Chapter 2

The Nitrogen Cycle

Plants need at least seventeen elements to grow. Three of these elements—carbon, oxygen, and hydrogen—are referred to as "building blocks." Plants get these elements from air and water. The other fourteen elements, such as nitrogen, potassium, and phosphorus, are referred to as "nutrients." Plants usually get nutrients from the soil.

Nitrogen has traditionally been considered one of the most important plant nutrients. This chapter describes the importance of nitrogen as a plant nutrient, the role that biosolids can play in providing nitrogen and other nutrients to enhance soils and crop yields, and the mechanics of the naturally occurring nitrogen cycle as they relate to biosolids application.

The importance of nitrogen as a plant nutrient

Nitrogen gas comprises about 78 percent of the earth's atmosphere. Nitrogen (N) in various forms is also found in rocks, soils, sediment, oceans, and living matter. Growing plants, animals, and microbial populations need a continual source of N. It is an essential component of the proteins that build cell material and plant tissue. In addition, it is necessary for the function of other essential biochemical agents, including chlorophyll (which makes photosynthesis possible), many enzymes (which help organisms carry out biochemical processes and assimilate nutrients), and nucleic acids such as DNA, RNA (which are involved in reproduction). Most microorganisms and plants obtain N from the surrounding soil and water. Animals get N from the food they eat. A few organisms obtain N directly from the pool of nitrogen gas (N_2) in the atmosphere, but this requires the organism to expend energy.

Of all the major plant nutrients, N is often the most important determinant of plant growth and crop yield. Plants lacking N show stunted growth and yellowish leaves. Plant growth and crop yield usually increase when N is added, despite the presence of N in soils. This is because most of the N in soils is stored within the soil humus in forms that plants cannot access. Chemical fertilizers add N in forms that plants can use immediately or after a brief conversion. Organic materials such as manure, biosolids, and compost add some readily available N, but most of the N in these materials is contained in organic compounds that must decompose before plants can use the N. Although some of the decomposition occurs relatively quickly (within a year), most of the organic N takes years to change into plant-available forms. In the meantime, microorganisms in the soil assimilate and convert some of the N released through decomposition back into unavailable organic forms that are eventually incorporated and stored within the soil humus.

Just as too little N can cause problems, too much N can also cause problems. These problems can extend to plants, humans, animals, and the environment. For example, in plants, too much N can produce weak stems in grain crops (lodging), reduce quality in fruit such as peaches and apples, and lower sugar content in sugar beets. Excess N can lead to an accumulation of nitrate in the edible foliage of plants such as spinach and forage crops. Ingestion of such high-nitrate foods can pose possible health risks for animals and humans.

The problems posed to the environment occur when excess N in soils is carried away with surface runoff and water moving through soils and then finds its way to water and other ecosystems, which can also receive N from precipitation. Most of this N is in soluble forms, such as nitrate and ammonium. N entering lakes, streams, and other surface water changes the character of the water body and contributes to its accelerated aging, or "eutrophication." In this process, the N increases the growth of algae and aquatic vegetation, which create aesthetic problems and deplete the oxygen content of the water as they eventually die and decompose. Much of the N from the

decomposed algae and aquatic vegetation remains in the water to nourish new organisms, thus continuing the cycle of growth, decomposition, and oxygen depletion.

High levels of ammonium are toxic to fish and use up dissolved oxygen in the water as the ammonium converts to nitrate. Nitrate poses a particular environmental concern because of its mobility. Nitrate readily moves with water moving through soils. It can contaminate groundwater to the point at which it becomes a health risk (10 ppm). The primary health concern is methemoglobinemia (called the "blue baby" syndrome). Human infants and some animals are especially susceptible. In this condition, the digestive system reduces nitrate to nitrite, which interferes with the blood's ability to carry oxygen.

