4

Nitrogen

Nitrogen (N) is the most frequently deficient nutrient in nonlegume plants, while quantities of N_2 fixed by legumes can be sufficient for their growth. Because most soils cannot supply sufficient amounts of plant available N, inorganic and/or organic N sources must be applied to meet plant N requirements (Fig. 4-1). Globally, agricultural N use has substantially increased over the last 50 years, contributing to our ability to feed a growing planet (Chapter 1). However, global N use has also increased N loading in the environment (Chapter 12). Understanding the biology and chemistry of N in the soil-plant-atmosphere continuum is essential for maximizing plant growth and productivity, while reducing the impacts of N inputs on the environment.

THE N CYCLE

The ultimate source of all N used by plants is N_2, which constitutes 78% of the earth's atmosphere. Unfortunately, higher plants cannot metabolize N_2 directly into protein. N_2 must first be converted to plant available N by:

- microorganisms that live symbiotically on legume roots,
- free-living or nonsymbiotic soil microorganisms,
- atmospheric electrical discharges forming N oxides, or
- the manufacture of synthetic N fertilizers.

The large reservoir of atmospheric N_2 is in equilibrium with all fixed forms of N in soil, seawater, and living and nonliving organisms (Table 4-1). Cycling of N in the soil-plant-atmosphere system involves many transformations between inorganic and organic forms (Fig. 4-2). The N cycle can be divided into N inputs or gains, N outputs or losses, and N cycling within the soil, where N is neither gained nor lost (Table 4-2). Except for industrial fixation and combustion, all of these N transformations occur naturally; however, humans influence many of these N processes. This chapter describes the chemical and microbial cycling of N and how humans influence or manage these transformations to optimize N availability to plants.

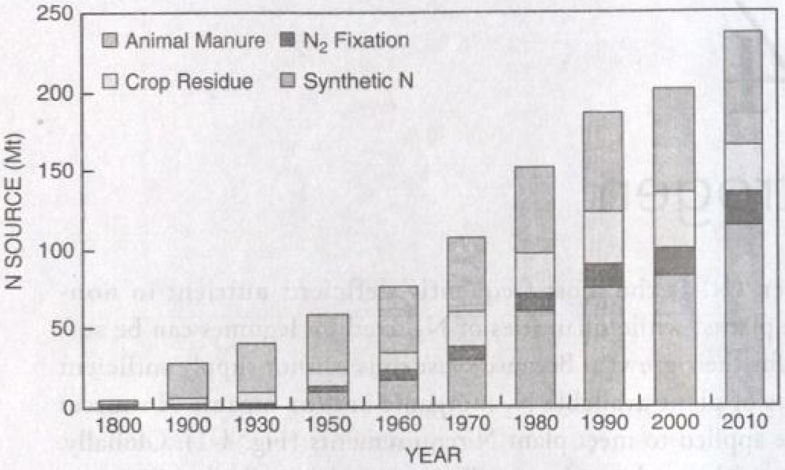


Figure 4-1
Global agricultural N sources from 1800 to 2010. Synthetic N use is increasing relative to other N sources.
(Adapted from Mosier, 2001, *Plant and Soil*, 228:17–27.)

Table 4-1
Approximate Distribution of N Throughout the Soil-Plant/Animal-Atmosphere System[1]

N Source	Metric Tons	% of Total
Atmosphere	3.9×10^{15}	99.3840
Sea	2.4×10^{13}	0.6116
Soil	4.5×10^{11}	0.0038
Plants	1.5×10^{10}	0.00038
Microbes in soil	6×10^{9}	0.00015
Animals (land)	2×10^{8}	0.000005
People	1×10^{7}	0.00000025

[1] Not included in the above is ~180 × 10^{15} t of N contained in rocks and other materials unavailable to soil-plant-atmosphere system.

FUNCTIONS AND FORMS OF N IN PLANTS

Forms

Plants contain 1–6% N by weight and absorb N as both nitrate (NO_3^-) and ammonium (NH_4^+) (Fig. 4-2). In moist, warm, well-aerated soils, soil solution NO_3^- is generally greater than NH_4^+. Both move to plant roots by mass flow and diffusion.

The rate of NO_3^- uptake is usually high, causing an increase in rhizosphere pH. When plants absorb high levels of NO_3^-, there is an increase in anion (HCO_3^-, OH^-, organic anions) transport out of cells. Plants metabolize NO_3^- to NH_4^+ to amino acids and to proteins. NO_3^- reduction to NH_4^+ is an energy requiring process that uses two nitrate reductase (NADH) molecules for each NO_3^- reduced in protein synthesis. Thus, NH_4^+ is the preferred N source since energy is conserved compared to NO_3^- (one less step in the reduction process). Plants supplied with NH_4^+ may have increased carbohydrate and protein levels compared with NO_3^-.

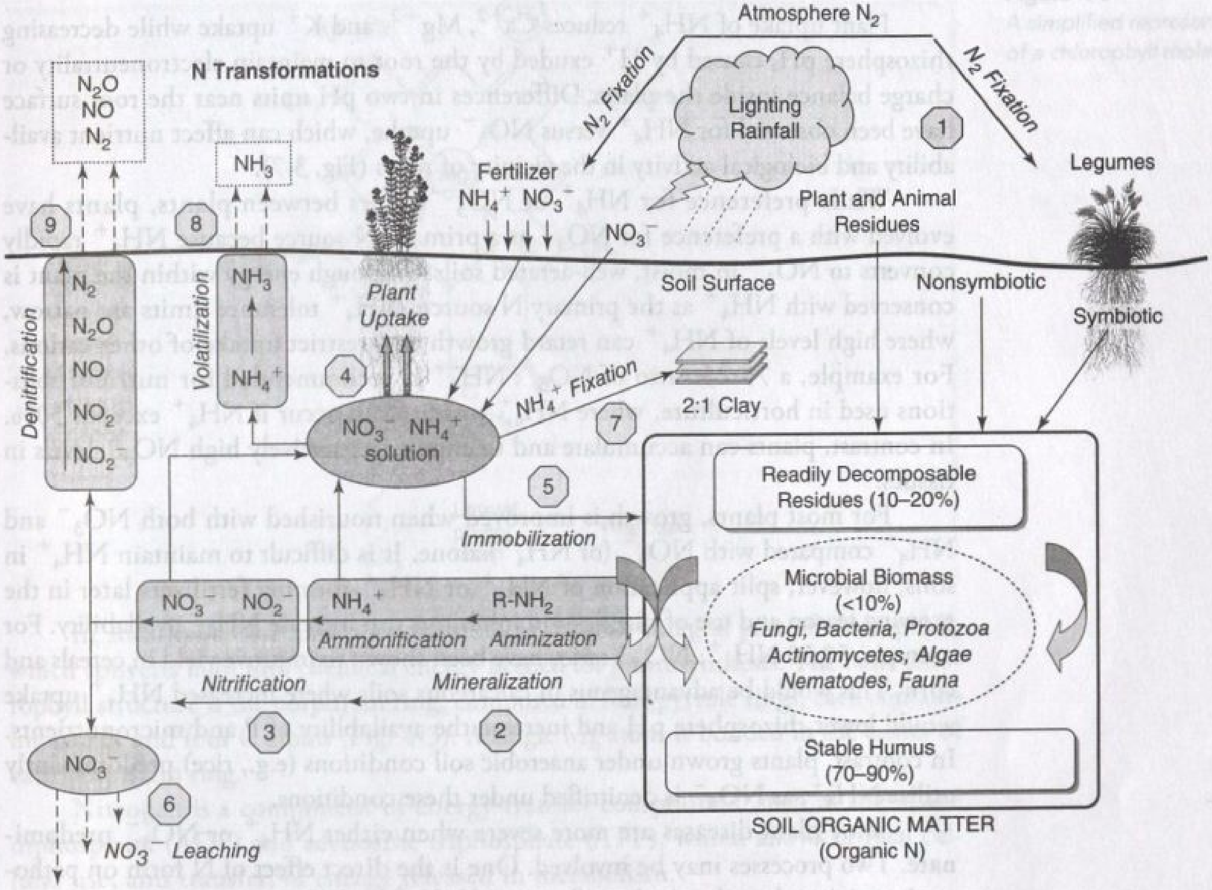


Figure 4-2
The N cycle. Most of the **N transformations** *(italics) are facilitated by the microbial biomass and cycle through the organic fraction in soil. In step 1, N in plant and animal residues and N derived from the atmosphere through electrical discharges, legumes, and industrial processes (N_2 is combined with H_2 or O_2) are added to the soil. In step 2, organic N is* **mineralized** *to NH_4^+ by soil organisms. Much of the NH_4^+ is converted to NO_3^- by bacteria through* **nitrification** *(step 3). In step 4, NO_3^- and NH_4^+ in soil solution are taken up by plant roots. In step 5, some solution NH_4^+ and NO_3^- are converted back to organic N through* **immobilization**. *Solution NO_3^- can be lost by* **leaching** *to groundwater or drainage systems as a result of downward movement below the root zone in percolating water (step 6). In step 7, NH_4^+* **fixation** *by 2:1 clay minerals can occur. In step 8, NH_4^+ can be* **volatilized** *to gaseous NH_3. NO_3^- derived from nitrification, fertilization, or rainfall can be converted by denitrifying bacteria to N_2, N_2O, NO that escape into the atmosphere* (**denitrification**; *step 9), completing the cycle.*

TABLE 4-2

N INPUTS, OUTPUTS, AND CYCLING IN THE SOIL-PLANT-ATMOSPHERE SYSTEM[1]

N Inputs (Gains)	N Outputs (Losses)	No Net N Gain or Loss (Cycling)
Fixation	Plant uptake	Mineralization
Biological (bacteria)	Denitrification	Immobilization
Industrial (Haber-Bosch)	Volatilization	Nitrification
Electrical (lightning)	Leaching	
Combustion (fossil fuel)	NH_4^+ fixation[2]	
Animal manure		
Crop residue		

[1] Some N inputs, outputs, and cycling components can be influenced by management but generally are not managed.

[2] Some fixed NH_4^+ can be released (input).

Plant uptake of NH_4^+ reduces Ca^{+2}, Mg^{+2}, and K^+ uptake while decreasing rhizosphere pH, caused by H^+ exuded by the root to maintain electroneutrality or charge balance inside the plant. Differences in two pH units near the root surface have been observed for NH_4^+ versus NO_3^- uptake, which can affect nutrient availability and biological activity in the vicinity of roots (Fig. 3-7).

While preference for NH_4^+ or NO_3^- differs between plants, plants have evolved with a preference for NO_3^- as a primary N source because NH_4^+ rapidly converts to NO_3^- in moist, well-aerated soils. Although energy within the plant is conserved with NH_4^+ as the primary N source, NH_4^+ tolerance limits are narrow, where high levels of NH_4^+ can retard growth and restrict uptake of other cations. For example, a 75:25 ratio of $NO_3^-:NH_4^+$ is recommended for nutrient solutions used in horticulture, where NH_4^+ toxicity can occur if NH_4^+ exceeds 50%. In contrast, plants can accumulate and tolerate comparatively high NO_3^- levels in tissues.

For most plants, growth is improved when nourished with both NO_3^- and NH_4^+ compared with NO_3^- (or NH_4^+) alone. It is difficult to maintain NH_4^+ in soils; however, split application of NH_4^+ or NH_4^+-forming fertilizers later in the growing season and use of nitrification inhibitors can increase NH_4^+ availability. For example, 50:50 $NH_4^+:NO_3^-$ ratios have been shown to improve yield in cereals and corn. This would be advantageous in calcareous soils where increased NH_4^+ uptake would lower rhizosphere pH and increase the availability of P and micronutrients. In contrast, plants grown under anaerobic soil conditions (e.g., rice) predominantly utilize NH_4^+, as NO_3^- is denitrified under these conditions.

Some plant diseases are more severe when either NH_4^+ or NO_3^- predominate. Two processes may be involved. One is the direct effect of N form on pathogenic activity; the other is the influence of NH_4^+ or NO_3^- on organisms affecting the availability of micronutrient cations. For example, high NO_3^- supply stimulates certain bacteria, which lowers Mn availability in wheat. The effect of N form on rhizosphere soil pH is partially responsible for differences observed in disease incidence and severity.

Functions

Before NO_3^- can be used in the plant, it must be reduced to NH_4^+. Nitrate reduction involves two enzyme-catalyzed reactions that occur in roots and/or leaves, depending on the plant species. Both reactions occur in series so that toxic nitrite (NO_2^-) does not accumulate.

	Reduction Reaction	**Enzyme**	**Reaction Site**
Step 1	$NO_3^- \rightarrow NO_2^-$	Nitrate reductase	Cytoplasm
Step 2	$NO_2^- \rightarrow NH_3$	Nitrate reductase	Chloroplast

The NH_3 produced is assimilated into amino acids that are subsequently combined into proteins and nucleic acids. Proteins provide the framework for chloroplasts, mitochondria, and other structures in which most biochemical reactions occur. The type of protein formed is controlled by a specific genetic code in nucleic acids, which determines the quantity and arrangement of amino acids in each protein. The nucleic acid, deoxyribonucleic acid (DNA), present in the nucleus and mitochondria of the cell (Fig. 2-22), duplicates genetic information in the chromosomes of the parent cell to the daughter cell. Ribonucleic acid (RNA), present in the nucleus and cytoplasm of the cell, executes the instructions coded within DNA molecules. Most enzymes controlling these metabolic processes are also proteins and are continually metabolized and resynthesized.

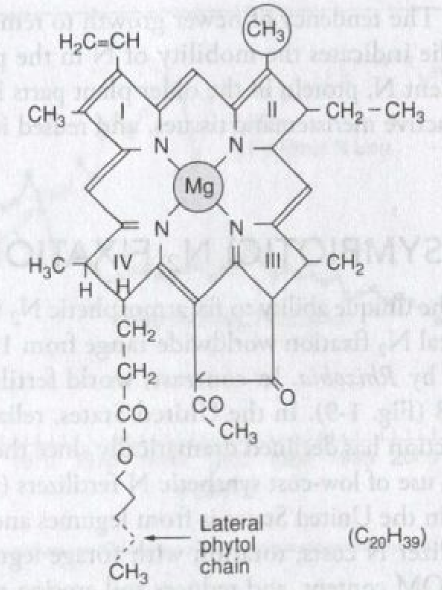


Figure 4-3
A simplified representation of a chlorophyll molecule.

In addition to the formation of proteins, N is an integral part of chlorophyll, which converts light into chemical energy needed for photosynthesis. The basic chlorophyll structure is the porphyrin ring, composed of four pyrrole rings, each containing one N and four C atoms (Fig. 4-3). A single Mg atom is bonded in the center of each porphyrin ring.

Nitrogen is a component of energy-transfer compounds, such as adenosine diphosphate (ADP) and adenosine triphosphate (ATP), which allows critical cellular use, and transfer, of energy released in metabolism.

An adequate supply of N is associated with high photosynthetic activity, vigorous vegetative growth, and a dark green color. An excess of N in relation to other nutrients, such as P, K, and S, can delay crop maturity. In many plants grown in humid environments, excess N stimulates vegetative growth and increases the incidence of foliar diseases. In semi-arid and arid climates, stimulation of heavy vegetative growth early in the season can reduce soil moisture during the reproductive growth stage, where plants are most sensitive to water stress.

The supply of N influences carbohydrate utilization. Under low N, carbohydrates will be deposited in vegetative cells, causing them to thicken. When N supplies are adequate and conditions are favorable for growth, proteins are formed from the manufactured carbohydrates. With less carbohydrate deposited in the vegetative portion, more protoplasm is formed, and because protoplasm is highly hydrated, a more succulent plant results. Excessive succulence in cotton weakens the fiber, and with grain crops, lodging may occur, particularly with a low K supply or with varieties not adapted to high levels of N. In some cases, excessive succulence enhances susceptibility to diseases or insects. Crops such as wheat and rice have been modified for growth at higher densities and at higher levels of N fertilization. Shorter plant height and improved lodging resistance have been bred into plants, which respond in yield to much higher N rates.

Visual Deficiency Symptoms

When plants are N deficient, leaves or leaf veins appear yellow. The loss of protein N from chloroplasts in older leaves produces the yellowing, or chlorosis, indicative of N deficiency. Chlorosis usually appears first on the lower leaves, the upper leaves remaining green; under severe N deficiency, lower leaves turn brown and die. This necrosis begins at the leaf tip and progresses along the midrib until the entire leaf is dead (see color plates). The tendency of newer growth to remain green as the lower leaves turn yellow or die indicates the mobility of N in the plant. When roots are unable to absorb sufficient N, protein in the older plant parts is converted to soluble N, translocated to the active meristematic tissues, and reused in the synthesis of new protein.

BIOLOGICAL (SYMBIOTIC) N_2 FIXATION

Many organisms have the unique ability to fix atmospheric N_2 (Table 4-3). Estimates of total annual biological N_2 fixation worldwide range from 130 to 180 × 10^6 Mt, with about 50% fixed by *Rhizobia*. In contrast, world fertilizer N use was about 100 × 10^6 Mt in 2008 (Fig. 1-9). In the United States, reliance on biological N_2 fixation for crop production has declined dramatically since the 1950s because of increased production and use of low-cost synthetic N fertilizers (Fig. 4-4). About 20% of N supplied to crops in the United States is from legumes and crop residues (Table 4-4). Under high fertilizer N costs, rotation with forage legumes is generally cost effective, increases soil OM content, and reduces soil erosion potential. Inclusion of grain legumes in the rotation will also reduce fertilizer N costs; however, soil erosion potential may increase.

In addition to forage and grain legumes, N_2 fixation by leguminous trees is important to the ecology of forests and agroforestry systems. Numerous leguminous tree species fix appreciable amounts of N_2. In the United States, mimosa, acacia, and black locust are common. Three woody leguminous species—*Gliricidia sepium*, *Leucaena leucocephala*, and *Sesbania bispinosa*—are used as green manure crops in rice-based cropping systems.

Some widely distributed non-leguminous plants also fix N_2 by a mechanism similar to legume and rhizobial symbiosis. *Frankia*, an actinomycete, is responsible for N_2 fixation by several non-leguminous woody plants including Betulaceae, Elaeagnaceae, Myricaceae, Coriariaceae, Rhamnaceae, and Casuarinaceae (Table 4-3). For example, alder and ceanothus, two species commonly found in the Douglas fir forest region of the Pacific Northwest, contribute substantial N to the ecosystem.

