total Nitrogen Levels of A and B Horizons of Four Cultivated Virginia Soils and the Percentage of the Nitrogen Present as Nonexchangeable or Fixed NH\(_4^+\).**

<table>
<thead>
<tr>
<th>Soil great group (series)</th>
<th>Total N, mg/kg</th>
<th>Nitrogen fixed as NH(_4^+), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A horizon</td>
<td>B horizon</td>
</tr>
<tr>
<td>Hapludults (Bojac)</td>
<td>812</td>
<td>516</td>
</tr>
<tr>
<td>Paleudults (Dothan)</td>
<td>503</td>
<td>336</td>
</tr>
<tr>
<td>Hapludults (Groseclose)</td>
<td>1792</td>
<td>458</td>
</tr>
<tr>
<td>Hapludults (Elioak)</td>
<td>1110</td>
<td>383</td>
</tr>
</tbody>
</table>


**Figure 13.6** Ammonia volatilization is markedly affected by temperature and pH. Here, urea fertilizer (NH\(_2\)-CO-NH\(_2\)) was applied to a silt loam soil surface. Urea absorbs moisture from the air or soil and then hydrolyzes to form ammonia. The loss of ammonia gas is especially rapid when pH exceeds 7 and temperature exceeds 16 °C. Ammonia loss can be even faster from animal feces (manure) than from urea. Ammonia-forming amendments should not be left on the surface of warm, high pH soil for more than a day. [Redrawn from Gilbert et al. (2006) using data in Franzen (2004).]
Volatilization from Wetlands. Gaseous ammonia loss from nitrogen fertilizers applied to
the surface of fishponds and flooded rice paddies can also be appreciable, even on slightly acid
soils. The applied fertilizer stimulates algae growing in the paddy water. As the algae photo-
synthesize, they extract CO₂ from the water and reduce the amount of carbonic acid formed.
As a result, the pH of the paddy water increases markedly, especially during daylight hours,
to levels commonly above 9.0. At these pH levels, NH₃ gas is released from ammonium com-
ounds and goes directly into the atmosphere. As with upland soils, this loss can be reduced
significantly if the fertilizer is placed below the soil surface. Natural wetlands lose NH₃ gas by
a similar daily cycle.

Ammonia Absorption. By the reverse of the ammonium loss mechanism just described,
both soils and plants can absorb ammonia from the atmosphere. Thus the soil–plant system
can help cleanse ammonia from the air, while deriving usable nitrogen for plants and soil
microbes. In the Rocky Mountain region of the United States, NH₃ gas carried by wind from
fertilized cropland and cattle feedlots has been shown to provide significant amounts of nitro-
gen to forests on mountain slope hundreds of kilometers away.

13.7 NITRIFICATION

As ammonium ions appear in the soil, they are generally oxidized quite rapidly by certain soil
bacteria and archaea, yielding first nitrates and then nitrates. The prokaryotes that carry out
this enzymatic oxidation are classed as autotrophs because they obtain their energy from ox-
idizing the ammonium ions rather than organic matter. The process termed nitrification (see
Figure 13.3) consists of two main sequential steps. The first step results in the oxidation of
ammonium to nitrite. Molecular research has shown that certain archaea (Crenarchaeota) may
be active ammonia-oxidizing organisms in soils. In other soils, a specific group of autotrophic
bacteria of the genus Nitrosomonas is thought to carry out most of the ammonia oxidation. In
any case, the nitrite so formed is then immediately acted upon by a second group of autotrophs
(the best known being the bacteria of the genus Nitrobacter). Therefore, when NH₄⁺ is re-
leased into the soil it is usually converted rapidly into NO₃⁻ (see Figure 13.8). The enzymatic
oxidation releases energy and may be represented very simply as follows:

Step 1

\[
\text{NH}_4^+ + \frac{3}{2} \text{O}_2 \xrightarrow{\text{Nitrosomonas bacteria}} \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} + 275 \text{ kJ energy} \quad (13.4)
\]
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NH$_4^+$ + $\frac{1}{2}$O$_2$ → NO$_2^-$ + 2H$^+$ + H$_2$O + 275 kJ energy

Step 1

NO$_2^-$ + $\frac{1}{2}$O$_2$ → NO$_3^-$ + 76 kJ energy

Step 2

So long as conditions are favorable for both reactions, the second transformation is thought to follow the first closely enough to prevent accumulation of much nitrite. This is fortunate, because even at concentrations of just a few mg/kg, nitrite is quite toxic to most plants. When oxygen supplies are marginal, the nitrifying bacteria may also produce some NO and N$_2$O, which are potent greenhouse gases (see Sections 12.9 and 13.8). The chemical reaction below (Eq. (13.6)), which combines steps 1 and 2, illustrates the production of hydroxylamine and possible production of N$_2$O gas between the initial oxidation of NH$_4^+$ and the production of nitrite and nitrate during nitrification.

\[
\begin{align*}
\text{NH}_4^+ & \xrightarrow{\text{Ammonia oxidation}} \text{NH}_2\text{OH} \\
& \xrightarrow{\text{hydroxylamine}} \text{NO}_2^- \\
& \xrightarrow{\text{Nitrite oxidation}} \text{NO}_3^- \\
& \xrightarrow{\text{Nitrogen oxides}} \text{H}_2\text{O} + 2\text{H}^+
\end{align*}
\]

Regardless of the source of ammonium (i.e., ammonia-forming fertilizer, sewage sludge, animal excreta, or any other organic nitrogen source), nitrification will significantly increase soil acidity by producing H$^+$ ions, as shown in Reaction (13.6). See also Sections 9.6 and 13.14.

Soil Conditions Affecting Nitrification

The nitrifying bacteria are much more sensitive to environmental conditions than the broad groups of heterotrophic organisms responsible for the release of ammonium from organic nitrogen compounds (ammonification). Nitrification requires a supply of ammonium ions, but excess NH$_4^+$ can be toxic to *Nitrobacter*. The nitrifying organisms, being aerobic, require oxygen to make NO$_2^-$ and NO$_3^-$ ions and are therefore favored in well-drained soils. The optimum moisture for these organisms is about the same as that for most plants (about 60% of the pore space filled with water, Figure 13.9). Since they are autotrophs, their carbon sources are bicarbonates and CO$_2$. They perform best when temperatures are between 20 and 30 °C and perform very slowly if the soil is cold (below 5 °C).

Nitrification proceeds most rapidly where there is an abundance of exchangeable Ca$^{2+}$ and Mg$^{2+}$ and nutrient levels are optimum for the growth of higher plants. Nitrification is often constrained in soils high in smectite or allophane clays. These clays hold certain nitrogen-containing organic compounds in their intercolloid pores, thereby protecting them from microbial attack, including nitrification.

Nitrifying organisms are quite sensitive to some pesticides applied at high rates, but most studies suggest that at ordinary field rates, the majority of the pesticides have only a

Figure 13.8 Transformation of ammonium into nitrite and nitrate by nitrification. On day zero, the silt loam soil was amended with enough (NH$_4$)$_2$SO$_4$ to supply 170 mg of N/kg soil. It then underwent a warm, well-aerated incubation for 14 days. Every second day, soil samples were extracted and analyzed for various forms of nitrogen. Note that the increase in nitrate-N (NO$_3^-$-N) almost mirrored the decline in ammonium-N (NH$_4^+$-N), except for the small amount of nitrite-N (NO$_2^-$-N) that accumulated temporarily between day 2 and 10. This pattern is consistent with the two-step process depicted by Eqs. (13.4) and (13.5).

*Data selected from Khalil et al. (2004).*

No plants were grown during the study.
minimal effect on nitrification. Agrochemical companies have marketed a number of compounds that can inhibit or slow down the nitrification process, thereby reducing the nitrate leaching potential. Such compounds, as well as others that retard the dissolution of urea, are discussed in Section 13.15.

Provided that all the preceding conditions are favorable, nitrification is such a rapid process that nitrate is generally the predominant mineral form of nitrogen in most soils. Irrigation of an initially dry arid-region soil, the first rains after a long dry season, the thawing and rapid warming of frozen soils in spring, and sudden aeration by tillage are examples of environmental fluctuations that typically cause a flush of soil nitrate production (Figure 13.10). The growth patterns of natural vegetation and the optimum planting dates for crops are greatly influenced by such seasonal changes in nitrate levels.

**Figure 13.9** (Left) Rates of nitrification, ammonification, and denitrification are closely related to the availability of oxygen and water as depicted by percentage of water-filled pore space. Both nitrification and ammonification proceed at their maximal rates near 55–60% water-filled pore space; however, ammonification proceeds in soils too waterlogged for active nitrification. Only a small overlap exists in the conditions suitable for nitrification and denitrification. (Right) Nitrous oxide (N₂O), is mainly produced by denitrification, but it is also a minor by-product of nitrification, with abrupt shift from one process to the other at water-filled porosities between 60 and 70%. (Bar graph from Bateman and Baggs (2005).)

**Figure 13.10** Seasonal patterns of nitrate-N concentration in the A horizons of representative soils with and without growing plants. (Upper) In a representative northern hemisphere humid temperate region with cool winters and rainfall rather uniformly distributed throughout the year, NO₃⁻-N accumulates as the soil warms up in May and June. The nitrates are lost by leaching in the fall. (Lower) In a representative tropical region with four rainy months followed by eight months of dry, hot weather, a large flush of NO₃⁻-N appears when the rains first moisten the dry soil. This nitrate flush is caused by the rapid decomposition and mineralization of the dead cells of microorganisms previously killed by the dry, hot conditions. Note that soil nitrate is lower in both climates when plants are growing, because much of the nitrate formed is removed by plant uptake. (Diagrams courtesy of R. Weil.)
Several anaerobic microbial processes can in effect “reverse” nitrification. **Dissimilatory nitrate reduction to ammonium** is an anaerobic bacterial process that reduces \( \text{NO}_3^- \) to \( \text{NO}_2^- \) and then to \( \text{NH}_4^+ \). However, the best known and most common process that “reverses” nitrification is termed **denitrification**, an anaerobic process by which heterotrophic bacteria (or in some cases archaea or fungi) reduce nitrate to such gases as \( \text{NO} \), \( \text{N}_2\text{O} \), and \( \text{N}_2 \), as discussed next in Section 13.8.

### 13.8 GASEOUS LOSSES BY DENITRIFICATION AND ANAMMOX

#### Denitrification

Nitrogen is commonly lost to the atmosphere when nitrate ions are converted to gaseous forms of nitrogen by a series of widely occurring biochemical reduction reactions termed **denitrification**. The organisms that carry out this process are widespread and generally present in large numbers. They are mostly facultative anaerobic bacteria in genera such as *Pseudomonas*, *Bacillus*, *Micrococcus*, and *Achromobacter*. However, certain archaea and fungi are also known to carry out denitrification. Most denitrifying organisms are **heterotrophs**, which obtain their energy and carbon from the oxidation of organic compounds. Other denitrifying bacteria are **autotrophs**, such as *Thiobacillus denitrificans*, which obtain their energy from the oxidation of sulfide. The exact mechanisms vary depending on the conditions and organisms involved. In the reaction, \( \text{NO}_3^- [\text{N(V)}] \) is reduced in a series of steps to \( \text{NO}_2^- [\text{N(III)}] \), and then to nitrogen gases that include \( \text{NO} [\text{N(II)}] \), \( \text{N}_2\text{O} [\text{N(I)}] \), and eventually \( \text{N}_2 [\text{N(0)}] \):

\[
2\text{NO}_3^- \rightarrow 2\text{NO}_2^- \rightarrow 2\text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2
\]

Although not shown in the simplified reaction given here, the oxygen released at each step would be used to form \( \text{CO}_2 \) from organic carbon (or \( \text{SO}_4^{2-} \) from sulfides if *Thiobacillus* is the nitrifying organism).

For these reactions to take place, sources of organic residues should be available to provide the energy the denitrifiers need. The soil air in the microsites where denitrification occurs should contain no more than 10% oxygen, and lower levels of oxygen are preferred. Optimum temperatures for denitrification are from 25 to 35 °C, but the process will occur between 2 and 50 °C. Very strong acidity (pH < 5.0) inhibits rapid denitrification and favors the formation of \( \text{N}_2\text{O} \).

Generally, when oxygen levels are very low, the end product released from the overall denitrification process is dinitrogen gas (\( \text{N}_2 \)). It should be noted, however, that \( \text{NO} \) and \( \text{N}_2\text{O} \) are commonly also released during denitrification (Figure 13.11), especially under the fluctuating aeration conditions that often occur in the field. The proportion of the three main gaseous products seems to be dependent mainly on the degree of oxygen depletion, as well as the prevalent pH, temperature, and concentrations of nitrate and nitrite ions available. For example, release of nitrous oxide (\( \text{N}_2\text{O} \)) is favored over dinitrogen gas (\( \text{N}_2 \)) if soil pH is acidic, carbon supply is relatively low, the soil is not overly wet (some \( \text{O}_2 \) is present) and the concentrations of nitrite and nitrate are high (see Figures 13.9 and 7.13). Under very acid conditions, almost all of the loss occurs in the form of \( \text{N}_2\text{O} \). Nitric oxide (\( \text{NO} \)) formation is generally quite small.

#### Codenitrification

**Codenitrification** is a related microbial process by which nitrite (\( \text{NO}_2^- \)) in the soil solution is reduced to \( \text{N}_2\text{O} \) and \( \text{N}_2 \) gases by such nitrogen compounds as ammonium (\( \text{NH}_4^+ \)) or hydroxylamine (\( \text{NH}_2\text{OH} \)). Codenitrification is carried out by bacteria (e.g., *Streptomyces* spp.) and fungi.

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7For a review of recently revealed N cycle pathways of importance in ecosystems see Thamdrup (2012).

8Nitrate can also be reduced to nitrite and to nitrous oxide gas by nonbiological chemical reaction and under some circumstances by nitrifier bacteria, but these reactions are relatively minor in comparison with biological denitrification.
and sulfur economy of soils chapter thirteen

(e.g., *Fusarium oxysporum*) and has been measured in various aerobic soils, including those in agroecosystems and grasslands. In fact, fungal codenitrification may be the main source of N₂ emissions from grassland soils.