Biosolids as a means to provide nitrogen and other nutrients to soils and plants

If appropriate calculations are made and proper management practices are observed, biosolids can provide a viable means to enhance soil and plant N. Biosolids contain N and all of the other nutrients necessary for plants to grow—and in fairly well balanced ratios compared to what plants need. As can be seen in Figure 2.1, the amount of N in biosolids is relatively high compared to the amount of N in the soil.
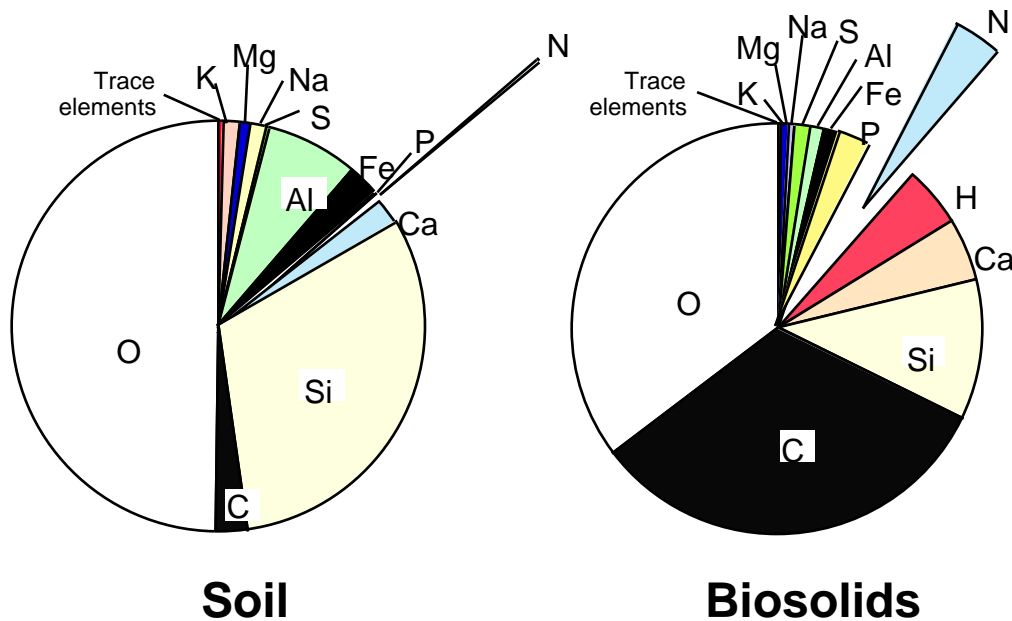

Soil   **Biosolids**

Figure 2.1. Comparison of the chemical composition of a typical soil to a typical biosolids.

Mechanics of the nitrogen cycle

N occurs in several chemical forms, sometimes referred to as "oxidation states." These forms vary greatly not only in their characteristics—from the proteins of solid organic matter to gaseous ammonia—but also in the way they behave. These forms are classified as either organic or inorganic N. Organic forms of N are found in compounds such as amino acids, protein, and more resistant N compounds (ultimately, humus). Inorganic forms include ammonium (NH_4^+), ammonia (NH_3), nitrate (NO_3^-), and nitrite (NO_2^-). Inorganic forms of N are the "available" forms that plants and microorganisms can use or that can move in the soil as water moves through it. Most N in the soil is in the unavailable organic form. This is N that has been taken up by plants or other

organisms and then incorporated into soil organic matter when the plants die and decompose. In biosolids, the majority of N added to the soil is in organic forms; the remainder is in inorganic forms (NH_4^+ and NO_3^-).

Many forms of N are present in any environment at any point in time, mainly because N readily shifts from one form to another. NO_3^-, NH_4^+ and N_2 can be converted to organic N (ON) by plants and microorganisms; ON can be converted back to inorganic forms as the organic compounds decompose. N can also shift between inorganic forms (for example, NH_3 to NH_4^+ or NO_3^- to N_2). These shifts occur as nature attempts to establish an equilibrium among the various forms as environmental conditions change. N in the soil interacts with the atmosphere, soil particles, soil solution (the water that surrounds or moves through the soil), microorganisms, and plants. If a new source of N is added to alter the balance or if environmental conditions (such as temperature and moisture) change, N transformations take place. Because environmental conditions are constantly changing, N transformations are constantly occurring. This continual movement of N from one form to another is known as the "nitrogen cycle."