TABLE 4-3

ECONOMICALLY IMPORTANT MICROORGANISMS INVOLVED IN BIOLOGICAL N_2 FIXATION

Organisms	General Properties	Agricultural Importance
Azotobacter	Aerobic; free fixers; live in soil, water, rhizosphere, leaf surfaces	Minor benefit to agriculture; found in vascular tissue of sugarcane, with sucrose as an energy source for N_2 fixation
Azospirillum	Microaerobic; free fixers; or found in association with roots of grasses	Inoculation benefits some non-legume crops, shown to increase root hair development
Rhizobium	Fix N_2 in legume-Rhizobium symbiosis	Legume crops are benefited by inoculation with proper strains
Actinomycetes	Fix N_2 in symbiosis with non-legume wood trees—alder, Myrica, Casuarina	Potentially important in reforestation, wood production
Cyanobacteria (Anabaena)	Contains chlorophyll, mostly aquatic, some terrestrial	Enhance rice in paddy soils; Azolla (a water fern) symbiosis; used as green manure

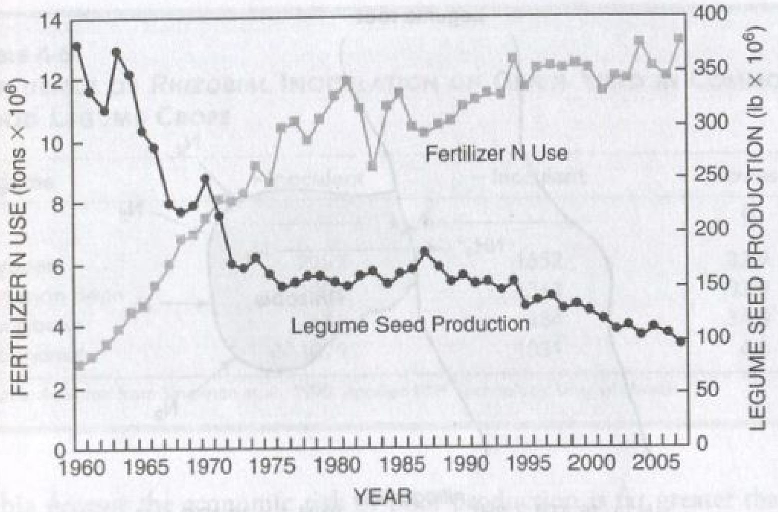


Figure 4-4
Inverse relationship between N fertilizer use and legume seed production in the United States. Part of the decrease in U.S. production is offset by increased production in Canada.

TABLE 4-4
ESTIMATED PERCENTAGE OF TOTAL N ADDED TO U.S. CROPLAND BY VARIOUS SOURCES

N Source	Total (million tons)	% of Total
Commercial N	13.2	57
Legumes, crop residues	5.6	24
Animal manures	3.4	15
Other sources	0.9	4

Source: USDA-ERS, 2008; Howarth et al., 2002, *Ambio*, 31:89–96.

N_2 Fixation by Legumes

When legume root growth begins, N_2-fixing bacteria in soil invade root hairs and multiply. Legume roots respond by forming tumor-like structures called *nodules* on the root surface (Fig. 4-5). The specialized bacteria called rhizobia inside the nodule absorb N_2 from soil air and convert it to NH_4^+ (Fig. 4-6). Rhizobia use

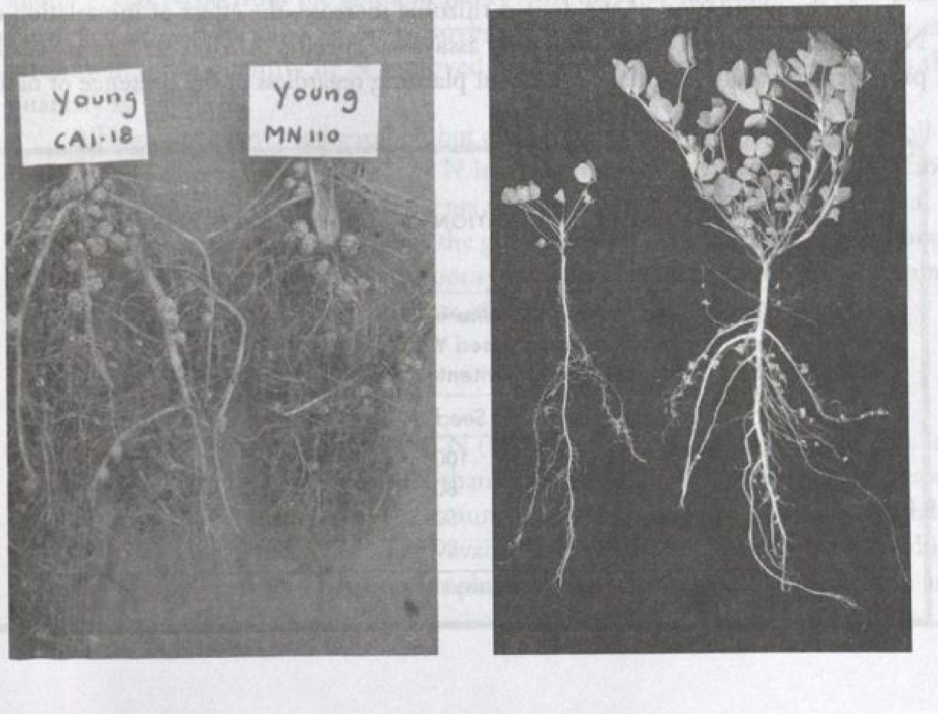
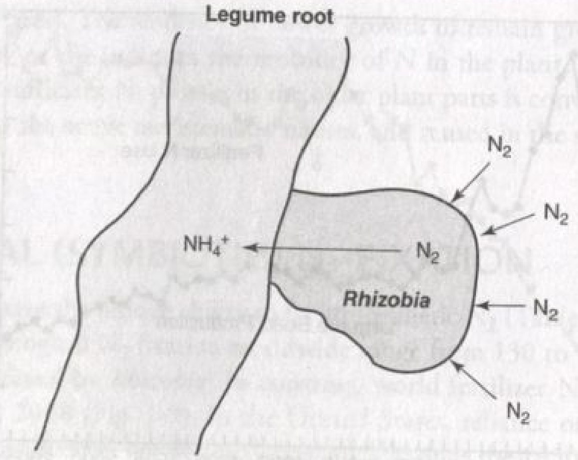


Figure 4-5
Example of nodules on soybean (left) showing differences in nodulation between varieties, and alfalfa (right) showing non-inoculated (left) and inoculated (right) with proper rhizobia bacteria.
(Courtesy D. Israel (soybean) and J. Burns, D. Chamblee, and J. Green (alfalfa), NC State University.)



$$N_2 + 16\ ATP + 2H^+ \xrightarrow{nitrogenase} 2NH_4^+ + 16\ ADP + H_2$$

Figure 4-6
Conversion of N_2 to NH_4^+ by rhizobia inside a legume root nodule.

the enzyme nitrogenase and energy from the transformation of ATP to ADP to break the strong triple bond (N≡N) in N_2. The *symbiotic* relationship between legume host plant and nodule bacteria is mutually beneficial. Plants provide energy (sugars, carbohydrates, ATP) for rhizobia to fix N_2, and rhizobia in turn provide NH_4^+ for production of proteins by the host plant. Most of the fixed N_2 is utilized by the host plant, although some may be excreted from the nodule into the soil and used by other nearby plants, or released as nodules decompose after the plant dies.

Numerous rhizobium species exist in soil, each requiring a specific host legume plant. For example, symbiotic bacteria specific to soybean will not fix N_2 with alfalfa. Inoculation of the legume seed with the correct inoculum is recommended the first time a field is planted to a new legume species. Carefully matching cultivars with inoculum strains will increase N_2 fixation, which increases plant yield and protein content (Table 4-5). A wide range in yield increases to inoculation has been observed (10–90%), but commonly are 15–25% with 5–20% increases in protein content. Typical legume response to inoculation is shown in Table 4-6.

As the population of the desired rhizobia increase, the effect of inoculation on N_2 fixation decreases. Since laboratory assays for specific rhizobia strains are costly, producers generally inoculate legumes at planting regardless of the presence of native

TABLE 4-5
INFLUENCE OF *RHIZOBIAL* INOCULATION ON LEGUME SEED YIELD AND N CONTENT

Legume Species	No. of Trials Where Inoculation Increased Yield or Seed N Content-		Average Seed N (%)	
	Yield	*Seed N*	*Inoculated*	*Uninoculated*
Soybean	83	100	6.2	5.7
Lima bean	60	80	3.2	3.0
Common bean	33	50	3.0	2.8
Cowpea	0	80	4.2	3.9

Source: J. Thies, Ph.D. Dissertation, University of Hawaii, 1990.

TABLE 4-6
INFLUENCE OF *RHIZOBIAL* INOCULATION ON GRAIN YIELD IN COMMON FOOD LEGUME CROPS

Legume	+ Inoculant	− Inoculant	Increase
	kg/ha		%
Soybean	2195	1652	32.9
Common Bean	1825	1363	33.9
Mungbean	651	484	34.5
Groundnut	1079	1031	4.6

Source: Adapted from Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.

rhizobia *because* the economic risk of poor production is far greater than the cost of the inoculum. Sufficient native rhizobia occur when legume crops are frequently grown in the same fields or with previous legume inoculations. Inoculation assures the producer an adequate population of rhizobia for the crop.

The presence of nodules on legume roots does not necessarily indicate N_2 fixation by active rhizobia. Mature effective alfalfa nodules tend to be elongated (2–4 by 4–8 mm), clustered on the primary roots, and have pink to red centers. The red color is due to leghemoglobin, which indicates that rhizobia are actively fixing N_2. Ineffective nodules are small (<2 mm in diameter), usually numerous, and scattered over the entire root system. In some cases, they are very large (>8 mm in diameter), few in number, and have white or pale-green centers.

Quantity of N_2 Fixed Generally, nodule bacteria fix 25–90% of the total legume N (Table 4-7). Under optimum conditions, N_2 fixation by most perennial forage legumes exceeds short-season annual legumes. Most of the N_2 fixed is found in the above-ground plant material (Table 4-8). These data also illustrate that N_2 fixation represented 63% of total N uptake, increasing through the season as the contribution from soil N decreased.

The amount of N_2 fixed by rhizobia varies with yield level, effectiveness of inoculation, amount of soil N, and environmental conditions. Soybeans remove about 1.5 lb N/bu from the soil and fix 40% or more of the total N in the plant. However, on sandy, low-OM soils, soybeans may fix 80% or more. In many environments, the quantity of N removed by soybean grain at harvest exceeds the quantity of N_2 fixed.

All legumes recover some soil N, but grain legumes generally remove more soil N than forage legumes since most of the N is transferred to the seed and removed from the field at harvest. Forage legumes generally increase soil N, reducing additional N needed for subsequent crops, because the growth period is usually longer with forage legumes, developing more extensive root systems than grain legumes. Forage legume roots and nodules contain high amounts of N that ultimately increase soil N.

Factors Affecting N_2 Fixation

Soil Nutrient Supply

As with any plant, legumes prefer soil N (NO_3^- and NH_4^+) because it requires less energy for the plant to take up soil N than to fix N_2. As soil N availability decreases, N_2 fixation generally increases. Maximum N_2 fixation occurs only when available soil N is at a minimum. Excess NO_3^- availability reduces nitrogenase activity, which reduces N_2 fixation by competition for photosynthate between NO_3^- reduction and N_2-fixation reactions.

TABLE 4-7
RANGE IN QUANTITY OF N_2 FIXED BY SELECTED LEGUMES

Legume	N fixed (lb/a/yr) *Range*	*Typical*
Alfalfa	50–300	200
Beans	20–80	40
Birdsfoot Trefoil	50–100	70
Black gram	80–140	100
Chickpeas	20–100	50
Clovers (general)	50–300	150
Cluster beans	30–200	60
Common Bean	10–120	40
Cowpeas	60–120	90
Crimson clover	30–180	80
Faba beans	50–240	130
Field peas	50–180	100
Green gram	30–60	40
Groundnut	70–120	90
Hairy vetch	50–200	140
Kudzu	20–150	110
Ladino clover	80–200	150
Lentils	40–130	60
Leucaena	350–480	450
Lespedezas (annual)	30–120	85
Lucerne	180–250	220
Lupin	60–100	80
Mung bean	170–225	200
Peanuts	20–200	60
Pigeon Pea	140–220	200
Red clover	70–160	115
Soybean	20–260	100
Sweet clover	20–80	20
White clover	30–150	100
Winter peas	10–80	50

TABLE 4-8
N BUDGET FOR FIRST-YEAR ALFALFA

N Budget Component	Harvest *1st*	 *2nd*	 *3rd*	 Total
		lbs/a		
Forage yield	3,128	2,727	1,032	6,887
Total plant N	105	113	53	271
N from N_2 fixation[1]	51 (49%)	91 (81%)	30 (57%)	172 (63%)
Leaves/stems	46	66	20	132
Roots/crown	4	25	11	40
N from soil	54	22	22	99
Leaves/stems	48	16	14	79
Roots/crown	6	6	8	21

[1] Percent of total plant N.

Source: Heichel and Barnes, 1981, *Crop Sci.*, 21:330–35.

Even under adequate soil N supply, inoculation of the legume seed is still important for optimum yields (Fig. 4-7). Sometimes a small amount of N fertilizer at planting provides young legume seedlings adequate N until rhizobia become established on the roots. Early spring N application can also benefit legume crops where rhizobial activity is restricted by cold, wet conditions. With some legumes, N_2 fixation is low and usually unreliable (e.g., common bean), so N fertilization is recommended.

In acid soils, Ca^{+2} and $H_2PO_4^-$ deficiencies can limit rhizobial growth and reduce host plant productivity (Fig. 4-8). N_2 fixation requires more Mo than the host plant because Mo is a component of nitrogenase; thus, Mo deficiency is the most important micronutrient deficiency affecting N_2 fixation. Initiation and development of nodules can also be affected by B, Fe, and Cu deficiencies. Differences exist in the sensitivity of various rhizobial strains to nutrient stress.

Soil pH

Soil acidity can restrict the survival and growth of rhizobia in soil and severely affect nodulation and N_2-fixation process. Generally at pH < 5.5, rhizobial infection, root growth, and legume productivity can be severely reduced. Significant differences in sensitivity of rhizobia to soil acidity exist. For example, soil pH < 6 drastically reduces *Rhizobium meliloti* population, degree of nodulation, and alfalfa yield, whereas soil pH 5.0–7.0 has little effect on *Rhizobium trifoli* associated with red clover. Liming acid soils increases alfalfa growth dependent on *Rhizobium meliloti.* For locations where lime may not be readily available, high levels of inoculum and coating inoculated seeds with lime can improve inoculation. Another approach is to select and use acid-tolerant rhizobia (Fig. 4-9).

Environment

A high rate of photosynthate production is strongly related to increased N_2 fixation by rhizobia. Factors that reduce the rate of photosynthesis will reduce N_2 fixation, including reduced light intensity, moisture stress, and low temperature.

Legume Management

In general, any management practice that reduces legume stands or yield will reduce the quantity of N_2 fixed by legumes. These factors include water and nutrient stress, excessive weed and insect pressure, and improper harvest management. Harvest

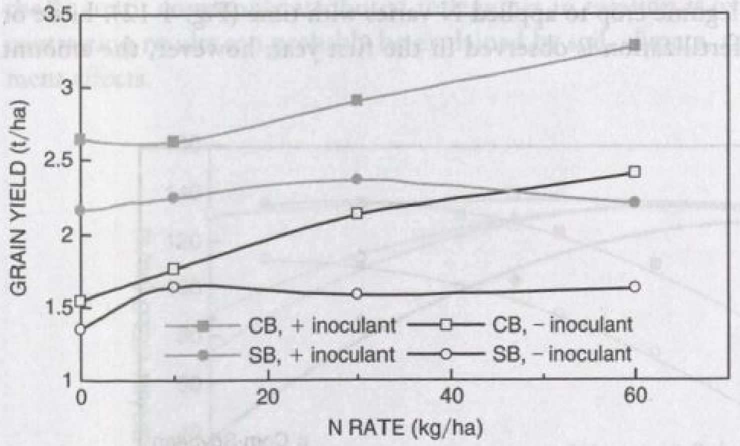


Figure 4-7
Influence of inoculation and N rate on soybean (SB) and common bean (CB) yield.
(Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.)

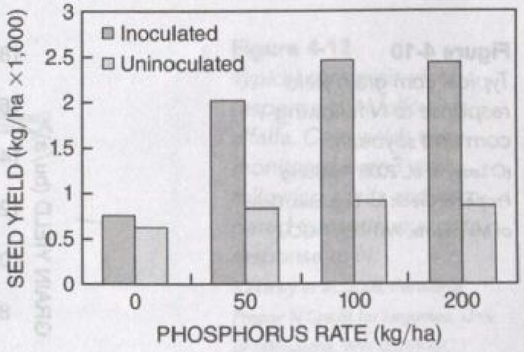


Figure 4-8
Soybean yield as influenced by P availability and inoculation.
(Singleton et al., 1990, Applied BNF Technology, Univ. of Hawaii.)

