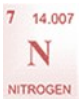
Technical Note 12. Essential Nitrogen



12.0 Background

Nitrogen (chemical symbol N) is one of the most important elements to living organisms and in industrial applications. The plants we cultivate for food and fiber, as well as the plants grown to produce all of the beef, pork, poultry we intend to eat, are heavy users of nitrogen. Nitrogen or nitrogen-containing compounds such as ammonia, urea, ammonium nitrate, and nitric acid are five of the top fifteen synthetically produced chemicals in the USA. Nitrogen makes up about 78 per cent of the Earth's atmosphere but it is not involved with the breathing function of living organisms. Plants are surrounded by a vast reservoir of invisible elemental N; in fact, the atmosphere above every terrestrial hectare on Earth is suffused with about 83 million kilograms of N. Under normal conditions atmospheric nitrogen occurs as a colorless, odorless, inert diatomic gas N_2, rather than a single N atom. The two atoms of N are joined by a very strong triple covalent bond making diatomic N_2 chemically unreactive. Despite the great abundance of nitrogen in the Earth's atmosphere, nitrogen deficiency is one of the most pervasive plant nutritional problems affecting agriculture, worldwide.

12.1 Nitrogen in Plants

Plants absorb most of their nitrogen as ammonium (NH_4^+) or nitrate (NO_3^-) ***ions*** from the soil. Complex molecules as water -soluble amino acids may be absorbed directly and used by plants. These latter compounds do not normally exist in the soil in significant quantities. Plant preference for either NH_4^+ or NO_3^- is influenced mainly by the age and type of plant. Many plants show a preference for NH_4^+ when they are young and again as they mature. Varieties of rice growing in flooded 'paddy' soil absorb mainly NH_4^+, but most of the nutrient-N absorbed by terrestrial plants is in the NO_3^- form due to ***oxidation*** of NH_4^+ to NO_3^- in soil by microorganisms. From the plant's point of view NO_3^-N is less efficient because the plant must convert NO_3^- to NH_4^+ before it can be used for biosynthesis. In the process, energy is used up.

The functions of N in the plant are:

- Nitrogen is necessary for chlorophyll synthesis and, as part of the chlorophyll molecule, is the focal point of photosynthesis. Chlorophyll is a complex organic molecule present in all green plant tissue consisting of a central magnesium ion bonded to four atoms of nitrogen. Each of the nitrogen atoms is bonded to other elements like carbon, hydrogen and oxygen in a porphyrin ring structure (**Figure 1**). The dark green color of plants is produced by the chlorophyll molecule. Chlorophyll absorbs energy from sunlight which is needed for photosynthesis. Chlorophyll molecules convert carbon (C), hydrogen (H) and oxygen (O) from carbon dioxide (CO_2) and water (H_2O), to simple sugars with help from the nitrogen-containing leaf enzyme, RUBP carboxylase. These sugars and their conversion products are used for the growth and development of plants.

- Nitrogen is a component of vitamins and energy systems driving carbon fixation and metabolism in the plant.

- Nitrogen is an essential component of amino acids, the building blocks of protein. Nitrogen is directly responsible for increasing the protein content of plants. Protein-N is the largest N fraction and amounts to 80-85% of the total plant N.

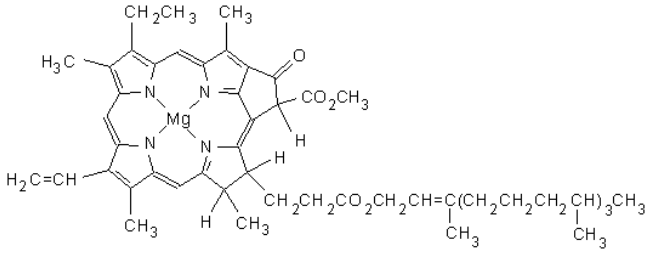


Figure 1. Chemical structure of chlorophyll. There are several types of chlorophyll; the one above is chlorophyll *a*. Note that the element chlorine is not part of the molecule. The prefix '*chloro*' is from the Greek *chloros,* meaning yellowish-green. Chlorine is a yellowish-green gas and the name is from the same Greek root.

Symptoms of nitrogen deficiency include:

- Yellowing of the leaves (chlorosis) due to declining chlorophyll content. Nitrogen is mobile in the plant. In annual plants, symptoms develop first on older leaves, and then progress to the younger leaves as the deficiency becomes more acute.

- Slow growth, stunting, and inefficient water use also are indicators of nitrogen deficiency.

- Low protein content of seeds, fruit, and vegetables.

Nitrogen uptake from the soil is a continuous process during the life of most plants, enabling them to reach maturity. Excess nitrogen supply that is not balanced by an increase in the supply of other nutrients often leads to excessive vegetative growth, which may delay maturity and reduce fruit set. Over fertilization with nitrogen may influence the quality of certain food products and induce harmful environmental effects. Some plant diseases are encouraged by too much fertilizer nitrogen.

12.2 Nitrogen in the Soil

The amount of nitrogen in the soil that is available to plants at any given time is small. This is mainly due to the fact that the primary rock and mineral matter from which soil is formed contains very little nitrogen[1]. Most nitrogen found in the soil originated from the Earth's atmosphere. Gaseous, atmospheric N_2 is of nutritive value only to legumes and some trees which are able to 'fix' it through the mediation of bacteria occupying specialized root nodules, as well as some free-living bacteria in the soil that are able to convert atmospheric N_2 to plant-available nitrogen.

The nitrogen (N) present in the soil, apart from the soil air, occurs in three major forms:

- *Organic N*, part of soil organic matter and unavailable to plants. Organic N represents about 98% o f the total N in the soil. Inorganic N generally represents less than 3% of the total organic N.
- *Ammonium-N*, or *NH_4^+-N*, is a positively charged ion that is held on the negatively charged surfaces of clay minerals and organic colloids (humus). Ammonium-N is usually not present in large quantities in the soil except following the application of ammonium-based fertilizers. Ammonium is an soluble inorganic, or *mineral*, form of nitrogen that can be utilized by many plants.
- *Nitrate-N*, or *NO_3^--N*, a negatively charged ion that is the most common soluble inorganic form of nitrogen in the soil. Nitrate-N is readily available for plant uptake. Nitrogen fertilizers are rapidly converted to this form when applied to soil. In warm, moist soil the NO_3^- content may be 10-fold greater than NH_4^+. Because nitrate-N is a negatively charged ion it is repelled by negatively charged soil colloid particles; thus, most of the nitrate-N remains in the soil solution and is subject to leaching in free-draining soils.

Nitrogen is perhaps the most fickle plant-essential nutrient as it has seven routes that it can take to change its form or cause it to disappear completely from the soil: *mineralization, immobilization, nitrification*, *denitrification, volatilization, leaching* and *erosion*. These processes are grouped into a global system called the 'nitrogen cycle' (**Figure 2**). Because microorganisms are involved in most of these processes, they occur very slowly when the soil temperature is below 10°C (50°F), but their rates increase rapidly with warming.

12.3 Nitrogen Mineralization and Immobilization

The biological conversion of organic nitrogen that is unavailable to plants, to plant-available nitrogen is called ***mineralization***. This process is constantly going on in soil as microorganisms decompose organic materials for their energy supply. Nitrogen can also be converted from mineral to organic forms, as shown by the double arrow in **Figure 3**. This process is the reverse of mineralization and is called ***immobilization***. Immobilization occurs when crop residues

[1] The N reservoir in the earth's crust (mainly as mineral-fixed NH_4^+ ions) is many times that of the atmosphere but the majority of plant-available N in soil comes from the atmosphere. Sedimentary rock, such as coal, may contain up to 1% N.

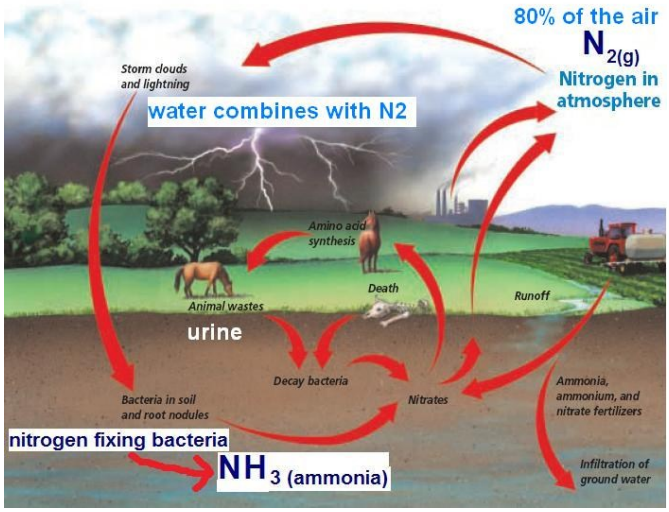


Figure 2. The nitrogen cycle represents the flow of nitrogen through the environment. Microorganisms are a key element in the cycle, providing different forms of nitrogen that can be assimilated by higher organisms.

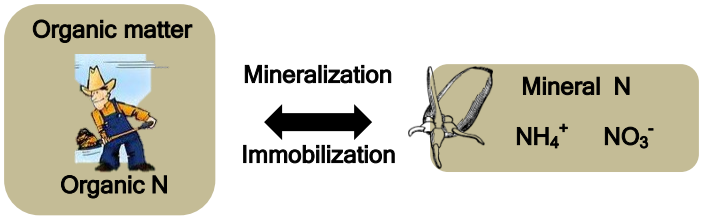


Figure 3. Most soil nitrogen is contained in the organic pool and is not available for plant use.

high in carbon and low in nitrogen, are incorporated into the soil. These residues are assimilated by free-living microbes for their metabolism. Immobilization can be thought of as nature's recycling process because the nitrates released from plant residue are assimilated by microbes for their metabolism and temporarily unavailable to plants. After a period of time the microbe population dies off and the nutrients are again available for uptake by plants (**Figure 4**).

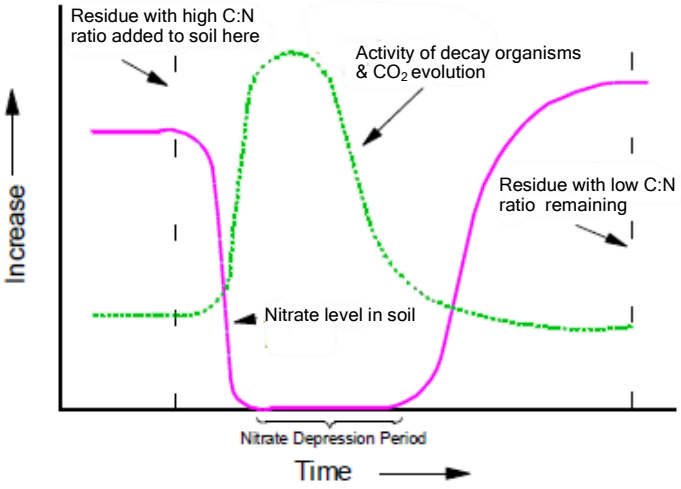


Figure 4. The period of nitrate immobilization corresponds to the nitrate depression period when microbial populations are increasing rapidly. The activity of microbes is observed as a large spike in CO_2 which is 'exhaled' during respiration. *source: R.B. Ferguson, University of Nebraska.*

The reactions of mineralization and immobilization can also occur at the same time. Whether the soil shifts toward an organic or inorganic nitrogen 'pool' depends mainly on the carbon to nitrogen (C:N) ratio of the decomposing organic material. Residue with wide C:N ratio (above 30:1), such as straw or woodchips, favor immobilization. Materials with a narrow C:N ratio (less than 20:1) favor more rapid mineralization. A C:N ratio in the range of 20 to 30:1 would mean the two processes are about equal. Soil organic matter contains an average of 50% carbon and 5% nitrogen, or a C:N ratio of 50/5=10. This ratio is fairly constant for organic matter. The C:N ratio of plant tissue ranges from 10:1 in annual herbaceous legumes like clover to over 100:1 in corn stalks and wheat straw. The potential for fertilizer-N immobilization can be reduced by placing the fertilizer below the plant residue zone, instead of incorporating the fertilizer in the soil with residue. The most direct method for farmers to accomplish this is by machine ***slitting*** and ***knifing***.