The nitrogen cycle both affects and is affected by living organisms (Figure 2.2). N compounds created by biological activity are eventually available for later use by other organisms. N enters the soil from a variety of sources. Unlike other nutrients, only a small amount of N is contributed from the mineral part of the soil (i.e., rocks). Most naturally occurring N enters the soil either as NO_3^- or NH_4^+ in rainfall (atmospheric deposition) or by special plants, such as alfalfa, ceanothus, and red alder, that are called "nitrogen fixers" (Figure 2.3). Humans also increase the N in soils by fertilizing with either chemical or organic fertilizers. Once in the soil, the N will transform through the processes of mineralization, immobilization, volatilization, nitrification, denitrification, and plant uptake. Two of these transformations—volatilization and denitrification—result in losses of N from the soil. N is also lost through leaching and runoff.
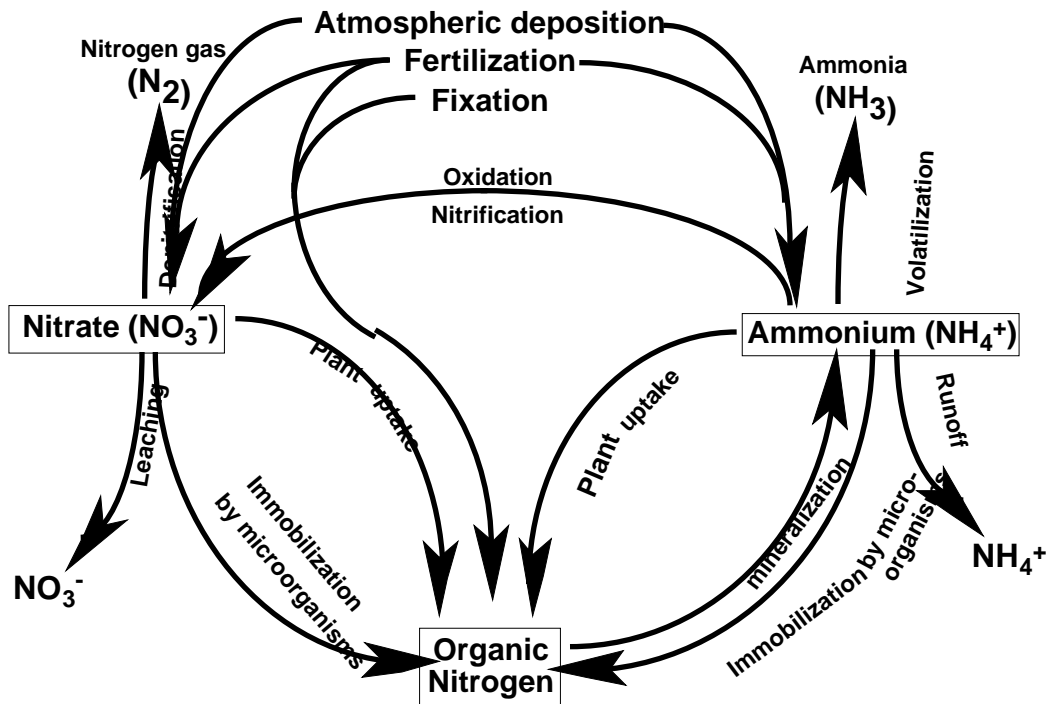

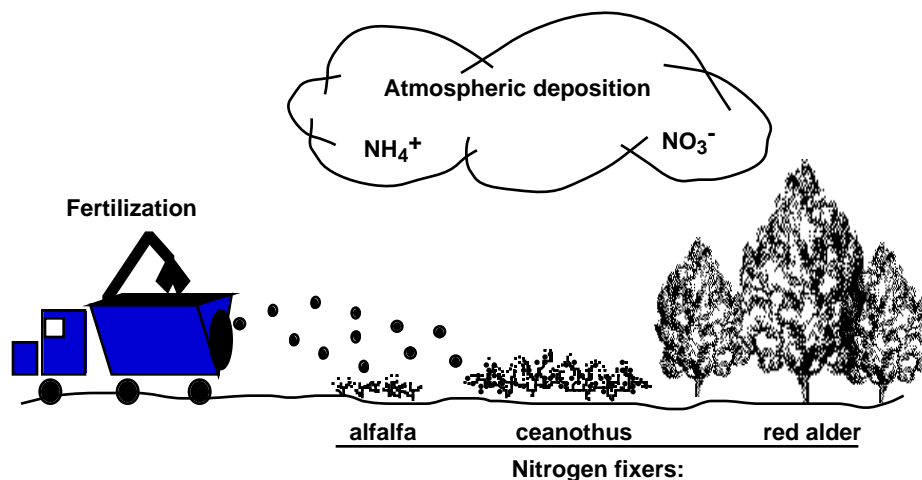**Figure 2.2. The nitrogen cycle: inputs to soil, nitrogen transformations, and losses from soil.**

Figure 2.3. Nitrogen inputs to soil: atmospheric deposition, nitrogen fixing plants, and fertilization.