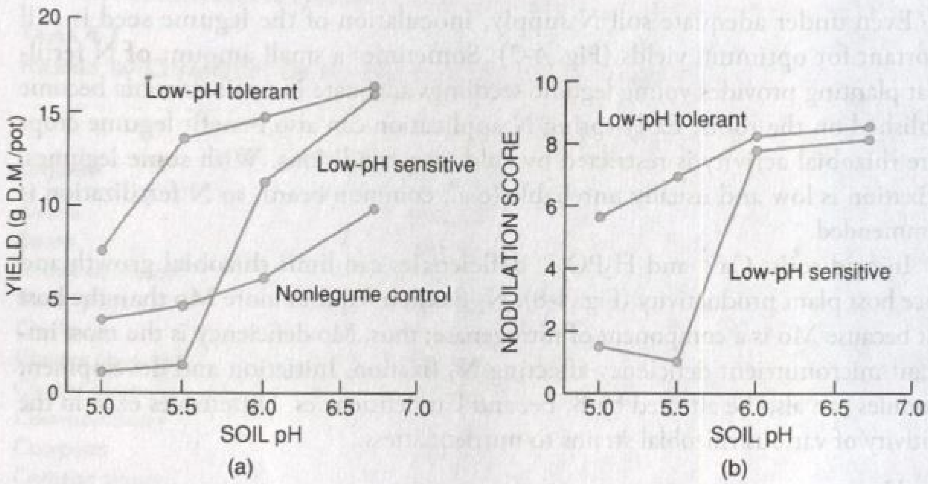


Figure 4-9
Forage yields (a) and nodulation scores (b) of alfalfa inoculated with low-pH-tolerant and low-pH-sensitive strains of Rhizobium meliloti. Barley was the non-legume control.
(Rice, 1989, Can. J. Plant Sci., 62:943.)

practices vary greatly with location, but excessive cutting frequency, premature harvest, and delayed harvest, especially in the fall, can reduce legume stands and the quantity of N_2 fixed.

Legume N Availability to Non-Legume Crops Yields of non-legume crops are often increased when grown following legumes. For example, when corn follows soybean, the N required for optimum yield is less than that required for corn after corn (Fig. 4-10). Similarly, less N is needed to maximize wheat grain yield following lupins (Fig. 4-11). Reduced N rates with the non-legume crop following a legume, compared to continuous non-legume rotations, are due to:

- decomposition of legume residue providing plant available N
- greater N immobilization in continuous non-legume rotations
- enhanced soil microbial activity resulting in increased N mineralization in legume rotations

For example, recent studies showed that soil organic N at planting decreased ≈10% by corn harvest but increased ≈10% from soybean planting to harvest (Table 4-9). Rotation benefits can also be related to reduced soilborne diseases and improved soil physical properties (Chapter 12).

When a perennial legume such as alfalfa is used in rotation, the response of the following non-legume crop to applied N varies with time (Fig. 4-12). Little or no response to N fertilization is observed in the first year; however, the amount

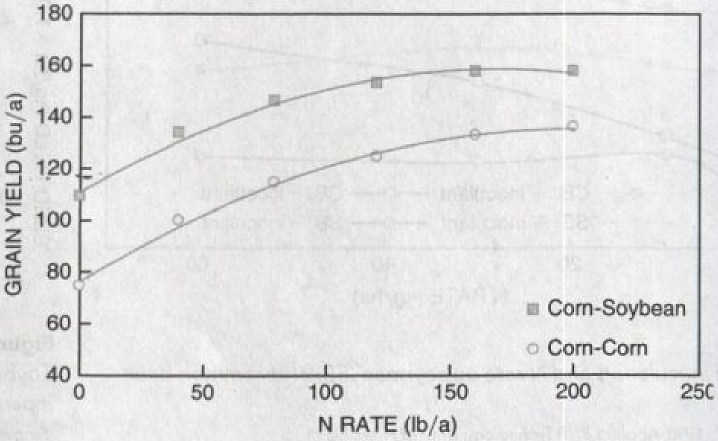


Figure 4-10
Typical corn grain yield response to N following corn and soybean.
(O'Leary et al., 2008, Providing Proper N Credit for Legumes, Univ. of Minnesota, WW-03769-GO.)

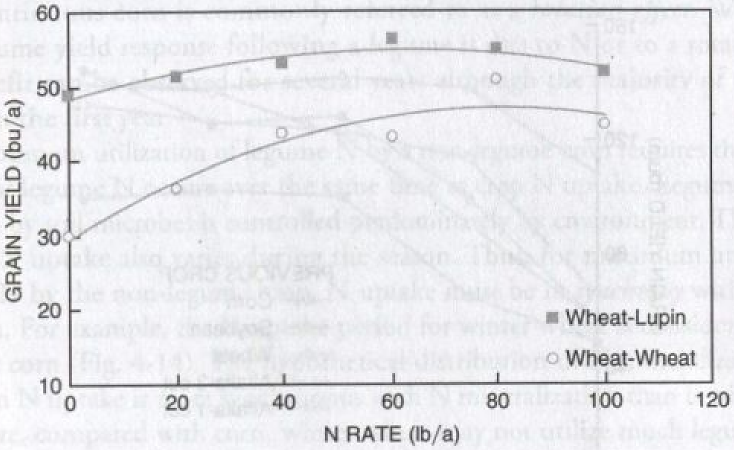


Figure 4-11 *Typical wheat grain yield response to N following wheat and lupin.*
(Doyle et al., 1988, *Aust. J. Agric. Res., 39:1029–1037.*)

TABLE 4-9
CHANGE IN SOIL ORGANIC N BETWEEN PLANTING AND HARVEST OF CORN AND SOYBEAN GROWTH (0–6-IN. DEPTH)

	Organic N			
Crop	*Planting*	*Harvest*	Change	
	kg/ha			%
Corn	3661	3294	−367	−11
Soybean	3304	3623	+319	+12

Note: Values are averaged over 10 locations.
Source: Martens et al., 2006, *Soil Sci. Soc. Am. J.*, 70:382–392.

of N required for optimum crop production increases with time as the legume N reserves are depleted. N availability in the legume cropping system depends on the quantity of N_2 fixed, the amount and type of legume residue returned, and soil and environmental conditions influencing residue decomposition and N mineralization. Legume N incorporated into the soil from first year alfalfa varies between 35 and 300 kg/ha. Vigorous, high N_2 fixing, alfalfa stands can usually supply all or most of the N to a non-legume crop in the first year. Several studies suggest that the N credit commonly attributed to legumes in rotation is overestimated. These contrasting results can probably be explained by soil, climate, and legume management effects.

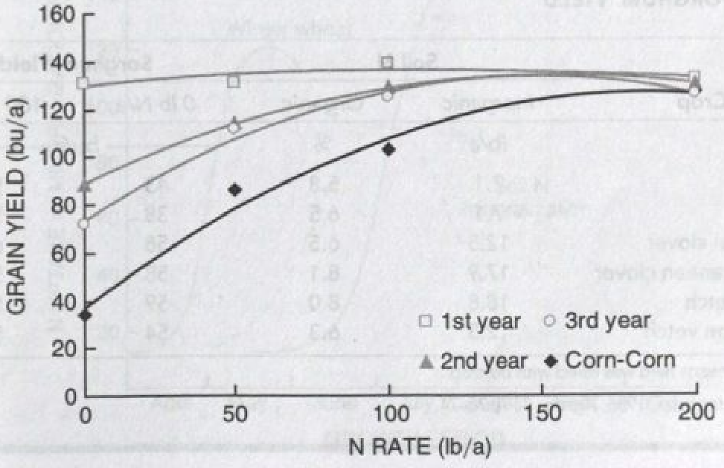


Figure 4-12 *Typical corn grain yield response to N following alfalfa. Corn yields were monitored over 3 years following alfalfa and compared to continuous corn response to N.*
(O'Leary et al., 2008, *Providing Proper N Credit for Legumes*, Univ. of Minnesota, WW-03769-GO.)

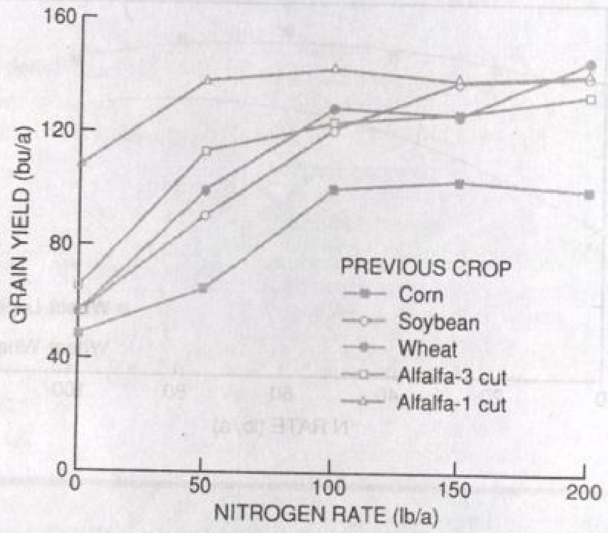


Figure 4-13
Corn grain yields as influenced by previous crop and fertilizer N.
(Heichel, 1987, *Role of Legumes in Conservation Tillage Systems*, Soil Cons. Soc. Am., p. 33.)

Forage legumes are used for green manure and animal feed, where all or part of the legume biomass is incorporated into the soil. Since the majority of legume N is in above-ground plant material, the quantity of N returned can be substantial. With forage legumes grown for animal feed, a smaller part of the N_2 fixed is returned to the soil because most of the forage is harvested. For example, legume N availability can be greater in a one-cut system compared with a three-cut system because of the increased amount of N incorporated with less-frequent harvests (Fig. 4-13). Forage legumes generally return more N than grain legumes, because most of the fixed N is in the grain compared to residue N left on the field.

Forage legumes are also used as winter cover crops to protect surface soil from erosion. Depending on the legume and amount of growth (N_2 fixation), winter cover crops will provide some of the N needed by the subsequent non-legume crop (Table 4-10). As a non-legume, using rye as a cover crop will provide protection from erosion, but has little influence on N availability.

The yield benefit of rotations with some legumes may not always be related to the legume N supply. Figure 4-13 illustrates that corn yield response to fertilizer N was similar following soybean or wheat. The rotation response compared

TABLE 4-10
INFLUENCE OF LEGUME AS A WINTER COVER CROP ON SOIL N AND SORGHUM YIELD

	Soil N		Sorghum Yield	
Cover Crop	*Inorganic*	*Organic*	*0 lb N/a*	*100 lb N/a*
	lb/a	%	*bu/a*	
Fallow[1]	7.1	5.8	43	58
Rye	7.1	6.5	38	58
Crimson clover	12.5	6.5	58	63
Subterranean clover	17.9	8.1	58	57
Hairy vetch	18.8	8.0	59	56
Common vetch	12.5	6.3	54	59

[1] Fallow means field was idled with no crop.

Source: Hargrove, 1986, *Agron. J.*, 78:70–74.

with continuous corn is commonly referred to as a *rotation effect.* Whether the non-legume yield response following a legume is due to N or to a rotation effect, the benefit can be observed for several years although the majority of the benefit occurs in the first year.

Optimum utilization of legume N by a non-legume crop requires that mineralization of legume N occurs over the same time as crop N uptake. Legume N mineralization by soil microbes is controlled predominately by environment. The quantity of crop N uptake also varies during the season. Thus, for maximum utilization of legume N by the non-legume crop, N uptake must be in *synchrony* with N mineralization. For example, the N uptake period for winter wheat is considerably earlier than for corn (Fig. 4-14). The hypothetical distribution of N mineralization shows that corn N uptake is more synchronous with N mineralization than is winter wheat. Therefore, compared with corn, winter wheat may not utilize much legume N and, when mineralization occurs, the inorganic N is subject to leaching and other losses. Therefore, efficient management of legume N requires careful crop selection.

Legumes grown with forage grasses generally supply N for both crops, where 50–70% of the grass N originates from the legume. Legume N availability to a companion crop is not well understood. Small amounts of amino acids and other organic N compounds may be excreted by the legume roots. Microbial decomposition of the sloughed off root and nodule tissue may also contribute N to the crop growing with legumes. Under some conditions, the quantity of fixed N_2 and/or legume N availability is not sufficient, and N fertilization is required for optimum production of both non-legume and legume crops.

Fertilizer N Value of Legumes Direct measures of the quantity of N fixed by legumes in rotation are difficult; however, the legume value in rotation with non-legume crops can be estimated in fertilizer N units. Crop yield response to N must be determined for the non-legume crop grown in rotation with a legume and grown continuously (Fig. 4-15). In this example, N response was measured with corn grown in rotation with soybean compared to continuous corn. The fertilizer N value of the previous soybean crop is the N rate needed in continuous corn to produce the same yield in rotation with soybean without N fertilizer. Notice in this example corn yields are higher in rotation with soybean than in continuous corn even at high N rates. The additional yield is due to rotation effects other than the N value from the soybean.

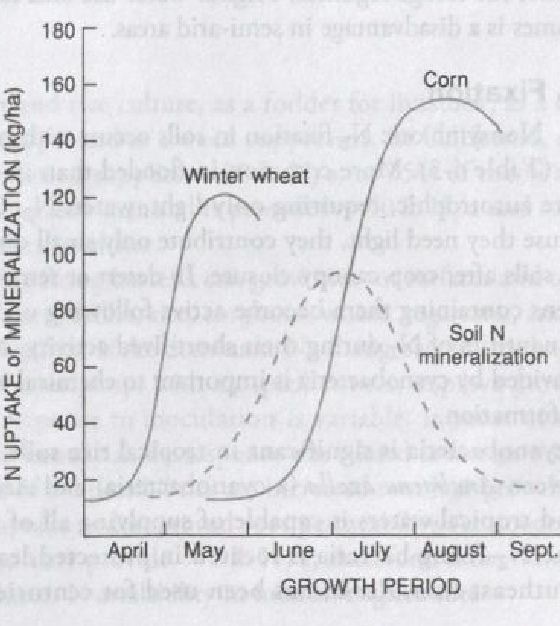


Figure 4-14
Synchrony of soil N mineralization and crop N uptake in corn and winter wheat.

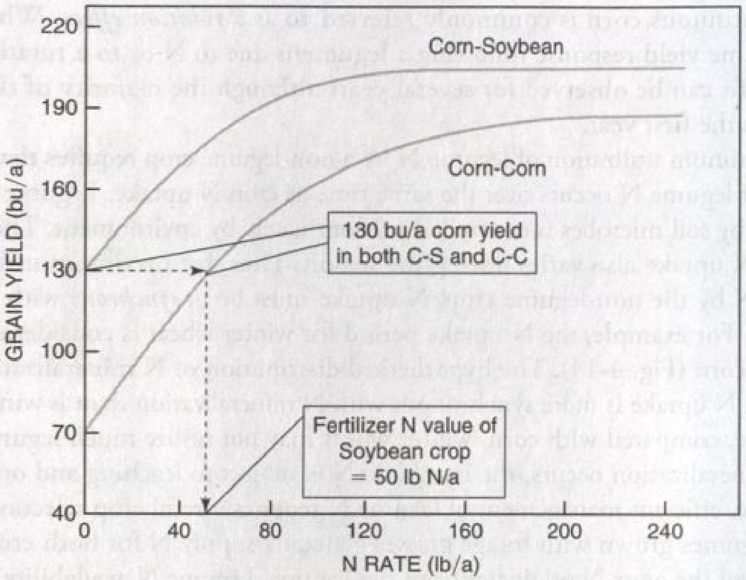


Figure 4-15
Estimating the fertilizer N value of soybean in rotation with corn. With no fertilizer N, corn yield is 130 bu/a in the corn-soybean rotation; however, 50 lb N/a are needed in continuous corn to produce the same yield (130 bu corn/a).

Legume Rotations The primary reason for including legumes in a rotation is to supply N, but with development and availability of relatively inexpensive fertilizer N, most agricultural production does not involve legume N (Fig. 4-4). In a livestock farming system, the main purpose of legumes is to supply large amounts of high-quality forage (hay or pasture). Legumes are generally of superior quality, with higher protein and mineral concentrations compared with N-fertilized grasses.

Management decisions regarding the use of legumes or fertilizer N are based on the highest net return on investment. Fertilizer N costs have increased in recent years because of greater global demand and higher fossil fuel costs. As a consequence, interest in legumes to substitute partially for the fertilizer N requirements of non-legume crops has increased. In some developing countries, commercial N may not be available or is too expensive. Therefore, cropping systems that include legumes are essential to supply some or all of the N needed for non-legumes.

In spite of the advantages of legume rotations, it may not always be economical and thus varies greatly between regions (Table 4-11). For example, producers may not have a use or market for forage legumes. Higher water use and lower drought tolerance in some legumes is a disadvantage in semi-arid areas.

Nonsymbiotic N_2 Fixation

Soil Microorganisms Nonsymbiotic N_2 fixation in soils occurs with certain strains of free-living bacteria (Table 4-3). More common in flooded than in well-drained soils, cyanobacteria are autotrophic, requiring only light, water, N_2, CO_2, and essential nutrients. Because they need light, they contribute only small quantities of N in upland agricultural soils after crop canopy closure. In desert or semi-arid regions, cyanobacteria or lichens containing them become active following occasional rains and fix considerable quantities of N_2 during their short-lived activity. N availability to other organisms provided by cyanobacteria is important to chemical weathering in the early stages of soil formation.

N_2 fixation by cyanobacteria is significant in tropical rice soils. The symbiotic relationship between *Anabaena azolla* (a cyanobacteria) and *Azolla* (a water fern) in temperate and tropical waters is capable of supplying all of the N needs of the host plant. The N_2-fixing bacteria is located in protected leaf cavities of the water fern. In southeast Asia, *Azolla* has been used for centuries as a green

TABLE 4-11
EXAMPLES OF REGIONAL USE OF LEGUMES IN THE UNITED STATES

Region	Legume Species	Cropping or Tillage System
Southeast	Crimson clover, hairy vetch	Winter cover crop—no-till corn
	Bigflower vetch, crown vetch, alfalfa, lupine, arrowleaf clover, red clover	Winter cover crops preceding grain sorghum and cotton
Northeast	Alfalfa, birdsfoot trefoil, red clover	Legumes grown for hay or silage in rotations that include conventional or no-till corn as feed grain or silage; also used as living mulches
North Central	Soybean, pea	Grown in rotation with nonlegume, possibly in conservation tillage; peas may precede soybean in double-crop system
	Alfalfa, red clover, white clover, alsike clover	Grown for 2+ years in 3-5 year rotations with small grains or corn, possibly in conservation tillage
	Birdsfoot trefoil, crown vetch, sweet clover	Used for forage, silage, or pasture
Great Plains	Native legumes	Rangeland for grazing
Pacific Northwest	Dry pea, lentil, chickpea Austrian winter pea	Rotation or double cropped with grains, green manure or alternated with winter wheat
	Alfalfa	Grown in rotation with winter wheat, spring barley, and winter peas
	Fava bean	Grown in rotation for silage
California	Dry bean, lima bean, blackeye pea, chickpea	Grown for grains in various rotations
	Alfalfa	Grown for seed on irrigated land and for erosion control and forage on steeply sloping soils
	Subterranean clover	Rangeland for grazing

Source: Heichal, 1987, Role of Legumes in Conservation Tillage Systems, Soil Cons. Soc. Am.

manure in wetland rice culture, as a fodder for livestock, as a compost for production of other crops, and as a weed suppressor. In California, the *Azolla-Anabaena* N_2-fixing association supplies ≈ 90 lb N/a, or 75% of the N requirements of rice. When used as a green manure, it provides ≈ 50 lb N/a and substantially increases yields over unfertilized rice.