**Anammox**

A more recently discovered bacterial process, the *anaerobic oxidation of ammonium* (*anammox*), converts ammonium to N₂ gas using nitrite as an electron acceptor. The nitrite required for this reaction may come from nitrifying bacteria or archaea that carry out aerobic ammonium oxidation as described in Section 13.6:

\[
\begin{align*}
\text{NH}_4^+ + \frac{3}{2} \text{O}_2 & \rightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O} \quad \text{(aerobic)} \\
\text{NH}_4^+ + \text{NO}_2^- & \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad \text{(anaerobic)} \\
2\text{NH}_4^+ + \frac{3}{2} \text{O}_2 & \rightarrow \text{N}_2 + 2\text{H}^+ + 3\text{H}_2\text{O} \quad \text{(combined net anammox reaction)}
\end{align*}
\]

Anammox bacteria are a very unusual group of organisms within the phylum Planctomycetes; in addition to cellular properties typical for bacteria, they also appear to have some features more typical of archaea and fungi. Their carbon source for growth is CO₂ and therefore a supply of organic carbon is not required for anammox to occur.

Although originally thought to be of widespread importance only in ocean water, sediments, and hydric soils, recent evidence suggests this reaction is also important in many (but not all) upland soils as well, so long as boundary conditions exist between aerobic and anaerobic environments. As suggested by the anammox equations above, the process requires the presence of linked oxidizing and reducing environments and typically occurs in redox transition zones such as the upper layers of saturated soils, the capillary fringe above the water table, the rhizosphere of plant roots, or the interior of macroaggregates in moderately wet soils (see Figure 7.10).

---

Figure 13.11 Changes in various forms of nitrogen during the process of denitrification in a moist soil incubated in the absence of atmospheric oxygen. [From Leffelaar and Wassel (1988).]

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For a review of the unique characteristics of anammox reactions and bacteria see van Niftrik and Jetten (2012).
Atmospheric Pollution and Greenhouse Gas Emissions

Denitrification and anammox processes are ecologically important both because of the removal of nitrogen from an ecosystem, and because of the nitrogen gases they emit into the atmosphere. Nitrogen losses from soil during even a brief period of denitrification can bring about serious nitrogen deficiency in plants (Figure 13.12), while losses from nitrogen-laden groundwater or surface water can markedly improve the water quality. Dinitrogen (N₂) gas is quite inert and environmentally harmless, but the oxides of nitrogen are very reactive gases and have the potential to do serious environmental damage in at least four ways. First, when N₂O rises into the upper atmosphere, it contributes to climate change and global warming by absorbing infrared radiation (as much as 300 times the effect of an equal amount of CO₂) that would otherwise escape into space (see Section 12.9). Second, the nitrogen oxide gases can react with volatile organic pollutants to form ground-level ozone, a major air pollutant in the photochemical smog that plagues many urban areas. Third, NO and N₂O released into the atmosphere by denitrification can contribute to the formation of nitric acid, one of the principal components of acid rain.

Finally, as N₂O moves up into the stratosphere, it may participate in reactions that result in the destruction of ozone (O₃), a gas that helps shield the Earth from harmful ultraviolet solar radiation. In recent decades this protective ozone layer has been measurably depleted by reaction with industrial chlorofluorocarbons as well as with N₂O and other gases. As this protective layer is further degraded, thousands of additional cases of skin cancer are likely to occur annually. While there are other important sources of N₂O, such as automobile exhaust fumes, a major contribution to the problem is being made by denitrification in soils, especially in rice paddies, wetlands, and heavily fertilized or manured agricultural soils.

Quantity of Nitrogen Lost Through Denitrification

As might be expected, the exact magnitude of denitrification loss is difficult to predict and will depend on management practices and soil conditions. Studies of forest ecosystems have shown that during periods of adequate soil moisture, denitrification results in a slow but relatively steady loss of nitrogen from these undisturbed natural systems. In contrast, most field measurements of gaseous nitrogen loss from agricultural soils reveal that the losses are highly variable in both time and space. The greater part of the annual nitrogen loss often occurs during just a few days in summer, when rain or irrigation water temporarily waterlog the warm, nitrogen-fertilized, carbon-rich soils (Figure 13.12).

Low-lying, organic-rich areas and other hot spots may lose nitrogen ten times as fast as the average rate for a typical field. Although as much as 10 kg/ha of nitrogen may be lost in a single day from the sudden saturation of a well-drained, humid-region soil, such soils rarely lose more than 5–15 kg N/ha annually by denitrification. But where aeration is restricted and
large amounts of nitrogen fertilizer are applied, losses of 30–60 kg N/ha/yr of nitrogen have been observed (Figure 13.13).

Much of the nitrogen dissolved in water moving from watersheds into shallow streams and slow-moving rivers is lost by denitrification. As the water moves through these shallow transport channels, there is opportunity for the nitrogen to come in contact with the river bottoms where the denitrification occurs. Research suggests that 5–20% of the nitrogen in some streams or rivers may be lost by denitrification.

**Denitrification in Flooded Soils**

In flooded soils, such as those found in natural wetlands or rice paddies (Figure 13.14), losses by denitrification may be very high. The soils of rice paddies are commonly subject to alternate periods of wetting and drying. Nitrates that are produced by nitrification during the dry periods are often subject to denitrification when the soils are submerged. Even when submerged, the soil permits both reactions to take place at once—nitrification occurs at the soil–water interface where some oxygen derived from the water is present and denitrification occurs at lower soil depths (see Figure 13.15). Nonetheless, nitrogen losses from rice soils can be dramatically reduced by keeping the soil flooded and by deep placement of the fertilizer into the reduced zone of the soil. In this zone, because there is insufficient oxygen to allow nitrification to proceed, nitrogen remains in the ammonium form and is not susceptible to loss by denitrification.

The sequential combination of nitrification and denitrification also operates in natural and artificial wetlands. Tidal wetlands (see Figure 13.14c), which become alternately anaerobic and aerated as the water level rises and falls, have particularly high potentials for converting nitrogen to gaseous forms. Often the resulting rapid loss of nitrogen is considered to be a beneficial function of wetlands, in that the process protects estuaries and lakes from
Denitrification can be very efficient in removing nitrogen from flooded systems that combine aerobic and anaerobic zones and have a large supply of microbial available carbon. Examples of such systems include: (a) flooded rice paddies, (b) lagoons in which animal liquid manure is stored, (c) natural tidal marsh wetlands, and (d) constructed wetlands designed to remove nitrogen (and sediments) from urban storm water runoff. (Photos courtesy of R. Weil.)

Figure 13.15 Nitrification–denitrification reactions and dynamics of the related processes controlling nitrogen loss from the aerobic–anaerobic layers of a flooded soil system. Nitrates, which form in the thin aerobic soil layer just below the soil–water interface, diffuse into the anaerobic (reduced) soil layer below and are denitrified to the $N_2$ and $N_2O$ gaseous forms, which are lost to the atmosphere. In the case of fertilized rice paddies, placing the urea or ammonium-containing fertilizers deep in the anaerobic layer prevents N oxidation of ammonium ions to nitrates, thereby greatly reducing N loss. (Modified from Patrick (1982).)
the eutrophying effects of too much nitrogen (see Section 13.9). In fact, wastewater high in organic carbon and nitrogen can be cleaned up quite efficiently by allowing it to flow slowly over or through a specially designed water-saturated soil system such as stormwater retention wetlands (see Figure 13.14) or overland flow wastewater treatment systems.

Denitrification in Groundwater
In many cases studied, contaminated groundwater loses most of its nitrate nitrogen load as it flows through the riparian zone on its way to the stream. The apparent removal of nitrate may be quite dramatic, whether the nitrate source is suburban septic drainfields (Figure 13.16), livestock feeding operations, or fertilized cropland. Most of nitrate is believed to be lost by denitrification, stimulated by organic compounds leached from the decomposing forest litter and by the anaerobic conditions that prevail in the wet riparian zone soils.

Constructed wetlands can be used to reduce the nitrate content of surface waters moving toward streams. When coupled with buffer strips, such wetlands can remove half or more of the nitrates of the surface water before it enters the stream channel (see Figure 13.17).

We have just discussed a number of biological processes (e.g., nitrate leaching, ammonia volatilization, N₂ production by denitrification) that lead to loss of nitrogen from the soil system. Were such losses not matched by N inputs, ecosystems would have long ago run out of reactive N and life in them would have ground to halt. To understand why such a dire situation has not come to pass, we turn our attention next to the principal biological process by which soil nitrogen is replenished.

13.9 BIOLOGICAL NITROGEN FIXATION

Next to plant photosynthesis, biological nitrogen fixation is probably the most important biochemical reaction for life on Earth. This process converts the inert dinitrogen gas of the atmosphere (N₂) to reactive nitrogen that becomes available to all forms of life through the nitrogen cycle. The process is carried out by a limited number of bacteria, including several species of *Rhizobium*, actinomycetes, and cyanobacteria (formerly termed blue-green algae).

Globally, enormous amounts of nitrogen are fixed biologically each year. Terrestrial systems alone fix an estimated 139 million Mg. However, the amount that is fixed in the manufacture of fertilizers is now nearly as great (see Figure 13.18).
The Mechanism. Regardless of the organisms involved, the key to biological nitrogen fixation is the enzyme nitrogenase, which catalyzes the reduction of dinitrogen gas to ammonia

\[ \text{N}_2 + 8\text{H}^+ + 6e^- \xrightarrow{\text{Nitrogenase}} 2\text{NH}_3 + \text{H}_2 \]  

(13.10)

The ammonia, in turn, is combined with organic acids to form amino acids and, ultimately, proteins

\[ \text{NH}_3 + \text{organic acids} \rightarrow \text{amino acids} \rightarrow \text{proteins} \]  

(13.11)

The site of \( \text{N}_2 \) reduction is the enzyme nitrogenase, a complex consisting of two proteins, the smaller of which contains iron while the larger contains molybdenum, sulfur, and
iron (Figure 13.19). Several salient facts about this enzyme and its function are worth noting, for nitrogenase is unique and its role in the nitrogen cycle is of great importance to humankind.

1. Breaking the strong \( \text{N} = \text{N} \) triple bond in \( \text{N}_2 \) gas requires a great deal of energy. Therefore, this microbial process is greatly enhanced when it is carried out in association with plants, which can supply energy from photosynthesis.

2. Nitrogenase is destroyed by free \( \text{O}_2 \), so organisms that fix nitrogen must protect the enzyme from exposure to oxygen. When nitrogen fixation takes place in root nodules (see Section 13.11), one means of protecting the enzyme from free oxygen is the formation of leghemoglobin. This compound, which gives actively fixing nodules a red interior color, binds oxygen in such a way as to protect the nitrogenase while making oxygen available for respiration in other parts of the nodule tissue. Leghemoglobin is virtually the same molecule as the hemoglobin that gives human blood its red color while carrying oxygen to our body cells.

3. The reduction reaction is end-product inhibited—for example, an accumulation of ammonia will inhibit nitrogen fixation. Also, too much nitrate in the soil will inhibit the formation of nodules (see Section 13.11).

4. Nitrogen-fixing organisms have a relatively high requirement for molybdenum, iron, phosphorus, and sulfur, because these nutrients are part of the nitrogenase molecule and also needed for its synthesis and use.

**Fixation Systems.** Biological nitrogen fixation occurs through a number of microbial systems that may or may not be directly or indirectly associated with plants (Table 13.2). Although the legume–bacteria symbiotic systems have received the most attention, the other systems involve many more families of plants worldwide and may supply large amounts of biologically fixed nitrogen to the soil. Each major system will be discussed briefly.

### 13.10 SYMBIOTIC FIXATION WITH LEGUMES

Plants of the legume family (Fabaceae) are famous for their distinctive ability to provide the major biological source of fixed nitrogen in agricultural soils. They do so in association with several genera of bacteria (in the subclass Alpha-Proteobacteria) collectively termed *rhizobial bacteria*. These bacteria include species in the genera *Rhizobium*, *Mesorhizobium*, *Bradyrhizobium*, and *Ensifer*. The legume plants and rhizobial bacteria form a *symbiosis* (a mutually beneficial relationship) in which the host plant supplies the bacteria with carbohydrates for energy, and the bacteria reciprocate by supplying the plant with reactive nitrogen with which to make essential plant compounds such as proteins and chlorophyll. In a complex biochemical “conversation” involving many specific signaling compounds, the rhizobial bacteria find and infect the legume plant root hairs and colonize the cortical cells. Here the rhizobial bacteria ultimately induce the formation of *root nodules* that serve as the site of nitrogen fixation (Figure 13.20).
Organisms Involved. A given rhizobial bacteria species will infect some legumes but not others. For example, *Rhizobium trifolii* inoculates *Trifolium* species (most clovers), but not sweet clover, which is in the genus *Melilotus*. Likewise, *Rhizobium phaseoli* inoculates *Phaseolus vulgaris* (beans), but not soybeans, which are in the genus *Glycine*. This specificity of interaction is one basis for classifying rhizobia (see Table 13.3). Legumes that can be inoculated by a given *Rhizobium* species are included in the same cross-inoculation group.
In soils which have grown a given legume for several years, the appropriate species of rhizobial bacteria is probably present. Often, however, the natural rhizobial population in the soil is too low or the strain of the rhizobial bacteria species present is not effective (Figure 13.21). In such circumstances, special mixtures of the appropriate rhizobial bacteria may be applied as an inoculant, either by coating the legume seeds or by applying the inoculant directly to the soil. Effective and competitive strains of rhizobial bacteria are available commercially, and often give significant yield increases if used on the proper crops. You may want to refer to Table 13.3 when planting legume plants or purchasing commercial inoculant. Always check the inoculant label to be sure it will work for the intended plant species.

### Table 13.3

**Classification of Rhizobia Bacteria and Associated Legume Cross-Inoculation Groups**

The genera *Rhizobium* and *Ensifer* contain fast-growing, acid-producing bacteria, while those of *Bradyrhizobium* are slow growers that do not produce acid.