12.4 Nitrification and Denitrification

Under conditions favoring plant growth, much of the ammonium-N in soils is converted to nitrate-N by nitrifying bacteria (principally *Nitrosomonas* and *Nitrobactor*). This process is called ***nitrification***. Nitrification is important for two key reasons:

- Nitrate is readily available for use by plants and micro-organisms.
- Nitrates are highly mobile in soil. Large amounts of nitrate-N may leach down in the soil profile, especially deep, sandy free-draining soils under high rainfall. Sound fertilizer nitrogen management practices can reduce the leaching of nitrates into groundwater, increase productivity, and mitigate environmental costs.

Nitrification is an *acid-forming* process wherein hydrogen ions are released:

$$2NH_4 + 3O_2 \xrightarrow{\text{Nitrifying bacteria}} 2NO_3^- + 8H^+ \qquad \text{Eq. [1]}$$

Ammonium — Oxygen — Nitrate — Hydrogen ions

Equation 1 shows that for each mole of ammonium that is nitrified, four moles of hydrogen (acidity) are produced ($2NH_4^+ \times 4H^+ = 8H^+$). Therefore, sources of fertilizer nitrogen containing, or producing, ammonium-N, contribute to soil acidity, unless all the ammonium-N is absorbed by plants.

Soil conditions which have the greatest influence on nitrification are:

- *Soil pH.* Nitrification rates are reduced in very acid soil. A soil pH between 6 and 7 is optimum for nitrification. Liming acid soil generally benefits nitrifying bacteria.
- *Moisture*. Nitrifying bacteria are most active in moist, aerated soil, but are inactive in water logged or very dry soil. Soils with sufficient moisture to grow crops will also have enough moisture for normal nitrification. Poorly drained or water logged soils do not contain enough oxygen to support nitrifying bacteria. As a result, very little nitrate is generated under these conditions.
- *Temperature.* Nitrification begins at temperatures just above the freezing point. It continues to increase as soil temperature increases, up to about 29°C (85°F). Above 29°C, the rate of nitrification decreases.
- *Aeration*. Nitrification is an aerobic process requiring oxygen. Well drained, medium to coarse textured soils are sufficiently oxygenated to support rapid nitrification. Good internal drainage and air movement between the soil and the atmosphere facilitate the process. In flooded soils under cultivation for rice, ammonium-based fertilizers are preferred because the lack of oxygen blocks the formation of nitrate that otherwise would escape from the paddy field as gaseous N_2 (see discussion of *denitrification* below).

Nitrates that are generated via nitrification can be lost through ***denitrification***, a process whereby anaerobic microorganisms use oxygen from the nitrate as an electron acceptor in metabolism, reducing the NO_3^- molecule to gaseous N_2. The reactions are shown in **Figure 5**.

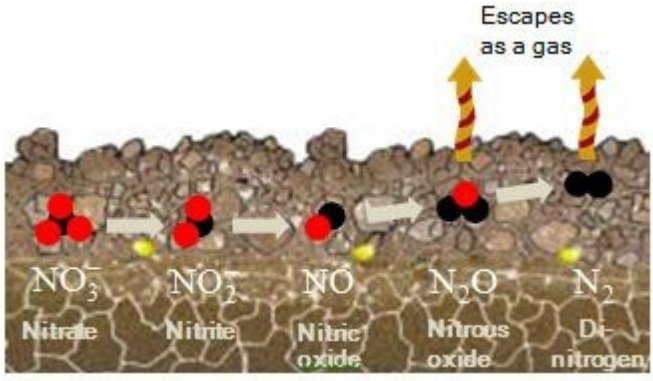


Figure 5. Denitrification is caused by soil microbes that can use the oxygen in nitrate as an electron acceptor during metabolism of organic matter, reducing the NO_3^- molecule to N_2. Conditions that favor this are warm, wet soil with lots of plant residue.

The process of denitrification is a major mechanism of soil nitrogen loss in most crop producing areas. Conditions that favor this are warm weather and wet, oxygen-depleted soil with lots of plant residue. It is not necessary for water to be standing on the soil surface for denitrification to occur. Denitrification can occur below the surface wherever oxygen diffusion is limited and nitrate is present. **Table 1** shows the relationship of denitrification to soil temperature, saturation, and loss of applied nitrogen.

Table 1. Estimated rates of denitrification in saturated soils

Soil temperature	Days saturated	Loss of applied N
55-60° F	5	10%
	10	25%
75-85° F	5	75%
	7	85%
	9	95%

source: Shapiro, University of Nebraska

12.5 Nitrogen Volatilization

Ammonia (NH_3) is a natural product of nitrogen mineralization. Where soil conditions favor the formation of NH_3 it does not remain in the soil but escapes to the atmosphere as a gaseous vapor. This is called ***volatilization***. Only small amounts of NH_3 are volatilized during mineralization. Much larger amounts of NH_3 may be lost from surface applied fertilizers and manure. The reaction is:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad \text{Eq. [2]}$$

The amount of NH_3 gas lost from the soil depends on several factors.

- *Soil pH*. Ammonia volatilization losses occur when ammonium (NH_4^+) is dissolved in a basic solution (pH >7). This condition occurs naturally in calcareous soil with a high carbonate content. When NH_4^+ fertilizers are added to acidic to near-neutral soil, little or no NH_3 volatilization occurs (see section 12.10 for more on NH_3/NH_4^+ equilibrium in solution).

- *N Source and Placement*. Ammonium containing fertilizers (e.g. nitrate and sulfate salts of ammonium) added to acidic soil produce little or no NH_3 therefore they can be broadcast without incorporation. Rainfall or irrigation effectively washes the fertilizer into the root zone. Urea is a popular fertilizer nitrogen source because of its high analysis (46% N) and good handling and storage characteristics. When applied to the soil urea hydrolyzes to form NH_4^+ and consumes H^+ ions, thus raising the pH in the surrounding fertilizer micro-zone. The enzyme ***urease*** mediates this reaction (see 'Urea' in section 12.7 for reaction specifics). Urease is a naturally occurring enzyme found in many soil dwelling bacteria and fungi, as well as in plants, and plant residues. Urea containing fertilizers (solid or liquid) are most effective when injected or incorporated into the soil; if broadcasted, urea volatilization can be minimized by irrigation or rainfall soon after application. Volatilization can also reduce the fertilizer value of manure. NH_3 volatilization can be as high as 40% of the total nitrogen content of animal manure. Immediate incorporation of broadcast manure will reduce volatilization losses.

- *Soil Environment*. Warm, moist, mineral soils with pH >7 pose the highest risk of NH_3 volatilization because urease is most active under alkaline conditions.

Because N volatilization is influenced by so many factors it is not easy to know how much of the applied nitrogen is lost in agro-ecosystems. Annual volatilization losses of NH_3-N from synthetic fertilizer and animal manure has been estimated at 14% and 23%, respectively (Bouwman et al. 2005), and contributes to the observed low nitrogen use efficiency in agriculture.

12.6 Leaching of Soil Nitrogen

Both ammonium and nitrate ions are very soluble in water. But the positively charged ammonium ion is bound by the negatively charged colloid particles (e.g. clay), thereby resisting movement in or out of the soil. Nitrate ions are negatively charged, and have no chemical bindings to the soil colloidal fraction. Consequently, they are subject to movement as water percolates through the soil. When the quantity of water infiltrating the soil exceeds the rate of water lost through evaporation and transpiration by the crop, and if the excess water is freely draining, some of the nitrate will move out of the root zone in the drainage water. This process is called ***leaching***, portrayed in **Figure 6**.

Leaching is more severe in sandy, coarse-textured soil than in loamy or clay soils. Nitrogen losses from the soil vary with the crop, pattern of rainfall, and timing and rate of fertilizer nitrogen application. In sandy soil where fertilizer application timing does not coincide with plant uptake, or during periods of heavy rainfall, leaching losses up to 80 kg/ha nitrogen annually can be realized (Miller and Donahue, 1990).

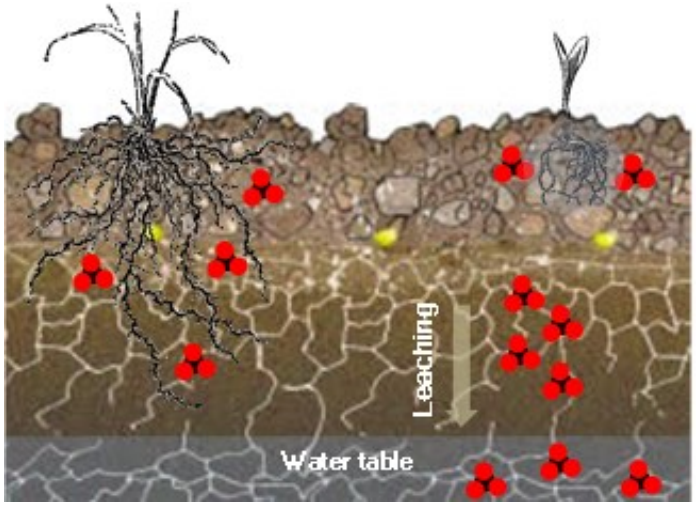


Figure 6. At right, leaching of fertilizer nitrate from the plant root zone under free drainage when application does not coincide with plant uptake. At left, a mature plant with a deep, well developed root system captures the nitrates. Nitrate that leaches into the water table is a pollutant and represents an economic loss to agriculture.

12. 7 Nitrogen Fixation

When atmospheric N_2 combines with hydrogen or oxygen, a process called ***fixation***[2] occurs. All atmospheric N_2 must undergo conversion to a chemically ***reduced*** form of nitrogen via fixation before it is rendered plant available. Fixation occurs in three principle ways:

1. *Biological*. Biological fixation may be *symbiotic* or *non-symbiotic*. Symbiotic fixation refers to micro-organisms fixing nitrogen while growing in association with a host plant. This process benefits both the organism and the host plant. The most widely known example is the association between species of ***Rhizobium*** bacteria and

[2] In agronomics the term 'fixation' has two meanings that are opposite. When used with *nitrogen*, the term fixation refers to converting from plant unavailable to plant available forms. When referring to nutrients, especially phosphorus, potassium, ammonium, the term fixation means converting from available to unavailable forms.

a ***legume*** (e.g. beans, peas, clovers, alfalfa). The bacteria form nodules directly on the roots (**Figures 7a and 7b).** The bacteria, in occupying the legume root nodules, fix nitrogen from the atmosphere thereby making it available to the plant. In turn, the legume furnishes carbohydrates to the bacteria as an energy source for fixation. Nitrogen fixation by legumes varies widely: annual production of a few tens of kilograms of nitrogen per hectare, to >200 kg per hectare per year are possible (see **Table 5**). Nitrogen fixed by symbiotic bacteria is considered the most important natural source of nitrogen in mineral soils. Non-symbiotic nitrogen fixation is also carried out by certain free-living bacteria in the soil (*Azotobactor*, blue-green algae, photosynthetic bacteria). The amount of non-symbiotic nitrogen fixed by free-living bacteria is much less than the amount fixed symbiotically. In average soil conditions this generally amounts to >15 kg/ha per year and is considered unimportant to the overall nitrogen budget for crops.