Certain N_2-fixing bacteria can grow on root surfaces and to some extent within root tissues of corn, millet, rice, sorghum, wheat, sugarcane, and many other grasses. *Azospirillum brasilense* is the dominant N_2-fixing bacterium that has been identified. Inoculation of cereal crops with azospirillum can improve growth and N nutrition, although the response to inoculation is variable. In most of the studies in which inoculation was beneficial, the response was related to factors other than increased N_2 fixation. Some of the possibilities are increased root hair growth that enhances water and nutrient uptake and improved root permeability. Azotobacter- and clostridium-inoculated seed may provide ≈ 5 lb N/a; therefore, these nonsymbiotic organisms are of little value to N availability in intensive agriculture.

Atmospheric N N compounds in the atmosphere are deposited with rain and snow as NH_4^+, NO_3^-, NO_2^-, and organic N. Because of the small amount of NO_2^- present in the atmosphere, NO_3^- and NO_2^- are combined and reported as NO_3^-. About 10–20% of the NO_3^- is formed during atmospheric electrical discharges, with the remainder from industrial waste gases or denitrification from soil. NH_4^+ comes largely from industrial sites where NH_3 is used or manufactured. Soil has a high capacity for adsorbing NH_3 gas from the atmosphere. NH_3 also escapes (volatilization) from the soil surface (Fig. 4-2). Finely divided organic residues swept into the atmosphere from the earth's surface are deposited in rainfall.

Total N deposition as $NH_4^+ + NO_3^-$ in rainfall is usually <8 lb N/a/yr, depending on the location, where ≈75% is NO_3^- (Fig. 4-16). Total N deposition is higher around areas of intense industrial and agricultural activity and is greater in tropical than in polar or temperate zones. Localized NH_4^+ deposition can depress soil pH (Fig. 4-17). NH_3 emissions from confined poultry facilities are greater than with other confined animal production systems.

Greenhouse Gases

Nitrous oxide (N_2O) is emitted to the atmosphere from numerous sources and is ≈300 times more effective than CO_2 in trapping heat in the atmosphere; however, N_2O contributes only a few percent to overall greenhouse warming. Although N_2O is unreactive and long-lived in the lower atmosphere (troposphere), it slowly rises into the stratosphere reacting with ozone (O_3). Decreasing upper atmospheric O_3 increases ultraviolet radiation reaching the earth's surface. Global atmospheric N_2O has increased ≈18% since 1750 and is ≈4% higher than in 1990. In the United States, agricultural soil management and fertilizer use contributes 67% of atmospheric N_2O with fossil fuel combustion contributing 15% (Chapter 12).

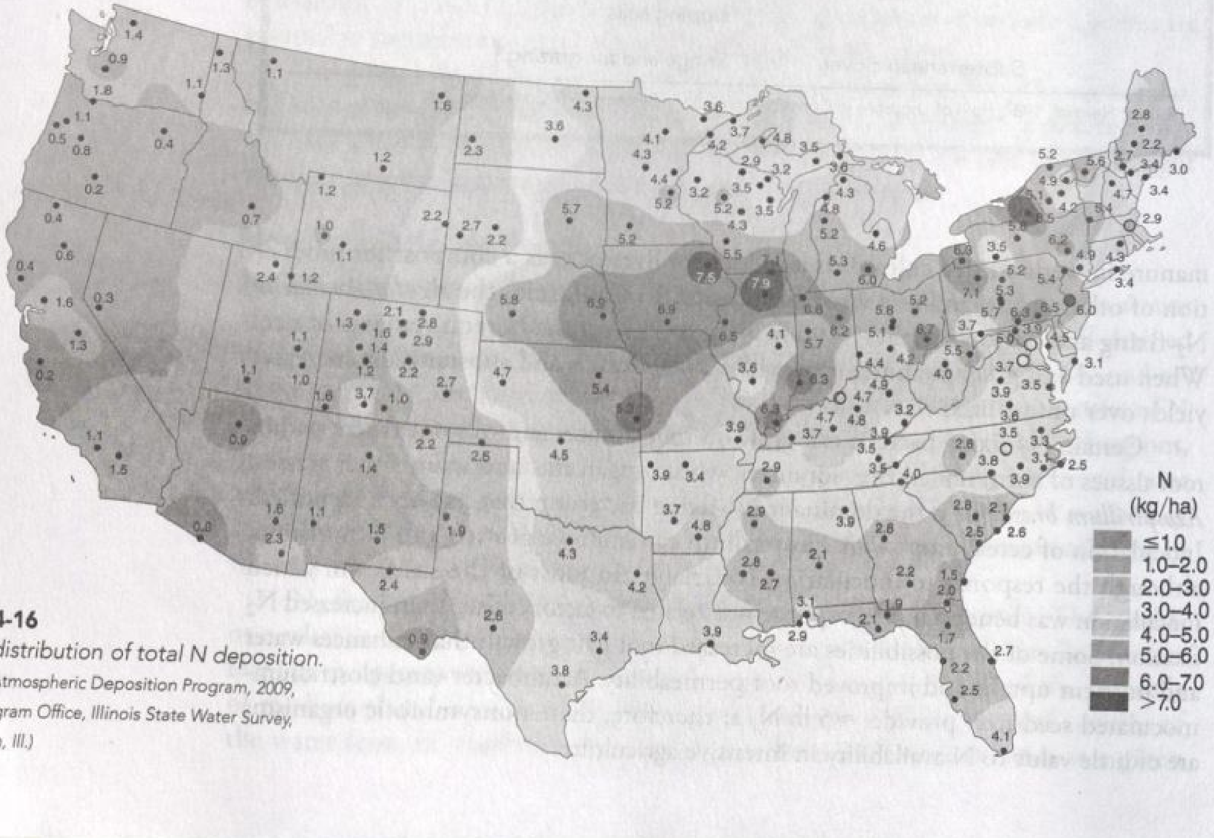


Figure 4-16
Spatial distribution of total N deposition.
(National Atmospheric Deposition Program, 2009, NADP Program Office, Illinois State Water Survey, Champaign, Ill.)

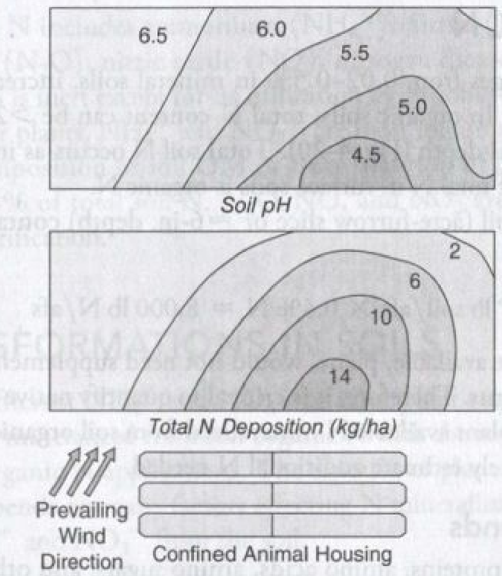


Figure 4-17
NH_3 produced from the poultry houses (20,000 animals) deposits NH_4^+ downwind and reduces soil pH. Field is approximately 20 acres and poultry houses had been operated for 18 years before air and soil sampling in 1986. NH_4^+ deposition data were collected over 1 month.
(Adapted from Speirs and Frost, 1987, Research & Development in Agriculture, 4:83–86.)

Ammonia and NO_x (NO_2 + NO) are highly reactive and short-lived in the troposphere, thus contribute little to atmospheric warming. Nitric oxide (NO) catalyzes the formation of smog. In sunlight, NO and O_2 react with hydrocarbons emitted by automobile exhausts to form ozone, the most dangerous component of smog. Ground-level ozone has serious detrimental effects on human health as well as the health and productivity of crops and forests. NO_x also combines with H_2O and O_2 to form atmospheric HNO_3, a component of acid rain (Fig. 3-4). Combustion (fossil fuel, deforestation, etc.) and denitrification are the dominant sources of NO_x. In contrast, NH_3 neutralizes acids in the atmosphere by:

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

Nearly 70% of global NH_3 emissions are related to NH_3 losses from fertilizer use, storage and application of animal wastes, and forest combustion.

Industrial N Fixation The industrial fixation of N_2 is by far the most important source of N to plants. Industrial N_2 fixation is based on the Haber-Bosch process (Fig. 4-18). The NH_3 produced can be used directly as a fertilizer (anhydrous NH_3), although numerous other fertilizer N products are manufactured from NH_3 (see Fig. 4-49). Development of the NH_3 synthesis process was essential to world food security through increased crop yields with fertilizer N; however, contamination of water and air resources has also increased.

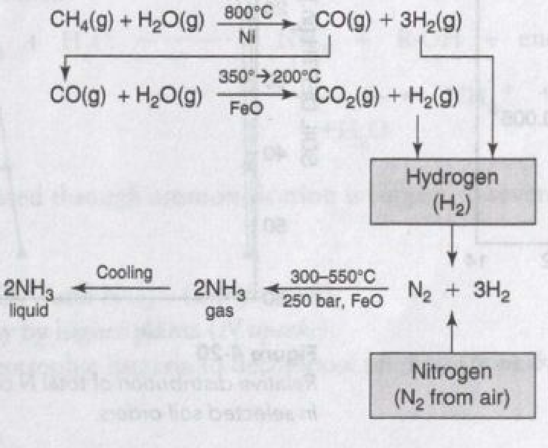


Figure 4-18
Industrial synthesis of NH_3 in the Haber-Bosch process.

FORMS OF SOIL N

Total soil N content ranges from 0.02–0.5% in mineral soils, increasing with soil OM content (Fig. 4-19). In organic soils, total N content can be >2.5%. Total N content decreases with soil depth (Fig. 4-20). Total soil N occurs as inorganic or organic N, where ≈95% of total N in surface soils is organic N.

Assuming surface soil (acre-furrow slice or ≈6-in. depth) contains an average of 0.4% total N, then:

$$2 \times 10^6 \text{ lb soil/afs} \times 0.4\% \text{ N} = 8{,}000 \text{ lb N/afs}$$

If this entire N were plant available, plants would not need supplemental N as fertilizers or organic amendments. Therefore, it is critical to quantify native plant available N in soils, and potential plant available N mineralized from soil organic N during the growing season to accurately estimate additional N needed.

Organic N Compounds

Organic soil N occurs as proteins, amino acids, amino sugars, and other complex N compounds. The proportion of soil organic N in these various fractions is:

amino acids	30–45%
bound NH_4^+	20–35%
acid insoluble	20–35%
amino sugars	5–10%
unidentified	10–20%

The exact origin of each fraction is not clearly defined. Most are associated with humic and fulvic acids that comprise soil OM and are characterized by their solubility in acids or bases. For example, humic acids are acid insoluble, whereas fulvic acids are both acid and base soluble. Proteins are commonly found in combination with clays, lignin, and other materials resistant to decomposition. While all of these forms contribute to plant available N to some extent, the easily decomposable compounds (amino acids) and organic bound NH_4^+ comprise the majority of mineralizable N during the growing season. Dependence on these reserves to meet non-legume plant N requirements will result in N deficiency and reduce growth and yield.

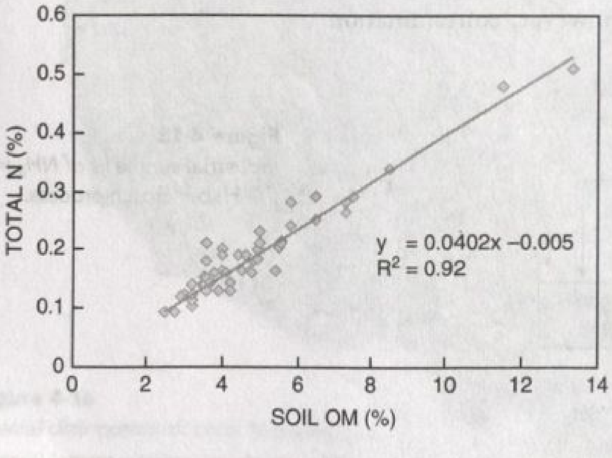


Figure 4-19
Influence of soil OM on total soil N content.
(Zheng, 2008, M.S. Thesis, Dept. Earth Sci., Indiana Univ.)

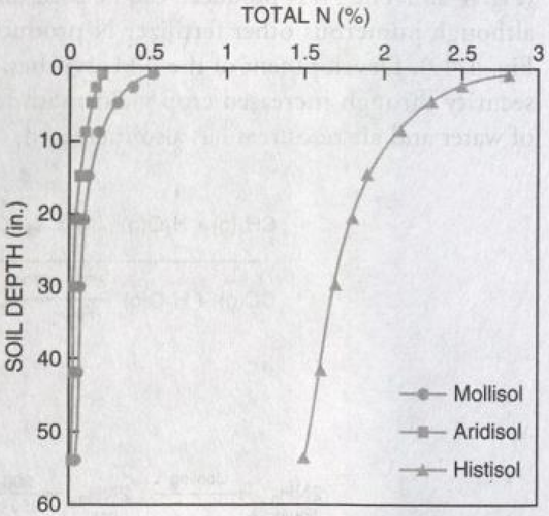


Figure 4-20
Relative distribution of total N content with soil depth in selected soil orders.

Inorganic N Compounds

Inorganic soil N includes ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and elemental N (N_2) which is inert except for its utilization by rhizobia and other N-fixing microorganisms. For plants, NH_4^+ and NO_3^- are most important and are produced from aerobic decomposition of soil OM or from addition of N fertilizers. These forms represent 2–5% of total soil N. N_2O, NO, and NO_2 are important N forms lost through denitrification.

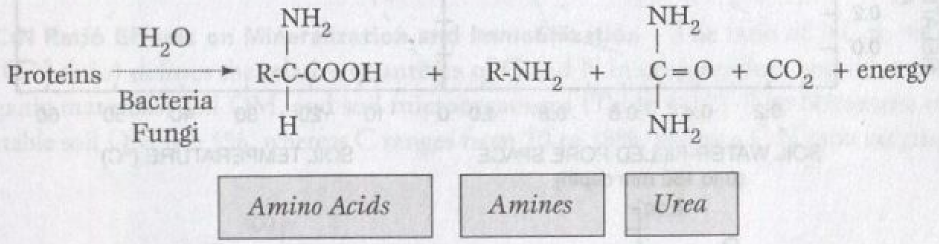
N TRANSFORMATIONS IN SOILS

Supplying sufficient NH_4^+ and NO_3^- to meet plant requirement depends on the quantity of N mineralized from soil organic N with the remainder provided through fertilizer or organic N applications. The amount of plant available N released from organic N depends on many factors affecting N mineralization, immobilization, and losses of NH_4^+ and NO_3^- from the soil.

N Mineralization and Immobilization

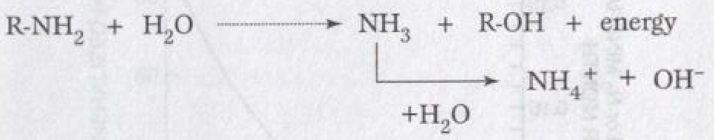
Mineralization N *mineralization* is the conversion of organic N to NH_4^+ through two reactions, *aminization* and *ammonification* (Fig. 4-2). Mineralization occurs through the activity of heterotrophic microorganisms that require organic C for energy. Heterotrophic bacteria dominate the breakdown of proteins in neutral and alkaline environments, with some involvement of fungi, while fungi predominate in acid soils. The end products of the activities of one group furnish the substrate for the next and so on until the material is decomposed. Aminization converts proteins in residues to *amino acids, amines,* and *urea* (Step 1). These are organic N compounds that are further converted to inorganic NH_4^+ by ammonification (Step 2). A diverse population of aerobic and anaerobic bacteria, fungi, and actinomycetes is capable of converting the products of aminization to NH_4^+.

Step 1. *Aminization*



$$\text{Proteins} \xrightarrow[\text{Bacteria, Fungi}]{H_2O} R\text{-}\underset{H}{\overset{NH_2}{C}}\text{-}COOH + R\text{-}NH_2 + \underset{NH_2}{\overset{NH_2}{C}}{=}O + CO_2 + \text{energy}$$

Step 2. *Ammonification*



$$R\text{-}NH_2 + H_2O \longrightarrow NH_3 + R\text{-}OH + \text{energy}$$

$$NH_3 \xrightarrow{+H_2O} NH_4^+ + OH^-$$

The NH_4^+ produced through ammonification is subject to several fates (Fig. 4-2). NH_4^+ can be:

- converted to NO_2^- and NO_3^- (*nitrification*),
- absorbed directly by higher plants (*N uptake*),
- utilized by heterotrophic bacteria to decompose residues (*immobilization*),

- fixed as biologically unavailable N in the lattice of certain clay minerals (NH_4^+ *fixation*), or
- converted to NH_3 and released back to the atmosphere (*volatilization*).

Soil moisture content regulates the proportions of aerobic and anaerobic microbial activity (Fig. 4-21). Maximum aerobic activity and N mineralization occur between 50 and 70% water-filled pore space. Soil temperature also influences microbial activity and N mineralization (Fig. 4-21). Most biological reactions are influenced by temperature, where optimum soil temperature for microbial activity ranges between 25 and 35°C. The temperature coefficient, Q_{10}, is 2 over the range of 5–35°C. Thus, a twofold change in mineralization is associated with a shift of 10°C (Fig. 4-22). While N mineralization can occur over a wide range in soil moisture and temperature, N mineralization rates generally increase as temperature and moisture increase (Fig. 4-23). However, increasing moisture to saturation and temperature above 50°C will dramatically reduce N mineralization potential due to reduced microbial activity (Fig. 4-21).

Soil OM contains about 5% N and during a growing season 1–3% of organic N is mineralized to inorganic N. As total soil N content increases, the quantity of N mineralized from soil organic N increases (Fig. 4-24). Therefore, soil and crop management strategies that conserve or increase soil OM will result in a greater contribution of mineralizable N to plant N availability.