Because most of the transformations and losses are caused by microbial action, all the processes are slowed down considerably when temperatures are low. For example, for each decrease of 18°F in the soil temperature, microbial action decreases by about half. At about 40°F, microbial action is fairly slow. Through much of the winter, the average soil temperature is at or below this temperature, especially under forest stands in Washington; therefore, mineralization, nitrification, and denitrification are very slow. The nutrients from applications made during the winter will essentially be stored in the forest floor and soil layers until temperatures increase. Significant NO_3^- leaching will not occur from winter applications because NO_3^- generally will not be formed. Only NO_3^- present in the soil at the time of application will be lost. Although this inactivity can also be the case in agricultural soils, winter sunshine can warm up the surface of the soil enough for short periods to allow some transformations to occur. If there is no corresponding plant uptake, NO_3^- leaching can occur.

The various transformations are shown in Table 2.1 and then described in the following sections.

Nitrogen mineralization and immobilization

Mineralization of N occurs when the organic matter in biosolids decomposes (Figure 2.4). The soil microorganisms break organic bonds to obtain energy. When the organic matter is completely broken down (oxidized), carbon dioxide (CO_2), water (H_2O), and minerals are left. The inorganic (available) form of N resulting from decomposition is NH_4^+.

The rate of decomposition and release of available N depends on the nature of the N compounds, which are greatly influenced by the type of treatment or stabilization process the biosolids receive, the duration of the process, and the type of organic matter in the biosolids. Decomposition is slower when the biosolids are more stable. Typical N mineralization rates for the first year range from 0 to 60 percent of the ON. Decomposition is not complete in the first year. It continues during the next few years at progressively slower rates. Some of the N is retained in stable organic matter (such as humus), which continues to mineralize very slowly. As much as half of the ON in some biosolids may remain stable for decades.

Table 2.1. Transformations and chemical reactions in the nitrogen cycle.

Transformation	Chemical Reaction	Description
N fixation	$0.5N_2 \twoheadrightarrow R\text{-}NH_2$	Plants and some microorganisms use N_2 from the air and convert to ON in a symbiotic relationship with microbes
N mineralization	$R\text{-}NH_2 + H_2O + H^+ \twoheadrightarrow R\text{-}OH + NH_4^+$	Transformation of organic N to inorganic N (NH_4^+) as microorganisms decompose organic matter.
N immobilization		Transformation of inorganic N to organic N as microorganisms incorporate N into their cell structures or soil humus during the decomposition process
From NO_3^- (first step)	$NO_3^- + 2e \twoheadrightarrow NO_2^- + 6e \twoheadrightarrow NH_4^+$	
From NH_4^+	$NH_4^+ + R\text{-}OH \twoheadrightarrow R\text{-}NH_2 + H_2O + H^+$	
NH₃ volatilization		Loss of ammonia (NH_3) from soil water to air
First stage (in water)	$NH_4^+ \twoheadrightarrow NH_{3(aq)} + H^+$	
From water to air	$NH_{3(aq)} \twoheadrightarrow NH_{3(air)}$	
Nitrification		Transformation of ammonium (NH_4^+) to nitrite (NO_2^-) nitrate (NO_3^-) by microorganisms
By *Nitrosomonas*	$NH_4^+ + 1.5O_{2(aq)} \twoheadrightarrow NO_2^- + H_2O + 2H^+$	
By *Nitrobacter*	$NO_2^- + .5O_{2(aq)} \twoheadrightarrow NO_3^-$	
Denitrification		Transformation of nitrate (NO_3^-) to nitrogen gases (N_2 or N_2O)
To N_2	$NO_3^- + 1.25[HCHO] \twoheadrightarrow 0.5N_2 + .75H_2O + 1.25CO_2 + OH$	
To N_2O	$NO_3^- + [HCHO] \twoheadrightarrow 0.5N_2O + .5H_2O + CO_2 + OH$	

R = organic compound.