2. *Natural oxidation*. The energy released by lightning discharge in the atmosphere causes O_2 molecules to react with N_2 molecules, eventually generating nitrate-nitrogen. On average, rain and snow add only about 5-10 kg/ha nitrogen per year to the soil.

3. *Industrial*. The most important industrial process of nitrogen fixation is the reversible Haber-Bosch process whereby ammonia is synthesized as follows:

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+ \qquad \text{Eq. [3]}$$

The dihydrogen (H_2) feedstock is natural gas (methane, NH_4) whereas the nitrogen feedstock is atmospheric N_2. These raw materials are subject to high temperature (450-500˚C) and pressure (20 MPa) in the presence of an iron catalyst to generate ammonia. The energy cost of breaking nitrogen's triple bond is high: 946 kilojoules per mole of nitrogen, almost twice that needed to break a single O_2 molecule. The Haber-Bosch process was developed in Germany just prior to WWI, ushering the modern era of synthetic fertilizers needed for high-yield, intensive agriculture. Today, about 40% of human dietary protein can be traced back to Haber-Bosch and industrial ammonia synthesis (Smil, 2002).

12.8 Mineral N Sources

Before the era of ammonia synthesis, all agricultural sources of nitrogen were obtained from wastes and manures, decomposing crop residue, or from mined sources. Huge deposits of Chilean nitrate or saltpeter (essentially sea-bird droppings), found in coastal Chile and in its northern Atacama desert, have been mined and sold under various trade names since the 1800s (**Figure 8**).

Virtually all of the commercial fertilizer nitrogen today is manufactured, usually from ammonia. Such products are less expensive, more concentrated, and available in a wide array of formulations, while being just as plant available as the older organics. Major fertilizer N sources include:

Anhydrous Ammonia (NH_3) and Aqua Ammonia (NH_3OH) Anhydrous ammonia is formed from two gaseous elements, hydrogen and nitrogen. The word *anhydrous* is

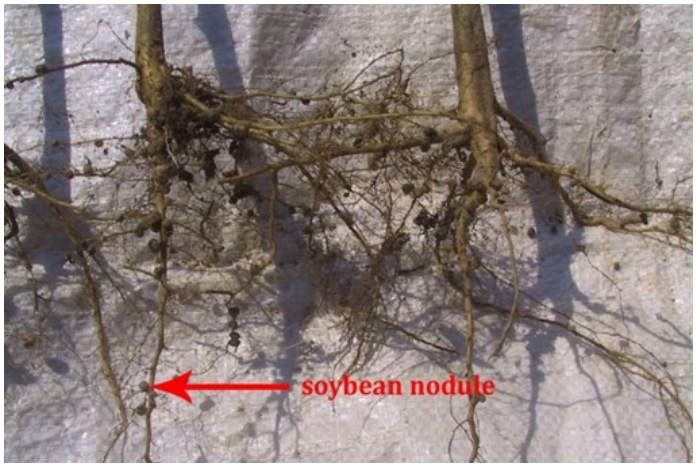


Figure 7a. *Rhizobium japonicum* bacteria nodule on soybean root.

Figure 7b. *Rhizobium* nodule cut in half showing pink interior, a sign of a healthy bacteria colony. The pink color is caused by an iron-containing molecule called *legheamoglobin*. The purpose of the leghaemoglobin is to absorb free oxygen because a low-oxygen environment is needed for the nitrogenase enzyme to fix nitrogen. If the nodules are brown or black inside, the bacteria are dead.

Figure 8. Left: Ad extolling the virtues of Chilean nitrate, containing 'vital' elements. Right: The Champion brand of Chilean nitrate, known as 'bulldog soda'. The importance of Chilean nitrate as a nitrogen source in agriculture waned during the 1920s as synthetic ammonia production advanced. Today it occupies a niche market.

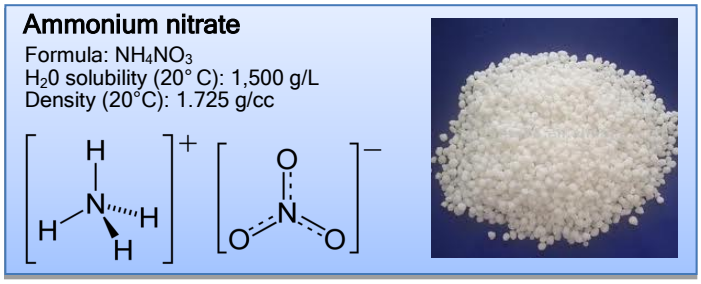
from the Greek and emphasizes the absence of water. The composition of anhydrous ammonia is 82.35% nitrogen and 17.65% hydrogen. Anhydrous ammonia is a gas under normal atmospheric temperature and pressure. Because anhydrous ammonia is stored under pressure as a liquid, special equipment is needed for handling, transport, and application (**Figure 9**). Aqua ammonia is a mixture of ammonia gas and water (ammonium hydroxide) and is sometimes used as a fertilizer. It is 21% nitrogen and is applied as a non-pressurized liquid.

Figure 9. Anhydrous ammonia application rig. Because anhydrous ammonia is a gas at normal atmospheric temperature and pressure, it is stored as a liquid under ~ 1.4 MPa pressure (about 200 psi) and applied via trailing 'nurse' tanks equipped with special valves, hoses, and fittings. Inset: close-up of an anhydrous applicator chisel or 'knife' shank showing injection of anhydrous ammonia gas into soil slit. *Photo by Todd Nelson, University of Wisconsin; inset image from Crops and Soils magazine.*

In agronomics, anhydrous and aqua ammonia are injected in bands several inches below the soil surface. The moisture content of the soil must be in a range to dissolve the ammonia gas to form soluble ammonium (NH_4^+) ions but not waterlogged. The ideal moisture content is when the soil is slightly below ***field capacity***. Anhydrous ammonia must be applied deeper in sandy, low cation-exchange capacity (CEC) soils compared to loamy soils. Anhydrous ammonia application equipment cannot be used to apply other fertilizers, so its use is limited to broad-acre operations able to justify the cost of single-purpose equipment. Ammonia gas is toxic to plants and animals, including micro-organisms[3]. However, long-term field experiments have shown that the population of soil micro-organisms returns to the normal level of unfertilized soil about one month after application. There are no known detrimental effects to the soil that are associated with using anhydrous ammonia.

Ammonium nitrate (NH_4NO_3) Ammonium nitrate is the ammonium salt of nitric acid. Ammonium is the basic part and the nitrate is the acid. Fertilizer grade ammonium nitrate contains 33-34% nitrogen and is usually applied as a solid prill.

[3] Ammonia (NH_3) and ammonium (NH_4^+) ions are toxic to plants in high enough concentration. In most temperate well-drained soil, ammonium formed from organic matter decomposition is quickly converted to nitrate during the process of nitrification. The toxic effect of ammonium salts (e.g. ammonium nitrate) is quite different from that of ammonia gas or ammonium ions in solution. Injury from over-fertilization with ammonium salts is due to negative osmotic pressure developed in the soil solution around the root hairs, which prevents water uptake (fertilizer 'burn') or, from high salt concentration in the leaf due to evaporation of moisture through the leaf pores (stomata).



In agronomics, it may be applied directly or blended with other liquid and dry fertilizers. Since ammonium nitrate contains over 50% of its nitrogen in the nitrate form, it is more susceptible to denitrification after application than other ammonium-based fertilizers. The other hand, it is not volatile and can be surface applied in situations where incorporation is not feasible. Ammonium nitrate is very hygroscopic; under high humidity in storage it hardens to brick irreversibly. Under certain conditions ammonium nitrate can be explosive; however modern fertilizer grades are conditioned such that when stored and handled properly, no hazard is posed.

Urea ($CO(NH_2)_2$) Urea, or carbamide, is a neutral (uncharged), naturally occurring organic compound with two amine ($-NH_2$) groups attached to a carbonyl (C=O) functional group. It is usually marketed as a dry material containing 45-46% nitrogen. Unlike other mineral fertilizers, urea is an organic compound synthesized by reacting ammonia with carbon dioxide under high temperature and pressure. It is chemically similar to animal urine. Its nitrogen, although in organic form, is water soluble, and becomes available to plants upon contact in warm soil. Urea's high N analysis, stability in storage, and desirable handling properties, make it one of the most important nitrogen fertilizers, worldwide. Urea may contain trace amounts of biuret (carbamylurea) from the thermal decomposition of urea in manufacturing, which is toxic to some crops. However urea manufactured under good control practices seldom contains toxic levels of biuret.

In agronomics, urea is applied as a solid or liquid fertilizer. When applied to soil, urea is ***hydrolyzed***, or decomposed, to produce NH_4^+ and bicarbonate (HCO_3^-) ions by the enzyme *urease:*

$$CO(NH_2)_2 + 2H_2O + H^+ \xrightarrow{\text{urease}} 2NH_4 + HCO_3^- \qquad \text{Eq. [4]}$$

During hydrolysis one mole of acidity (H^+) is consumed and the HCO_3^- reacts with another mole of acidity, producing carbon dioxide (CO_2) and water:

$$HCO_3^- + H^+ \rightleftharpoons CO_{2(gas)} + H_2O \qquad \text{Eq. [5]}$$

Therefore two moles of acidity are consumed from the soil solution for each mole of urea that is hydrolyzed. The net reaction raises soil pH temporarily in the zone of the hydrolysis[4]. The excess OH^- ions react with NH_4^+ to produce gaseous NH_3 according to the reaction in Eq. [2] in section 12.5.

Serious nitrogen losses can occur when the micro-zone surrounding the urea molecules becomes alkaline due to hydrolysis, or when urea-containing fertilizer is applied to warm, moist surface soil, especially where crop residues are thick or where surface soil pH is naturally high. Urea that is diffused via tillage or precipitation (0.5 inches or more), or applied to cold soil can significantly reduce ammonia volatilization. In this case the ammonia is converted to ammonium ions which are then adsorbed by the negatively charged surfaces of soil colloid particles. Some urea fertilizers are impregnated or mixed with a ***urease inhibitor*** to prevent the conversion of urea to ammonium carbamate during hydrolysis.

Non-pressure nitrogen solutions These include a versatile category of solutions composed of urea and ammonium nitrate dissolved in water. When used as fertilizer they react in the same manner as the individual components. The most popular are urea-ammonium-nitrate (UAN) solutions. The nitrogen content generally ranges from 19-32%. Because the solubility of the nitrogen salts in these solutions decreases as temperature decreases, the more concentrated products tend to precipitate or 'salt out', limiting their storage and use in colder climates.

Non-pressure (UAN) solutions

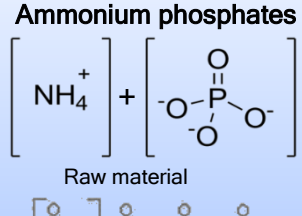
Grade, %N	28	30	32
NH_4N0_3,%	40	42	45
$(CO(NH_2)_2)$,%	30	33	35
Water,%	30	25	20
Density@16°C	1.283	1.303	1.320
Salt-out temp. (°C)	-18	-10	-2
pH	---------- 7 ----------		

In agronomics, UAN solutions are used as carriers for herbicides or applied with irrigation water. Spray pumps, valves, fittings, and nozzles used to apply herbicides can also be used to apply UAN solutions. Because they contain some urea, UAN solutions ideally should be injected in the soil; when surface applied, nitrogen volatilization can be minimized by dribbling in narrow bands rather than broadcasting. Broadcast or post-directed with herbicides, UAN solutions can enhance weed-killing activity. When applied in this manner, care must be taken to avoid contact with crop foliage.