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Genus</th>
<th>Species/subgroup</th>
<th>Host legume</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ensifer</strong></td>
<td><em>E. meliloti</em></td>
<td></td>
<td>Mililotus (sweet clovers), <em>Medicago</em> (alfalfa), <em>Trigonella</em> spp. (fenugreek)</td>
</tr>
<tr>
<td><strong>Rhizobium</strong></td>
<td><em>R. leguminosarum</em></td>
<td></td>
<td><em>Vicia</em> spp. (vetches), <em>Pisum</em> (peas), <em>Lens</em> (lentils), <em>Lathyrus</em> (sweet pea), <em>Vicia faba</em> (faba bean)</td>
</tr>
<tr>
<td></td>
<td><em>bv. viceae</em></td>
<td></td>
<td><em>Trifolium</em> spp. (most clovers)</td>
</tr>
<tr>
<td></td>
<td><em>bv. trifoli</em></td>
<td></td>
<td><em>Phaseolus</em> spp. (dry bean, string bean, etc.)</td>
</tr>
<tr>
<td></td>
<td><em>bv. phaseoli</em></td>
<td></td>
<td><em>Glycine</em> spp. (e.g., soybean)</td>
</tr>
<tr>
<td><em>R. Fredii</em></td>
<td></td>
<td></td>
<td><em>Securigera varia</em> (crown vetch)</td>
</tr>
<tr>
<td><em>R. spp.</em></td>
<td></td>
<td></td>
<td>Trees in <em>Leucaena</em> group: <em>Leucaena</em> spp. <em>Sesbania grandiflora</em> <em>Calliandra calothyrsus</em> <em>Glicicida sepium</em> <em>Prosopis</em> spp.</td>
</tr>
<tr>
<td><em>R. lupini</em></td>
<td></td>
<td></td>
<td><em>Lupinus</em> spp. (lupins)</td>
</tr>
<tr>
<td><strong>Bradyrhizobium</strong></td>
<td><em>B. japonicum</em></td>
<td></td>
<td><em>Glycine</em> spp. (e.g., soybean)</td>
</tr>
<tr>
<td></td>
<td><em>B. spp.</em></td>
<td></td>
<td><em>Vigna</em> (cowpeas, mung bean), <em>Arachis</em> (peanut), <em>Cajanus</em> (pigeon pea), <em>Pueraria</em> (kudzu), <em>Crotalaria</em> (crotalaria), and many other tropical legumes; <em>Phaseolus lunatus</em> (lima bean) <em>Acacia</em> spp. (acacia trees), <em>Desmodium</em> spp., <em>Stylosanthes</em> spp., <em>Centroama</em> sp., <em>Psophocarpus</em> tetragonolobus (winged bean), <em>Lablab</em> purpureus (Lablab bean), <em>Pueraria</em> phaseoloides</td>
</tr>
<tr>
<td><strong>Mesorhizobium</strong></td>
<td><em>M. loti</em></td>
<td></td>
<td><em>Lotus</em> (trefoils), <em>Lupinus</em> (lupins), <em>Cicer</em> (chickpea), <em>Anthyllis, Leucaena</em>, and many other tropical trees</td>
</tr>
<tr>
<td><strong>Azorhizobium</strong></td>
<td><em>A. spp.</em></td>
<td></td>
<td>Produces stem nodules on <em>Sesbania rostrata</em></td>
</tr>
</tbody>
</table>

In soils which have grown a given legume for several years, the appropriate species of rhizobial bacteria is probably present. Often, however, the natural rhizobial population in the soil is too low or the strain of the rhizobial bacteria species present is not effective (Figure 13.21). In such circumstances, special mixtures of the appropriate rhizobial bacteria may be applied as an inoculant, either by coating the legume seeds or by applying the inoculant directly to the soil. Effective and competitive strains of rhizobial bacteria are available commercially, and often give significant yield increases if used on the proper crops. You may want to refer to Table 13.3 when planting legume plants or purchasing commercial inoculant. Always check the inoculant label to be sure it will work for the intended plant species.

### Quantity of Nitrogen Fixed

The rate of biological fixation is greatly dependent on soil and climatic conditions. The legume–*Rhizobium* associations generally function best on soils that are not too acid (although *Bradyrhizobium* associations generally can tolerate considerable acidity) and that are well supplied with essential nutrients. However, high levels of available nitrogen, whether from the soil or added in fertilizers, tend to depress biological nitrogen fixation (Figure 13.22). Apparently, plants make the heavy energy investment required for symbiotic nitrogen fixation only when supplies of mineral nitrogen from the soil are quite limited.

Although quite variable from site to site, the amount of nitrogen biologically fixed can be quite high, especially for those systems involving nodules, which supply energy from photosynthates and protect the nitrogenase enzyme system (Table 13.4). Nonnodulating or nonsymbiotic systems generally fix relatively small amounts of nitrogen. Nonetheless, many natural plant communities and agricultural systems (generally involving legumes) derive the bulk of their nitrogen needs from biological fixation.
Effect on Soil Nitrogen Level. Over time, the presence of nitrogen-fixing species can significantly increase the nitrogen content of the soil and benefit nonfixing species grown in association with fixing species (see Figure 13.23).

Although some direct transfer may take place via mycorrhizal hyphae connecting two plants, most of the transfer results from mineralization of nitrogen-rich compounds in root exudates and in sloughed-off root and nodule tissues. Ammonium and nitrate thus released into the soil are available to any plant growing in association with the legume. The vigorous development of a grass in a legume–grass mixture is evidence of this rapid release (Figure 13.24), as are the relatively high nitrate concentrations sometimes measured in groundwater under legume crops. Some legumes are relatively weak nitrogen fixers so most of the nitrogen they absorb must come from the soil. Consequently, it should not be assumed that the symbiotic systems always increase soil nitrogen. Only in cases where the soil is low in available nitrogen and vegetation includes strong nitrogen fixers would this be likely to be true.

In the case of legume crops harvested for seed or hay, most of the nitrogen fixed is removed from the field with the harvest. Nitrogen additions from such crops should be considered as nitrogen *savers* for the soil rather than nitrogen builders. On the other hand, considerable buildup of soil nitrogen can be achieved by perennial legumes (such as alfalfa or kudzu) and by annual legumes (such as hairy vetch) if the entire growth is returned to the soil as green manure. If managed to maximize the return of their high-nitrogen biomass, legume
### Table 13.4
**Typical Levels of Nitrogen Fixation from Different Systems**

<table>
<thead>
<tr>
<th>Crop or plant</th>
<th>Associated organism</th>
<th>Typical levels of nitrogen fixation, kg N/ha/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Symbiotic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Legumes (nodulated)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ipil-ipil tree (Leucaena leucocephala)</td>
<td>Bacteria (Rhizobium)</td>
<td>100–500</td>
</tr>
<tr>
<td>Locust tree (Robina spp.)</td>
<td></td>
<td>75–200</td>
</tr>
<tr>
<td>Alfalfa (Medicago sativa)</td>
<td></td>
<td>150–250</td>
</tr>
<tr>
<td>Clover (Trifolium pratense L.)</td>
<td></td>
<td>100–150</td>
</tr>
<tr>
<td>Lupine (Lupinus)</td>
<td></td>
<td>50–100</td>
</tr>
<tr>
<td>Vetch (Vicia villosa)</td>
<td></td>
<td>50–150</td>
</tr>
<tr>
<td>Bean (Phaseolus vulgaris)</td>
<td></td>
<td>30–50</td>
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<tr>
<td>Cowpea (Vigna unguiculata)</td>
<td>Bacteria (Bradyrhizobium)</td>
<td>50–100</td>
</tr>
<tr>
<td>Peanut (Arachis)</td>
<td></td>
<td>40–80</td>
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<tr>
<td>Soybean (Glycine max L.)</td>
<td></td>
<td>50–150</td>
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<tr>
<td>Pigeon pea (Cajanus)</td>
<td></td>
<td>150–280</td>
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<tr>
<td>Kudzu (Pueraria)</td>
<td></td>
<td>100–140</td>
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<tr>
<td><strong>Nonlegumes (nodulated)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alders (Alnus)</td>
<td>Actinomycetes (Frankia)</td>
<td>25–150</td>
</tr>
<tr>
<td>Ironwoods (Casuarina)</td>
<td></td>
<td>10–20</td>
</tr>
<tr>
<td>Species of Gunnera</td>
<td>cyanobacteria* (Nostoc)</td>
<td>10–20</td>
</tr>
<tr>
<td><strong>Nonlegumes (nonnodulated)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pangola grass (Digitaria decumbens)</td>
<td>Bacteria (Azospirillum)</td>
<td>5–30</td>
</tr>
<tr>
<td>Bahia grass (Paspalum notatum)</td>
<td>Bacteria (Azobacter)</td>
<td>5–30</td>
</tr>
<tr>
<td>Azolla</td>
<td>cyanobacteria* (Anabaena)</td>
<td>150–300</td>
</tr>
<tr>
<td><strong>Nonsymbiotic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bacteria (Azobacter, Clostridium)</td>
<td></td>
<td>5–20</td>
</tr>
<tr>
<td>Cyanobacteria* (various)</td>
<td></td>
<td>10–50</td>
</tr>
</tbody>
</table>

Note: *Formerly referred to as blue-green algae.

**Figure 13.23** Nitrogen concentrations in forest soil horizons showing the effects of New Mexican locust trees (Robinia neomexicana) growing in association with ponderosa pine (Pinus ponderosa) in a region of Arizona receiving about 670 mm of rainfall per year. The data are means from 20 stands of ponderosa pine, half of them with the nitrogen-fixing legume trees (locust) in the understory. The soils are Eutrustalfs and Argiustolls with loam and clay loam textures. (Data from Klemmedson [1994]).
For a scientific review of microbial N fixation in association with nonleguminous plants, see Santi et al. (2013).

Green manures can be used to replace most or even all of the nitrogen fertilizer typically used in certain crop rotations. In any case, the nitrogen contributions from legumes should be taken into account when estimating nitrogen fertilizer needs for maximum plant production with minimal environmental pollution (Section 13.15).

### 13.11 Symbiotic Fixation with Nonlegumes

#### Nodule-Forming Nonlegumes

Some 220 species from eight plant families are known to develop nodules and to accommodate symbiotic nitrogen fixation when their root hairs are invaded by soil actinomycetes of the genus *Frankia*. Most of these *actinorhizal* plants are woody shrubs and trees that form distinctive nodules (Figure 13.25, inset). Table 13.5 lists several of the more important actinorhizal in certain forests and wetlands.

The rates of nitrogen fixation per hectare compare favorably with those of the legume–*Rhizobium* associations (see Table 13.4). On a worldwide basis, the total nitrogen fixed in this way may even exceed that fixed by agricultural legumes. Because of their nitrogen-fixing ability, certain of the tree–actinomycete associations are able to colonize infertile soils and newly forming soils on disturbed lands, which may have extremely low fertility as well as other conditions that limit plant growth (Figure 13.25). Once nitrogen-fixing plants become established and begin to build up the soil nitrogen supply through leaf litter and root exudation, the land becomes more hospitable for colonization by other species. *Frankia* thus play a very important role in the nitrogen economy of areas undergoing succession, as well as in established wetland forests.

Certain cyanobacteria are known to develop nitrogen-fixing symbiotic relations with green plants. One involves nodule formation on the stems of *Gunnera*, an angiosperm common in marshy areas of the southern hemisphere. In this association, cyanobacteria of the genus *Nostoc* fix 10–20 kg N/ha/yr (see Table 13.4).

#### Symbiotic Nitrogen Fixation Without Nodules

Among the most significant nonnodule nitrogen-fixing systems are those involving cyanobacteria. One system of considerable practical importance is the *Azolla–Anabaena* complex, which flourishes in certain rice paddies of tropical and semitropical areas (Figure 13.26). The *Anabaena* cyanobacteria inhabit cavities in the leaves of the floating fern *Azolla* and fix quantities of nitrogen comparable to those of the more efficient *Rhizobium*–legume complexes (see Table 13.4).

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10For a scientific review of microbial N fixation in association with nonleguminous plants, see Santi et al. (2013).
A more widespread but less intense nitrogen-fixing phenomenon is that which occurs in the rhizosphere of certain nonlegume plants, especially tropical grasses. As discussed in Section 11.12, bacteria adapted to life in the rhizosphere are called rhizobacteria. Rhizobacteria that benefit plant growth and development are referred to as plant growth–promoting rhizobacteria (PGPR). Many PGPR bacteria belong in the genera *Spirillum*, *Rhizobium*, and *Azotobacter* (see Table 13.4). These microorganisms obtain their energy supply for their nitrogen-fixation from the exudates of plant roots.

Scientists have reported a wide range of rates for rhizosphere nitrogen fixation with the highest values observed in association with certain tropical grasses. Even if typical rates are only 5–30 kg N/ha/yr, the vast areas of tropical grasslands suggest that the total quantity of nitrogen fixed by rhizosphere organisms is likely very high (see Table 13.4). There may also be some potential to harness this type of nitrogen fixation for agriculture. In some cases inoculation of soil with certain GPB has stimulated sufficient nitrogen fixation under field conditions to significant increase productivity of food crops such as corn, rice, and wheat.
13.12 NONSYMBIOTIC NITROGEN FIXATION

Certain free-living microorganisms present in soils and water are able to fix nitrogen. Because these organisms are not directly associated with higher plants, the transformation is referred to as nonsymbiotic or free-living.

Fixation by Heterotrophs

Several different groups of bacteria and cyanobacteria are able to fix nitrogen nonsymbiotically. In upland mineral soils, the major fixation is brought about by species of several genera of heterotrophic aerobic bacteria, *Azotobacter* and *Azospirillum* (in temperate zones) and *Beijerinckia* (in tropical soils). Certain anaerobic bacteria of the genus *Clostridium* are also active in fixing nitrogen. Because pockets of low oxygen supply exist within aggregates even in well-drained soils (see Section 7.4), aerobic and anaerobic bacteria probably work side by side in many well-drained soils. These organisms obtain their carbon either from root exudates in the rhizosphere or by saprophytic decomposition of SOM, and they operate best where soil nitrogen is limited.

The amount of nitrogen fixed by these heterotrophs varies greatly with the pH, soil nitrogen level, and sources of organic matter available. In some natural ecosystems these organisms undoubtedly make an important contribution to the nitrogen needs of the plant community. Because of limited carbon supplies, in conventional agricultural systems they probably fix only 5–20 kg N/ha/yr (see Table 13.4); however, with proper organic matter management, it is thought that the rates may be considerably higher. If agriculturalists are able to take advantage of these organisms, the benefits would go beyond increased crop yields to include reducing the need to manufacture nitrogen fertilizer (and therefore lowering the amount of reactive nitrogen circulating in the environment) as well as reductions in N₂O emissions.