Often N released from biosolids organic matter may be taken up by soil microorganisms and converted back to organic forms. This process is called "immobilization" (Figure 2.4). When biosolids are applied, the available N allows microbial populations to expand rapidly and decompose the soil organic matter, temporarily locking up the N in microbial biomass or in long-term stable humus. The N incorporated into the cell structure of the microorganisms will be released gradually as the microorganisms die and decompose. Immobilization generally occurs in nutrient-poor soils, in soils with a lot of matter that is low in N and high in carbon (such as woody material or straw), or in soils where organic amendments (such as sawdust or low-N compost) have been added.

The carbon-to-nitrogen (C:N) ratio is often used as an indication of whether mineralization or immobilization will occur. The C:N ratio is the total concentration of C divided by the total concentration of N. When surface soil layers have a C:N ratio greater than 30:1, then immobilization is highly likely to occur. This is because microorganisms need N to assimilate the available C. When the C:N ratio is below 20:1, N mineralization is likely to occur. When the C:N

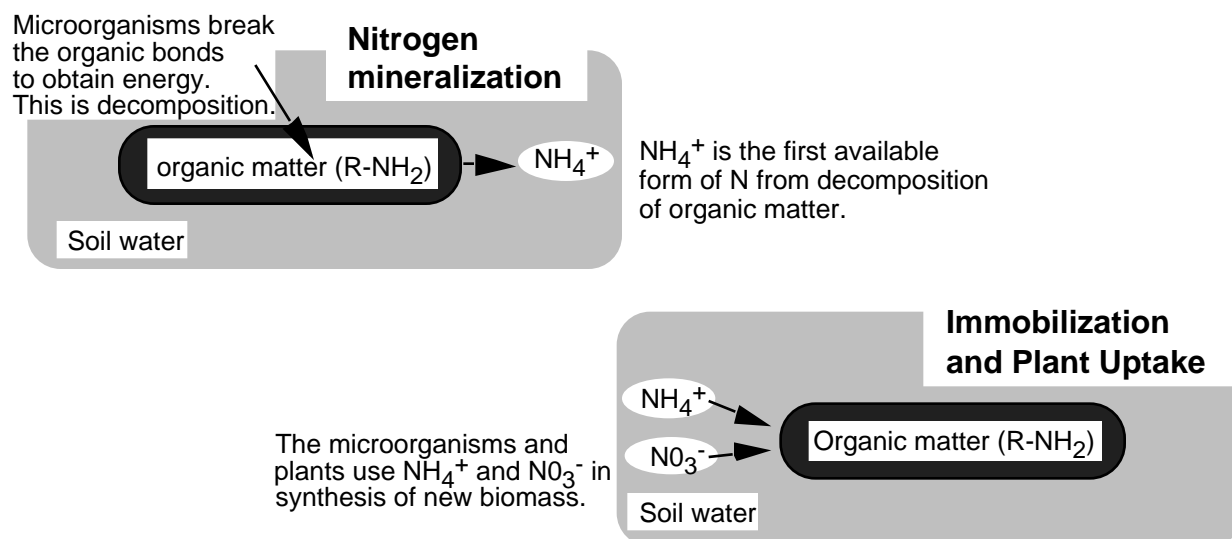ratio is between 20-30:1, both mineralization and immobilization may occur but they will generally balance.

**Figure 2.4. The processes of nitrogen mineralization and immobilization from biosolids.**

Ammonia volatilization

The potential for loss of ammonia gas (NH_3) to the air depends on several equilibrium relationships in the soil (Figure 2.5). Ammonium (NH_4^+) plays an important role in these relationships. Most of the NH_4^+ is bound to soil surface exchange sites; the remainder is dissolved in soil solution. If some NH_4^+ is removed from the soil solution through plant uptake or other means, NH_4^+ will move from the soil surface sites into the soil solution to reestablish equilibrium.

The NH_4^+ in the soil solution also tries to maintain an equilibrium with the NH_3 in the soil solution. If more NH_3 is needed to maintain the equilibrium in the soil solution, NH_4^+ will transform to NH_3. If more NH_4^+ is needed in the soil solution, NH_4^+ will move from the soil exchange sites. This equilibrium depends on the soil pH (Figure 2.6). At pH 6.0, only 0.1 percent of the total of these two is NH_3; at pH 7.0, 1 percent is NH_3; and at pH 9.0, the ratio is one to one. When a significant amount of NH_3 is present in the soil solution, some will "volatilize" into the air. When this happens, all the relationships try to reestablish. More NH_4^+ transforms to NH_3, and more NH_4^+ comes off the soil exchange sites. When the soil solution evaporates, the concentration of NH_3 increases and the potential for loss increases.