[4] Several different carbonate ions may form in urea hydrolysis. The pH of the hydrolysis reaction in near-neutral soils is 7-9; in this range HCO_3^- predominates. Smaller amounts of HCO_3^{-2} are produced under these conditions, with the amount of HCO_3^{-2} increasing at pH >8. In acid soil with pH <6.3 H_2CO_3 predominates. In all reactions two moles of acidity are consumed per mole of urea hydrolyzed. See Ferguson et al. (1984) for details.

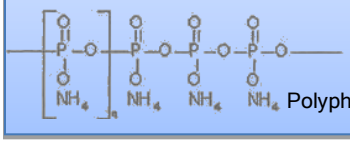
Ammonium Phosphates These include mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP) and ammonium polyphosphate (APP). Ammonium phosphates are inorganic salts synthesized by treating phosphoric acid with ammonia (anhydrous or aqueous); the main difference is the ratio of ammonia to phosphoric acid, for example, MAP has the formula $NH_4H_2PO_4$, DAP is produced by reacting two units of ammonia per unit phosphoric acid and has the formula $(NH_4)_2H_2PO_4$, and APPs are ammonium salts of polyphosphoric acid and ammonia such as triammonium pyrophosphate $[(NH_4)_3P_2O_7)]$, penta-ammonium tripolyphosphate $[(NH_4)_5P_2O_{10})]$. Ammonium phosphates are manufactured as solid or liquid. They are used mainly as phosphorus sources (APs supply ~50% of all agricultural phosphate, worldwide), but can also contribute significantly to nitrogen balance programs. Fertilizer grade MAP is 10-12% nitrogen (11-52-0 is the typical NPK grade), DAP is 18% nitrogen (18-46-0), and APP, in liquid form, is 10-11% nitrogen (10-34-0 and 11-55-0).

Ammonium phosphates



Raw material

Mono-ammonium phosphate (MAP)



Polyphosphate chain

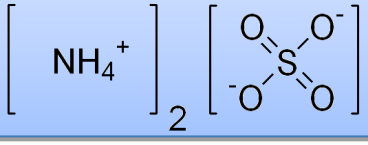
In agronomics, ammonium phosphates are row-applied as starter or 'pop-up' fertilizers. Ammonium phosphates are highly water soluble and therefore of equal agronomic value, when applied in irrigation water. Ammonium phosphates are applied in bands several inches from the seed to avoid salt and ammonia injury. This is particularly true for DAP, which will initially have a high pH around the granules due to the higher ammonium content. Under alkaline soil conditions, the risk of ammonia injury and volatilization will be higher for DAP than MAP.

Ammonium sulfate $[(NH_4)_2SO_4]$ Ammonium sulfate is the crystalline ammonium salt of sulfuric acid. It is a by-product of many industrial processes and one of the oldest manufactured fertilizer nitrogen sources. It can also be synthesized but is generally uneconomical to do so. It contains 20-21% nitrogen, all in ammonium form. It also contains 23-24% sulfur (S), all in the sulfate (SO_4^{-2}) form. Sulfur deficiencies are on the rise due to more stringent air pollution controls, and increasing use of high grade, low-S inorganic fertilizers. In future, ammonium sulfate may become more popular as a source of plant-available sulfur.

Ammonium sulfate

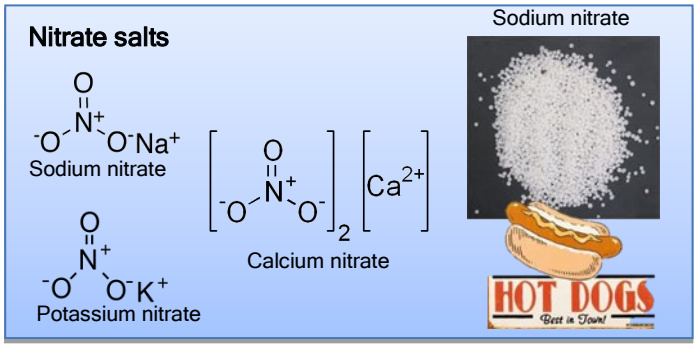
Formula: $(NH_4)_2SO_4$

H_20 solubility (20°C): 750 g/L



In agronomics, the use of ammonium sulfate for nitrogen nutrition is limited by its low nitrogen content and relatively high transportation cost. Ammonium sulfate has an acidifying effect on soil due to the nitrification process (see section 12.9). The acid-producing potential of ammonium sulfate is greater than the same nitrogen application from ammonium nitrate, since all the nitrogen in ammonium sulfate will be converted to nitrate, while only half of the N from ammonium nitrate will be converted to nitrate. The sulfate ion *does not* cause acidity. Under alkaline soil conditions (above pH 7.0), acid-forming fertilizers can increase the availability of micronutrients such as iron and zinc, and help control some diseases, for example, potato scab. Where soils are naturally acidic, the extra acidity produced by these fertilizers must be countered by more frequent liming. Ammonium sulfate has low hygroscopicity and can be blended with most of the raw materials used by the fertilizer industry. However, it is not compatible with alkaline materials and thus should not be mixed with lime, Cyanamid, urea, calcium nitrate, or basic slag. Most ammonium sulfate is applied in a dry form.

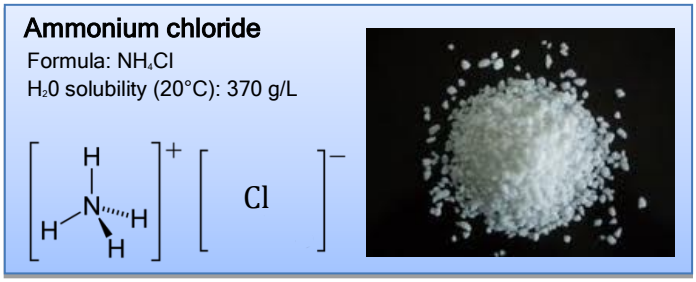
Nitrate salts This group includes principally, potassium nitrate (KNO_3, 12-14% N), sodium nitrate ($NaNO_3$, 16% N), and calcium nitrate ($Ca(NO_3)_2$, 15.5% N). All of the nitrogen is in the soluble nitrate form, immediately available for plant uptake and requiring no additional microbial transformation in the soil. Because these products contain no ammonium, they have a neutral, to slightly basic, reaction in the soil. Nitrate salts are sometimes preferred by growers of high-value tobacco, citrus, and vegetable crops where chloride-free sources of nitrogen and potassium improve quality and yield.



In agronomics, the fertilizer nitrate salts are niche products and their production and use, as compared to high-grade N sources is limited, worldwide. Potassium nitrate (aka 'saltpeter') is synthesized by reacting potassium chloride (KCl) with a nitrate source, for example nitric acid, ammonium nitrate, or sodium nitrate. The end product is the same regardless of the nitrate source. Fertilizer grade KNO_3 is typically sold as a water-soluble, crystalline material primarily intended for dissolving and application with water or, as a prill for soil application via truck or tractor-mounted applicator. It is also a valuable source of soluble potash (44% as K_2O). It is only slightly hygroscopic and can be blended, mixed, and stored without caking. Sodium nitrate (aka 'Chilean saltpeter') occurs in natural deposits, but is also synthesized by reacting nitric acid with sodium carbonate. Sodium nitrate has chemical and physical properties similar to potassium nitrate.

Field crops that have, historically, been associated with sodium nitrate application are sugar beet and cotton. Sodium ions, if present in high amounts in the soil, cause deflocculation (dispersion of clay particles) and can damage soil structure. Normal applications of 100-200 kg sodium nitrate per hectare per year do not affect the soil structure. Calcium nitrate is synthesized by reacting nitric acid with calcium carbonate (limestone). Production of fertilizer grade calcium nitrate is carried out largely in Europe (Norway, Netherlands, Portugal, and Ukraine) and in Egypt. In the prilled form it is suitable for mixing with bulk blended fertilizer, and the crystalline power can be mixed with water. It finds application in the control of blossom end rot of tomatoes and is used as a source of nitrogen in European horticulture. As a fertilizer, calcium nitrate is advantageous on saline soils because the calcium displaces the sodium that is adsorbed by the clay in soils. For this reason, it may be the preferred fertilizer where soil salinity problems exist. The fertilizer value of calcium nitrate is offset somewhat by its hygroscopicity, which requires sealed, moisture-proof containers for shipping and handling.

Ammonium chloride (NH_4Cl) Ammonium chloride, like other salts of ammonium, is used as a fertilizer. Its principal raw materials depend on the manufacturing process: salt (NaCl) and anhydrous ammonia in the case of the dual-salt (Solvay) process or, anhydrous ammonia and hydrochloric acid (HCl) for the direct-neutralization method. Fertilizer grade ammonium chloride contains 26% nitrogen and is used as such, or combined with fertilizer phosphorus and potassium. Coarse crystalline or granular forms are the most common, the latter being preferred for direct application. Ammonium chloride is hygroscopic; transportation and storage in moisture-proof bags is necessary to prevent clumping. Ammonium chloride has a higher N content than ammonium sulfate (20.5%), thus a slightly lower per unit cost.



As a fertilizer, ammonium chloride is popular in Asia and southeast Asia, where it has some agronomic advantage for paddy rice due to its slower rate of nitrification compared to urea and ammonium sulfate. Nitrogen loss is, therefore, lower and yields, higher. However, it is much less economical than urea and only slightly more so than ammonium sulfate. The disadvantages of ammonium chloride are its acid reaction in the soil, which is equal to ammonium sulfate per unit of N; and, its high chloride (66%) content. Crops that have been successfully tested with ammonium chloride are rice, wheat, barley, sorghum, sugar cane and fiber crops. Other crops, such as tobacco, potato grapes, and chilies are not ideal as the chloride lowers the quality and storability of these crops.

Slowly Available N Sources There are a number of products available that release nitrogen slowly in the soil, rather than a short burst after application. Situations where the grower does not want high levels of soluble nitrogen in

the soil solution at any one time, due to potential loss, salt injury, or in promoting excessive plant growth, are prime situations, for example, container-based horticultural production and turfgrass management. Inorganic compounds, such as magnesium ammonium phosphate, and organic compounds, such as ureaformaldehyde (ureaform), isobutylidene diurea (IBDU), and crotonylidene diurea (CDU), are often preferred to supply nitrogen at slow but fairly predictable rates.

Slowly Available N Sources

Name: Nitroform
Parent material: Urea+formaldehyde
N content: 38%, consisting of
4.5% urea
6.9% slowly available N
26.6% H_20-insoluble N

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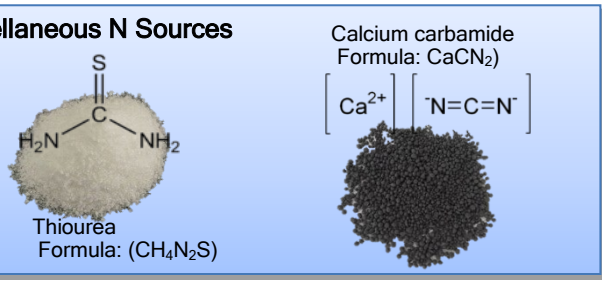
Nitrogen release from these compounds is slowed by very low solubility in water, and release from the organic materials is usually related to rate of microbial degradation. Simpler nitrogen compounds, such as urea, can be coated with less soluble materials, including polymers and waxes, and nitrogen release controlled by the rate at which the coating deteriorates. Sulfur-coated urea (SCU), made by spraying urea granules with molten sulfur, is a common example of such a product. All of these products are relatively expensive sources of nitrogen; as such, their use is restricted to specialty markets and high-value crops.