Fixation by Autotrophs

In the presence of light, certain photosynthetic bacteria and cyanobacteria are able to fix carbon dioxide and nitrogen simultaneously. The contribution of the photosynthetic bacteria is

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Footnote:
11 For insights into the exploitation of nonsymbiotic N fixation for agriculture, see Kennedy et al. (2004).
uncertain, but that of cyanobacteria is thought to be of some significance, especially in wetlands (including in rice paddies). In some cases, cyanobacteria contribute a major part of the nitrogen needs of rice, but nonsymbiotic species rarely fix more than 20–30 kg N/ha/yr. Nitrogen fixation by cyanobacteria in upland soils also occurs (including in the desert microbiotic crusts discussed in Section 11.14), but at much lower levels than found under wetland conditions.

13.13 NITROGEN DEPOSITION FROM THE ATMOSPHERE

As the Earth’s growing human population puts ever more reactive nitrogen into circulation, its unwanted deposition is becoming an increasingly serious global environmental problem.

Reactive nitrogen in the atmosphere consists of small, but increasing, quantities of ammonia and nitrogen oxide gases that originated as emissions from soils, oceans, vegetation, and fossil fuel combustion (especially in vehicle engines—see Section 9.6). These nitrogen gases are generally transformed into \( \text{NH}_4^+ \) or \( \text{NO}_3^- \) by reactions in clouds, and additional nitrates are formed in the atmosphere by reaction of \( \text{N}_2 \) and \( \text{O}_2 \) during lightning flashes. The term nitrogen deposition refers to the addition of these atmosphere-borne reactive nitrogen compounds to soils through rain, snow, dust, and gaseous absorption.

The quantity of ammonia and nitrates in precipitation varies markedly with location (see Figure 13.27). Global N deposition totals some 105 Tg N yr\(^{-1}\) while that in the contiguous 48 United States totals about 5 Tg N yr\(^{-1}\). Deposition is greatest in high-rainfall areas downwind from cities (nitrate from nitrogen oxides in car exhaust and coal burning power plants), concentrated animal-feeding operations (CAFOs) (ammonium volatilized from manure), and fertilized wetland rice production. The ratio of nitrate to ammonium nitrogen deposited varies with location, the nitrate share ranging from about one-third to two-thirds. In recent decades in the United States, the nitrate proportion has declined while the ammonium proportion has increased.

Although the deposited nitrogen may stimulate greater plant growth in agricultural systems, the effects on forests, grasslands, and aquatic ecosystems are quite damaging. Nitrates in particular are associated with acidification of rain (as discussed in Section 9.6), but since the ammonium soon nitrifies, both forms lead to soil acidification. Nitrogen added by deposition as ammonium and nitrate from the atmosphere (or by fertilization) also impacts another soil process with important global change implications, namely, methane oxidation (Figure 13.28).
Methane is an important greenhouse gas affecting climate change, and its removal from the atmosphere by soil oxidation helps maintain its global balance (see also Section 12.9, Table 12.7). Forested soils have particularly high rates of methane oxidation, but also may be hardest hit by nitrogen deposition. The methane oxidation capacities of grasslands and crop-lands are also significantly reduced by mineral nitrogen.

Effects on Forest Ecosystems

Nitrogen in precipitation might be considered beneficial fertilizer when it falls on farmland, but it can be a serious pollutant when chronically added to some forested soils. Most forest soils are nitrogen limited—that is, they contain a surplus of carbon so that any nitrogen added is quickly tied up by microbial and chemical immobilization and very little nitrate is lost by leaching. However, a condition known as nitrogen saturation has been found to result from high levels of nitrogen deposition on certain mature forests in northern Europe and to a lesser extent in North America. Nitrogen saturation refers to the inability of the forest system to retain all or even most of the nitrogen received by deposition, leading to the leaching of nitrates and the associated soil acidification and loss of calcium and magnesium (as described in Sections 9.6 and 13.21). Nitrogen deposition can eventually reduce tree growth and disrupt the forest soil ecosystem in numerous ways, many of which are probably related to nitrogen saturation (Figure 13.29). Nitrogen deposition greater than about 8 kg N/ha/yr can be expected to eventually cause damage to sensitive forest and aquatic ecosystems.

The amounts of nitrogen deposited; the type of forest (e.g., deciduous or evergreen); soil properties such as texture, mineralogy, and acidity; the history of land use and age of the forest; and climatic variables all seem to influence how chronic nitrogen additions will impact forest soils and ecosystems. For example, mature coniferous forests on poorly buffered soils may reach a state of nitrogen saturation more rapidly than young, rapidly growing forests such as those subject to frequent logging or recently converted from agriculture.

Effects on Rangeland Systems

Natural rangeland ecosystems contain a wide variety of native plant species that are known for their ability to conserve nitrogen and efficiently utilize low levels of deposited nitrogen (2–5 kg N/ha/yr). However, research using deliberate nitrogen additions suggests that as nitrogen deposition increases, certain plants—often exotic species—that are highly responsive to high levels of nitrogen quicklycrowd out many of the desirable native species that are adapted to grow efficiently at low nitrogen levels. Attempts that have been made to increase rangeland productivity by adding fertilizer nitrogen may increase productivity temporarily, but again, the low-nitrogen-requiring native species are soon crowded out and replaced by high-nitrogen-requiring exotic species that are generally considered weeds. The resulting systems are
lower in biological diversity and productivity than the original native rangelands. This case illustrates that well-meaning efforts to increase productivity of complex, poorly understood natural ecosystems can, in fact, have the exact opposite effect.

### 13.14 THE NITRATE LEACHING PROBLEM

Subsurface flow of dissolved nitrogen is commonly the pathway accounting for the greatest losses of nitrogen from upland ecosystems, especially agroecosystems (Figure 13.30). Although in some cases subsurface flow carries substantial amounts of DON, the main form of nitrogen subject to leaching loss is nitrate. In contrast to positively charged ammonium ions, negatively charged nitrate ions are not adsorbed by the negatively charged colloids that dominate most soils. Therefore, nitrate ions move downward freely with drainage water and are readily leached from the soil. The loss of nitrogen in this manner is of concern for...
three basic reasons: (1) the loss of this valuable nutrient is a waste that impoverishes the ecosystem (as discussed in Section 13.1), (2) leaching of nitrate anions stimulates the acidification of the soils and the co-leaching of such cations as Ca$^{2+}$, Mg$^{2+}$, and K$^+$ (as described in Section 9.6), and (3) the movement of nitrate to groundwater causes several serious water-quality problems downstream. We will now examine the nature of these environmental impacts.

**Water-Quality Impacts.** The main water quality problem attributed to nitrogen is the leaching of nitrate to groundwater. Nitrate may reach and contaminate drinking water, causing health hazards (see Box 13.2) for people as well as livestock. The key factor for health hazards is the concentration of nitrate in the drinking water and the level of exposure (amount of water ingested, especially over long periods). The nitrates may also eventually flow underground to surface waters, such as streams, lakes, and estuaries. The damages to surface waters are even more widespread, impairing water quality and the health of aquatic ecosystems, especially those with salty or brackish water (Box 13.3). The key factor for this kind of damage is often the total load (mass flux) of nitrogen delivered to the sensitive ecosystem.

**Box 13.2**

**SOIL, NITRATE, AND YOUR HEALTH**

Mismanagement of soil nitrogen can result in levels of nitrates in drinking water (usually in groundwater) and food (mainly leafy vegetables) that may seriously threaten human health. While nitrate itself is not directly toxic, once ingested, a portion of the nitrate is reduced by bacterial enzymes to nitrite, which is considered toxic.

The most widely known (though actually quite rare) malady caused by nitrite is methemoglobinemia, in which the nitrites decrease the ability of hemoglobin in the blood to carry oxygen to the body cells. Since inadequately oxygenated blood is blue rather than red, people with this condition take on a bluish skin color. This symptom, and the fact that infants under three months of age are much more susceptible to this illness than older individuals, accounts for the condition being commonly referred to as “blue baby syndrome.” Most known deaths from this disease have been caused by infant formula made with high-nitrate water. With the aim of protecting infants from methemoglobinemia, governments have set standards to limit the nitrate concentrations allowed in drinking water (Figure 13.31). In the United States this limit is 10 mg/L nitrate-N ($= 45$ mg/L nitrate) and in the European Union it is 50 mg/L nitrate ($= 11$ mg/L nitrate-N).

Of greater potential concern is the tendency of nitrate to form N-nitroso compounds in the stomach by binding with such organic precursors as amines derived from proteins. Certain N-nitroso compounds are known to be highly toxic, causing cancer in some 40 species of test animals, so the threat to humans must be given serious consideration. Nitrates (or nitrites formed therefrom) have also been reported to promote certain types of diabetes, stomach cancers, interference with iodine uptake by the thyroid gland, and certain birth defects. While documenting cause and effect in chronic diseases is always uncertain, many of these effects appear to be associated with nitrate concentrations much lower than the drinking water limits just mentioned.

On the other hand, several research studies suggest that ingestion of nitrate does no harm and may actually provide protection against bacterial infections and some forms of cardiovascular diseases and stomach cancers. Therefore, while a precautionary approach is probably wise, we must conclude that the “jury is still out” on the health risks of nitrates in drinking water and vegetables.

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*For reviews of nitrate effects on health, see Santamaria (2006) and L’hirondel and L’hirondel (2002). For a contrary view, see Addiscott (2006).
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**Box 13.3**

**Nitrogen Pollution: Dead Zone in the Gulf of Mexico**

Under natural conditions, low levels of nitrogen limit aquatic algae growth—especially in estuaries where salty or brackish water inhibits N-fixing algae. Increased human input of nitrogen can remove this constraint, causing choking and sometimes toxic growth of aquatic plants and algae. The resulting degradation of aquatic ecosystems is undoubtedly the most widespread water-quality problem induced by nitrogen pollution. Worldwide, more than 400 estuaries have suffered severe declines in water quality and biodiversity. Major examples include the Yangtze River and Pearl River estuaries on the coast of China, the lower Chesapeake Bay on the Atlantic Coast of the United States, and the Mississippi River estuary in the Gulf of Mexico.

In the Gulf of Mexico off the coast of Louisiana, an enormous “dead zone” of water some 4–60 m deep reaches from the mouth of the Mississippi River westward nearly 500 km to Texas. Nutrient-rich freshwater carried by the river glides over the cooler, saltier (and therefore heavier) Gulf water. The nutrients (mainly N, but also P and Si) stimulate explosive growth of algae, which sink to the bottom when they die (Figure 13.32). While decomposing this dead tissue, microorganisms deplete the oxygen dissolved in the water to levels unable to sustain animal life. Fish, shrimp, and other aquatic species either migrate out of the zone or die. This state of low oxygen in the water (less than 2–3 mg O₂/L) is known as hypoxia, and the process that brings it about is called eutrophication (see also Box 14.1 for eutrophication caused by phosphorus mainly in fresh waters).

Concentrations of N in the Mississippi river have tripled in the past 30 years, mainly due to human activities, especially those in agriculture. Critical assessments suggest that only about 10% of the N delivered by the river comes from sewage treatment plants and other point sources; some 75% comes from farmland runoff carrying N from fertilizers, soil, and manure. Major efforts are required to help farmers and others improve their N use efficiency and reduce the transformation of this valuable nutrient into a pollutant.

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**Figure 13.32** Eutrophication process leading to hypoxia. From CAST (1999). For a detailed account of the causes and effects of the Gulf of Mexico dead zone, see Boesch et al. (2009).

The total nitrogen load may be comprised partly of organic and ammonium forms of N transferred from the land in surface runoff or on eroded soil material, but N leached through the soil profile as nitrate (along with soluble organic N) is often the main contributor. The quantity of nitrate lost in drainage water depends on two factors: (1) the volume of water leaching through the soil and (2) the concentration of nitrates in that drainage water.
**Volume of Leaching Water.** The volume of leaching water is influenced by rates of precipitation, irrigation, and evapotranspiration (Section 6.1), as well as by soil texture and structure. Sandy soils in humid regions are therefore highly susceptible to leaching. By contrast, unirrigated soils in arid regions are expected to undergo very little leaching (yet over 1000s of years, occasional rains may leach substantial amounts of nitrate deep into desert soils!). Conservation tillage increases water infiltration at the expense of surface runoff, thereby also increasing the volume of water available for leaching. Growth of perennial vegetation or use of cover crops can decrease leaching by removing both nitrogen (by uptake) and water (by transpiration).

**Concentration of Nitrogen.** The concentration of nitrate in the leaching water is largely dependent on the size of the soil nitrate pool during periods of leaching. The nitrate present, in turn, reflects the balance between removal of nitrogen from this pool by plant uptake or immobilization and the input of nitrogen into the nitrate pool by mineralization, fertilization, and atmospheric deposition. For example, pristine mature forests usually maintain a very close balance between nitrogen taken up by trees and nitrogen returned as litter. Leaching water contains only about 0.1 mg nitrate-N/L, and only 1 or 2 kg of N/ha is lost annually to groundwater. However, deposition from the atmosphere can increase inputs to the nitrate pool, while disturbances such as timber harvest can reduce plant uptake out of the pool, leading to leachate concentrations of 2–3 mg nitrate-N/L and annual leaching losses greater than 25 kg N/ha.

Groundwater and streams draining watersheds with intense agricultural land use are commonly much higher in nitrate than those draining forested watersheds. Heavy nitrogen fertilization of crops (especially vegetables and some grain crops) can be a major source of excessive nitrate because the crops rarely absorb more than half of the nitrogen applied. Watersheds with many CAFOs are often the most polluted with nitrate because of the enormous quantities of nitrogen-rich animal manure produced (see Sections 13.15 and 16.4).

**Timing of Nitrogen Input.** In humid-temperate (Udic) and Mediterranean (Xeric) climates, the potential for nitrate leaching is lowest in midsummer when plants are using large amounts of both water and N. Leaching water volumes and nitrate levels are commonly highest in early spring and late fall and winter (if soils are not frozen) when plants are not intensively using water or N, leaving both available to leach. The synchrony between the production of nitrate by mineralization and the uptake of N by plants is greatest where perennial vegetation is grown and poorest where annual crops leave the soil bare in early spring and late fall.

Application of the entire amount at the beginning of the season may result in much of the nitrogen leaching below the root zone before annual plants have had a chance to use it (as in the high N-rate example in Figure 13.33). This is especially true where soils are sandy or where precipitation (rainfall and irrigation) is high early in the season. Under these conditions, it is advisable to delay N application until plants have established an extensive root system and are about to enter their phase of rapid growth and high N uptake rate. The amount of nitrogen to side dress at this time may be determined by: (1) measuring the nitrate accumulated so far in the soil (a pre-sidedress nitrate soil test, PSNT) or (2) feeding site-specific soil, weather and management data into a sophisticated computer program that models the gains and losses of nitrogen in the soil up to that point in the season (e.g., Adapt-N, http://adapt-n.cals.cornell.edu/). At the end of the season, a cornstalk nitrate test (CSNT) can be used to assess whether too much or too little nitrogen was applied that year. Widespread experience shows that such improved management allows the application of less nitrogen while increasing economic returns, maintaining crop yields, reducing the level of N susceptible to leaching loss after crop harvest.

