

NITROGEN IN SOIL AND THE ENVIRONMENT

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Nitrogen is the seventh most abundant element in the universe. It's the single most common element in the earth's atmosphere, comprising about 78% (4,000 trillion tons) of the gas that makes up our atmosphere. Nitrogen is found in all soils, and is required by all living creatures. In plants, nitrogen is the nutrient required in the largest amounts. It is a key constituent of critical organic molecules such as amino acids, nucleic acids, and proteins. Nitrogen is found in marine and freshwaters and is present in some minerals. In short, nitrogen is found in every ecosystem and in every part of the global environment.

Atmospheric Nitrogen

In the atmosphere, the predominant form of nitrogen is dinitrogen gas (N₂), which is relatively inert and must be converted into different forms to be utilized by most organisms. There are several avenues for these conversion processes, collectively called *nitrogen fixation*, in which N₂ gas is converted to ammonium (NH₄⁺). A small amount of nitrate (NO₃⁻) is produced by high voltage electrical discharged in the atmosphere during lightning storms.

Certain microorganisms produce the ammonium biologically. Some biological nitrogen fixation is associated with free-living soil microorganisms, but most is attributed to microorganisms living symbiotically with higher (green) plants. A well-known example is rhizobium bacteria living within the roots of legume (bean family) plants such as clover, alfalfa, beans, and peas, however there are also other nitrogen fixing symbiotic pairs.

Another prominent form of nitrogen fixation is industrial. The Haber-Bosch process, developed in 1913, is now the primary source of nitrogen in fertilizers. About as much nitrogen is fixed by this process as is fixed by all natural processes combined. In the Haber-Bosch process dinitrogen gas is combined with hydrogen gas (H₂) to form ammonia (NH₃), which can then be used to make numerous other nitrogen compounds. This process uses large amounts of energy and usually depends on natural gas as the source for both hydrogen and energy.

Organic Soil Nitrogen

In undisturbed, natural soils, roughly 95% of the nitrogen is found in soil organic material. Organisms, including plants, animals, and microorganisms contain nitrogen rich compounds, including amino acids, nucleic acids, and proteins in their tissues. When wastes or dead bodies of these organisms are deposited in the soil, this material and its breakdown products form soil organic matter. Organic nitrogen is largely unavailable to growing plants. As various soil microorganisms decompose organic material, excess nitrogen may be converted to the

inorganic ammonium and nitrate forms which plants and other soil organisms use.

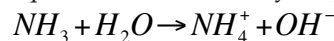
If organic matter is sufficiently rich in nitrogen, degradation of the organic matter will result in the release of ammonium and nitrate nitrogen, a process called *mineralization*. On the other hand, degradation of organic matter with low levels of nitrogen will consume or immobilize ammonium and nitrate nitrogen as degrading microorganisms scavenge available nitrogen from the soil system. This is called *immobilization*. In general, decomposition of organic materials with a C:N (carbon to nitrogen) ratio of less than 40:1 will mineralize nitrogen, whereas degradation of those with a C:N ratio greater than 40:1 will immobilize nitrogen (Vigil and Kissel, 1991).

Nitrogen mineralization can be divided into *ammonification* (Equation 1), conversion of organic nitrogen to ammonia (NH₃), and *hydrolysis*, which is the conversion in water of ammonia to ammonium (NH₄⁺) (Equation 2).

Equation 1. Ammonification



Equation 2. Ammonia hydrolysis



Ammonium Nitrogen

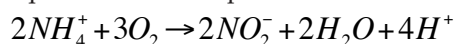
Ammonium and ammonia nitrogen are closely related, as indicated in Equation 2. Ammonia, on the left side of the equation, is a gas. High pH levels favor this form. Ammonium, on the right side of the equation is a soluble ion, and is favored by low to moderate pH. Ammonium is a positively charged ion (a cation) and is therefore attracted to negatively charged soil particles. It is held as an exchangeable cation in soil and does not easily leach. Ammonia, on the other hand, is a gas. Once formed, it can quickly escape from soil into the air. Thus ammonium is a common soil nitrogen form; ammonia is not.

Ammonium can also be trapped between the layers of clay minerals that exhibit shrinking and swelling. This is called *ammonium fixation*.

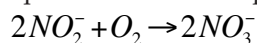
Ammonium is energy-rich and relatively unstable in aerobic (oxygen-rich) soils. In the presence of oxygen, ammonium is rapidly converted (oxidized) to nitrate through *nitrification*. In nitrification, the conversion of ammonium takes place in two steps: the transformation of ammonium into nitrite (NO₂⁻) by oxidizing bacteria such as *Nitrosomonas* (Equation 3), and the oxidation of nitrite to nitrate by *Nitrobacter* (Equation 4). Oxidation of nitrite usually proceeds at a more rapid rate, so

nitrite is a relatively rare form of inorganic soil nitrogen. Note that nitrification produces a large amount of hydrogen ions (H^+), or acidity. Ammonium and nitrate make up the bulk of soil inorganic nitrogen, and are the principle forms available for plant growth.