Miscellaneous N Sources A catch-all including calcium cyanamide ($CaCN_2$) and thiourea ($SC(NH_2)_2$). Fertilizer grade calcium cynamide (aka cyanamid) is a dark colored, granulated organic material containing 21% nitrogen and 11% calcium. The presence of carbon as calcium carbide gives it a dark color. It is manufactured by reacting calcium carbide (CaC_2) with elemental nitrogen. It has a basic reaction and is hydrolyzed to urea in the soil. The conversion process is postulated to produce several toxic products that have been exploited as pre-plant weed killers, especially in tobacco seedbeds.

Miscellaneous N Sources



Curiously, the synthesis of calcium cyanamide by Adoph Frank and Nicoderm Caro in 1898 predates the Haber-Bosch process for nitrogen fixation, presaging the era of industrial ammonium production. Thiourea is a sulfur analogue of urea containing 38.6% nitrogen. It is crystalline and a water-insoluble solid manufactured by reacting technical-grade calcium cyanamide ($CaCN_2$) and hydrogen sulfide (H_2S) or one of its precursors in aqueous solution e.g., ammonium sulfide ($(NH_4)_2S$) or calcium hydrogen sulfide ($Ca(HS)_2$). Thiourea has industrial uses but its total global use as a fertilizer is less than 1%. It is nitrified slowly in the soil and its fertilizer value has not been well tested.

12.9 Fertilizers and Soil Acidity

There is a great deal of confusion over the reaction of nitrogenous fertilizers in solution and the effect they have on the soil reaction (pH). Let us consider ammonia, the prime source of fertilizer nitrogen. When dissolved in water, it reacts as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4 + OH^- \qquad \text{Eq. [6]}$$

Note that, Eq. [6] is the same as Eq. [2] in section 12.5, only reversed (the double arrow means this can happen). Equation [6] shows that for each mole of ammonia dissolved in water, one mole of hydroxyl (OH^-) ions is formed. A solution with an excess of OH- ions is basic whereas an excess of hydrogen ions is acidic (see Technical Note 3 for a discussion of acids and bases). Ammonia therefore is a base (actually a weak base). However, the pH of a solution has an effect on the relative amounts of ammonia (a gas) and ammonium (a dissolved ion) that are formed, illustrated in **Figure 10.**

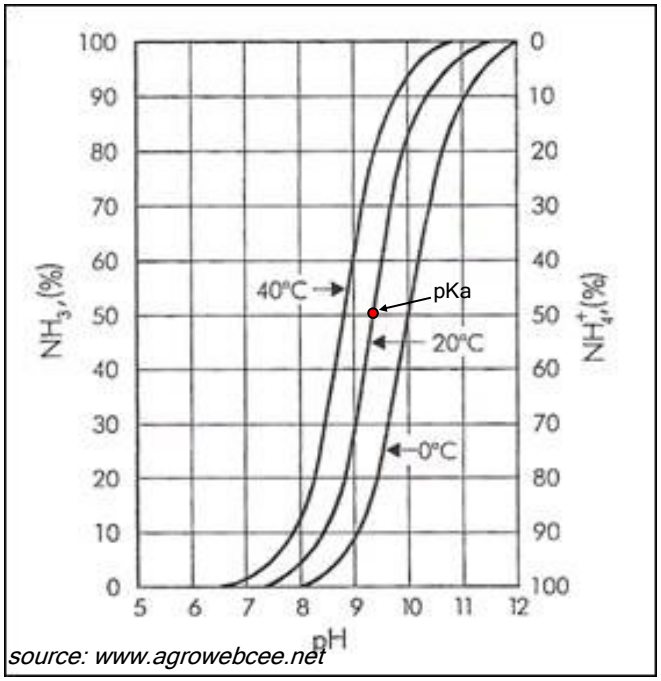


Figure 10. Equilibrium relationship for NH_3 and NH_4^+ concentration in a dilute solution as affected by pH and temperature.

The ***pKa*** of an acid (or base) is the pH at which the concentration of undissociated (non-ionized) ***conjugate base*** is numerically equal to the dissociated (ionized) ***conjugate acid***. Here, ammonia (NH_3) is the conjugate base and ammonium (NH_4^+) the conjugate acid. We see from the graph that ammonia has a pKa of ~9.4 (at 20° C); in other words, at a pH of 9.4, a solution of ammonia would consist of 50% ammonia and 50% ammonium. At pH ≤ 7.5 the graph predicts a negligible (closer to zero) amount of ammonia whereas a pH ≥ 11.5 predicts nearly 100% ammonia. This relationship is important because ammoniacal nitrogen (i.e. ammonium + ammonia) may be mixed in irrigation water or applied directly to the soil where it dissolves in water. As the solution around the ammonia molecules becomes more basic (> pH ~7.5) there is increasing risk of N volatilization. You can test this fact by

sniffing a jug of household ammonia which has a pH of ~11. The ammonia vapors tell the truth. Because the concentration of ammonia in the soil solution is tiny compared to a jug of household ammonia, nitrogen volatilization is a process that humans cannot perceive so we must fall back on the fundamentals of chemistry to understand what is happening.

Now consider urea, also highly soluble. When dissolved in water, it reacts as follows:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 + H_2O \qquad \text{Eq. [7]}$$

Equation 7 shows that the reaction of urea in water is neutral because ***hydrolysis*** (splitting by water) of the urea molecule produces no H^+ or OH^- ions. However, ammonia is a product of urea hydrolysis and it obeys the pKa relationship in **Figure 10**. This concept is important because when urea is applied to the soil, it rapidly hydrolyzes in the presence of the enzyme urease to produce NH_4^+ and bicarbonate ions (HCO_3^-):

$$CO(NH_2)_2 + 2H_2O + H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- \qquad \text{Eq. [8]}$$

Note that one mole of acidity (H^+ ions) is consumed per mole of urea that is hydrolyzed. Further, the bicarbonate ions also react with one mole of H^+ around the urea molecule, temporarily raising the pH:

$$HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O \qquad \text{Eq. [9]}$$

If urea is exposed to the atmosphere while pH in the vicinity of the urea molecule rises above 7.5, some free ammonia will be formed according to the pKa relationship. At pH ≤ 7.5, less than 5% of the ammoniacal-N is in the form of ammonia over the range of temperatures likely for field conditions (0-40° C).

Lastly, we examine ammonium nitrate, also highly soluble. When dissolved in water, it reacts as follows:

$$NH_4NO_3 \rightarrow NH_4^+ + NO_3^- \qquad \text{Eq. [10]}$$

Because ammonium nitrate is a salt, it ionizes in water to produce ammonium and nitrate ions. The reaction is neutral but again, the ammonium ion will obey the pKa relationship in **Figure 10**. We could substitute ammonium sulfate ($(NH_4)_2SO_4$) and the same reaction would occur, but instead of nitrate ions we would get sulfate (SO_4^-) ions. The effect of nitrate and sulfate anions on pH is negligible.

When ammoniacal-N fertilizers such as anhydrous ammonia and urea are applied to soil, the reaction is initially basic in the micro-zone around the fertilizer but over time the macro-scale effect is acidic due to nitrification of ammonium to nitrate (Eq. [1], section 12.4). Nitrogen fertilizers that contain NO_3^- but not NH_4^+ make the soil slightly less acidic over time, but are generally used in much less quantity than ammoniacal-N fertilizers.

The standard index for comparing the acidity of different fertilizers is called the Calcium Carbonate Equivalent (CCE). This number is often found on fertilizer labels, spec sheets, and in fertilizer tables published by the USDA and affiliated State Cooperative Extension Services in the United States. Some reference numbers are shown in **Table 2**.

Table 2. Acidity or basicity of fertilizer materials

Material	% N	CCE, lb/Ton of Material
Anhydrous ammonia	82	-2,960
Ammonium sulfate	21	-2,200
Urea	46	-1,680
Diammonium phosphate	18	-1,400
Monoammonium phosphate	10	-1,300
Ammonium nitrate	33.5	-1,180
Urea-form	38	-1,360
UAN solutions	19-49	-750 to -1,760
Calcium nitrate	15	+400
Potassium nitrate	13	+580
Sodium nitrate	16	+520

source: Zublena, et al. (1991). Nutrient Content of Fertilizer and Organic Materials. Soil Facts AG-439-18.

Numbers in **Table 2** (English units) show the pounds of calcium carbonate ($CaCO_3$) equivalent needed (minus sign) to neutralize the acid formed by one ton of the fertilizer material in question. A plus sign indicates the material is basic in nature. Note that the CCE values are given in terms of pounds of *pure* $CaCO_3$. Other aglime materials would require more than this amount depending on the CCE (see Technical Note 3 for a discussion of aglime and CCEs).

It is fair to question how the CCE values in **Table 2** are calculated. We would expect the reaction of a given fertilizer material to vary with soil characteristics, cropping, and environment. The CCE numbers in **Table 2** are, however, widely published and accepted as official, fixed values. In theory, we can calculate the number of neutralizing equivalents in a pound of $CaCO_3$ and the number of acidic equivalents in a pound of a given fertilizer. The carbonate in limestone reacts with hydrogen to neutralize acidity, as follows:

$$CaCO_3 + 2H^+ \rightarrow Ca^{+2} + H_20 + CO_2 \qquad \text{Eq. [11]}$$

From this equation we see that one mole of $CaCO_3$ will combine with two moles of hydrogen. The number of molecules in one mole of $CaCO_3$, and the number of molecules in one mole of hydrogen, is numerically equal (Avogadro's number). The formula weight of $CaCO_3$ is 100 g/mole. Therefore one pound of $CaCO_3$, or 454 g, contains 4.54 moles. One pound of $CaCO_3$ will neutralize (4.54) x (2), or about 9 equivalents of acidity.

Table 2 shows that ammonium sulfate is an acid fertilizer requiring 2,200 pounds of $CaCO_3$ to neutralize the acidity in one ton (2,000 lb), or 1.1 pound of $CaCO_3$ per pound of ammonium sulfate. When ammonium sulfate is applied to

the soil, all the ammonium is oxidized to nitrate via nitrification (section 12.4). The net reaction is:

$$(NH_4)_2SO_4 + 4O_2 \rightarrow 4H^+ + 2NO_3^- + SO_4^- + 2H_2O \qquad \text{Eq. [12]}$$

Equation 12 shows that one mole of ammonium sulfate produces 4 moles of acid hydrogen ions. The formula weight for ammonium sulfate is 132 g/mole. One pound (454 g) of ammonium sulfate contains 454/132, or 3.44 moles. Since each mole of ammonium sulfate produces 4 moles of hydrogen ions, one pound of ammonium sulfate will produce (3.44) x (4) = 13.8 equivalents of acidity. Therefore it will take, theoretically, 13.8/9, or 1.5 pounds of $CaCO_3$ to neutralize the acidity in one pound of ammonium sulfate. This answer does not agree with 1.1 pound $CaCO_3$ for each pound ammonium sulfate in **Table 2**. What is the reason for the discrepancy?

Turns out, the official AOAC[6] method to calculate the equivalent acidity and basicity of fertilizers is based on early greenhouse experiments of W.H. Pierre, in which he observed the actual acidity produced by fertilizers under field conditions was less than expected on the basis of theoretical calculation (Pierre, 1928a).