An even more conservative alternative is to split the total N application for the growing season into several small doses. For example, split application for an annual crop might involve applying a small portion (10–20%) of the N at planting time, and providing most of the N in a second—and possibly third—application latter in the season when the plants are larger and their rate of N uptake is high. Although split or delayed application of fertilizer may require some extra effort and special machinery, it often is justified by improved N use efficiency, increased yields, and greater profitability.
Management to Reduce Losses. Even in regions of high leaching potential, careful soil management can prevent excessive nitrate losses. Applications of fertilizer and manure should be modest in amount and timed to provide nitrogen when actively growing plants are able to absorb it. Nitrogen-scavenging winter cover crops (Section 16.2) should be planted immediately following summer annual crop harvest to take up the unused nitrates before they can leach away (see Figure 13.33). If such guidelines are followed, nitrogen leaching may be kept to less than 5–10% of the nitrogen applied.

Reversing Nitrate Leaching in the Humid Tropics. Much of the nitrate mineralized in certain highly weathered, tropical Oxisols and Ultisols leaches below the root zone before annual crops such as corn can take it up. Soil scientists in Africa have discovered that some of this leached nitrate is not lost to groundwater. Instead, the highly weathered and acid clays deep in the subsoil adsorb the nitrate on their anion exchange sites (see Section 8.11). Deep-rooted woody perennials such as *Sesbania* trees or pigeon peas are capable of taking up this subsoil nitrate. If grown in association with annual food crops, the perennials subsequently enrich the surface soil when they shed their leaves, making this pool of once-leached nitrogen available again for food production (Figure 13.34). Such agroforestry practices have the potential to improve both crop production and environmental quality in the humid tropics (see also Section 20.10).

### 13.15 PRACTICAL MANAGEMENT OF SOIL NITROGEN

Sustainable nitrogen management aims to achieve three goals: (1) the maintenance of SOM to ensure adequate long-term nitrogen supplies in the soil, (2) the regulation of the soluble forms of nitrogen to ensure that plant needs are met, and (3) the minimization of environmentally damaging losses of nitrogen from the soil–plant system, including nitrate and soluble organic nitrogen in leaching and runoff water, as well as ammonia and nitrogen oxides in gaseous emissions.

A particular type of soil in any given combination of climate and farming system tends to assume what may be called a *normal* or *equilibrium content* of nitrogen. Consequently, under ordinary methods of cropping and manuring, any attempt to permanently raise the nitrogen content to a level higher than this will result in unnecessary waste as nitrogen
leaches, volatilizes, or is otherwise lost before it may be used. The equilibrium level of soil nitrogen is governed by the management practices employed and is likely to change as they are changed. For example, if cultivated soil that is initially low in organic matter and nitrogen is planted to perennial grass and fertilized or mixed with legumes, the cessation of tillage and high rate of root matter return will cause SOM to build up quickly (see Section 12.8). If this long-term grassland is then plowed under, the reverse will take place, and the nitrogen stored over the years will be rapidly released—possibly causing a flush of nitrate leaching.

**Using Nitrogen Fertilizers Wisely**

Ammonium and nitrate ions from fertilizer are taken up by plants and participate in the nitrogen cycle in exactly the same way as ammonium and nitrate derived from organic matter mineralization or other sources. In fact, most of the N added as soluble fertilizers enters the biological cycle before the fertilized plants use it (see Figure 13.35). Nonetheless, the application of soluble fertilizers results in greater concentrations of these nitrogen ions than would be found in unfertilized soils. Plants and microorganisms may not be able to assimilate the applied nitrogen fast enough to prevent major losses by leaching, surface runoff, denitrification, and ammonia volatilization. Box 13.4 describes some technologies that can make nitrogen fertilizers less prone to these environmentally damaging losses. However, even with the best fertilizer technologies, it is still important to avoid applying more nitrogen than is actually needed.

Fertilizer nitrogen should be considered only as a supplement to the nitrogen made available from nitrogen deposition from the atmosphere, mineralization from SOM, fixation by legumes, and release from current or past applications of animal manure or other organic materials. That is, the amount of N applied as fertilizers should be reduced in accordance with contributions from these sources to the pool of plant-available nitrogen. This strategy is often referred to as “taking nitrogen credits” for these nonfertilizer sources.

**Preventing N Losses**

Nitrogen losses by leaching and denitrification from agricultural land generally become problematic only when nitrogen fertilization exceeds the amount needed to fill the gap between crop uptake needs and the supply from the other sources just mentioned. The need for

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**Figure 13.34** Depth distribution of nitrates in an Oxisol in western Kenya before planting either corn or a fast-growing tree, Sesbania, and after growing three crops of fertilized corn (in 16 months) and continuous Sesbania. Note that the Sesbania markedly decreased soil nitrates to a depth of about 2 m. Separate root studies (Mekonnen et al., 1997) showed that 31% of the Sesbania roots were located between 2.5 and 4 m in depth. Compare to Figure 13.34.[From Sanchez et al. (1997).]
Crop rotation can increase yields and reduce fertilizer requirements. (a) The amount of fertilizer nitrogen required (T) for optimal corn yields was about 150 kg N/ha in the corn–soybean rotation (green line), but over 250 kg N/ha in the continuous corn system (gold line). These Flanagan silt loam (Aquic Argiudoll) soils supported either corn every year or corn every second year alternating with soybeans for five corn crops. (b) The use of isotopically labeled fertilizer (15NH4NO3) in another study showed that even when a relatively high rate was applied (168 kg N/ha), most of the corn’s N needs did not come directly from the fertilizer but from the mineralization of soil organic matter. This was especially true in the latter part of the growing season. By harvest time, the fertilizer-derived nitrogen taken up by the corn represented less than one-third of the nitrogen taken up by the plants and accounted for less than one-third of the fertilizer nitrogen applied to the soil. (c) Corn grown in rotation with soybeans took up more nitrogen from both soil and fertilizer sources than did corn grown after corn. These data are averages for two years and two soils (a silt loam Ustoll and a loam Udoll) in Kansas, but the results are typical of those found in many parts of the world (compare to Table 16.15). The rotation corn maintained some yield advantage even when high amounts of nitrogen were applied, indicating that in addition to increased nitrogen availability after soybeans, the crop rotation conferred other benefits, such as pest reduction or improved soil microbial activity. Crop rotations involving more than two crops usually produce even greater benefits, especially if they include cover crops, perennial grass-legume hay or pasture. [Data in (a) from Gentry et al. (2013) and in (b,c) from Omay et al. (1998).]

commercial nitrogen fertilizer will be governed by the degree to which the manager is able to integrate symbiotic nitrogen fixation, manure and residue recycling, and loss minimization practices into the farming system. Not every system needs to export a nitrogen-containing product. In the case of lawn grass, the aim of management is to produce a healthy lawn, not grass clippings for harvest. In contrast to the heavy fertilization used on many lawns, the nitrogen-balance principles just discussed suggest that if the clippings are not removed after every mowing, then little or no nitrogen will be removed and little fertilizer need to be applied (see Figure 13.39).

Legume Cover Crops Reduce the Need for Nitrogen Fertilizer

A legume cover crop system may be able to replace part or all of the nitrogen fertilizer normally used to grow an annual cash crop (Figure 13.40). The cover crop is usually killed mechanically or by herbicide spray before the main crop is planted. The cover crop residues can be left on the surface as a mulch in a no-till system (see Section 17.6) or plowed under in a conventional tillage system. When evaluating the feasibility of using cover crops, consideration should be given to the many other benefits of cover crops in addition to nitrogen supply (Section 16.2) as well as the costs and risks of growing the cover crop.

As cover crop residues decay, nitrogen is supplied to the following main crop over a period of several months, rather than all at once as with a soluble fertilizer application. In most cases low C/N ratio legume residues decay rapidly enough to keep up with crop nitrogen demands (see Section 12.3). Legume cover crop systems have been adapted for vineyards, rice paddies, grain crops, vegetable fields, and home gardens wherever there is sufficient water to support both the cover crop and the main (summer) crop. Cover crops are increasingly important in organic farming systems because environmental restrictions on excessive phosphorus application (Sections 16.2 and 16.12) are forcing organic farmers to reduce their traditional
BOX 13.4

CONTROLLING NITROGEN LOSSES WITH FERTILIZER TECHNOLOGY

A major challenge in managing nitrogen (N) fertilizers is to supply plant-available N at the proper time, in sufficient but not excessive amounts, and with a minimum of loss to the environment. Here we will discuss three types of fertilizer technology that can help meet this goal (Figure 13.36).

1. **Slow-release fertilizers.** Most synthetic nitrogen fertilizers contain readily water soluble N, but the N in slow-release fertilizers is formulated to dissolve in moist soil slowly over a period of weeks or months. In this way, ammonium and nitrate concentrations may be better synchronized with plant N uptake requirements, thus avoiding excessive N losses. Figure 13.37 illustrates dramatic reductions in nitrate leaching under turfgrass that can be achieved by replacing water-soluble fertilizers with organic or slow-release materials. Slow release of N may be achieved by the mineralization of compost (see Section 12.10), digested sewage sludge (e.g., Milorganite®) or other stabilized organic materials. However, most slow-release N fertilizers are made by treating highly soluble urea fertilizer with materials that slow its dissolution or inhibit its hydrolysis to ammonium (Figure 13.36). Urea–formaldehyde, isobutylidene diurea (IBDU), resin-coated fertilizers (e.g., Osmocote®), polymer and sulfur-coated urea are all examples of slow-release N fertilizers. In the case of the latter, the sulfur content (10–20%) itself may be beneficial where sulfur is in low supply (Section 13.18) or problematic where the extra acidity generated by the sulfur (Section 13.22) would be undesirable. Sulfur-coated urea should not be used in flooded rice paddies as reduced iron will combine with the sulfur to form insoluble FeS, locking up the N in the fertilizer. Excellent controlled release characteristics have recently been achieved with polymer coatings that do not react with iron in anaerobic soils. Figure 13.38 describes dramatic reductions in emissions of ammonia and nitrous oxide gases using plastic polymer coatings to make fertilizer granules release urea slowly during an entire rice growing season instead of dissolving immediately upon application to flooded paddy soils. Slow-release fertilizers cost from 1.5 (for sulfur-coated urea) to 5 times as much as plain urea per unit of N. Therefore, they are most widely used for high-value plant production (e.g., certain vegetables, turfgrass, and ornamentals) where the cost of fertilizers is not critical. Their use on turfgrass is popular because they are not likely to cause fertilizer burn and because they provide the convenience of fewer applications.

2. **Urease inhibitors.** The enzyme urease is ubiquitous in soils and on surface residues. When urea is applied in the field, urease rapidly catalyzes the hydrolysis of urea to form ammonium carbonate which in turn releases ammonium ions into the soil solution. If the urea is applied to the soil surface, and especially if the soil pH is above 7.0, the ammonium ions (NH₄⁺) will readily convert to ammonia gas (NH₃) and volatilize from the soil. Urease inhibitors, such as N-(n-butyl) thiophosphoric triamide (NBPT), added to urea fertilizer can conserve N if conditions favor NH₃ loss. Yield increases that repay the added cost of NBPT fertilizer have been observed in about 1/3 of such cases.

3. **Nitrification inhibitors** are compounds that inhibit the activity of the Nitrosomonas bacteria, which convert NH₄⁺ to NO₂⁻ in the first step of nitrification. (Note from Eq. (13.5) that a chemical inhibiting Nitrobacter would not be useful, as this would cause toxic nitrite (NO₂⁻) to accumulate.) As long as N remains as NH₄⁺ it has little susceptibility to loss by leaching and does not transform into the greenhouse-forcing gases (N₂O and NO) by denitrification. Therefore, N fertilizers might be used more efficiently if the conversion of NH₄⁺ to NO₃⁻ could be slowed down until the crop is ready to make use of the mobile NO₃⁻. To this end chemical companies have developed such nitrification inhibitors as dicyandiamide (DCD), nitrapyrin (N-Serve®), 3, 4-Dimethylpyrazole phosphate (DMPP), Ca-carbide and etridiazol (Dwell®). When mixed with nitrogen fertilizers, these compounds can temporarily prevent NO₃⁻ formation. The key word here is temporarily, for when conditions are favorable for nitrification, the inhibition usually lasts only a few weeks (less if soil temperatures are above 20 °C). Fertilizers treated

![Figure 13.36: Three types of inhibitors (jagged blades) designed to make fertilizer nitrogen less prone to loss: (1) Coatings that inhibit slow the release of urea from fertilizer granules; (2) chemicals that inhibit the urease enzyme thus slowing hydrolysis of urea to ammonium thus limiting formation of ammonia gas and nitrates; and (3) nitrification inhibitors that slow nitrate formation from ammonium, thus reducing losses by leaching and denitrification. (Diagram courtesy of R. Weil.)](https://example.com/diagram)
with these chemicals are expensive and typically pay for themselves by saving N only in rainy conditions on sandy soils (by reduced leaching) and on temporarily waterlogged soils (by reduced denitrification).

Biological inhibition of nitrification may offer a new way of controlling nitrate formation without the limitations and expense of synthetic fertilizer additives. Researchers have discovered that root exudates produced by a tropical forage grass (*Brachiaria humidicola*) effectively inhibit *Nitrosomonas*, accounting for the high efficiency of N use in certain pasture systems. Scientists hope to transfer the nitrification inhibition gene from *B. humidicola* to other plants, with the aim of achieving widespread improvements in N use efficiency and reductions in N impacts on groundwater and greenhouse gases.

For a meta-analysis of research on nitrification inhibitors and their potential benefits, see Qiao et al. (2015). For information on biological nitrification inhibition in tropical pastures, see Ishikawa et al. (2003).
dependence on purchased manure and compost for nitrogen (which contain high levels of phosphorus).