Most volatilization occurs within the first few days of biosolids application. The amount of NH_3 that volatilizes depends on a number of environmental factors and biosolids management techniques. The important ones, in addition to the pH, include temperature and wind speed, and whether the biosolids are incorporated, injected, or surface applied. As much as 100 percent of the initial NH_3 and NH_4^+ in biosolids that are surface applied to agricultural soils can be lost to volatilization. Even when the biosolids have been mixed in with the soil the majority of the NH_3 may volatilize if the soil has a high pH (over 8.0). Little volatilization may occur in sites such as

forest environments in western Washington state because of the low pH of the forest floor, the low wind speed in the forest stands, and the low amounts of radiation reaching the forest floor.
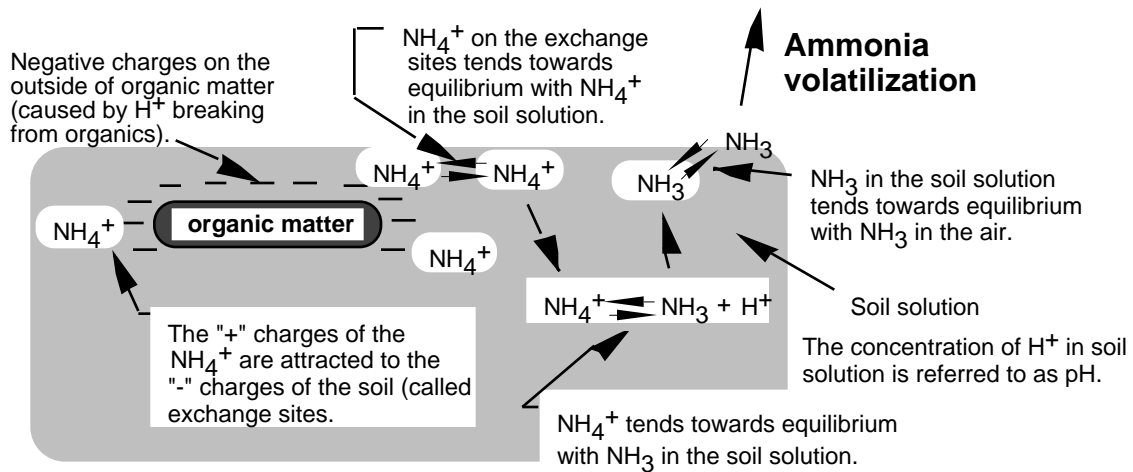
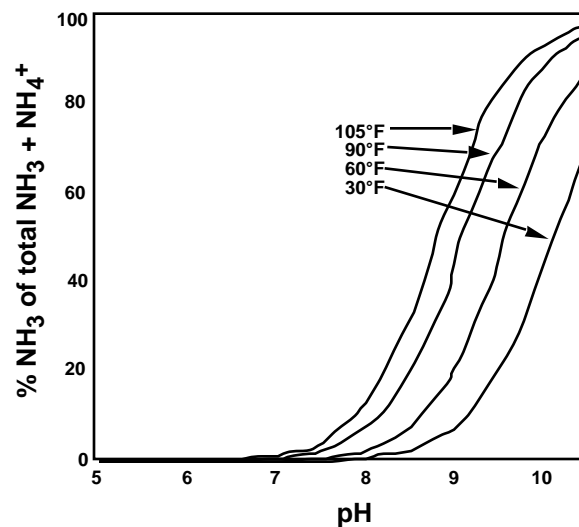**2.5. The process of ammonia volatilization from biosolids.**

Figure 2.6. The change in percentage of ammonia versus ammonium in solution as the pH and temperature change.

Plant uptake

Plants use inorganic N and convert it to ON. Agricultural crops, trees, and understory use the available N from biosolids to increase growth. Crop N uptake varies widely, depending on crop type, growing conditions (moisture and temperature), and management practices, but can be higher than 300 lb/ac/yr (340 kg-N/ha/yr). N requirements for different forest systems also vary widely, from older stands with little N requirements to rapidly growing hybrid poplar stands with requirements greater than 300 lb/ac/yr (340 kg-N/ha/yr).