To support his claim, Pierre invoked the concept of physiological acidity and basicity, which results from the unequal uptake by plants of cation and anion equivalents[7]. In a paper describing his methods, Pierre argues that 'on this basis ammonium sulfate should only develop three-quarters of its potential acidity if plants are growing in the soil' (Pierre, 1933). Recent work by Chien et al. (2008) suggests that acidity produced by different ammoniacal-N fertilizers deviates from the official AOAC data, evidently from differences in soil clay and organic matter content.

To conclude our discussion of fertilizers and soil acidity, the following points may be taken:

- The reaction of ammoniacal-N fertilizers in solution is different from the reaction of the same fertilizers in soil.
- Ammonia in solution has a basic reaction, and the equilibrium concentration of its conjugate acid (ammonia) and conjugate base (ammonium) is governed by the pH and temperature of the solution.
- The equilibrium relationship of ammonia- ammonium in solution is important because ammoniacal-N fertilizers initially raise the pH of the soil solution in a micro-zone around the fertilizer.
- Ammonia, if not converted immediately to ammonium in the soil, may be lost through volatilization.
- The long-term effect of ammonium fertilizers on the soil reaction is acidic due to nitrification of ammonium to nitrate by micro-organisms.
- Nitrate and sulfate anions in fertilizers do not cause acidity.
- The acidic effect of ammonium fertilizers can be easily countered by liming the soil.
- Liming should be done on the basis of pH measured in the field, not on the basis of fertilizer application.

[6] Association of Official Analytical Chemists

[7] The concept of physiological acidity and basicity is based on the principle of electrical neutrality, where each cation equivalent absorbed by the plant is balanced by the release of one acid equivalent, and each anion absorbed is balanced by the release of one basic equivalent. Since nitrogen uptake in the form of nitrate, is greater than all other nutrient elements, the logical conclusion is that nutrient uptake by plants has a net basic effect that partly offsets the acidity produced by fertilizers.

12.10 Organic N Sources

As the cost of fertilizer increases, there is increasing interest in using animal manure, municipal waste, and legume cover crops to supply some of the nitrogen for agriculture. Organic wastes, in whatever form, contain valuable quantities of plant-essential nutrients and, there are many environmental benefits of composting wastes rather than disposing of them in landfills. Further, organic growers who are producing for the certified organic market must use approved organic and unprocessed nutrient sources.

Organic wastes vary tremendously in their physical, chemical, and biological properties due to the mixed composition of the raw materials and specific treatment practices. Compared to manufactured fertilizers, manures contain a relatively small amount of plant essential nutrients, with exception for micronutrients. The decay of organic materials depends on the activity of microorganisms that convert nutrients to a soluble form that can be used by plants. Conversely, the nutrients in commercial fertilizers are generally soluble, so predicting their availability to plants is much easier. Some challenges using organic sources of nitrogen are:

- Predicting nitrogen mineralization and, synchronizing the release from organic sources with plant demand over the growing season is more difficult (**Figure 11**).
- The N-P-K profile of animal manure is often unbalanced, such that manure applied at rates to satisfy N demand for crops may result in over- or under-applying P and K.
- Animal diet supplements, for example lime in poultry, antibiotics, etc. will also be present in the manure.
- Moisture content of manure is between 70-85% increasing the cost of transportation and handling.
- Special precautions need to be observed when stockpiling manure to avoid groundwater contamination and nutrient loss.

Since animal manures are low in nitrogen (1-6%), larger amounts are needed to satisfy agronomic demand for this nutrient. A fringe benefit is that more organic matter is added to the soil, improving physical quality and microbiological activity. Recycling nutrients via compost and manure is an environmentally sound practice that is likely to intensify as pressure on non-renewable resources increases.

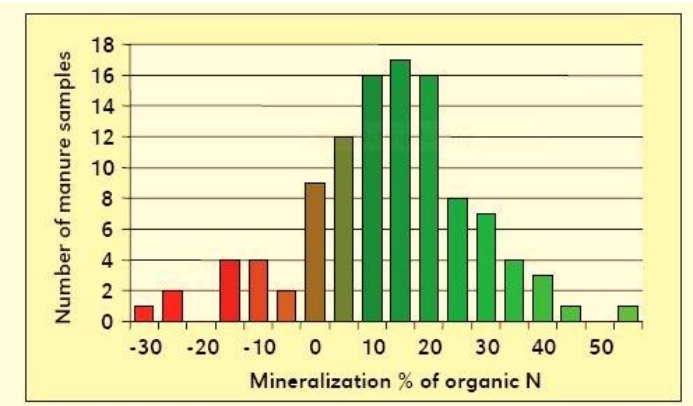


Figure 11. Nitrogen mineralization from 107 different dairy manure samples after 8 weeks incubation. Figure 9 points up that predicting N availability from organic waste can be difficult. On average, 13% of the organic N was mineralized, but 13 samples had net immobilization. Net N mineralization from the remaining 94 samples ranged from zero to 55%. *source: Mikkelsen and Hartz (2008); reinterpreted from Van Kessel and Reeves (2002).*

Efficient use of organic nitrogen sources involves knowing both the amount of nitrogen applied and the rate of nitrogen release from organic matter. Nitrogen availability 'coefficients' are used to estimate the fraction of total N that will be available for crop uptake during the first growing season (called *plant available N* or PAN). Examples of PAN coefficients are shown in **Table 3**.

Using PAN coefficients requires some understanding of the physical and chemical properties of organic matter for maximum efficiency in management. Properties such as C:N ratio, lignin content, as well as agronomic practices (e.g. placement) and climate factors (e.g. time of the year) affect nitrogen mineralization and, consequently PAN coefficients.

Table 3. First-year N availability coefficients for different manures and application methods.

Manure type	Soil incorporated	Surface applied BC¥	Surface applied IR§
	Fraction of N available in first year		
Poultry litter	0.6	0.5	-
Layer manure	0.6	0.4	-
Scraped swine manure	0.6	0.4	-
Scraped dairy manure	0.6	0.4	-
Swine lagoon effluent	0.8	0.5	0.5
Dairy lagoon effluent	0.8	0.5	0.5
Municipal sludge			
aerobic	0.3	0.2	0.3
anaerobic	0.2	0.2	0.2
lime-stabilized	0.4	0.3	-
Compost (C:N of 15:1 to 20:1)	0.05	0.03	-
			-
Compost (C:N of > 25:1)	0	0	-

¥ Broadcast; § Irrigated

source: adapted from Mikkelsen and Hartz (2008); Baldwin and Greenfield (2006); and North Carolina Dept. of Agriculture (2011).

Following is an example showing how to calculate field application rates with PAN coefficients such as in **Table 3**.

Problem: Farmer Jones has a supply of layer manure he wishes to use for sweet corn production. How many metric tons per hectare would he apply to satisfy an agronomic demand of 140 kg N/ha (125 lbs. N/acre), assuming there is no nitrogen carryover from the previous year?

Solution: There are three PAN coefficients for layer manure listed in **Table 3**, depending on the application method. The layer manure will be soil incorporated with a disk, so we choose a coefficient of 0.60. This is *the fraction of the total nitrogen* estimated to become available in one growing season[5]. To calculate the field application rate we need to know the *total nitrogen content* (or Total Kjeldhal Nitrogen, TKN) of the manure and its moisture content. The most reliable way of getting this information is by submitting a sample of manure to a laboratory for analysis. Failing that, published tables showing typical values for waste products may be consulted although this is less accurate. For this example, assume the total nitrogen content was reported as 30,000 mg N/kg (dry-weight basis), and the moisture content is 20%.

To convert mg/kg, which is the same as parts per million (ppm), to parts per hundred (per cent) basis, we divide 30,000 by 10,000 (1,000,000/100) which is 3%. To find the % dry matter (i.e. 'solids') we subtract the % moisture from 100:

$$\%\ \text{dry matter} = 100 - 20 = 80 \qquad \text{Eq. [13]}$$

The total amount of layer manure (**lm**) to apply is given by:

$$\frac{140\ \text{kg N}}{\text{ha}} \times \frac{\text{kg lm}}{0.03\ \text{kg N}} \times \frac{1}{0.60} \times \frac{1}{0.80} \qquad \text{Eq. [14]}$$

Canceling units in Eq.[14] and doing the math we obtain:

$$\frac{140}{(0.03 \times 0.60 \times 0.80)} = \frac{9722\ \text{kg lm}}{\text{ha}} \checkmark$$

Or, 9.7 metric tons layer manure per hectare (4.3 tons/acre).

This is amount of layer manure *estimated* to satisfy the nitrogen demanded by the sweet corn crop. Actual efficiency may differ depending on timing, weather, management practices, tillage intensity, method of placement, and application uniformity. Note that, in Eq. [14] we express per cent values for total nitrogen and dry matter as their decimal (1/100) fractions. The PAN coefficients are normally expressed as decimal fractions and used directly.

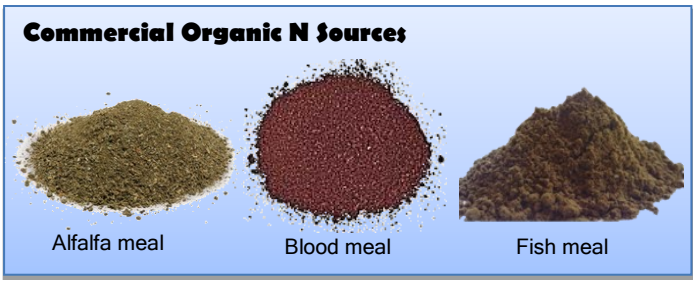
[5] Greater efficiency can be achieved with separate PAN coefficients for organic N and for inorganic N. This involves the added expense of testing for inorganic N (NH_4^+ and NO_3^-), which is sometimes required if waste application is close to environmentally sensitive areas. See NCDA&CS Waste and Compost Analysis Guide for details.

There are also commercial organic fertilizers supplying nitrogen. Such products are generally derived from protein-rich plant and animal parts and may contain essential nutrients other than nitrogen. Because the chemical composition of plant or animal parts remains fairly constant, fertilizers derived from them have a relatively consistent nutrient value.

Plant Products *Alfalfa meal* (4% N), *cottonseed meal* (6% N), *corn gluten* (9% N), and *soybean meal* (7% N) are examples of plant products commonly used as nitrogen sources for organic production. These protein-rich feed products are processed to a finely-divided state to facilitate digestion of the nutrients and minerals by livestock. When applied to soil, they must be mineralized by microbes before the nitrogen is made available to plants.

Alfalfa meal is derived from the alfalfa plant, a high-protein, nitrogen-fixing legume commonly grown for hay. If plant grinding facilities are available, a wide variety of legumes such as white, red, crimson, and alsike, can be used for the same purpose as alfalfa meal. Grinding the plant to a fine powder accelerates mineralization of the nitrogen, but otherwise the plant meal has the same fertilizer nitrogen value as the whole plant from which it is derived.

Nitrogen derived from legume plants is sometimes called 'free' nitrogen. This is not true. There are costs associated with buying legume seed and for the energy needed to plant, fertilize, (P and K), lime, harvest and process the plants. Up to 25% of legume carbohydrate is needed to sustain the legume-bacteria symbiosis. In addition, bacteria inoculants often are needed to jump-start the nitrogen fixation process. This may not deter home gardeners from legume fertilizer like alfalfa meal, but they are generally uneconomical on a commercial scale. Legumes are more efficient when deployed as a multi-purpose ***cover crop*** supplying nitrogen, improving infiltration, reducing erosion and NO_3^- -N leaching. In addition, their decomposed bodies contribute organic matter and nutrients to subsequent crops.