The quantity of N mineralized during the growing season can be estimated. For example, if a soil contained 2% OM with 2% mineralization rate, then:

$$2\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times (5\%\ \text{N}) \times (2\%\ \text{N mineralized}) = 40\ \text{lb N/a}$$

Thus, each year, 40 lb N/a as NH_4^+ are mineralized, which can be utilized by plants or other soil N processes (Fig. 4-2). Depending on the nature of the previous crop residue being degraded, 50–75% of organic N mineralized can be utilized by the crop.

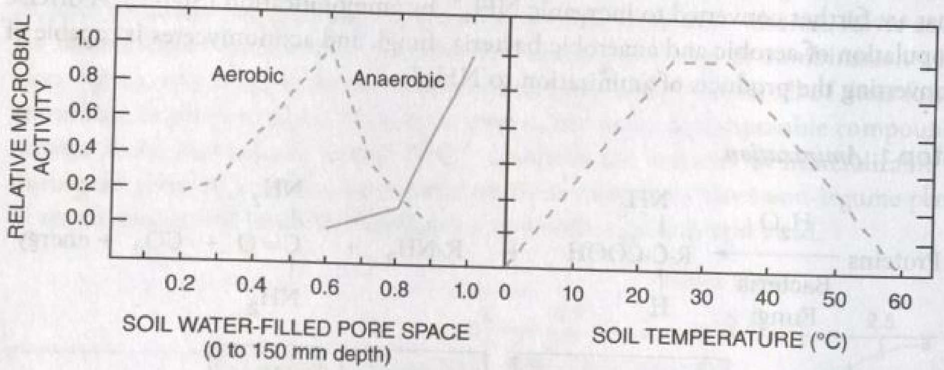


Figure 4-21
Influence of soil moisture (water-filled pore space) and temperature on relative microbial activity in soil.
(Doran and Smith, 1987, SSSA Spec. Publ. 19.)

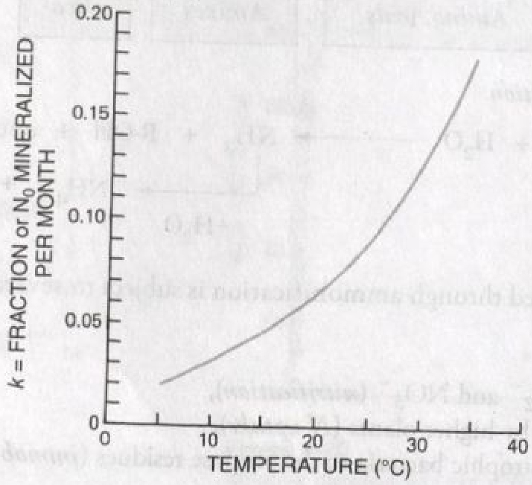


Figure 4-22
Fraction of N mineralized per month, k, in relation to temperature (k was estimated graphically for observed average monthly air temperatures).
(Stanford et al., 1977, Agron. J., 69:303.)

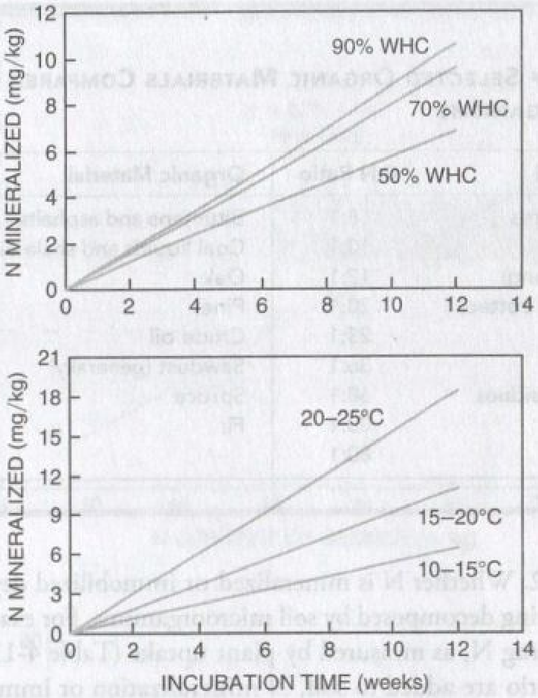


Figure 4-23
Effect of temperature and moisture on cumulative N mineralization (mg N/kg soil). Sandy clay loam soil contained 3.6% OM and 0.44% total N. WHC represents water holding capacity.
(Agehara and Warncke, 2005, SSSAJ, 69:1844–1855.)

Immobilization N immobilization is the conversion of inorganic N (NH_4^+ and NO_3^-) to organic N (Fig. 4-2). If decomposing residues contain low N, microorganisms will immobilize NH_4^+ and NO_3^- in the soil solution. Microbes need N in a C:N ratio of ~8:1; therefore, inorganic soil N is utilized by the rapidly growing population, reducing NH_4^+ and NO_3^- to very low levels. Microorganisms outcompete plants for NH_4^+ and NO_3^- during immobilization, and plants can readily become N deficient. Fortunately, in most cropping systems, sufficient N is applied to compensate for N immobilization by microbes and crop N uptake. If added organic material contains high N, immobilization will not proceed because the residue contains sufficient N to meet microbial demand, and inorganic N will increase from mineralization of organic N in the residue.

C:N Ratio Effects on Mineralization and Immobilization The ratio of %C to %N (C:N ratio) defines the relative quantities of C and N in crop residues and other organic materials, soil OM, and soil microorganisms (Table 4-12). The N content of stable soil OM is ~5%, whereas C ranges from 50 to 58%, giving a C:N ratio ranging

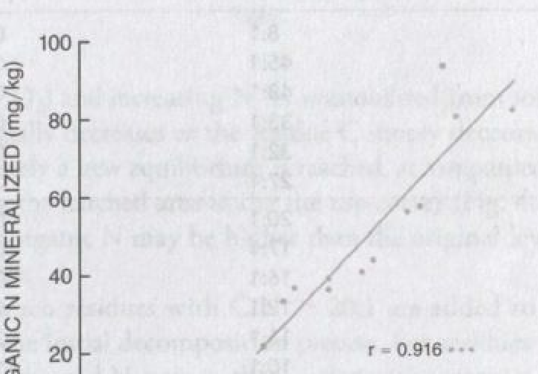


Figure 4-24
Influence of total soil N on quantity of N mineralized.

TABLE 4-12

C:N RATIOS OF SELECTED ORGANIC MATERIALS COMPARED TO SOIL OM AND MICROORGANISMS

Organic Material	C:N Ratio	Organic Material	C/N Ratio
Soil microorganisms	8:1	Bitumens and asphalts	95:1
Soil OM	10:1	Coal liquids and shale oils	125:1
Sweet clover (young)	12:1	Oak	200:1
Barnyard manure (rotted)	20:1	Pine	300:1
Clover residues	23:1	Crude oil	400:1
Green rye	36:1	Sawdust (generally)	400:1
Corn/sorghum residues	60:1	Spruce	1000:1
Grain straw	80:1	Fir	1200:1
Timothy	80:1		

between 10 and 12. Whether N is mineralized or immobilized depends on the C:N ratio of the OM being decomposed by soil microorganisms. For example, a typical soil mineralizes 0.294 mg N, as measured by plant uptake (Table 4-13). When residues of variable C:N ratio are added to soil, N mineralization or immobilization would be indicated if plant uptake was greater or less than 0.294 mg N, respectively. In this study, a C:N ratio of ~20:1 was the dividing line between immobilization and mineralization. The N content of the residue being added to soil also can be used to predict whether N is immobilized or mineralized (Fig. 4-25). Generally, N mineralization occurs with residue N content >2% under aerobic conditions.

The progress of N mineralization and immobilization following residue addition can be estimated (Fig. 4-26). During the initial stages of decomposition of added residue, there is a rapid increase in the number of heterotrophic organisms, indicated by the increased evolution of CO_2. If the C:N ratio of the fresh material is >20:1, N immobilization occurs, as shown in the hatched area under the top curve (Fig. 4-26). As residue decay proceeds, residue C:N ratio decreases, due to decreasing

TABLE 4-13

N MINERALIZED FROM VARIOUS RESIDUES AS MEASURED BY PLANT UPTAKE

Plant Residue*	C:N Ratio	N Uptake (mg)
Check soil	8:1	0.294
Tomato stems	45:1	0.051
Corn roots	48:1	0.007
Corn stalks	33:1	0.038
Corn leaves	32:1	0.020
Tomato roots	27:1	0.029
Collard roots	20:1	0.311
Bean stems	17:1	0.823
Tomato leaves	16:1	0.835
Bean stems	12:1	1.209
Collard stems	11:1	2.254
Collard leaves	10:1	1.781

*Residues above the dashed line have a C:N ratio >20:1 (net immobilization). Residues below the dashed line have a C:N ratio <20:1 (net mineralization).

Source: Iritani and Arnold, 1960, Soil Sci., *89:74.*

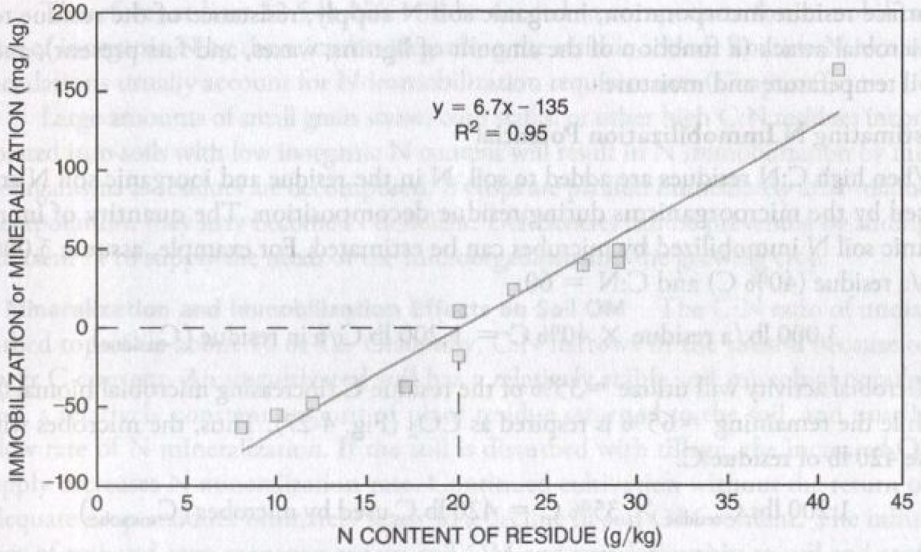


Figure 4-25
Effect of N content of organic materials on apparent N immobilization or mineralization.
(Goos, 1995, J. Nat. Resources Life Sci. Educ., 24:68–70.)

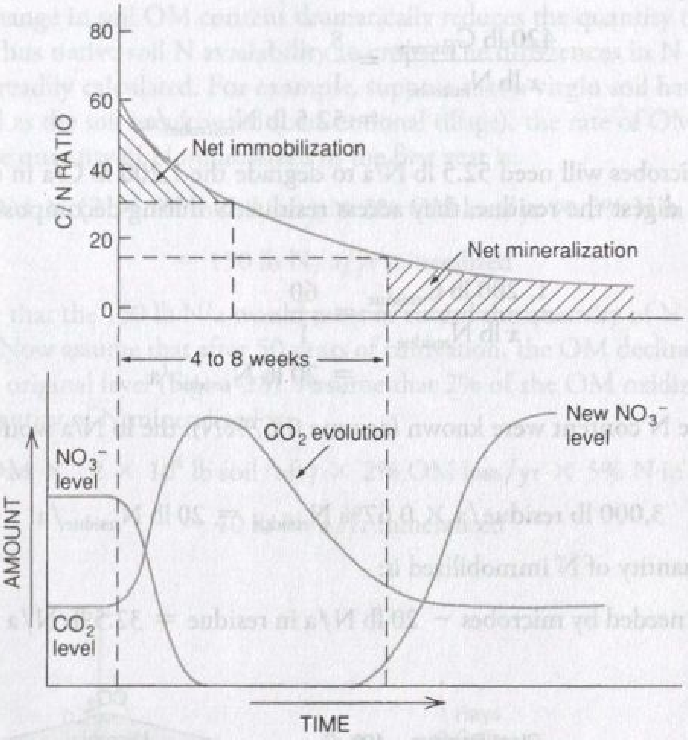


Figure 4-26
General description of N mineralization and immobilization following addition of residue to soil.
(Adapted from B. R. Sabey, Univ. of Illinois.)

C (respiration as CO_2) and increasing N (N immobilized from soil solution). Microbial activity eventually decreases as the residue C supply decreases (decreasing CO_2 evolution). Ultimately a new equilibrium is reached, accompanied by mineralization of N (indicated by the hatched area under the top curve) (Fig. 4-26). The net result is that final soil inorganic N may be higher than the original level, as a result of N added in the residue.

Generally, when residues with C:N > 20:1 are added to soil, soil N is immobilized during the initial decomposition process. For residues with C:N < 20:1, there is a release of mineral N early in the decomposition process. Soil OM may also increase, depending on the quantity and type of residue added and the quantity of OM loss through oxidation (mineralization) or physical soil loss (Chapter 12). The time required for residue decomposition depends on the quantity added, degree of surface residue incorporation, inorganic soil N supply, resistance of the residue to microbial attack (a function of the amount of lignins, waxes, and fats present), and soil temperature and moisture.

Estimating N Immobilization Potential

When high C:N residues are added to soil, N in the residue and inorganic soil N are used by the microorganisms during residue decomposition. The quantity of inorganic soil N immobilized by microbes can be estimated. For example, assume 3,000 lb/a residue (40% C) and C:N = 60.

$$3{,}000 \text{ lb/a residue} \times 40\%\text{ C} = 1{,}200 \text{ lb C/a in residue } (\text{C}_{\text{residue}})$$

Microbial activity will utilize ≈35% of the residue C (increasing microbial biomass), while the remaining ≈65% is respired as CO_2 (Fig. 4-27). Thus, the microbes will use 420 lb of residue C.

$$1{,}200 \text{ lbs C}_{\text{residue}} \times 35\%\text{ C} = 420 \text{ lb C used by microbes } (\text{C}_{\text{microbe}})$$

The increasing microbe population will require N governed by microbe C:N = 8:1 (Table 4-12):

$$\frac{420 \text{ lb C}_{\text{microbe}}}{x \text{ lb N}_{\text{microbe}}} = \frac{8}{1}$$
$$= 52.5 \text{ lb N}_{\text{microbe}}/\text{a}$$

Thus, the microbes will need 52.5 lb N/a to degrade the 1,200 lb C/a in the residue. As microbes digest the residue, they access residue N during decomposition determined by:

$$\frac{1{,}200 \text{ lb C}_{\text{residue}}}{x \text{ lb N}_{\text{residue}}} = \frac{60}{1}$$
$$= 20 \text{ lb N}_{\text{residue}}/\text{a}$$

If the residue N content were known (assume 0.67%N), the lb N/a would be determined by:

$$3{,}000 \text{ lb residue/a} \times 0.67\% \text{ N}_{\text{residue}} = 20 \text{ lb N}_{\text{residue}}/\text{a}$$

Thus, the quantity of N immobilized is:

$$52.5 \text{ lb N/a needed by microbes} - 20 \text{ lb N/a in residue} = 32.5 \text{ lb N/a immobilized}$$

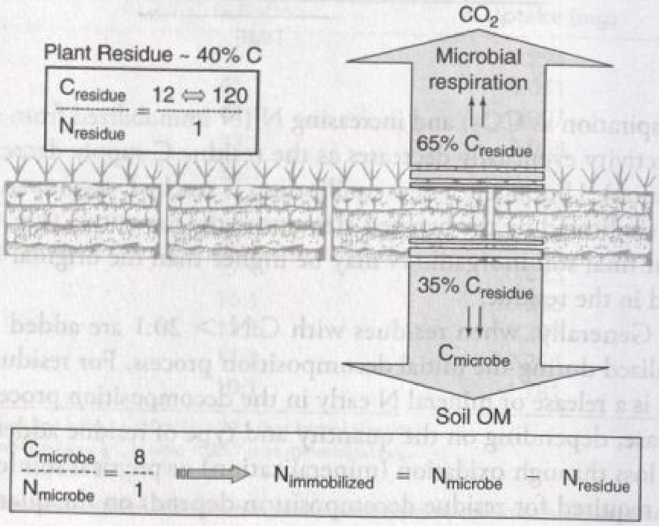


Figure 4-27
Partitioning of residue C added to soil into CO_2, soil microbe C, and soil OM, and its influence in N immobilization/mineralization. Plant residues contain an average of 40% C with variable C:N ratio. As microbes degrade the added residue, 65% of residue C is respired to the atmosphere as CO_2. The remaining 35% is incorporated into the microbes as their population increases because of the residue addition. The increase in microbe C is governed by its C:N ratio (8:1). Therefore, additional N needed by the microbes (N immobilization) is the difference in total N needed by the microbe to degrade the residue and the residue N content (see example calculation on this page).

Therefore, at least 32.5 lb N/a will be needed to compensate for immobilization of inorganic N by the microbes degrading the residue added. Routine N recommendations usually account for N immobilization requirements (Chapter 9).

Large amounts of small grain straw, corn stalks, or other high C:N residues incorporated into soils with low inorganic N content will result in N immobilization by microorganisms as residues are decomposed. If crops are planted immediately after residue incorporation, they may become N deficient. Deficiencies can be prevented by adding sufficient N to supply the needs of the microorganisms and the growing crop.

N Mineralization and Immobilization Effects on Soil OM The C:N ratio of undisturbed topsoil is about 10 or 12. Generally, C:N narrows in the subsoil because of lower C content. An uncultivated soil has a relatively stable soil microbial population, a relatively constant amount of plant residue returned to the soil, and usually a low rate of N mineralization. If the soil is disturbed with tillage, the increased O_2 supply increases N mineralization rate. Continued cultivation without the return of adequate crop residues ultimately leads to a decline in soil OM content. The influence of soil and crop management on soil OM and its relationship to soil and crop productivity is discussed in Chapter 12.