In temperate regions, winter annual legumes, such as vetch, clovers, and peas, can be sown in fall after the main crop harvest or, if the growing season is short, they can be seeded by airplane or helicopter while the main crop is still in the field. After surviving the coldest part of the winter in a dormant state, the cover crop will resume growth in spring and associated microorganisms will fix as much as 3 kg/ha of nitrogen daily during the warmer spring weather. The amount of nitrogen provided is therefore partially determined by how long the cover crop is allowed to grow.

### Legume Main Crops in Rotations

A detailed consideration of different cropping sequences (crop rotations) is beyond the scope of this book, but the nutrient-management aspects of rotating legumes with nonlegumes deserve mention here. A legume main crop grown one year may substantially reduce the amount of nitrogen fertilizer that needs to be used to grow a subsequent nonleguminous crop the next year. However, unlike for the legume cover crops just discussed, most of the biomass and accumulated nitrogen in the legume main crop is removed with the crop harvest. Perennial forage legumes like alfalfa tend to supply the greatest amounts of nitrogen because of their large root contribution, but the nitrogen contributions of grain legumes (e.g., soybeans or peanuts)
should also be taken into account when planning fertilizer applications to nonlegumes that follow in the rotation. For example, many studies have shown that compared to corn grown after corn, corn grown after soybeans responds less dramatically to nitrogen fertilizer and requires less of it for optimal growth (Figure 13.35a).

Growing the same crop year after year on the same land generally produces lower yields of that crop and engenders more negative impacts on the soil and environment than if that crop is grown in rotation with other crops. This is true even when legumes are not part of the rotation, so more than nitrogen fixation must be involved. The improved plant productivity may result from interruption of weed, disease, and insect pest cycles; from complementary soil exploitation by differing root systems; different types of residues and nutrient requirements; synergistic effects (see Section 11.14); and, possibly, positive effects on mycorrhizal diversity (see Section 11.9). These and other phenomena may explain why, even where pests and nutrient supply are optimally controlled, crops consistently yield 10–20% more in rotations than in continuous culture.

**Bringing Nitrogen Inputs into Balance with Outputs**

To effectively manage nitrogen or any other nutrient, it is important to consider the balance between inputs and outputs for the system in question. The features that make a system dominated by agriculture different from a natural ecosystem are mainly: (1) the import of nitrogen in fertilizer and feed and (2) the removal of nitrogen in the harvested product. If the total N input is greater than nitrogen output contained in harvested agricultural products, the land is considered to be subject to a nitrogen excess. A small amount of such nitrogen excess may initially remain on the land as accumulated soil organic N or in plant biomass, but eventually the excess nitrogen will take the form of environmentally (and financially) damaging losses from the system. The map in Figure 13.41 shows "hot spots" of excess nitrogen in China, Northern India, central USA, and Western Europe. Perhaps one third of the global nitrogen surplus is

![Figure 13.41](image)
concentrated on just 10% of the world’s croplands. The lost excess nitrogen ends up causing environmental damage via air (e.g., \( \text{N}_2\text{O}, \text{NH}_3 \) gases), water (e.g., \( \text{NO}_3^- \) and dissolved organic N), or soil (nitrogen saturation and acidification). In many agricultural areas devoted to intensive crop production, the excess nitrogen is mainly due to applications of fertilizer beyond what the crops can actually use (see Section 16.13). In other areas, where there are CAFOs (concentrated animal-feeding operations), the imbalance stems from the fact that much nitrogen is imported in the feed because the system for raising of animals is not well integrated on the land with the production of their feed (see Section 16.4). The data in Table 13.6 quantify changes, experienced, and expected, in the balance between various nitrogen inputs and outputs for the world’s agricultural land. The data specific to China in Table 13.6 illustrate the magnitude of nitrogen excess in a country that imports a significant proportion of the livestock feed for its many CAFOs. Note that for the country of China as a whole, the manure and atmospheric deposition nitrogen inputs to agricultural land were sufficient to meet the nitrogen taken off the land as harvested agricultural products.

The principles discussed in this chapter suggest several basic strategies for achieving a rational reduction of excessive nitrogen inputs while maintaining or improving production levels and profitability in agricultural enterprises. These approaches include: (1) taking into account the nitrogen contribution from all sources and reducing the amount of fertilizer applied accordingly; (2) improving the efficiency with which fertilizer and organic amendments (e.g., manure) are used; (3) avoiding overly optimistic yield goals that lead to fertilizer

### Table 13.6
**Inputs and Outputs of Nitrogen for Agricultural Land at Different Times**

Actual data are shown for estimates of global amounts of N for world agricultural land in the years 1970 and 2000 and for per hectare amounts of N in Chinese agricultural land in 2008. Projected data for the year 2050 is also shown as modeled simulation that assumes nine billion people on Earth, moderate economic growth, amelioration of environmental impacts, and some recycling of human nutrients in areas lacking sewers.

<table>
<thead>
<tr>
<th>Year</th>
<th>Global, actual</th>
<th>Global, simulation</th>
<th>China, actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>N inputs to global agriculture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer N</td>
<td>29</td>
<td>83</td>
<td>68</td>
</tr>
<tr>
<td>Manure N</td>
<td>76</td>
<td>101</td>
<td>144</td>
</tr>
<tr>
<td>Human N</td>
<td>0</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>Biologically fixed N</td>
<td>27</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>Atmospheric deposition N</td>
<td>27</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td>Irrigation water N</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d</td>
</tr>
<tr>
<td>Total N input to agricultural land</td>
<td>160</td>
<td>249</td>
<td>299</td>
</tr>
<tr>
<td>Outputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop harvest/grazing</td>
<td>58</td>
<td>93</td>
<td>146</td>
</tr>
<tr>
<td>Ammonia volatilization</td>
<td>18</td>
<td>34</td>
<td>47</td>
</tr>
<tr>
<td>Denitrification</td>
<td>56</td>
<td>82</td>
<td>71</td>
</tr>
<tr>
<td>Leaching/soil erosion</td>
<td>28</td>
<td>41</td>
<td>36</td>
</tr>
<tr>
<td>N loss or accumulation in the soil</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Notes: *Global values selected from (Bouwman et al., 2009); China values selected from Li et al. (2013).  
*bFor China livestock and human nutrients are combined.  
*cNot determined.  
*dFor China all pathways of environmental N loss are combined.
application rates designed to meet crop needs that are much higher than actually occur in most years; and (4) improving crop response knowledge, which identifies the lowest nitrogen application that is likely to produce optimum profit. These and other strategies of nutrient management will be discussed further in Chapter 16.

13.16 IMPORTANCE OF SULFUR

Sulfur (S) is a macronutrient element essential for life. It is used by plants in amounts similar to those of phosphorus. Yet S often is forgotten in discussions of soil fertility management which tend to focus on N, P, and K. In addition to its vital roles in plant and animal nutrition, sulfur is also responsible for several types of air, water, and soil pollution, and is therefore of increasing environmental interest. The environmental problems associated with sulfur include acid precipitation, certain types of forest decline, acid mine drainage, acid sulfate soils, and even some toxic effects in drinking water used by humans and livestock.

Roles of Sulfur in Plants and Animals

Sulfur is a constituent of the essential amino acids methionine, cysteine, and cystine, deficiencies of which result in serious human malnutrition. As part of storage proteins, these sulfur-containing amino acids tend to accumulate in plant seeds, including grains that are staples of the human diet. The vitamins biotin, thiamine, and B1 contain sulfur, as do many protein enzymes that regulate such activities as photosynthesis and nitrogen fixation. Sulfur-to-sulfur bonds link certain sites on long chains of amino acids, causing proteins to assume the specific three-dimensional shapes that are the key to their catalytic action.

Sulfur is closely associated with nitrogen in the processes of protein and enzyme synthesis. Sulfur is also an essential ingredient of the aromatic oils that give the cabbage and onion families of plants their characteristic odors and flavors. It is not surprising that among the plants, the legume, cabbage, and onion families require especially large amounts of sulfur.

Agronomic Deficiencies of Sulfur

Depending on the plant species, healthy plant foliage generally contains 0.15–0.45% sulfur, or approximately one-tenth as much sulfur as nitrogen. Plants deficient in sulfur tend to become spindly and to develop thin stems and petioles. Their growth is slow, and maturity may be delayed. They also have a chlorotic light green or yellow appearance (Figure 13.42). Symptoms of sulfur deficiency are similar to those associated with nitrogen deficiency (see Figure 13.1). However, unlike nitrogen, sulfur is relatively immobile in the plant, so the chlorosis develops first on the youngest leaves as sulfur supplies are depleted (in nitrogen-deficient plants, chlorosis develops first on the older leaves). Sulfur-deficient leaves on some plants show interveinal chlorosis or faint striping that distinguishes them from nitrogen-deficient leaves. Also, unlike nitrogen-deficient plants, sulfur-deficient plants tend to have low sugar but high nitrate contents in their sap.

As a result of the following three independent trends, sulfur deficiencies in agricultural plants have become increasingly common during the past several decades:

1. Enforcement of clean air standards in many countries has led to reduction of sulfur dioxide (SO2) emissions to the atmosphere from the burning of fossil coal and oil.
2. The sulfur contents of today’s highly concentrated N—P—K fertilizers are far lower than those of a generation ago, resulting in less sulfur in applied amendments.
3. As crop harvests have increased, larger amounts of sulfur are being removed from the soils. Consequently, the need for sulfur has increased just as the inputs from all sources have declined.

Areas of Deficiency. Sulfur deficiencies have been reported in most areas of the world but are most prevalent in areas where soil parent materials are sandy or inherently low in sulfur,

12Several reviews provide more detail on the subject of sulfur in soils (Eriksen, 2009; Jez, 2008; Kovar and Grant, 2011; Scherer, 2009).
Deficiency of sulfur is often mistaken for that of nitrogen as the plant symptoms for both include yellowish, chlorotic leaf tissue. However, S deficiency causes chlorotic leave uniformly throughout the plant or more typically the younger, uppermost leaves to become most chlorotic. This is in contrast to N deficiency which typically causes the oldest, lowest leaves on the plant to become chlorotic first. Photos (a)–(c) illustrate plant responses to S applied to soils as gypsum (CaSO₄). Photo (d) shows a sulfur-deficient tea bush in Malawi where this deficiency was first reported. (Photos courtesy of R. Weil.)

where extreme weathering and leaching have removed this element, or where there is little replenishment of sulfur from the atmosphere. In many tropical countries, one or more of these conditions prevail and sulfur-deficient areas are common. In the industrial countries, sulfur deficiencies are most common in areas far from heavy industry, fossil fuel power plants, and large cities.

The burning of plant biomass results in a loss of sulfur to the atmosphere. In many parts of the world, crop residues and native vegetation are routinely burned as a means of clearing the land. Soils of the African savannas are particularly deficient in sulfur as a result of the annual burning of plant residues during the dry season. Fire converts much of the sulfur in the plant residues to sulfur gases, such as sulfur dioxide. Sulfur in these gases and in smoke particulates is subsequently carried by the wind hundreds of kilometers away to areas covered by rain forest, where some of the sulfur dioxide is absorbed by moist soils and foliage and some is deposited with rainfall. Thus, the soils of the savannas tend to export their sulfur to those of the rain forest (e.g., Oxisols). Consequently, the latter often contain significant accumulations of sulfur deep in their profiles (see Figure 13.43).

13.17 NATURAL SOURCES OF SULFUR

The three major natural sources of sulfur that can become available for plant uptake are: (1) organic matter, (2) soil minerals, and (3) sulfur gases in the atmosphere. In natural ecosystems where most of the sulfur taken up by plants is eventually returned to the same soil, these three sources combined are usually sufficient to supply the needs of growing plants (Figure 13.44).
Organic Matter

In surface soils in temperate, humid regions, 90–98% of the sulfur is usually present in organic forms (see Figure 13.43). As is the case for nitrogen, the exact forms of the sulfur in the organic matter are not well known. Recent research using sophisticated spectroscopic analyses has shown that three principal groups of organic sulfur compounds exist in SOM. The first group consists of the most reduced forms of S bonded to carbon in compounds such as sulfides, disulfides, thiols, and thiophenes. These include proteins with amino acids such as cysteine, cystine, and methionine. A second group at intermediate redox state includes sulfoxides and sulfonates in which the sulfur is bonded to carbon but also to oxygen (C—S=O). The third group consists of highly oxidized forms of S in ester sulfates (C—O=S), in which S is bound to oxygen rather than directly to carbon.

Figure 13.43 The distribution of organic and inorganic sulfur in representative soil profiles of the soil orders (a) Mollisols, (b) Spodosols, and (c) Oxisols. In each, soil organic forms dominate the surface horizon. Considerable inorganic sulfur, both as adsorbed sulfate and calcium sulfate minerals, exists in the lower horizons of Mollisols. Relatively little inorganic sulfur exists in Spodosols. However, the bulk of the profile sulfur in the humid tropics (Oxisols) is present as sulfate adsorbed to colloidal surfaces in the subsol. (Diagram courtesy of R. Weil.)

Figure 13.44 Plants take up sulfur primarily from three sources: sulfur in atmospheric gases and dust, sulfate mineralized from soil organic matter, and sulfate adsorbed on soil minerals. Typical ranges of sulfur uptake from these sources are shown. Where these three sources are insufficient for optimal growth, the application of sulfur-containing fertilizers may be warranted. In areas downwind of coal-burning plants and metal smelters, the atmospheric contribution may be much larger than indicated here. (Diagram courtesy of R. Weil.)

For a study of organic sulfur forms in a range of soils, see Zhao et al. (2006).
Typically, undisturbed soils under grasslands, wetlands, and moist forest vegetation have much less than half of the organic sulfur that is in the most oxidized ester-sulfate group. The ester-sulfates appear to be most prominent in well-aerated soils that have a long history of tillage.

![Chemical structures](image)

Many of the S-compounds are probably somewhat protected from microbial attack by being bound to the humus and clay fractions. Compounds in the three main fractions of organic sulfur are characterized by sulfur in $+6$, $0$, and $-2$ oxidation states.

Over time, soil microorganisms break down these organic sulfur compounds into soluble forms analogous to the release of ammonium and nitrate from organic matter, discussed in Section 13.3. As with nitrogen, most soil sulfur is organic with only a very small percentage in the mineralized (sulfate) form, even in the sandy Spodosols described in Table 13.7 (compare with Figure 13.43).

In dry regions, less organic matter is present in the surface soils. Therefore, the proportion of organic sulfur is not likely to be as high in arid- and semiarid-region soils as it is in humid-region soils. This is especially true in the subsoils, where organic sulfur may constitute only a small fraction of the sulfur present and where inorganic sulfur in the form of gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$) is often present.