Equation 3. First step of nitrification



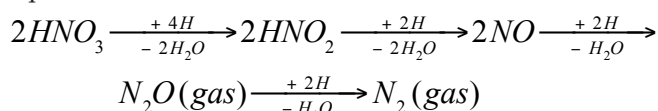
Equation 4. Second step of nitrification



Nitrate Nitrogen

Nitrate is a negatively-charged anion and, as such, is repelled by negatively charged soil colloids. Nitrate salts are highly soluble, so nitrate moves with soil water and can be easily *leached* through soil. Furthermore, nitrate can be chemically reduced through the process of *denitrification* (Equation 5). Denitrification, reduction of nitrate to nitrous oxide (N_2O) or dinitrogen (N_2) gas by anaerobic bacteria, can be a major mechanism for nitrogen loss from poorly aerated soils or when soils are saturated with rain or flooded by irrigation. Oxidation of organic matter provides energy and carbon for denitrifying bacteria and nitrate acts as the terminal electron acceptor.

Equation 5. Denitrification



Taken together, the reactions and various forms of nitrogen discussed above comprise the soil nitrogen cycle (Figure 1). In this diagram the arrows represent the processes already discussed. Red arrows represent chemical or abiotic reactions, whereas green arrows represent biological reactions.

Nitrogen, required by plants in larger amounts than any other nutrient, can be taken up in either of two forms, nitrate and ammonium. As noted, ammonium nitrogen is subject to conversion to nitrate by soil bacteria (nitrification). The rate at which nitrification takes place is largely dependent on soil temperature and occurs most rapidly in warm soils. Nitrate, on the other hand, can be converted to gaseous forms of nitrogen and lost to the atmosphere in waterlogged soils and is also easily leached from soil. To avoid nitrogen loss due to gaseous loss or leaching, nitrogen containing fertilizers should be applied when plants are growing actively.

Most plants are not particular about the form of nitrogen they take up and since the various nitrogen forms are easily converted in the soil, the choice of nitrogen fertilizer material is usually based on cost. However, when plants take up nitrate they need to use some energy to reduce nitrate to NH_2 forms that proteins are made of. Where supplemental nitrogen is required for plant growth, there are many fertilizer materials that can be used. Some common fertilizers are listed in Table 1. Ammonium sulfate and calcium nitrate are commonly used inorganic salts of nitrate or ammonium. All nitrogen salts are highly soluble, and immediately provide nitrogen in an available form. Urea is a simple organic nitrogen salt. It is highly soluble, but must

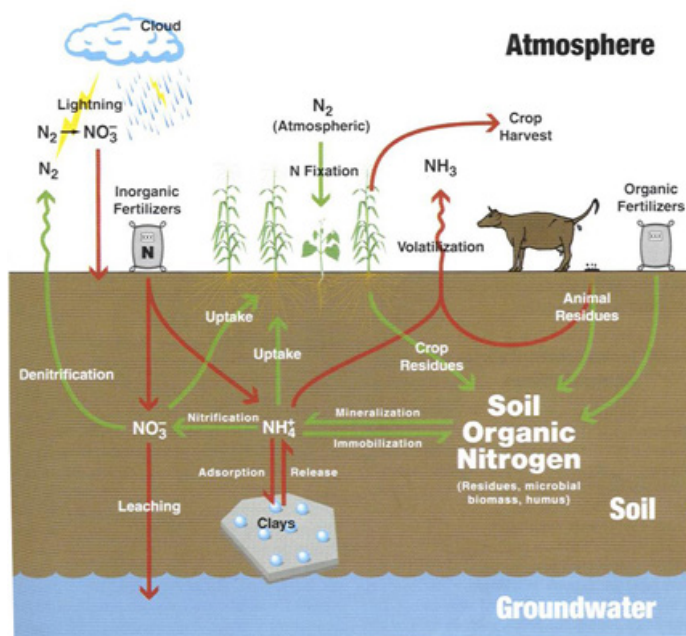
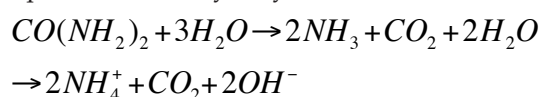


Figure 1. The Soil Nitrogen Cycle (Thompson, 1996).

be hydrolyzed by the urease enzyme to form ammonium before it can be utilized (Equation 6). If urea or ammonium fertilizers are used, attention should be paid to soil pH. At pH levels of 8.0 or above, volatilization of ammonia gas can cause large losses of nitrogen if fertilizer is not incorporated into the soil. In high pH soils urea should be incorporated into the soil immediately after application to prevent loss by ammonia volatilization. With the use of urea, soil pH can rise dramatically during hydrolysis (see equation 6), and substantial nitrogen can be lost by volatilization even in medium pH soils.