Any change in soil OM content dramatically reduces the quantity of N mineralized, and thus native soil N availability to crops. The differences in N mineralization can be readily calculated. For example, suppose that a virgin soil has a 5% OM content, and as the soil is cultivated (conventional tillage), the rate of OM loss is 3% per year. The quantity of N mineralized in the first year is:

$$5\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times 3\%\ \text{OM loss/yr} \times 5\%\ \text{N in OM}$$

$$= 150\ \text{lb N/a/yr mineralized}$$

Notice that the 150 lb N/a would meet or exceed the quantity of N required by most crops. Now assume that after 50 years of cultivation, the OM declined to 2% or one-half the original level (Fig. 4-28). Assume that 2% of the OM oxidizes per year; thus, the quantity of N mineralized is:

$$2\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times 2\%\ \text{OM loss/yr} \times 5\%\ \text{N in OM}$$

$$= 40\ \text{lb N/a/yr mineralized}$$

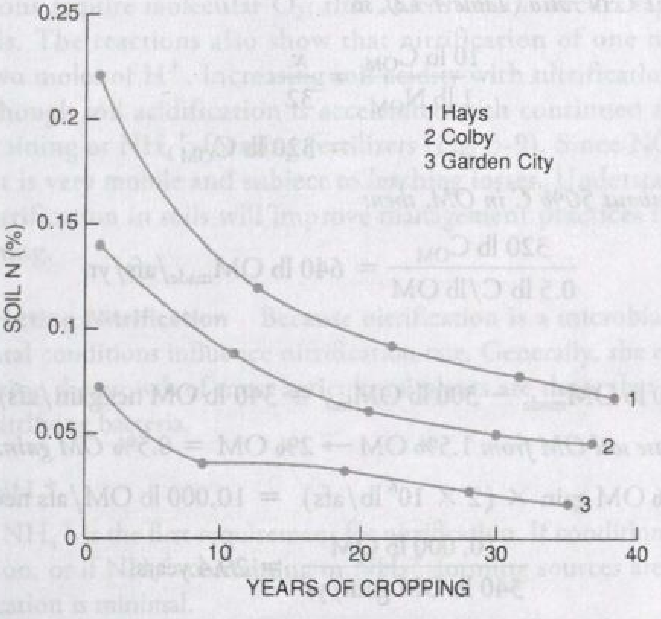


Figure 4-28
Decline in total soil N with years of cropping at three locations in Kansas. Each site was in wheat-fallow-wheat, with all residues incorporated with tillage. Total soil N represents soil OM, since 95% of total N is organic N.
(Haas and Evans, 1957, USDA Tech. Bull. No. 1164.)

The estimated N mineralized illustrates that cultivation of virgin soils mineralized sufficient N to optimize yields of most crops, especially at lower yield levels experienced 50 years ago. The excess N not utilized by the crop was subject to several losses, which include leaching and denitrification. However, at present yield levels, mineralization of 40 lb N/a is insufficient to meet crop demand and fertilizer or manure N is needed to optimize yields.

The decline in soil OM following cultivation is well documented. Depending on soil type, climate, cropping system, and tillage intensity, initial soil OM content can decline by 50% in 40–70 years. These observations indicate that the loss of soil OM can be extensive resulting in a loss of productivity. Maintaining or increasing soil OM content can dramatically improve soil productivity and crop yield. While soil and crop productivity relationships will be detailed in Chapter 12, we can use the N mineralization–immobilization calculations to estimate time required to increase soil OM.

Estimating Soil OM Production

A soil contains 1.5% OM with an annual decomposition rate of 1%. The producer wants to increase OM to 2%. How many years will it take if he produces 8,000 lb crop residue/yr (residue contains 40% C and C:N is 80:1). Also assume 80% of residue N ultimately ends up as N in soil OM.

Step 1. *Estimate annual soil OM loss.*

$$\text{OM}_{\text{lost}} \rightarrow 1.5\%\ \text{OM} \times (2 \times 10^6\ \text{lb soil/afs}) \times 1\%\ \text{loss rate}$$

$$= 300\ \textit{lb}\ \textit{OM}_{\textit{lost}}/\textit{afs}/\textit{yr}$$

Step 2. *Estimate annual soil OM produced.*

$$\text{OM}_{\text{made}} \rightarrow 8{,}000\ \text{lb residue/a} \times 40\%\ \text{C} = 3{,}200\ \text{lb C}_{\text{residue}}$$

$$\frac{3,200\ \text{lb C}_{\text{residue}}}{x\ \text{lb N}_{\text{residue}}} = \frac{80}{1}$$

$$= 40\ \text{lb N}_{\text{residue}}$$

About 80% of residue N goes into forming N in OM, thus:

$$40\ \text{lb N}_{\text{residue}} \times 0.8 = 32\ \text{lb N}_{\text{OM}} \quad \text{(this is N in soil OM from residue N)}$$

OM has a 10:1 C:N ratio (Table 4-12), so:

$$\frac{10\ \text{lb C}_{\text{OM}}}{1\ \text{lb N}_{\text{OM}}} = \frac{x}{32}$$

$$= 320\ \text{lb C}_{\text{OM}}$$

Since there is about 50% C in OM, then:

$$\frac{320\ \text{lb C}_{\text{OM}}}{0.5\ \text{lb C/lb OM}} = 640\ \text{lb OM}_{\text{made}}/\text{afs/yr}$$

Therefore,

$$640\ \text{lb OM}_{\text{made}} - 300\ \text{lb OM}_{\text{lost}} = 340\ \text{lb OM net gain/afs/yr}$$

want to increase soil OM from 1.5% OM → 2% OM = 0.5% *OM gain:*

$$0.5\%\ \text{OM gain} \times (2 \times 10^6\ \text{lb/afs}) = 10{,}000\ \text{lb OM/afs needed}$$

$$\frac{10,000\ \text{lb OM}}{340\ \text{lb OM gain/yr}} = 29.4\ \text{years}$$

The important concept is recognizing that soil OM can increase over time if the C added in the residue exceeds soil C lost. Therefore, increasing C inputs and reducing C loses will increase soil OM; however, it takes many decades to effect any measurable change (Chapter 12).

Nitrification

A major portion of the NH_4^+ produced from mineralization is converted to NO_3^- through microbial oxidation or *nitrification* (Fig. 4-2). Nitrification is a two-step process where NH_4^+ is converted to NO_2^- and then to NO_3^-. Oxidation of NH_4^+ to NO_3^- is represented by:

Step 1

$$2NH_4^+ + 3O_2 \xrightarrow{\textit{nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+$$

$$(-3) \xrightarrow[\textit{increasing oxidation of N}]{} (+3)$$

Step 2

$$2NO_2^- + O_2 \xrightarrow{\textit{nitrobactor}} 2NO_3^-$$

$$(+3) \xrightarrow[\textit{increasing oxidation of N}]{} (+5)$$

Net Reaction

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

Nitrosomonas and *Nitrobacter* are chemoautotrophic bacteria that obtain their energy from the oxidation of N and their C from CO_2. Other autotrophic bacteria (*Nitrosolobus*, *Nitrospira*, and *Nitrosovibrio*), and some heterotrophic bacteria, can oxidize NH_4^+ and other reduced N compounds (i.e., amines). Recently *Crenarchaeota* (*Archaea*) have been established as NH_4^+ oxidizers in soils, and may contribute more to nitrification than bacteria.

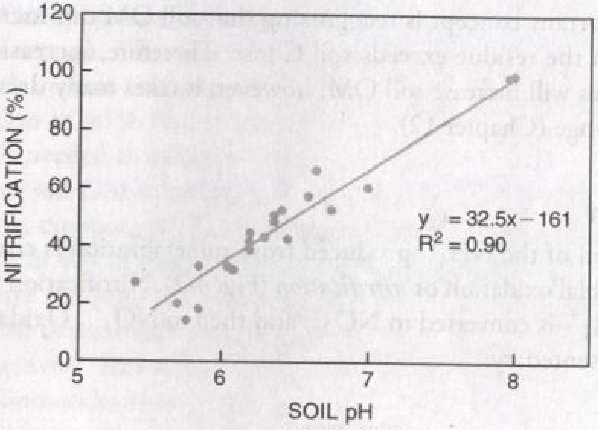
The source of NH_4^+ can be from N mineralization or N fertilizers or manures containing or forming NH_4^+. Nitrification reaction rates in well-drained soils are $NO_2^- \rightarrow NO_3^- \gg NH_4^+ \rightarrow NO_2^-$. As a result, NO_2^- generally does not accumulate in soils, which is fortunate since NO_2^- is toxic to plant roots. Both reactions require molecular O_2; thus, nitrification occurs rapidly in well-aerated soils. The reactions also show that nitrification of one mole of NH_4^+ produces two moles of H^+. Increasing soil acidity with nitrification is a natural process, although soil acidification is accelerated with continued application of NH_4^+-containing or NH_4^+-forming fertilizers (Fig. 3-9). Since NO_3^- is readily produced, it is very mobile and subject to leaching losses. Understanding factors affecting nitrification in soils will improve management practices that minimize NO_3^- leaching.

Factors Affecting Nitrification Because nitrification is a microbial process, soil environmental conditions influence nitrification rate. Generally, the environmental factors favoring the growth of most agricultural plants are those that also favor the activity of nitrifying bacteria.

Supply of NH_4^+

A supply of NH_4^+ is the first requirement for nitrification. If conditions do not favor mineralization, or if NH_4^+-containing or NH_4^+-forming sources are not added to soils, nitrification is minimal.

Figure 4-29
Influence of pH on % nitrification of fertilizer N. Anhydrous NH_3 fall applied, soils sampled after planting in spring.
(Kyveryga et al., 2004, SSSAJ, 68:545–551.)



Population of Nitrifying Organisms

Soils differ in their ability to nitrify NH_4^+ even under similar temperature, moisture, and NH_4^+ content. Variation in nitrifier population results in differences in the lag time between addition of NH_4^+ and buildup of NO_3^-. Because of the tendency of microbial populations to multiply rapidly, total nitrification is not affected by the number of organisms initially present, provided that temperature and moisture conditions are favorable for sustained nitrification.

Soil pH

Nitrification takes place over a wide range in pH (5–9), although optimum is ~ pH 8 (Fig. 4-29). Nitrifying bacteria need an adequate supply of Ca^{+2}, $H_2PO_4^-$, and micronutrients. The influence of soil pH and Ca^{+2} on activity of nitrifiers supports the importance of liming.

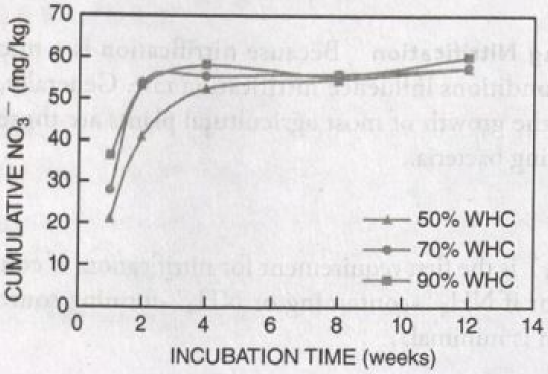
Soil Aeration

Aerobic nitrifying bacteria will not produce NO_3^- in the absence of O_2 (see reactions under "Nitrification"). Soil conditions that permit rapid gas diffusion are important for maintaining optimum soil aeration. Soils that are coarse textured or possess good structure facilitate rapid gas exchange and ensure an adequate supply of O_2 for nitrifying bacteria. Incorporation of crop residues and other organic amendments will help maintain or improve soil aeration.

Soil Moisture

Soil moisture and soil aeration are closely related in their effects on nitrification. Nitrification rates are generally highest at field capacity (Fig. 4-30). These data show that nitrification was initially slowed at the lower soil moisture content (50% WHC). N mineralization and nitrification are reduced when soil moisture exceeds field capacity (0.3 bar) or nears air dryness (>15 bar).

Figure 4-30
Influence of soil water content on cumulative nitrification of urea applied to soil.
(Agehara and Warncke, 2005, SSSAJ, 69:1844–1855.)



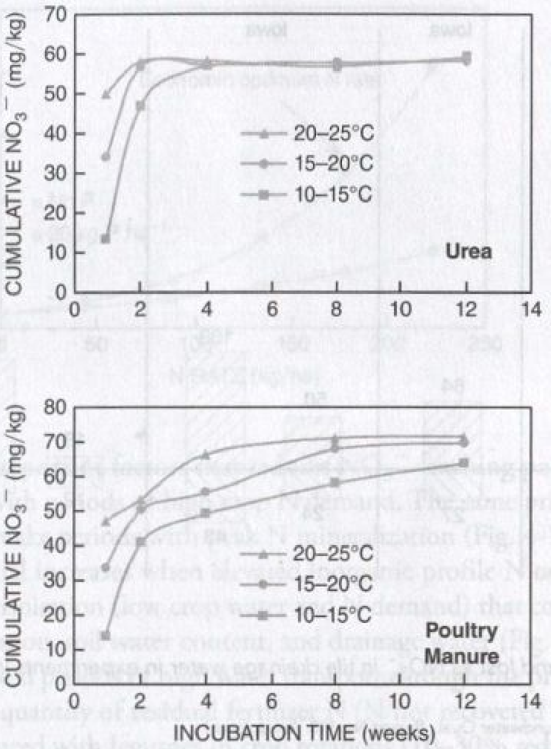


Figure 4-31

Effect of temperature on cumulative nitrification of N added as urea and poultry manure. Temperature range represents 10 h and 14 h at each temperature, respectively.

(Agehara and Warncke, 2005, SSSAJ, 69:1844–1855.)

Soil Temperature

Although nitrification occurs over a wide temperature range, optimum soil temperature is 25–35°C. Observe how nitrification of urea or poultry manure is slowed at the lower soil temperature regime (Fig. 4-31). For off-season application of NH_3 or NH_4^+-containing or NH_4^+-forming fertilizers, winter soil temperatures should be low enough to retard NO_3^- formation, thereby reducing the risk of leaching and denitrification losses. Fall NH_4^+ applications are most efficient when minimum air temperatures are below 40°F (4.4°C) or when soil temperatures are below 50°F (10°C). Application of nitrification inhibitors can help retard nitrification for several months. These are best used in moderately to well-drained soils under conditions optimum for nitrification (>50°F, pH>5.5, well-aerated soil, fall NH_4^+ applications).

Even if temperatures are occasionally high enough to permit nitrification of fall-applied NH_4^+, this is not detrimental if leaching does not occur. In low rainfall areas, moisture movement through the soil profile during the winter months is insufficient to leach NO_3^-. In humid areas, water movement through the soil profile can be excessive, and NO_3^- losses occur. Whether NH_4^+ can be applied in the fall without significant NO_3^- loss depends on local soil and weather conditions.

Nitrate Leaching

NO_3^- is very soluble in water and is not strongly adsorbed to the AEC. Consequently, it is highly mobile and subject to leaching losses when both soil NO_3^- content and water movement are high (Fig. 4-32). N leaching is considered a major pathway of N loss in humid climates (Fig. 3-5) and under irrigated cropping systems. NO_3^- leaching must be carefully controlled because of the serious impact on the environment. High NO_3^- levels in surface runoff and water percolating through soil can pollute drinking water sources and stimulate unwanted plant and algae growth in lakes and reservoirs. Some of the factors

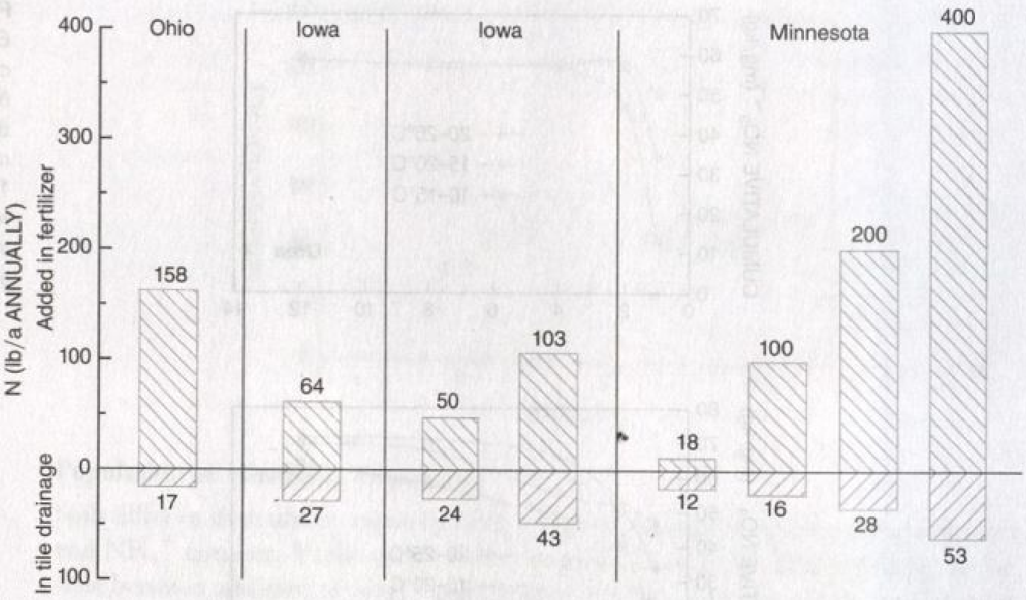
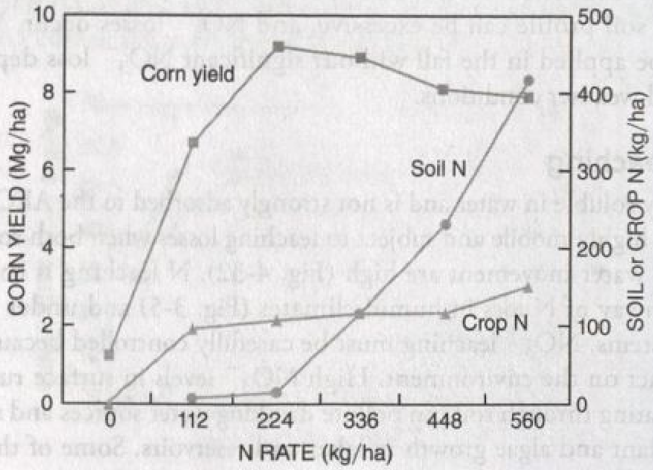


Figure 4-32
N added in fertilizer and lost as NO_3^- in tile drainage water in experiments in Ohio, Iowa, and Minnesota.
(CAST, 1985, Agric. and Groundwater Qual., Report No. 103, Ames, Iowa.)

that influence the magnitude of NO_3^- leaching losses are (1) rate, time, source, and method of N fertilization; (2) intensity of cropping and crop N uptake; (3) soil profile characteristics that affect percolation; and (4) quantity, pattern, and time of precipitation and/or supplemental irrigation. It is important to match crop N needs with soil and applied N so that leachable NO_3^- is minimized. NO_3^- leaching into water draining from tile lines located several feet below the soil surface occurs in many areas of the Midwest (Fig. 4-32). Generally, NO_3^- leaching losses in tile-drained systems can approach 30–40% of applied fertilizer or manure N, while under natural-drainage systems values between 10 and 30% are common.