Nitrification

Microorganisms oxidize available NH_4^+ to NO_3^- in order to get energy (Figure 2.7). This process is called "nitrification." During the process, the microorganism *Nitrosomonas* oxidizes NH_4^+ to NO_2^-, and the microorganism *Nitrobacter* oxidizes the NO_2^- to NO_3^-. Nitrification rates are highest when soils are warm and moist and the pH is neither strongly acidic nor alkaline. Over-application of inorganic N in arid climates will promote buildup of excess of NO_3^- in the soil. If leaching losses are insignificant, this buildup provides a bank of available nutrients for the next crop. However, in moist climates (where rainfall exceeds evapotranspiration), NO_3^- leaching may occur.
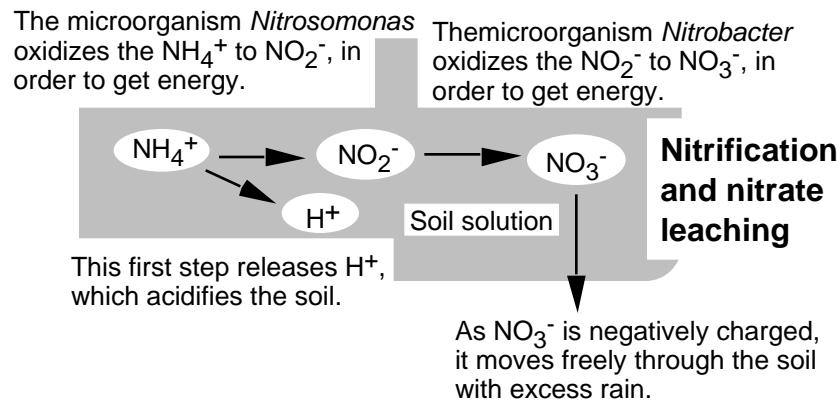
The microorganism *Nitrosomonas* oxidizes the NH_4^+ to NO_2^-, in order to get energy.

Themicroorganism *Nitrobacter* oxidizes the NO_2^- to NO_3^-, in order to get energy.

NH_4^+ → NO_2^- → NO_3^-

H^+

Soil solution

Nitrification and nitrate leaching

This first step releases H^+, which acidifies the soil.

As NO_3^- is negatively charged, it moves freely through the soil with excess rain.

Figure 2.7. The process of nitrification, which may lead to leaching.

Denitrification

Like higher plants and animals, many microorganisms use O_2 as an essential part of their metabolism. If the soil becomes depleted of O_2, some microorganisms can use the oxygen in NO_3^- as an alternative by reducing the NO_3^- to nitrogen gases (N_2 or N_2O). This process is called "denitrification."

The amount of denitrification depends on the availability of NO_3^-, on soil saturation, on soil temperature, and on availability of easily decomposable organic matter. When a site within the soil becomes saturated with water (either an entire soil layer or pockets within a layer), O_2 can no longer diffuse readily into that site. If microorganisms are active within that site, they will deplete the O_2 and then begin using the NO_3^-. If a soil is too cold for microbial activity or if there is too little food (organic matter) available for the microorganisms, the O_2 will not be depleted and denitrification will not occur. (Appendix C shows research results from the Northwest.)

N_2O N_2 **Denitrification**

NO_3^-

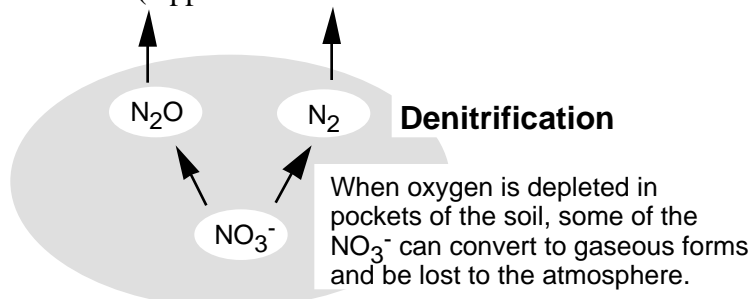When oxygen is depleted in pockets of the soil, some of the NO_3^- can convert to gaseous forms and be lost to the atmosphere.

Figure 2.8. The process of denitrification.