Equation 6. Urea hydrolysis



In addition to inorganic nitrogen salts, there are a number of slow-release or controlled-release nutrient sources. These materials may be coated fertilizers (sulfur-coated urea and Osmocote® are examples), slowly soluble materials (such as isobutylidene diurea – IBDU, and methylene ureas), or materials that must be microbially mineralized to release nitrogen (organic fertilizers and ureaformaldehydes, for example). To maximize effectiveness, controlled-release nutrients should be released at a rate equivalent to plant demand.

Ammonia, a gas at atmospheric pressure and ambient temperatures, is an effective nitrogen source which must be injected below the soil surface. Ammonia is highly water soluble. As it hydrolyzes to form the ammonium ion, hydrogen ions are consumed and soil pH can be raised to 9 or higher, which can adversely affect soil microorganisms in close proximity to the fertilizer (see Equation 2). With urea, ammonia, and ammonium fertilizers, the final pH of soil fertilized with ammonia may be lower than that of unfertilized soil because of acidification caused by nitrification of ammonium to nitrate (see Equation 4). Recently, many fertilizer dealers and producers are less

Fertilizer	% Nitrogen	Composition
Ammonium sulfate	20.5	$(\text{NH}_4)_2\text{SO}_4$
Calcium nitrate	16	$\text{Ca}(\text{NO}_3)_2$
Urea	45	$(\text{NH}_2)_2\text{CO}$
Anhydrous ammonia	82	NH_3
Diammonium phosphate	20	$(\text{NH}_4)_2\text{HPO}_4$
Ammonium polyphosphate	10 - 15	$(\text{NH}_4\text{PO}_3)_n$
Urea ammonium nitrate	28 - 32	$(\text{NH}_2)_2\text{CO}, \text{NH}_4\text{NO}_3$

inclined to handle anhydrous ammonia fertilizer, and for this reason, alternatives such as liquid urea ammonium nitrate are becoming more popular.

Sometimes ammonia is placed in irrigation water and applied during irrigation (this practice is called *fertigation*). Fertigation with ammonia is not recommended, as it can raise the pH of the water, precipitating calcium but leaving sodium in solution. The consequence is an increase in irrigation water sodium adsorption ratio (SAR), which may ultimately result in increased soil exchangeable sodium percentage (ESP), and problems such as soil crusting, and decreased water penetration and aeration. A better choice for fertigation is urea ammonium nitrate, a blend of urea and ammonium nitrate dissolved in water. A common form, containing 32% nitrogen, is known as UAN-32.

Soil Nitrogen Analysis

Nitrogen analyses are not difficult to conduct, but interpreting results can be problematic. This is because a major portion of soil nitrogen may be contained in the soil organic matter. Plant availability of organic nitrogen is dependent on organic matter breakdown, which is difficult to estimate. Therefore analyses of "total nitrogen", a sum of all forms of soil nitrogen are not routinely conducted. Instead, nitrogen in the nitrate form is assayed. Nitrate is directly available to plants, and this test provides an indication of short-term nitrogen availability. However, nitrate can be quickly lost from soil, either leached past the rooting zone, or lost to the atmosphere in gaseous forms, so soil nitrate level can change in just a few days.

The extractant used to remove nitrate from the soil is not particularly important. Some laboratories extract nitrate from soil with a salt solution, such as potassium chloride (KCl). However, other laboratories in the southwestern U.S. measure nitrate in the same extract used to measure other nutrients to reduce analysis costs. Results from these two kinds of extractants are directly comparable.

Nitrate analyses can provide an accurate determination of the nitrogen available to plants at the time of soil sampling, although

this may not provide reliable information concerning nitrogen availability later in the growing season. In the western U.S., soil samples for nitrate should be taken as deep as the expected plant root zone, usually three feet. If soil nitrogen analysis is to be used for making fertilizer recommendations, it is important that the sampling be done either shortly before planting time or during the growing season.

References

- Thompson, T. 1996. Agricultural Fertilizers as a Source of Pollution. In I.L. Pepper, C.P. Gerba, and M.L. Brusseau (eds) Pollution Science pp. 211-223. Academic Press, San Diego, CA.
- Vigil, M.F. and D.E. Kissel. 1991. Equations for estimating the amount of nitrogen mineralized from crop residues. Soil Sci. Am. J. 55, 757-761.



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