In general, increased leaching potential is related to N rates exceeding crop yield potential (Fig. 4-33). Exceeding the optimum N rate increases profile N content and N leaching potential. If other factors reduce yield potential, crop recovery of applied N will be reduced. For example, when corn yield was reduced by P deficiency, correcting the P deficiency increased yield and N uptake, decreasing profile N (Fig. 4-34).

Figure 4-33
Typical relationship between N rate, crop yield, and N accumulation in the soil profile.
(Schepers et al., 1996.)



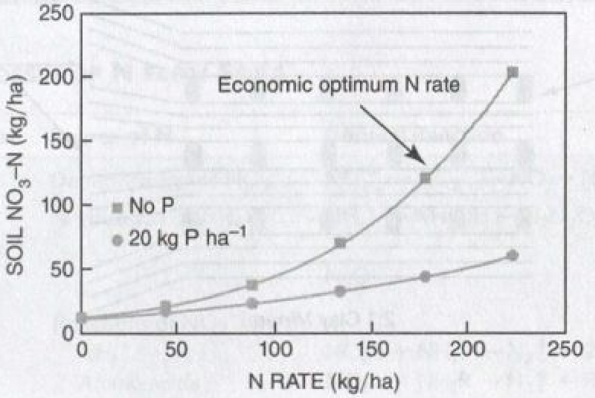


Figure 4-34
Influence of N rate on soil NO_3^- content (0–3 m depth) after 30 years of irrigated corn production. Economic optimum N rate occured at 180 kg N/ha. Addition of P reduced soil NO_3^-.
(Schlegel et al., 1996, J. Prod. Agric., 9:114.)

One of the most important factors that reduces NO_3^- leaching potential is applying N synchronous with periods of high crop N demand. The same principle holds for matching peak N uptake periods with peak N mineralization (Fig. 4-14). In addition, N leaching potential increases when elevated inorganic profile N occurs during periods of low evapotranspiration (low crop water and N demand) that coincides with periods of high precipitation, soil water content, and drainage water (Fig. 4-35). Timing N applications to avoid periods of high water transport through the profile reduces leaching potential. The quantity of residual fertilizer N (N not recovered by the crop) can be substantially reduced with legumes in crop rotations (10–30% reduction) and/or cover crops (20–80% reduction). N management and NO_3^- leaching impacts on environmental quality are discussed in Chapter 12.

Ammonium Fixation

Certain clay minerals, particularly vermiculite and mica, are capable of fixing NH_4^+ by replacement with cations in the expanded lattices of clay minerals (Fig. 4-36). Fixed NH_4^+ can be replaced by cations that expand the lattice (Ca^{+2}, Mg^{+2}, Na^+, H^+) but not by those that contract it (K^+). Coarse clay (0.2–2 mm) and fine silt (2–5 mm) are important fractions in fixing added NH_4^+. In a high NH_4^+-fixing clay soil dominated by mica, substantial amounts of added NH_4^+ were fixed, increasing with soil dryness (Fig. 4-37). Increasing moisture likely increases nitrification of the added NH_4^+. Greater NH_4^+ fixation occurs with broadcast application due to increased soil-fertilizer contact.

Alternate cycles of wetting-drying and freezing-thawing contribute to the stability of recently fixed NH_4^+. The presence of K^+ often restricts NH_4^+ fixation since K^+ can also fill fixation sites (Chapter 6). Consequently, K fertilization before

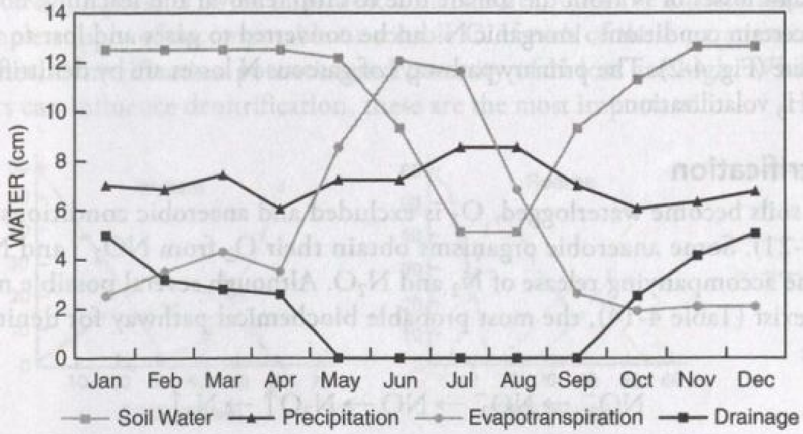


Figure 4-35
Typical soil-plant-water cycle for a humid region, sandy loam soil in the southeast United States. Soil water content in surface 1 m and water drainage below 1 m.

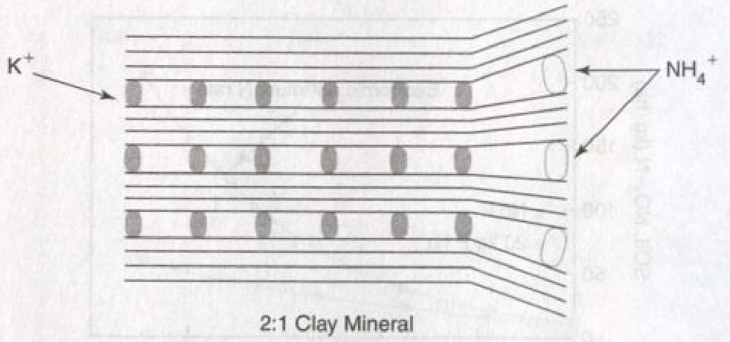


Figure 4-36
Diagram of an expanding clay mineral capable of fixing native or applied NH_4^+.

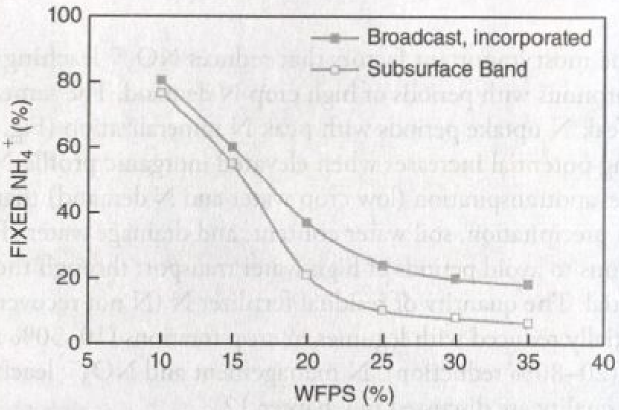


Figure 4-37
Influence of soil moisture content and NH_4^+ application method on relative fixation of NH_4^+ added as NH_4HCO_3 fertilizer.
(Tong et al., 2004, Pedoshere, 14:247–252.)

NH_4^+ application can reduce NH_4^+ fixation. The availability of fixed NH_4^+ ranges from negligible to relatively high. Clay fixation of NH_4^+ provides some degree of protection against volatilization, nitrification, and subsequent leaching. Although the agricultural significance of NH_4^+ fixation is not great, it is important in certain soils. For example, selected soils from Oregon and Washington fixed 1–30% of the applied NH_4^+. In certain soils of eastern Canada, 14–60% of fertilizer NH_4^+ can be fixed. Native-fixed NH_4^+ is significant in many of these soils and can amount to 10–30% of the total fixation capacity. Intensive cropping generally cannot readily remove native-fixed NH_4^+. In contrast, while some added NH_4^+ is fixed in soils, intensive cropping generally recovers recently fixed NH_4^+.

GASEOUS LOSSES OF N

The major losses of N from the soil are due to crop removal and leaching; however, under certain conditions, inorganic N can be converted to gases and lost to the atmosphere (Fig. 4-2). The primary pathways of gaseous N losses are by denitrification and NH_3 volatilization.

Denitrification

When soils become waterlogged, O_2 is excluded and anaerobic conditions occur (Fig. 4-21). Some anaerobic organisms obtain their O_2 from NO_2^- and NO_3^-, with the accompanying release of N_2 and N_2O. Although several possible mechanisms exist (Table 4-14), the most probable biochemical pathway for denitrification is:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow$$

TABLE 4-14
GASEOUS LOSSES OF N FROM SOILS

Form of N Lost	Source of N	General Reaction
N_2 and N_2O	Denitrification of NO_3^-	$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow$
	Nitrification of NH_4^+	$NH_4^+ \rightarrow NH_2OH \rightarrow H_2N_2O_2 \rightarrow NO_2^- \rightarrow NO_3^-$ $\downarrow$ N_2O
	Reactions of NO_2^- with:	
	NH_4^+	$NO_2^- + NH_4^+ \rightarrow N_2\uparrow + 2H_2O$
	Amino acids	$NO_2^- + NH_2R \rightarrow N_2\uparrow + R\text{-}OH + OH^-$
	Lignin	$NO_2^- + \text{lignin} \rightarrow N_2\uparrow + N_2O\uparrow + CH_3ONO$
	Decomposition of NO_2^-	
	H^+	$3NO_2^- + 2H^+ \rightarrow 2NO + NO_3^- + H_2O$
	Fe^{+2}	$NO_2^- + Fe^{+2} + 2H^+ \rightarrow Fe^{+3} + NO + H_2O$
	Mn^{+2}	$NO_2^- + Mn^{+2} + 2H^+ \rightarrow Mn^{+3} + NO + H_2O$
NH_3	Fertilizers	
	anhydrous NH_3	NH_3 (liquid) $\rightarrow NH_3$ (gas)
	urea	$(NH_2)_2CO + H_2O \rightarrow 2NH_3\uparrow + CO_2$
	NH_4^+ salts	$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$ (pH > 7)
	Residue decomposition	Organic N $\rightarrow NH_4^+ \rightarrow NH_3\uparrow$

Source: Modified from Kurtz, 1980, ASA Spec. Publ. 38, p. 5.

Conversion of NO_3^- to N_2 under anaerobic conditions can be monitored with time (Fig. 4-38). In this example, NO_3^- decreases as NO_2^- increases, then NO_2^- is replaced by N_2O, which is ultimately converted to N_2.

Large populations of denitrifying microorganisms exist, the most common are the bacteria *Pseudomonas*, *Bacillus*, and *Paracoccus*, and several autotrophs (*Thiobacillus denitrificans* and *Thiobacillus thioparus*). Denitrification potential is high in most field soils, but conditions must arise that cause a shift from aerobic respiration to a denitrifying metabolism involving NO_3^- as an electron acceptor in the absence of O_2. N_2O and N_2 losses are highly variable because of fluctuations in environmental conditions between years, between seasons, and within a given field. N_2 loss predominates, sometimes accounting for about 90% of the total denitrification, while N_2O loss is greater under less-reduced conditions.

Factors Affecting Denitrification When assessing the potential for denitrification and the magnitude of N loss, three major issues must be evaluated: (1) will the surface soil environment be waterlogged or anaerobic, (2) is NO_3^- and to a lesser extent NO_2^- present in the anaerobic zone, and (3) does the surface soil contain an ample supply of decomposable or soluble C. If each of these parameters occurs together, denitrification potential and quantity of N loss are high. While other factors can influence denitrification, these are the most important.

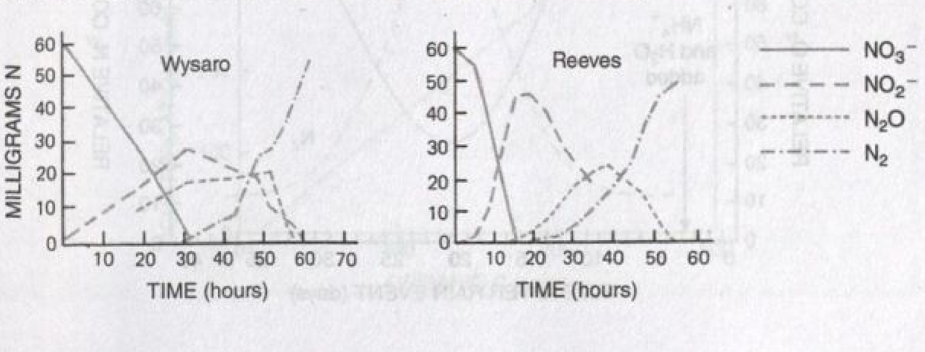


Figure 4-38
Sequence and magnitude of N products formed and utilized during anaerobic denitrification of Wysaro clay (pH 6.1) and Reeves loam (pH 7.8) at 30°C.
(Cooper and Smith, 1963, Soil Sci. Soc. Am. J., 27:659.)

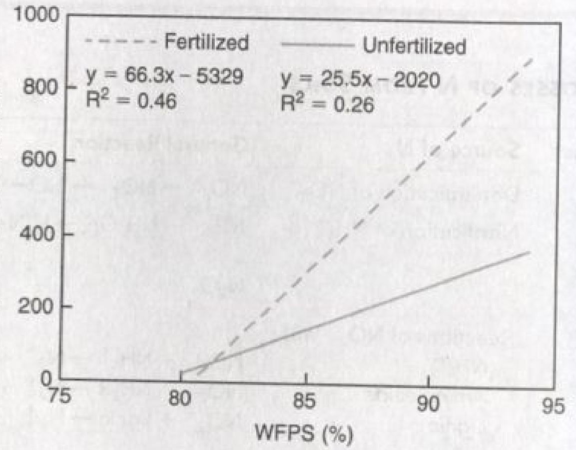


Figure 4-39
Relationship between denitrification rate (N_2O emission) and water-filled pore space (WFPS) in unfertilized soil and fertilized with 210 kg N/ha as urea.
(Sainz Rozas et al., 2001, SSSAJ, 65:1314–1323.)

Soil Drainage (Moisture and Aeration)

Soil moisture content is critical to denitrification because of its effect on aeration. Denitrification proceeds only when the O_2 supply is too low to meet aerobic microbial requirements. Generally, when soil water-filled pore space exceeds 60%, aerobic activity declines, while anaerobic microbial activity increases (Fig. 4-21); however, appreciable N loss generally occurs at >80% water-filled pore space (Fig. 4-39).

As soil moisture increases, O_2 diffusion through soil is impeded. Denitrification accelerates under low O_2 diffusion in soil and a high microbial respiratory demand (high C source). When O_2 content of well-aerated soil ($\approx$ 16–18% O_2) declines to 8–10% O_2, denitrification is optimized (Fig. 4-40). Denitrification can also occur in aerated soils, presumably in anaerobic microsites or aggregates, where O_2 diffusion is slow (Fig. 4-41).

Soil NO_3^- and NO_2^-

NO_3^- must be present for denitrification to occur, and high NO_3^- increases denitrification potential. Residual or freshly applied N from fertilizer, manure, or other waste materials in aerated soil will mineralize and/or nitrify to produce NO_3^-, which will be readily denitrified if anaerobic conditions occur after application (Fig. 4-42).

In flooded rice soils, NO_3^- fertilizers are not used because of rapid conversion to N_2 by denitrification. Only NH_4^+ or NH_4^+-forming N sources are used.

Although NO_2^- does not usually accumulate in soil, detectable amounts occur in high pH soils and in localized soil zones containing NH_4^+ or NH_4^+-forming fertilizers. High rates of band-applied urea, anhydrous NH_3, or $(NH_4)_2HPO_4$ fertilizers

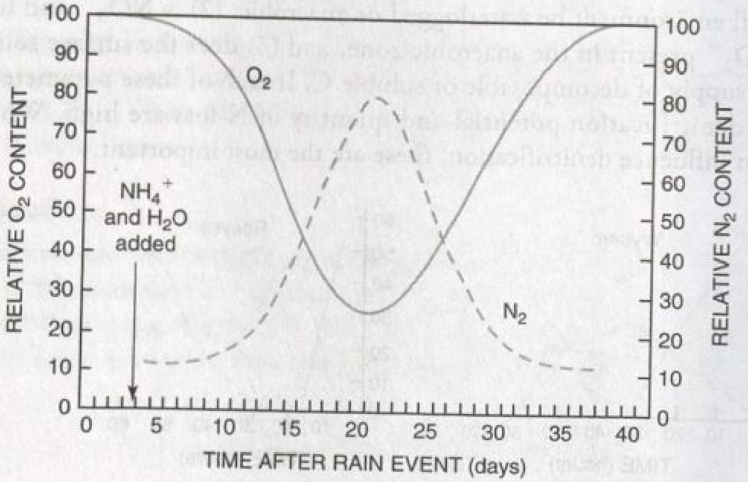


Figure 4-40
General relationship between reducing O_2 content in soil air following a rainfall event and increasing N_2 production. Release of N_2 peaked when soil O_2 decreases to ~25% of that observed at field capacity. Total N loss depends on duration of low O_2 conditions.

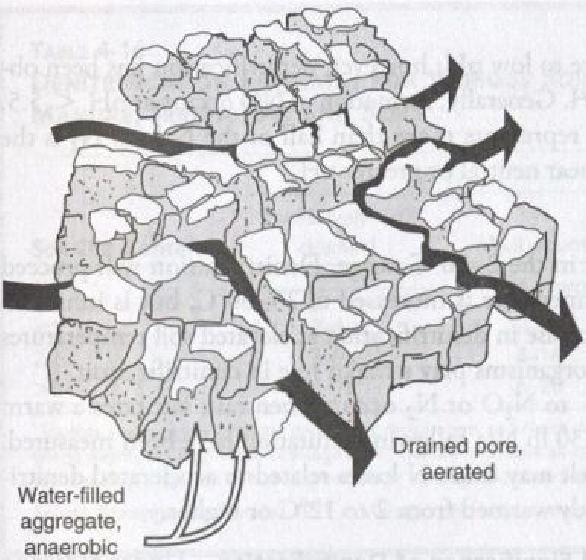


Figure 4-41
Diagram of microsites within an aerated soil that represent anaerobic, water-saturated aggregates in which native or applied N can be denitrified.