Animal Products These are by-products of animal carcass processing or derived from natural deposits, including:

- *Blood meal*, dried, powdered organic manure derived from slaughterhouse waste, containing about 12% nitrogen. The conventional method of preparing blood meal by drying has been superseded by reacting with chemicals like alum, aluminum sulfate, lime, etc. to increase recovery and reduce the time involved. Blood meal is completely soluble and rapidly mineralizes to available-N. As with other soluble fertilizers, care must be taken when placing blood meal near seeds or young seedlings due to the potential for injury.
- *Fish meal and fish emulsion,* dried, crushed, or powdered fishery by-product consisting mainly of processed scrap from the filleting operation or from whole parts of non-edible fish like menhaden and dogfish. The waste is pressed to separate solid and liquid fractions. Solid fish meal, containing 10-14% nitrogen, is used for fertilizer and animal feed. Oil is removed from the liquid fraction and, after addition of a thickening agent, the liquid is converted to fish emulsion (2-5% N). Fishmeal is generally applied at transplanting time whereas fish emulsion is often used for foliar-feeding of seedlings or young transplants. Both products are suitable for use on all crops and on all soils. In general fish meal and fish emulsion are quick-acting. Under conditions favoring mineralization, more than one -half the fishmeal-N may become plant available within two weeks after application (Mikkelsen and Hartz, 2008). Fertilizer-grade fishmeal should not contain more than 6% oil and 4% salt.
- *Feather meal,* a poultry by-product containing 70-90% protein in the form of non-soluble keratin. The resistant keratin is partially hydrolyzed by treatment with pressurized steam and animal enzymes, and furnishes, when ground, a dry fertilizer meal with 14-16% nitrogen. Much of the nitrogen in feather meal is initially unavailable but under warm conditions the amount mineralized from feather meal is comparable to fish meal and blood meal (Mikkelsen and Hartz, 2008). For this reason it is often soil-incorporated to speed the mineralization process. Feather meal is suitable for use by all crops and on all soils.
- *Guano,* a natural by-product of roosting colonies of sea birds and/or cave-dwelling bats, containing 8-12% nitrogen. In arid environments the excreta and remains of these animals forms large deposits which have been mined as a source of fertilizer for many years before the invention of synthetic nitrogen fertilizers. The largest known guano deposits are off the coast of Chile and Peru, where collection and marketing of guano still occurs. Guano has a high concentration of ammonia and nitrate salts, mainly as potassium and sodium, along with uric, phosphoric, oxalic, and carbonic acids. Guano can be applied directly to soil or used as a liquid fertilizer. The salts of ammonium and nitrate in guano are soluble and behave the same way in soil as their manufactured analogues. Usage of the term guano is not restricted to birds or bats excreta; in general it may include that of fish, whale, or other animals.

12.11 Nitrogen Efficiency

In nature, gains and losses of nitrogen in the ecosystem are roughly balanced, so that the quantity of nitrogen supplied by the soil depends on the rate of cycling between the living biomass and the organic and inorganic stores in the soil. Harvesting of the biomass will eventually exhaust the nitrogen stores. Consequently, biological productivity in the ecosystem will decrease. In agriculture, large amounts of biomass in the form of food, fiber, and animal products are removed annually from the land to feed, clothe, warm, and shelter a human population approaching 8 billion (as of 2020). Worldwide, the demand for protein, bioenergy, and

shelter is increasing rapidly, and nitrogen is the focal point in supplying that demand.

The cost of nitrogen exceeds all other essential plant nutrients and is a significant part of the farming budget. The amount of nitrogen fertilizer produced annually is approximately 130 billion kilograms (FAO, 2009). This is less than 50% of the nitrogen used in crop production (**Table 4**).

Table 4. Sources of nitrogen for crop production

Source of N	%
Biological N-fixation	16.3
Mineral fertilizers	45.7
Aerial fixation	8.1
Farm yard manure/biomass	13.6
Mineralization of soil organic matter	16.3
Total	100

source: IFDC/UNIDO Fertilizer Manual(1998)

The average efficiency of nitrogen in crop production hovers around 50%. In other words, on average, worldwide, for each pound of nitrogen supplied to a crop, only one-half of the nitrogen is utilized by the plant. The other half is lost, mainly through leaching, volatilization, denitrification, and erosion. This unpromising metric haunts a world in which population is predicted to reach 9+ billion by 2050. What are the prospects for increasing nitrogen use efficiency?

One prospect that beckons is biotechnology. Breeding crops that can use nitrogen (as well as other essential nutrients) under saline conditions or during periods of drought would boost fertilizer efficiency and usher another 'green revolution' in agriculture. Advances in remote sensing, combined with spatially-informed real-time kinematic (RTK) machine operating accuracy have made precision management of nitrogen possible over wide spatial extent. Aside from grand (and costly) technology breakthroughs, what can the average farmer do to boost nitrogen efficiency, today?

Farmers can increase nitrogen efficiency by adopting sound agronomic practices that limit the major mechanisms of nitrogen loss: leaching, volatilization, denitrification, and erosion. These practices include:

- *Fertilizer Rates.* Nitrogen fertilizer rates are determined by the crop grown, yield goal, and the amount of nitrogen that may be supplied by the soil. This information is usually determined by local testing and experience. The quantity of nitrogen supplied by the soil is determined by the quantity of nitrogen released from soil organic matter; organic residue from previous crops; nitrogen released from previous application of organic waste; and nitrogen carry-over from previous fertilizer applications. Such contributions are taken as credits (in kg N/ha or lb N/acre), so avoiding fertilizer nitrogen rates that exceed crop demand.

- *Soil Testing.* There is no test for soil nitrogen that has been adopted universally. Testing soil for nitrogen before planting has been used successfully as a substitute for taking credits in the drier regions in North America. In humid eastern North America, testing cornfields for NO_3^- -N after crop emergence (**Pre-Sidedress Nitrogen Test**, or PSNT) has, in some instances, been useful for predicting if additional nitrogen should be applied or not. Such tests are still under development and interpretation of the results is highly dependent on local testing and experience.

- *Fertilizer Placement.* Fertilizer should be placed where the plant can directly access the nutrients. Usually this is near the prime rooting zone. Applying fertilizer in shallow bands close to the plant row effectively accomplishes this. Broadcasting can also be effective if row spacing is close enough to eliminate gaps in the rooting zone. Incorporation via tillage, injection, or subsurface placement of ammoniacal-N fertilizer is effective in controlling losses due to volatilization.

- *Fertilizer Timing.* The timing of fertilizer application has a major effect on the efficiency of nitrogen use. Nitrogen applied near the time of peak demand reduces the potential for losses due to leaching or denitrification. On coarse sandy, well-drained soil where leaching is anticipated a split application, where most of the nitrogen is applied after crop emergence, can boost fertilizer efficiency. On medium to heavy-textured soils with limited leaching potential and good drainage, a single pre- or post-planting application may perform as well as split-application.

- *Soil Moisture.* Nutrient uptake depends on soil moisture content. Under dry soil conditions, placing nitrogen below the surface in a higher moisture zone can increase its availability because roots will be growing in this zone, and thus more likely to find it. Keeping the soil mulched with plant residue aids in conserving soil moisture and can increase nutrient efficiency.

- *Crop Rotation.* Alternating crops such as corn with a legume (alfalfa, soybean) takes advantage of the nitrogen credit and health benefit associated with the grass-legume rotation. **Table 5** shows the *average* amount of nitrogen fixed by legume crops; however, the actual amount may vary by two-fold depending on soil type, climate, fertility, and bacteria inoculant.

- *Fertilizer Additives.* Certain additives have proved to reduce nitrogen losses from volatilization and denitrification. Such additives, known as nitrogen stabilizers, work by suppressing nitrification of NH_4^+-N to NO_3^- -N, urease activity, or both. In principle, keeping soil nitrogen as NH_4^+ should increase nitrogen use efficiency by (i) reducing nitrogen loss due to leaching because the positively charged

Table 5. Average fixation of nitrogen by legume crops.

Crop	N fixed (kg/ha)
Alfalfa	217
Ladino clover	200
Sweet clover	133
Red clover	128
White clover	115
Cowpeas	101
Soybeans	112
Lespedeza	95
Vetch	90
Winter Peas	60
Garden Peas	81
Garden Beans	45
Peanuts	47

Source: adapted from Havlin, Tisdale and Nelson (1999).

ammonium ion is held by the negatively charged soil colloid particles (e.g. clay) and by organic matter; (ii) reduction in denitrification by preventing the formation of NO_3–N; and (iii) increase productivity by feeding the plant $NH4^+$-N that can be used directly for biosynthesis instead of using energy to reduce absorbed NO_3–N to $NH4^+$-N in the plant. Examples of nitrogen stabilizers include nitropyrin (*N-serve*), and NBPT (*Agrotain*). Nitropyrin, when added to NH_4^+-N fertilizer, delays its conversion to NO_3–N for several weeks by suppressing the bacteria responsible for the conversion of ammonium to nitrite in the nitrification process. The delay in nitrification reduces the loss of NO_3–N due to leaching and denitrification when wet conditions occur during the period of suppression. NBPT is a commercial urease inhibitor that can be impregnated onto granular urea or mixed with urea-ammonium nitrate (UAN) solutions. It prevents the conversion of urea to ammonium carbonate, reducing the potential for ammonia volatilization from urea and UAN solutions. It is most useful when urea or UAN are applied without incorporation to the surface of fields with high levels of crop residue, for example fields under no-tillage, or fields with high pH levels at the surface. The effect that nitrogen stabilizers have had on crop yield has not been consistent. (Walters and Malzer, 1990). In North Carolina, Cahill et al. (2010) tested several "enhanced efficiency" fertilizers and observed no consistent effect on corn or wheat grain yield compared to urea-ammonium nitrate. Despite these mixed results, there is great commercial interest in developing enhanced efficiency fertilizer (EEF) additives, particularly polymer coating technology.

- *Soil Compaction*. Known as the 'silent thief', compaction reduces nitrogen efficiency by increasing the volume of mineral solids at the expense of air, so increasing the potential for denitrification. It also increases runoff and erosion. Compacted soil reduces root growth which is essential for nutrient uptake (**Figure 12**). The best way to avoid compaction is by controlling field traffic (vehicle, machine, foot).

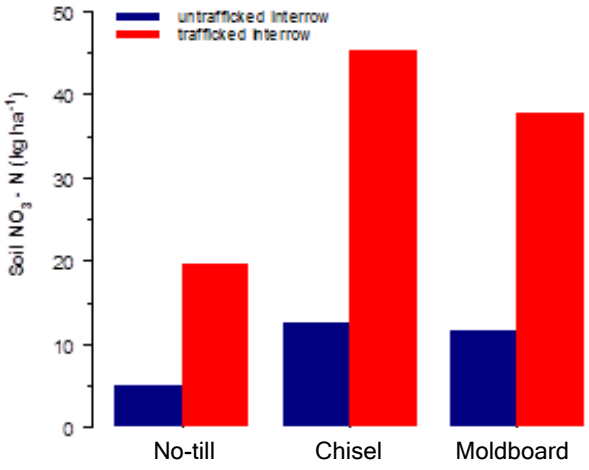


Figure 12. Effect of tillage and row position on soil NO_3–N concentration. Soil compaction from wheel traffic reduced NO_3– uptake under three tillage systems. *Source: R. Walters, and M.G. Wagger, North Carolina State University.*

- *Soil Drainage*. Adequate drainage is essential for nitrogen efficiency. Where drainage is naturally poor, it may be improved by subsurface tiling, ripping, bedding, and mole-plowing or a combination of these practices.