### Table 13.7

**Concentration of Sulfur Compounds in Forested Spodosols**

The organic layers (Oa) have high S levels and that the two organic forms (C-bonded and ester sulfate) contain 84–99% of the soil sulfur. However, the spodic horizons (Bh and Bs) can sorb significant amounts of sulfate ions.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Totals, μg S/g</th>
<th>C-bonded S</th>
<th>Ester sulfate</th>
<th>Sulfate S</th>
<th>Inorganic S*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Huntington Forest, NY</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oa</td>
<td>1780</td>
<td>77</td>
<td>22</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Bh</td>
<td>761</td>
<td>83</td>
<td>13</td>
<td>3.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Bs1</td>
<td>527</td>
<td>70</td>
<td>22</td>
<td>4.2</td>
<td>4.4</td>
</tr>
<tr>
<td><strong>Conifer site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oa</td>
<td>2003</td>
<td>88</td>
<td>11</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Bh</td>
<td>540</td>
<td>83</td>
<td>11</td>
<td>2.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Bs1</td>
<td>515</td>
<td>57</td>
<td>27</td>
<td>13</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Notes: *Inorganic sulfur compounds, such as sulfides.  
*From David et al. (1982).  
*From Mitchell et al. (1992).
Soil Minerals

While not as plentiful in surface soils as organic forms, inorganic sulfur compounds often supply soluble sulfur important for the nutrition of plants and soil microbes. Depending on the soil redox conditions (see Section 7.3), most inorganic sulfur is present either as sulfates (oxidized with $S^{6-}$) and sulfides (reduced with $S^{2-}$). The sulfate minerals are most easily solubilized, and the sulfate ion ($SO_4^{2-}$) is easily assimilated by plants. Sulfate minerals are most common in regions of low rainfall, where they accumulate in the lower horizons of some Molisols and Aridisols (see Figure 13.43). The most common sulfate mineral, gypsum, may also accumulate when sulfate-laden soil water evaporates near the soil surface (Figure 13.45c). Sulfate salts may contribute to salinity in soils of arid and semiarid regions.

Sulfides are found in some humid-region wetland soils, especially those formed from marine sediments (Figure 13.45a). Sulfides must be oxidized to the sulfate form before the sulfur can be assimilated by plants. When waterlogged sulfide-rich soil layers are drained or exposed by excavation, oxidation will occur, and ample available sulfate-S will be released. In fact, so much sulfur may be oxidized that problems of extreme acidity result (see Section 13.20).

Another mineral source of sulfur is the clay fraction of some soils high in Fe, Al oxides, and kaolinite. These clays are able to strongly adsorb sulfate from soil solution, especially at low pH, and subsequently release it slowly by anion exchange. Oxisols and other highly weathered soils of the humid tropics and subtropics may contain large stores of sulfate sorbed in their subsoil horizons (see Figure 13.43c). Considerable sulfate may also be bound by the metal oxides in the spodic horizons under certain temperate and boreal forests (Table 13.7).

Atmospheric Sulfur

The atmosphere contains varying quantities of carbonyl sulfide (COS), hydrogen sulfide (H$_2$S), sulfur dioxide (SO$_2$), and other sulfur gases, as well as sulfur-containing dust particles. These atmospheric forms of sulfur arise from volcanic eruptions, volatilization from soils, ocean spray, biomass fires, and industrial plants (such as metal smelters and electric-generation stations fired by high-sulfur coal). During the past century, the contribution from industrial sources has dominated sulfur deposition in certain locations.

In the atmosphere, most of the sulfur materials are eventually oxidized to sulfates, forming $H_2SO_4$ (sulfuric acid) and sulfate salts, such as CaSO$_4$ and MgSO$_4$. The “acid rain” problem caused by this atmospheric sulfur (as well as nitrogen) was discussed in Section 9.6 (see

Figure 13.45  Minerals containing oxidized or reduced sulfur can commonly be found in soils, especially those soils presently or in the geologic past associated with seawater which has high levels of sulfur. (a) The bluish-black color in the interior of the clayey clod embedded in a sandy soil on the Chesapeake Bay coast of Maryland is characteristic of iron sulfide that is formed under anaerobic reducing conditions. The zones where oxidation is taking place have turned the red-orange color of oxidized iron minerals. (b) The bright yellow color on the surface of these peds along the Pacific Ocean coast in California are characteristic of the potassium–iron sulfate mineral jarosite [KFe$_3^{3+}$OH$_2$[SO$_4$]$_2$] that is an end product of the sulfur oxidation process in formerly reduced soils. (c) The whitish efflorescence of gypsum (CaSO$_4$ ·2H$_2$O) crystals can be seen where laterally flowing groundwater evaporates from the subsoil exposed by a roadside ditch in semiarid Malawi. (Photos courtesy of R. Weil.)

14For a discussion of global sulfur deposition trends, see Klimont et al. (2013).
About half of the sulfur is returned to the Earth as dry deposition (dry particles and gases) and half as wet deposition (in snow and rain). Figure 13.46 shows how sulfur deposition is collected for measurement and a map of predicted global sulfur deposition.

After watching forests and lakes become seriously damaged by acid rain in the 1970s and 1980s, governments in North America and parts of Europe established regulatory programs to reduce sulfur emissions. As a result, sulfur emissions in these regions have declined by more than half since the late 1980s (although nitrogen oxide emissions have not been equally addressed). By 2008 in the eastern United States, annual sulfur deposition rarely exceeded 15 kg S/ha (= 37 kg sulfate) and was more commonly less than 6–12 kg S/ha (Figure 13.47). On the other hand, sulfur emissions are on the rise in China (until recently), India, and other newly industrializing regions, where burning of coal and oil cause as much as 50–75 kg S/ha to come down in a year. In other areas little affected by industrial emissions (e.g., most rural areas of the western United States), deposition is generally only 2–5 kg S/ha/yr. In rural Africa, as little as 1–4 kg S/ha/yr is deposited.

Figure 13.46. (Left) An apparatus for collecting both wet and dry sulfur deposition. A sensor (a) triggers the small roof (b) to move over and cover the dry deposition collection chamber (c) at the first sign of rain (or snow). The wet deposition chamber (d) is then exposed to collect precipitation. When the rain ceases, the sensor triggers the roof to move back over the wet deposition collection chamber so that dry deposition can again be collected. The map shows the geographic distribution of S deposition from the atmosphere as predicted for the year 2025 based on collected data and predictive models. (Photo courtesy of R. Weil; map modified from http://www-iam.nies.go.jp/aim/aipamph/S02ens.htm.)

Figure 13.47. The dramatic reductions in sulfur deposition achieved though environmental policies in the United States during a 23-year period. (Modified from USEPA.)
Atmospheric sulfur becomes part of the soil–plant system mainly as SO$_4^{2-}$ ions dissolve in soil solution, sorb to soil surfaces, or are directly absorbed by plant foliage (along with some SO$_2$ gas). The quantity that plants can absorb directly from the air is variable, but up to 1/3 of the sulfur in a plant may come from this source, even if available soil sulfate is adequate. In sulfur-deficient soils, about half of the plant needs can come from the atmosphere (see Figure 13.44).

The acid precipitation caused partly by atmospheric sulfur (and nitrogen) is a serious threat to the health of lakes, forests, and agroecosystems. In areas immediately downwind from industrial plants, sulfur deposition may be great enough to cause direct toxicity to trees and crops (not to mention respiratory problems in people). As far as 1000 km downwind, the deposited sulfate may mobilize toxic soil aluminum, acidify lakes, and deplete soils of needed calcium. On the other hand, recent reductions in sulfur emissions have resulted in sulfur deficiencies becoming increasingly common in some areas, especially for high-yield-potential agricultural crops. In these areas, improved sulfur recycling through cover crops and agroforestry may help provide enough of this element for high levels of crop production. Alternatively, farmers must spend more money on sulfur-fortified fertilizers and other S-containing amendments.

### 13.18 THE SULFUR CYCLE

The major transformations that sulfur undergoes in soils are shown in Figure 13.48. The inner circle shows the relationships among the four major forms of this element: (1) sulfides, (2) sulfates, (3) organic sulfur, and (4) elemental sulfur. The outer portions show the most important sources of sulfur and how this element is lost from the system.

Considerable similarity to the nitrogen cycle is evident (compare Figures 13.3 and 13.48). In each case, the atmosphere is an important source of the element in question. Both elements are held largely in the SOM, both are subject to microbial oxidation and reduction, both can enter and leave the soil in gaseous forms, and both are subject to some degree of leaching in the anionic form. Microbial activities are responsible for many of the transformations that determine the fates of both nitrogen and sulfur.

Figure 13.48 should be referred to frequently in conjunction with the following more detailed examination of sulfur in plants and soils.

### 13.19 BEHAVIOR OF SULFUR COMPOUNDS IN SOILS

**Mineralization**

Sulfur behaves much like nitrogen as it is absorbed by plants and microorganisms and moves through the sulfur cycle. The organic forms of sulfur must be mineralized by soil organisms if the sulfur is to be used by plants. The rate at which this occurs depends on the same environmental factors that affect nitrogen mineralization, including moisture, aeration, temperature, and pH. When conditions are favorable for general microbial activity, sulfur mineralization occurs, such that the amount of inorganic sulfur available in a soil is directly related to the amount of organic sulfur present (Figure 13.49). Some of the more easily decomposed organic compounds in the soil are sulfate esters, from which microorganisms release sulfate ions directly. However, in much of the SOM, sulfur in the reduced state is bonded to carbon atoms in protein and amino acid compounds. In the latter case the mineralization reaction might be expressed as follows:

\[
\text{Organic sulfur} \quad \rightarrow \quad \text{decay products} \quad O_2 \quad \rightarrow \quad \text{SO}_4^{2-} + 2H^+ \quad (13.12)
\]

- **Proteins and other organic combinations**
- **H$_2$S and other sulfides** are simple examples
- **Sulfates**
Because this release of available sulfate is mainly dependent on microbial processes, the supply of available sulfate in soils fluctuates with seasonal, and sometimes daily, changes in environmental conditions (Figure 13.50). These fluctuations lead to the same difficulties in predicting and measuring the amount of sulfur available to plants as were discussed in the case of nitrogen. It should be noted that for some plants, such as those in the Brassica family, a considerable amount of sulfur exists in actively growing plant tissue as sulfate or esters of sulfate that hydrolyze to chemically release soluble sulfate almost immediately when the plants are killed and added to soil as a green manure.
Immobilization

Immobilization of inorganic forms of sulfur occurs when relatively low-sulfur, but energy-rich organic materials are added to soils. As for nitrogen—the energy-rich material stimulates microbial growth, and the inorganic nutrient (sulfate in this case) is assimilated into microbial tissue. The critical C/S ratio of organic substrates, above which generally immobilization of sulfur is likely to occur, is thought to be between 300 and 400/1 (Figure 13.51). While immobilization can draw down the sulfate concentration in the soil solution to near zero, eventually most of the carbon will be used up, the microbial activity will subside, the C/S ratio in the remaining material will drop below the critical range, and the sulfate concentrations in the soil solution will begin to rise.

The pattern of S immobilization in soils suggests that, like nitrogen, sulfur in SOM may be associated with soil organic carbon and nitrogen in a relatively constant C/N/S ratio of about 85:7:1 (Table 13.8).

During the microbial breakdown of organic materials, several sulfur-containing gases are formed, including hydrogen sulfide (H₂S), carbon disulfide (CS₂), carbonyl sulfide (COS),

Figure 13.49 Sulfate-S mineralized from soil organic matter in seven diverse soils in relation to the soil organic S contents. The soils ranged in texture from sandy loam to clay, in pH from 4.8 to 8.0; in organic C from 8 to 50 g/kg; and in organic C/S ratio from 103 to 54. Organic S comprised 94–99% of the total S in these A horizons, except for two clay rice paddy soils in which the organic S was 53 and 62% of the total. (Graphed from data in Zhao et al. (2006).)

Figure 13.50 Seasonal sulfate concentration in the surface horizon of a soil (Argixerol, Oregon, USA) used to grow the oilseed crop, rape. This crop is sown in the fall, grows slowly during the winter, and then grows rapidly during the cool spring months. Data are shown for plots that were fertilized with either elemental S or calcium sulfate on the dates indicated by vertical arrows. Note that sulfate concentration was greater in the calcium sulfate-fertilized soils for the first few months after each application while the elemental S was slowly converted to sulfate by microbial oxidation. A distinct depression in sulfate concentration occurred each spring as the soil warmed up, stimulating both immobilization of sulfate into microbial biomass and uptake of sulfate into the rapeseed crop. Sulfate concentrations peaked in late summer and early fall, when crop uptake ceased after harvest and microbial mineralization was rapidly occurring. Movement of dissolved sulfate from the lower horizons up into the surface soil may also have occurred during hot, dry weather. (Modified from Castellano and Dick (1991).)
and methyl mercaptan (CH₃SH). All are more prominent in anaerobic soils. Hydrogen sulfide is commonly produced in waterlogged soils from reduction of sulfates by anaerobic bacteria. Most of the others are formed from the microbial decomposition of sulfur-containing amino acids and other reduced-S plant compounds. Although these gases can be adsorbed by soil colloids, some escape to the atmosphere, where they undergo chemical changes and eventually return to the soil in precipitation.

**13.20 SULFUR OXIDATION AND REDUCTION**

The Oxidation Process

During the microbial decomposition of organic carbon-bonded sulfur compounds, sulfides are formed along with other incompletely oxidized substances, such as elemental sulfur (S⁰), thiosulfates (S₂O₃²⁻), and polythionates (S₂O₅²⁻). These reduced substances are subject to oxidation, as

![Figure 13.51](image-url)
are the ammonium compounds formed when nitrogenous materials are decomposed. The oxidation reactions may be illustrated as follows, with hydrogen sulfide and elemental sulfur:

\[ \text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \]  
\[ 2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 \rightarrow 4\text{H}^+ + \text{SO}_4^{2-} \]

The oxidation of some sulfur compounds, such as sulfites (\(\text{SO}_3^{2-}\)) and sulfides (\(\text{S}^{2-}\)), can occur by strictly chemical reactions. However, most sulfur oxidation in soils is biochemical in nature, carried out by a number of autotrophic bacteria, which include five species of the genus \textit{Thiobacillus}. Since the environmental requirements and tolerances of these five species vary considerably, the process of sulfur oxidation occurs over a wide range of soil conditions. For example, sulfur oxidation may occur at pH values ranging from \(<2\) to \(>9\). This flexibility is in contrast to the comparable nitrogen oxidation process, nitrification, which requires a rather narrow pH range closer to neutral.

**The Reduction Process**

Like nitrate ions, sulfate ions tend to be unstable in anaerobic environments. They are reduced to sulfide ions by a number of bacteria of two genera, \textit{Desulfovibrio} (five species) and \textit{Desulfomonas} (three species). The organisms use the oxygen in sulfate to oxidize organic materials. A representative reaction showing the reduction of sulfur coupled with organic matter oxidation is as follows:

\[ 2\text{R} \text{CH}_2\text{OH} + \text{SO}_4^{2-} \rightarrow 2\text{R} \text{COOH} + 2\text{H}_2\text{O} + \text{S}^{2-} \]

In poorly drained soils, the sulfide ion reacts immediately with iron or manganese, which in anaerobic conditions are typically present in the reduced forms. By tying up the soluble reduced iron, the formation of iron sulfides helps prevent iron toxicity in rice paddies and marshes. This reaction may be expressed as follows:

\[ \text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS} \]  
\[ \text{Mn}^{2+} + \text{S}^{2-} \rightarrow \text{MnS} \]

Sulfide ions will also undergo hydrolysis to form gaseous hydrogen sulfide, which causes the rotten-egg smell of swampy or marshy areas (Figure 13.52). Sulfur reduction may take place with

**Figure 13.52** Using a handful of soil from a coastal marsh, soil scientist Robert Darmondy performs the “whiff test” he originated. The test checks for sulfidic material, which emits \(\text{H}_2\text{S}\) gas with an odor like that of a rotten egg. (Photo courtesy of R. Weil.)
sulfur-containing ions other than sulfates. For example, sulfites (SO₃²⁻), thiosulfates (S₂O₃²⁻), and elemental sulfur (S⁰) are readily reduced to the sulfide form by bacteria and other organisms.

The oxidation and reduction reactions of inorganic sulfur compounds play an important role in determining the quantity of sulfate (the plant-available nutrient form of sulfur) present in soils at any one time. Also, the state of sulfur oxidation is an important factor in the acidity of soil and water draining from soils.

**Acidity from Sulfur Oxidation**

Reactions 13.12–13.14 show that, like nitrogen oxidation, sulfur oxidation is an acidifying process. These reactions explain why elemental sulfur and iron or sulfide can be applied to lower soil pH if it is higher than desired (see Section 10.10).

Along with nitrogen, the sulfur in the atmosphere (as described in Section 13.17) forms strong acids that acidify rainwater to a pH of 4 or even lower from the normal pH of 5.6 or higher. Section 9.6 explains how "acid rain" forms and how it damages soils, forests, and lakes in many regions. As described in Section 13.21, part of the damage to these ecosystems stems from the leaching of sulfate anions, which can promote serious losses of calcium and magnesium.

**Extreme Soil Acidity.** The acidifying effect of sulfur oxidation can bring about extremely acid soil conditions that cause serious soil management problems and broader environmental pollution. Certain soils and sedimentary geologic materials are termed sulfidic because they contain high levels of reduced sulfur (sulfides), usually inherited from their present or past association with seawater (which is high in sulfur). A common form of reduced sulfur is the mineral pyrite (iron disulfide, FeS₂). The sulfides in these potential acid-sulfate materials are stable so long as oxygen is not present, but if submerged or buried materials are drained or excavated, the sulfides and/or elemental sulfur quickly oxidize and form sulfuric acid, driving pH levels as low as 1.5 (see Section 9.6, Reactions 9.18 and 9.19). Plants cannot grow under these conditions (Figure 13.53). The quantity of limestone needed to neutralize the acidity is so high that it is impractical to remediate these soils by liming (for reactions, solutions, and other details see Section 9.8). If allowed to proceed unchecked, the acids may wash into nearby streams. Thousands of kilometers of streams have been seriously polluted in this manner, the water and rocks in such streams often exhibiting orange colors from the iron compounds in the acid drainage (see Figure 9.21).

**Figure 13.53** Construction of this highway cut through several layers of sedimentary rock. One of these layers contained reduced sulfide materials. Now exposed to the air and water, this layer is producing copious quantities of sulfuric acid as the sulfide materials are oxidized. Note the failure of vegetation to grow below the zone from which the acid is draining. (Photo courtesy of R. Weil.)
13.21 SULFUR RETENTION AND EXCHANGE

The sulfate anion is the form in which plants absorb most of their sulfur from soils. Since many sulfate compounds are quite soluble, the sulfate would be readily leached from the soil, especially in humid regions, were it not for its adsorption by the soil colloids. As was pointed out in Chapter 8, most soils have some anion exchange capacity that is associated with iron and aluminum oxide coatings on soil particles and, to a limited extent, with 1:1-type silicate clays. Sulfate anions are attracted by the positive charges that characterize acid soils containing these clays. They also react directly with hydroxy groups exposed on the surfaces of these clays. Figure 13.54 illustrates sulfate adsorption mechanisms on the surface of some Fe, Al oxides, and 1:1-type clays. Note that adsorption increases at lower pH values as positive charges that become more prominent on the particle surfaces attract the sulfate ions. Some sulfate reacts with the clay particles, becoming tightly bound, and is only slowly available for plant uptake and leaching.

In warm, humid regions, surface soils are typically quite low in sulfur. However, because of the anion sorption mechanisms just discussed, much sulfate may be held in the subsoil horizons of Ultisols and Oxisols of these regions (see Figure 13.43). For example, symptoms of sulfur deficiency commonly occur early in the growing season on Ultisols with sandy, low-organic-matter surface horizons. However, the symptoms may disappear as the crop matures and its roots reach the deeper horizons where sulfate is retained. In other cases the zone of sorbed sulfate occurs too deep to be accessed by the roots of most annual crops, and deep rooted perennial vegetation is needed to “pump” the sulfur to the surface soil for crop access (Figure 13.55).

**Sulfate Adsorption and Leaching of Nonacid Cations**

When the sulfate ion leaches from the soil, it is usually accompanied by equivalent quantities of cations, including Ca and Mg and other nonacid cations. In soils with high sulfate adsorption capacities, sulfate leaching is low and the loss of companion cations is also low (Figure 13.56). In contrast, sulfate leaching losses from low-sulfate-adsorbing soils are commonly high and take with them considerable quantities of nonacid cations. Sulfur is thus seen as an indirect conserver of these cations in the soil solution. This is of considerable importance in soils of forested areas that receive acid rain.

![Figure 13.54](image_url)
The problem of maintaining adequate quantities of sulfur for mineral nutrition of plants is becoming increasingly important. Cleaner air as a result of environmental controls along with the increasing crop removal of sulfur make it essential that farmers be attentive to prevent deficiencies of this element. In some parts of the world (especially in certain semiarid grasslands), sulfur is already the next most limiting nutrient after nitrogen, deficiencies of S being even more common than those of P and K. However, the sulfur deficiencies often go unrecognized and untreated as the plant symptoms can be mistaken for N deficiency and traditional soil testing often does not include tests for S.

**Figure 13.55** Sulfur cycling by Faidherbia albida trees in an African corn-based agroforestry system. The trees are long lived with deep roots and leaves that fall off during the corn crop growing season. The trees, having translocated sulfur from sulfate sorbed deep in the subsoil, dropped their high-S content leaves to enrich the surface soil under their canopies. The darker corn under the trees appears to be a shadow from the tree, but measurements at six different sites confirmed that the darker green corn plants under the tree canopies were more vigorous and higher in S (bar graph). A similar phenomenon is illustrated in Figure 13.33 with respect to nitrate. [Data from Weil and Mughogho (1993).]

**Figure 13.56** Diagrams illustrating cation leaching losses as influenced by soil sulfate adsorption capacity. When acid rain containing SO$_4^{2-}$ and H$^+$ ions falls on soils with high SO$_4^{2-}$-adsorbing capacities (left), the small quantities of SO$_4^{2-}$ available for leaching are accompanied by correspondingly small amounts of cations such as Ca$^{2+}$ and Mg$^{2+}$. Where acid rain falls on soils with low SO$_4^{2-}$-adsorbing capacity (right), most of the sulfate remains in the soil solution and is leached from the soil along with equivalent quantities of cations, including Ca$^{2+}$ and Mg$^{2+}$. Al$^{3+}$ ions that commonly replace the Ca$^{2+}$ and Mg$^{2+}$ lost from the soil exchange complex are toxic to many forest species. This likely accounts for at least part of the negative effects of acid rain on some forested areas. [Redrawn from Mitchell et al. (1992).]
Crop residues and farmyard manures can help replenish the sulfur removed in crops, but these sources generally can help to recycle only those sulfur supplies that already exist within a farm. In regions with low-sulfur soils, greater dependence must be placed on regular applications of sulfur-containing materials. Fortunately, optimal plant growth on low-S soils can often be obtained with rather small application of about 5–15 kg S per hectare. The necessity for sulfur management will certainly increase in the future.

13.23 CONCLUSION

The cycles of sulfur and nitrogen have much in common, including many processes that operate in soils. Both elements are held by soil colloids in slowly available forms. In surface soil horizons, the bulk of both elements are found as constituents of SOM. Their release to inorganic ions (SO\(_4^{2-}\), NH\(_4^+\), and NO\(_3^-\)) is accomplished by soil microorganisms and makes them available to plants. Anaerobic soil organisms change both elements into gaseous forms, which are emitted to the atmosphere. While in the atmosphere, some serve as greenhouse gases that accelerate climate change. Both elements are subject to deposition from the atmosphere in the form of acid precipitation, seriously damaging lakes, soils, and plants in susceptible ecosystems.

Differences between nitrogen and sulfur also exist. In deeper soil layers much sulfur is found in gypsum and other sulfates (predominantly under dry climatic conditions) or pyrite and other sulfides (under low-oxygen conditions). No equivalent minerals commonly exist in soils with regard to nitrogen. Certain soil organisms have the ability to fix elemental N\(_2\) gas into compounds usable by plants. No analogous process occurs for sulfur.

Plants remove about 10–20 times as much nitrogen as sulfur. If plant material is regularly removed from the system, it is usually more critical for nitrogen than for sulfur that the supply be regularly replenished. On the other hand, while nitrogen fertilizers are expensive and energy intensive to manufacture and are usually needed in quite large amounts (~100 kg N/ha), sulfur deficiencies can be very easily corrected with small amounts (~10 kg S/ha) of inexpensive, plentiful materials such as gypsum.

Excessive amounts of nitrogen or sulfur cause serious environmental problems. Acid deposition and acid sulfate weathering are the main environmental concerns associated with sulfur cycling in soils. Progress has been greater in reducing excesses of sulfur than of nitrogen. Nitrogen also causes acidity, but eutrophication of coastal waters by nitrogen, especially in the highly mobile nitrate form, is probably its most ecologically damaging effect. The manufacture of fertilizer, along with combustion of fossil fuels, continues to magnify these problems by swelling the Earth’s total pool of reactive nitrogen.

Current knowledge of the nitrogen and sulfur cycles can help us alleviate environmental degradation and enhance life-supporting productivity. Nitrogen remains the most widely limiting—but also the most widely polluting—plant nutrient. Sulfur, whose supply to the soil was taken for granted during a century of intense industrial SO\(_2\) emissions, is now emerging as a widely limiting nutrient for plant growth. Outside the zones of heavy sulfur deposition from air pollution, plant requirements for sulfur should be given consideration equal to phosphorus and potassium—the topics of the next chapter.

**STUDY QUESTIONS**

1. The manager of a landscaping company is having a bit of an argument with the landscape architect about plans to fertilize and lime the soil in a new installation before planting turf and ornamental trees. The manager planned to use mostly urea for supplying nitrogen. The landscape architect says the urea will have an alkaline reaction and raise the soil pH. The manager says that urea will have an acid reaction and lower the soil pH. Who is correct? Explain, using chemical reactions to support your argument.

2. A sandy loam soil under a golf course fairway has an organic matter content of 3% by weight. Calculate the approximate amount of nitrogen (in kg N/ha) you would expect this soil to provide for plant uptake during a typical year. Show your work and state what assumptions or estimates you made to do this calculation.

3. The grass in the fairway referred to in question #2 is mowed weekly from May through October and produces an average of 200 kg/ha dry matter in clippings each time it is mowed. The clippings contain 2.5% N
on average (dry weight basis). How much N from fertilizer would need to be applied to maintain this growth pattern? Show your calculations and state what assumptions or estimates you made.

4. Both sulfur and nitrogen are added to soils by atmospheric deposition. In what situations is this phenomenon beneficial and under what circumstances is it detrimental?

5. About 2000 kg of wheat straw was applied to 1 ha of land. Tests showed the soil to contain 25 kg nitrate-N per ha. The straw contained 0.4% N. How much N was applied in the straw? Explain why two weeks after the straw was applied, new tests showed no detectable nitrate N. Show your work and state what assumptions or estimates you made to do this calculation.

6. Why do CAFOs (concentrated animal-feeding operations) on industrial-style farms present some environmental and health problems relating to nitrogen? What are these problems and how can they be managed?

7. What differences would you expect in nitrate contents of streams from a forested watershed and one where agricultural crops are grown, and why?

8. Microbial transformations of nitrogen involve oxidation and reduction reactions. Explain how the nitrogen from the protein in a leaf might cycle differently in a wetland soil than in an upland soil.

9. What is acid rain, what are the sources of acidity in this precipitation, and how does this acidity damage natural ecosystems?

10. Why might some farmers be willing to pay more for nitrogen fertilizer that contains a nitrification inhibitor chemical in it?

11. Nitrogen is said to be “fixed” from the atmosphere and is also “fixed” by vermiculite clays and humus. Differentiate between these two processes and indicate the role of microbes, if any, in each process.

12. Chemical fertilizers and manures with high N contents are commonly added to agricultural soils. Yet these soils are often lower in total N than are nearby soils under natural forest or grassland vegetation. Explain why this is the case.

13. Why are S deficiencies in agricultural crops more widespread today than 30 years ago?

14. How do riparian forests help reduce nitrate contamination of streams and rivers?

15. What are potential acid sulfate soils, where would you find them, and under what circumstances are they likely to cause serious problems?

16. In some tropical regions, agroforestry systems that involve mixed cropping of trees and food crops are used. What advantages in nitrogen and sulfur management do such systems have over monocropping systems that do not involve trees?

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