12.12 Core Intelligence

Conjugate acid (-base): The concept of a conjugate acid-base pair is central to the Brønsted-Lowry theory, where an acid is a molecule or ion able to lose or 'donate' a hydrogen cation (a proton, H^+), and a base is a molecule or ion able to gain or 'accept' a hydrogen cation. For a molecule to behave as an acid, donating a proton, a base must be present to accept the proton. The general equation for this is:

$$\text{acid} + \text{base} \rightleftarrows \text{conjugate acid} + \text{conjugate base}$$

For example, the protonation of ammonia, a base, yields ammonium ion, its conjugate acid:

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

In the above reaction water acts as an acid by donating a proton and ammonia is the base, or proton acceptor. The hydroxide ion (OH^-) is the conjugate base of water acting as an acid and the ammonium is the conjugate acid of the base, ammonia. The Brønsted-Lowry model is not the only framework for understanding acids and bases. The acid-base concept advanced by the Swedish chemist Arrhenius (1859-1927), stresses molecular dissociation, and the formation of hydroxyl (OH^-) and hydrogen (H^+) ions in an aqueous solution. The difference is that not all acid-base reactions form OH^- and H+ ions as required by Arrhenius; many acid-base reactions involve proton donor-acceptor relations described by Brønsted-Lowry.

Cover Crop: An annual or perennial crop planted to protect soil, absorb excess nutrients, add organic matter, protect another crop sown beneath it, or provide cover for game birds. A wide variety of plants including legumes and grasses are planted as cover crops in the fallow period between cash crops in a cropping cycle, or may be planted in the inter-row space in orchards and vineyards. Cover crops contribute nutrients to the following crop when they decay.

Denitrification: The conversion of nitrates (NO_3^-) and nitrites (NO_2^-) by soil bacteria under anaerobic conditions, followed by the release of gaseous nitrogen oxides (N_2O and NO) and nitrogen (N_2). Losses are greatest from water-logged, poorly aerated soils with large amounts of organic matter (e.g. crop residue). In most field soils, there is immense potential for denitrification. However, the soil must undergo a change in oxygen diffusion for microbes to shift from aerobic to anaerobic respiration; not all microbes can do this. The overall process of aerobic oxidation of carbohydrates can be generalized by a two-step reaction:

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^- \quad [1]$$

glucose water carbon dioxide protons electrons

$$24H^+ + 24e^- + 6O_2 = 12H_2O + energy \quad [2]$$

protons electrons oxygen water ATP

Step 1 in this reaction cannot happen on its own without linking to electron acceptors which are molecules than can be reduced. In aerobic respiration oxygen is the molecule that is reduced, shown in step 2.

Under anaerobic conditions some microbes use the oxygen in nitrate as the terminal electron acceptor:

$$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$$

nitrate protons electrons N-gas water

To summarize, organic matter is the carbohydrate source for microbial respiration. Under anaerobic conditions organic matter is the source of reducing equivalents (electrons) and the oxygen in nitrate is the acceptor. The end products are gaseous elemental dinitrogen (N_2) and water.

Field capacity: The amount of water remaining in the soil after free drainage. Water entering the soil from irrigation or natural precipitation initially moves downward due to the pull of gravity. The point at which drainage ceases (or becomes very small) is determined by soil particle shape and the packing density of the particles. Water remaining in the soil after free drainage is held by capillary forces (adhesion and the surface tension of water molecules), and represents the soil water content at 'field capacity'. In a sandy loam soil the capillary suction at field capacity is ~ -10 kPa, but clay soils may have higher (i.e. more negative) suctions. Field capacity is mainly used to infer some other soil physical condition like workability or available water capacity as related to water content. For most agricultural soils field capacity is reached within 24-48 h after wetting provided the soil is deep enough.

Fixation: It has two meanings in agronomics. When prefaced by the word 'nitrogen', fixation describes the action of microbes that convert the chemically inert nitrogen of the soil air into forms that are useful to plants. When referring to plant nutrients, fixation describes the process whereby available nutrients are made unavailable by reaction with soil components. Generally, nutrient fixation refers to reactions of phosphorus, potassium, and ammonium leading to decreasing availability.

Hydrolysis: A reaction between a compound and water in which the compound is split into two parts by the action of the water molecule. An example of hydrolysis is the catalysis of urea by the enzyme urease.

Hygroscopicity: The tendency of a substance to attract water by absorption or adsorption. The adsorbing or absorbing material becomes physically changed by an increase in volume, stickiness, or other physical characteristic of the material. Many fertilizer salts are hygroscopic, in varying degree. The main factors affecting hygroscopicity of fertilizer salts is the vapor pressure of moisture (humidity) and temperature.

Immobilization: The conversion of nutrients to forms that are unavailable or less available to plants. In immobilization, the soluble nutrient element is converted from an inorganic to organic form in the biomass of microbes or in plant tissue. Large amounts of N, P, K, and S thus get tied up, temporarily or for long periods. Immobilization is the reverse process of mineralization, where nutrients are converted from organic to soluble inorganic forms.

Ion(s): Atoms or groups of atoms that are electrically charged as a result of the loss of electrons (cations) or the gain of electrons (anions).

Leach(ing): In agronomics, to cause a soluble nutrient or chemical in the soil to move away from the root zone by the action of percolating liquid, e.g. rainwater. Leaching occurs when the amount of rainfall or irrigation water entering the soil becomes greater than its water-holding capacity.

Legume: Strictly, plants of the family Leguminosae (Fabacae) characterized botanically by a fruit called a *legume* or *pod* that opens along two sutures when ripe. In agronomics, *legume* refers to soybean, vetch, clover, peas, alfalfa, among others. Trees such as *Acacia* and locust are also legumes. Legumes in symbiotic relationship with *Rhizobium* bacteria fix atmospheric nitrogen in the nodules on the plant's roots, a characteristic that sets them apart from other plants.

Mineralization: The conversion of complex, unavailable organic nitrogen substances (e.g. proteins) to soluble, plant available inorganic forms such as NH_4^+. The conversion is brought about by the activities of certain soil microbes. The rate of mineralization increases with a rise in temperature, soil moisture, and oxygen supply. Water-logged conditions slow the rate of mineralization.

Nitrification: The conversion of ammonium (NH_4^+) and nitrites (NO_2^-) to nitrates (NO_3^-) brought about by soil microbes. Nitrification is a two-step biological process in which ammonium is first converted to nitrite by aerobic bacteria of the genera *Nitrosomonas, Nitrosospira*, *Nitrosococcus*, and *Nitrosolobus*. The nitrite is then converted to nitrate by bacteria of the genera *Nitrobactor*, *Nitrospina*, and *Nitrococcus*. Nitrification is a process that is constantly happening in the soil under warm, moist, and near neutral pH conditions. Not all of the nitrifying bacteria are soil-dwelling; some are found only in marine or freshwater environments. Soil temperature below about 10°C (50°F) slows the activity of nitrifying bacteria enough to reduce the risk of nitrate losses due to leaching; below about 3°C (37°F) the process halts entirely.

Nitrification inhibitor: Any substance that inhibits the biological oxidation of ammoniacal-N to nitrate-N. In agronomics, nitrification inhibitors may be added to fertilizers to selectively inhibit the activity of *Nitrosomonas* bacteria, decreasing the potential for nitrate-N loss via leaching and denitrification during wet periods and enhancing fertilizer-N recovery by the principle crop. There are several non-phytotoxic chemicals known to inhibit nitrification, including nitripyrin or *N-Serve*, AM (2-amino-4-chloro-6-methyl pyridine), DCD (dicyandiamide), thiourea, ATC ("nine–1,2,4 –triazole), potassium azide, and neem (*Azadirachta indica)* seed extract.

Oxidation: A chemical reaction in which the oxidation number (state) of a molecule, ion, or atom is increased (*cf.* **reduction**).

pKa: In chemistry, the acid dissociation constant on a logarithmic scale ('p-scale' as in pH). In acid-base reactions pKa is the quantitative measure of the tendency of an acid to dissociate in solution. The equilibrium can be generalized as:

$$HA \rightleftarrows A^- + H^+$$

Where HA is the generic acid that splits (dissociates) into A^-, known the conjugate base of the acid, and H^+ which in aqueous (water) solutions exists as the hydronium ion, H_3O. In the equation above HA represents any generic acid such as *citric acid* and A^- is the conjugate base known as *citrate*.

Pre-sidedress Nitrate Test (PSNT): A test developed to measure the soil's ability to supply nitrogen, expressed as an availability index. PSNT involves sampling the soil to 30 cm (12 inches) depth before side-dressing and analyzing for NO_3^- –N which, in certain regions, provides a more reliable index of available nitrogen. Its principle use is in deciding the amount of nitrogen fertilizer to be side-dressed. A major drawback of the PSNT is the (often) short time to complete the tasks of sampling, analyses, evaluation and decision making.

Reduction (pp. *reduced*): A chemical reaction in which the oxidation number (state) of a molecule, ion, or atom is reduced, typically (but not always) coupled with the gain of electrons. Oxidation is the opposite of reduction: loss of electrons, increasing the oxidation number. The following table shows the different oxidation states of nitrogen:

Oxidation State		
Formula	Chemical name	Oxidation number
NH_3	ammonia	-3
NH_4^+	ammonium	-3
N_2	diatomic N	0
N_2O	nitrous oxide	2
NO_2^-	nitrite	3
NO_3^-	nitrate	5

From this table we observe that mineralization ($NH_4^+ \rightarrow NO_3^-$) involves the oxidation of nitrogen whereas the opposite reaction, denitrification, is a reduction reaction. The fixation of atmospheric nitrogen by *Rhizobium* bacteria ($N_2 \rightarrow NH_4^+$) is also a reduction reaction because the oxidation number of nitrogen changes from 0 to -3.

Slitting (also knifing): Process where fertilizer is injected directly into the soil with a slender iron tool or tillage shank.

Urease: An enzyme, present in all soils, that catalyzes the hydrolysis of urea into ammonium carbamate [$(NH_4)_2CO_3$]. Ammonium carbonate easily converts to ammonium hydroxide which further breaks down to ammonia. When urea hydrolysis occurs at or near the soil surface, ammonia is lost via volatilization. If ammonia volatilizes at or near the seeds, they may not germinate or, if it is near the roots of plant seedlings, may prove to be toxic. Urease is a product of many different bacteria, fungi, and actinomycetes in the soil. It also occurs on living and dead plant tissue.

Urease inhibitor: An additive to urea fertilizer that slows the rate at which urea hydrolyzes in soil by selectively controlling the activity of the enzyme urease. In agronomics, the purpose of such an additive is to delay the hydrolysis of urea until surface-applied granular urea or urea-containing solutions have had time to leach into the soil. Thus, there will be less potential for nitrogen to be lost via ammonia volatilization. Several compounds are known to be urease inhibitors but at present NBPT (sold under the trade name Agrotain) is the only commercially viable product.

Volatilization: The conversion of nitrogen in organic or inorganic form, to gaseous forms such as ammonia (NH_3), nitrous oxide (N_2O), and dinitrogen (N_2). The nitrogen losses occur when (a) plant material is burned, (b) ammonia escapes from soil, fertilizer, or plants; and (c) microbes reduce nitrates to gaseous forms in the process of denitrification. In soil, conversion of ammonium to ammonia and denitrification are the principle mechanisms of volatile N losses. Ammonia volatilization is different from gaseous loss of applied anhydrous ammonia, which is not retained in the soil. Fire, whatever the cause, converts the nutrients in plant biomass to carbonates, oxides, and phosphates in the ash. Much of the nitrogen is converted to gaseous nitrous oxide (N_2O) that escapes to the atmosphere where it reacts with

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