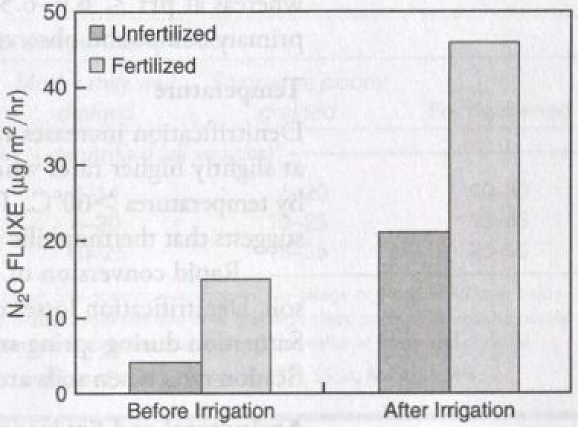


Figure 4-42
Influence of N fertilization and irrigation on rate of N_2O emission from winter wheat. Urea applied a 120 kg N/ha.
(Su et al., 1995, Terrestrial, Atmos., and Oceanic Sci., 6:409–417.)

cause temporary increases in pH, which encourages NO_2^- accumulation in the band, regardless of initial soil pH. Diffusion and/or dilution of NH_4^+ in the fertilizer bands will restore conditions suitable for conversion of NO_2^- to NO_3^-. NO_2^- can diffuse beyond the fertilizer band to a soil environment, where *Nitrobacter* will readily convert it to NO_3^-. If anaerobic conditions occur during the nitrification of applied N, some of the intermediate NO_2^- can be denitrified.

Decomposable OM

Decomposable soil OM or soluble C enhances denitrification potential in soil (Fig. 4-43). The reactions with available C required for microbial reduction of NO_3^- to N_2O or N_2 are:

$$4(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 4CO_2 + 2N_2O + 6H_2O$$

$$5(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$

Carbonaceous exudates from active roots support denitrifying bacteria growth in the rhizosphere. Under field conditions, freshly added crop residues can stimulate denitrification. Fields where animal wastes are regularly applied provide a high reservoir of soluble C.

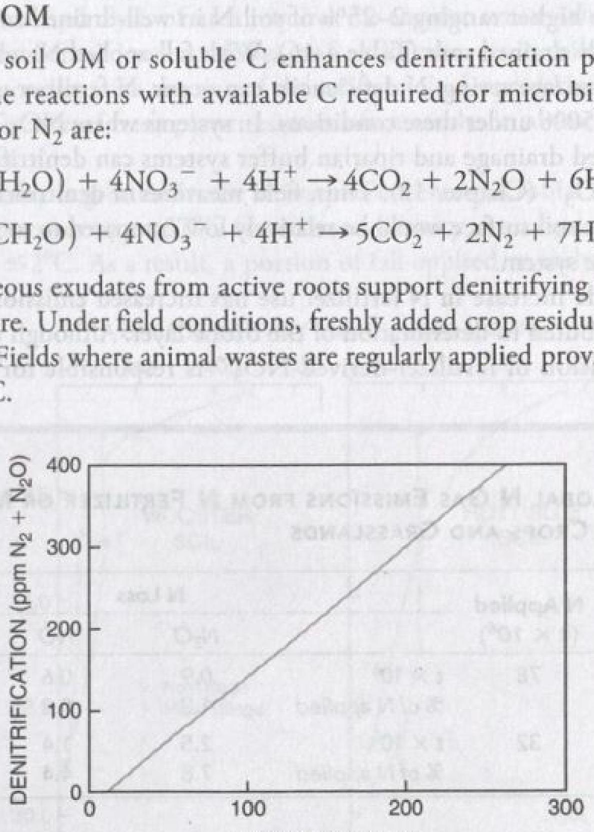


Figure 4-43
Relationship between denitrification capacity and water-soluble organic C.
(Burford and Bremner, 1975, Soil Biol. Biochem., 7:389.)

Soil pH

Denitrifying bacteria are sensitive to low pH; however, denitrification has been observed over a wide range in soil pH. Generally, formation of NO occurs at pH < 5.5, whereas at pH < 6.0–6.5 N_2O represents more than half of the N loss. N_2 is the primary compound observed at near neutral or greater pH.

Temperature

Denitrification increases rapidly in the 2–10°C range. Denitrification will proceed at slightly higher rates when temperature is increased to 25–60°C, but is inhibited by temperatures >60°C. The increase in denitrification at elevated soil temperatures suggests that thermophilic microorganisms play a major role in denitrification.

Rapid conversion of NO_3^- to N_2O or N_2 occurs when rain saturates a warm soil. Denitrification losses of 10–30 lb N/a following saturation have been measured. Saturation during spring snowmelt may cause N losses related to accelerated denitrification rates when soils are quickly warmed from 2 to 12°C or higher.

Agricultural and Environmental Significance of Denitrification Under reducing conditions, NO_3^- is subject to denitrification losses to the atmosphere. Since the earth's atmosphere is largely N_2 and the oceans are virtually NO_3^- free, denitrification is responsible for returning N_2 to the atmosphere (Fig. 4-2).

Two categories of N loss by denitrification exist: (1) rapid and extensive flushes associated with heavy rains, irrigation, and snowmelt; and (2) continuous small losses over extended periods in anaerobic microsites. Generally, as soil water-filled pore space increases >70–80%, loss of NO, N_2O, and N_2 increases (Fig. 4-39). Under conditions of high soil NO_3^-, temperature, and water content (low O_2), denitrification losses can reach 1 lb N/ac/day. While difficult to quantify, denitrification losses generally represent a small percentage of fertilizer N applied, and is usually greater with manure N (Table 4-15). Under high rainfall or irrigated conditions, denitrification loss can be higher ranging 2–25% of soil N in well-drained soils, compared to 6–55% in poorly drained soils (Table 4-16). With fall-applied N, when heavy winter snows persist into late spring, N deficiencies can occur. N fertilizer use efficiency can be reduced 25–50% under these conditions. In systems where NO_3^- enters drainage water, controlled drainage and riparian buffer systems can denitrify relatively large quantities of NO_3^- (Chapter 12). Thus, field measures of denitrification of fertilizer N applied to the soil surface would be relatively low compared to total eventual denitrification in the system.

Worldwide increase in N fertilizer use has increased emissions of N_2O from soils and contributed to deterioration of the ozone layer. Although there is evidence that denitrification of fertilizer-derived NO_3^- is responsible for N_2O emission,

TABLE 4-15
ANNUAL GLOBAL N GAS EMISSIONS FROM N FERTILIZER OR MANURE APPLIED TO CROPS AND GRASSLANDS

N Source	N Applied ($t \times 10^6$)		N Loss		
			N_2O	*NO*	*NH_3*
Fertilizer	78	*$t \times 10^6$*	0.9	0.6	11.2
		% of N applied	1.2	0.8	14.4
Manure	32	*$t \times 10^6$*	2.5	1.4	7.8
		% of N applied	7.8	4.4	24.4

Source: US EPA, 2007.

Table 4-16

Denitrification Estimates for Various Soils and Recommended Adjustments for Tillage, Manure, Irrigation, and Soils

Soil OM Content	Soil Drainage Classification *Excessively well drained*	*Well drained*	*Moderately well drained*	*Somewhat poorly drained*	*Poorly drained*
%	*% inorganic soil N denitrified (all sources)*[1]				
<2	2–4	3–9	4–14	6–20	10–30
2–5	3–9	4–16	6–20	10–25	15–45
>5	4–12	6–20	10–25	15–35	25–55

[1] Sources are primarily fertilizer, irrigation, precipitation, soil N not due to fertilizer. Site-specific adjustments: No-tillage or compacted layer below tillage depth use one wetter drainage class; manure N double all values; tile-drained soils use one drier drainage class; paddy systems use poorly drained only; irrigation or humid climates use value at upper end of range; semi-arid/arid sites (nonirrigated) use value at lower end of range.

Source: Meisinger and Randall, 1991. *In* Managing N for Groundwater Quality and Farm Profitability (pp. 85–122). *SSSA, Madison, Wis.*

contributions from natural transformations of soil OM and fresh crop and animal waste residues also contribute to N_2O emission.

Volatilization of NH_3

NH_3 is a natural product of N mineralization of which only small amounts are volatilized compared to NH_3 volatilization from surface-applied N fertilizers and manure (Fig. 4-2). The reversible reaction is:

$$NH_4^+ \leftrightarrows NH_3 + H^+ \ (pKa = 9.3)$$

Urea and other amines are products of N mineralization (aminization) and ammonification of urea mineralized from soil OM could be subject to NH_3 volatilization. The biological hydrolysis of urea requires the enzyme *urease,* which is abundant in soils. Large numbers of bacteria, fungi, and actinomycetes in soils possess urease. Urease activity increases with the size of the soil microbial population and with OM content. The presence of fresh plant residues often results in abundant supplies of urease (Fig. 4-44).

Urease activity is greatest in the rhizosphere where microbial activity is high. Although temperatures up to 37°C favor urease activity, urea hydrolysis occurs at temperatures of ≤2°C. As a result, a portion of fall-applied or early winter-applied

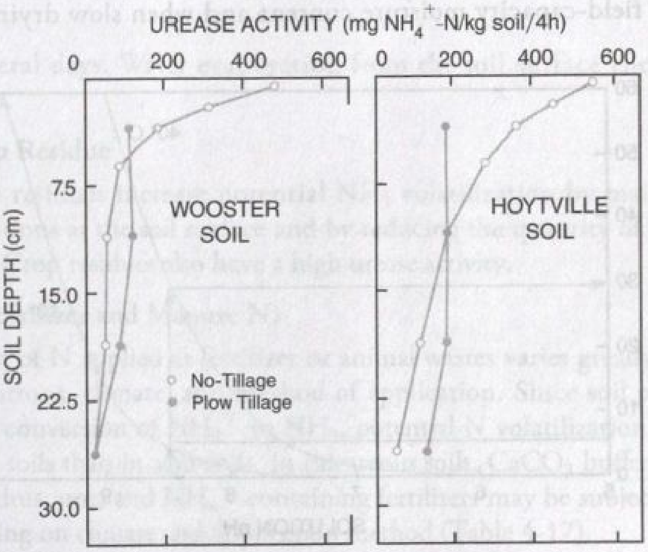


Figure 4-44

Distribution of urease activity in soil profiles as affected by tillage.

(Dick, 1984, SSSAJ, 48:569.)

urea may be converted to NH_3 or NH_4^+ before the spring. Urease activity is generally greater at optimum soil moisture content for plant growth.

While NH_3 volatilization is generally low in native unmanaged systems, adding fertilizer or manure N sources to soils can greatly increase N losses by volatilization. Understanding soil, environmental, and N management factors influencing volatilization reactions is essential to minimize NH_3 loss.

Factors Affecting Volatilization

Soil pH

Volatilization of NH_3 depends on the quantity of NH_3 and NH_4^+ in the soil solution, which is dependent on pH (Fig. 4-45). Appreciable quantities of NH_3 loss occur when soil solution pH > 7.5. When NH_4^+ fertilizers are added to acidic or neutral soils, little or no NH_3 volatilization occurs because of low soil solution pH. Recall that soil pH decreases slightly when the NH_4^+ is nitrified to NO_3^-. When NH_4^+-forming fertilizers (e.g., urea) are added to acidic or neutral soils, solution pH around the urea granule increases during hydrolysis:

$$CO(NH_2)_2 + H^+ + 2H_2O \leftrightarrows 2NH_4^+ + HCO_3^-$$

Solution pH increases above 7 because H^+ is consumed in the reaction; thus, the $NH_4^+ \leftrightarrows NH_3$ equilibrium shifts to the right to favor NH_3 loss. Therefore, in neutral and acidic soils, NH_4^+-containing fertilizers are less subject to NH_3 loss than urea and urea-containing fertilizers; however, NH_3 volatilization can occur with an NH_4^+ source depending on soil and environmental conditions (see "N Sources for Crop Production" for more detail).

Buffer Capacity (BC)

Soil BC greatly influences NH_3 volatilization loss (Fig. 4-46). Soil pH and subsequent NH_3 loss will be less in a soil with high BC compared with low BC because of increased adsorption of NH_4^+ on the CEC. Soil BC will increase with increasing CEC and OM content.

Environment

NH_3 loss by volatilization increases with increasing temperature up to about 45°C, which is related to higher reaction rates and urease activity (Fig. 4-45). With a dry soil surface, microbial activity and volatilization reaction rates are reduced (Fig. 4-47). Maximum potential NH_3 loss occurs when the soil surface is at or near field-capacity moisture content and when slow drying conditions

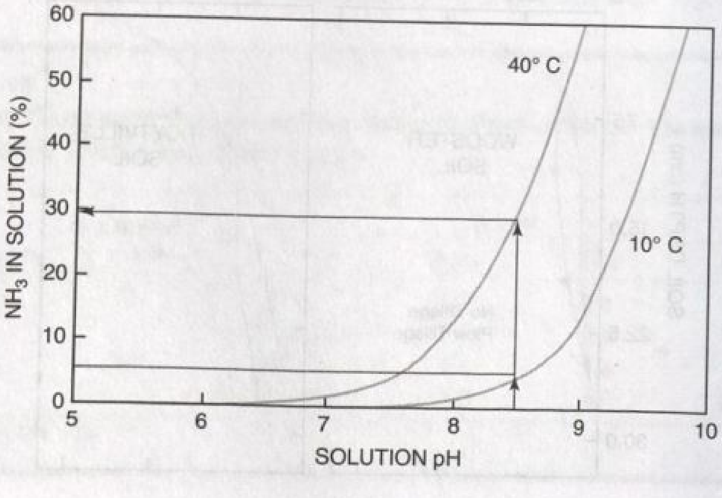


Figure 4-45
Influence of pH and temperature on the %NH_3 of total NH_3 + NH_4^+ in solution. At pH 8.5, %NH_3 in solution increases from 5 to 30% with increasing temperature.
(Adapted from Cabrera and Kissel, Univ. of Georgia, personal communication.)

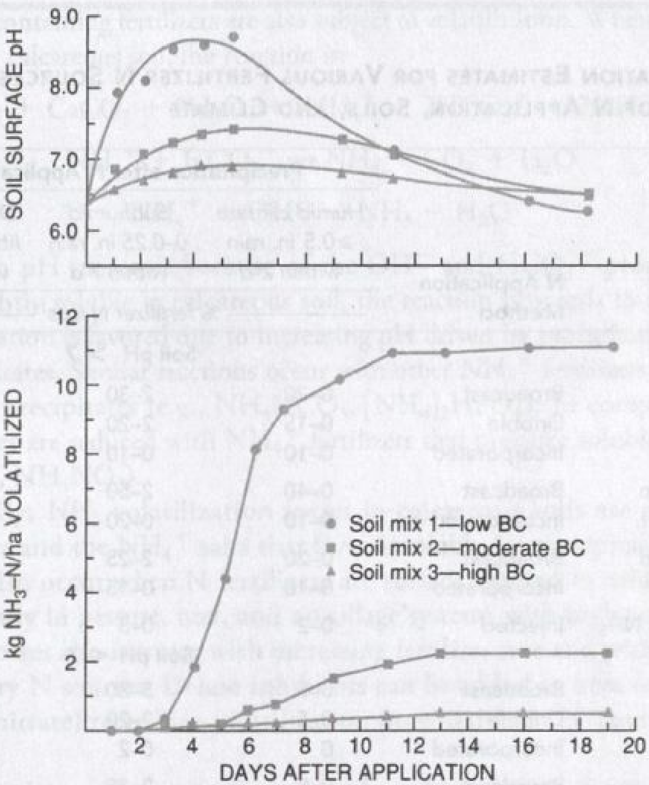


Figure 4-46
Soil BC effects on soil pH and NH_3 volatilization after N fertilizer application.
(Ferguson et al., 1984, SSSAJ, 48:578.)

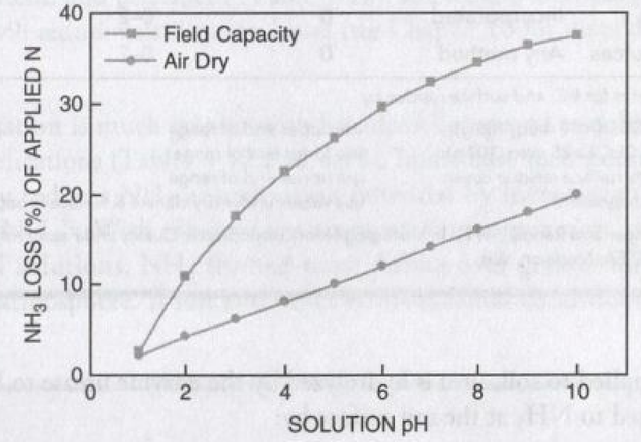


Figure 4-47
Influence of soil moisture on cumulative NH_3 loss from surface applied urea.
(Al-Kanani et al., 1991, SSSAJ, 55:1716–1766.)

exist for several days. Water evaporation from the soil surface encourages NH_3 volatilization.

Surface Crop Residue

Surface crop residues increase potential NH_3 volatilization by maintaining wet, humid conditions at the soil surface and by reducing the quantity of urea diffusing into the soil. Crop residues also have a high urease activity.

N Source (Fertilizer and Manure N)

Volatilization of N applied as fertilizer or animal wastes varies greatly and depends on soil conditions, climate, and method of application. Since soil pH has a large influence on conversion of NH_4^+ to NH_3, potential N volatilization loss is greater in calcareous soils than in acid soils. In calcareous soils, $CaCO_3$ buffers solution pH around 7.5; thus, urea and NH_4^+-containing fertilizers may be subject to volatilization, depending on climate and application method (Table 4-17).

TABLE 4-17
VOLATILIZATION ESTIMATES FOR VARIOUS FERTILIZER N SOURCES, METHOD OF N APPLICATION, SOILS, AND CLIMATE

Fertilizer N Source	N Application Method	Precipitation after N Application *Humid climate ≥0.5 in. rain within 2 d*	 *Subhumid 0–0.25 in. rain within 7 d*	 *Dry climate little/no rain within 7 d*
		% fertilizer N loss[1]		
			Soil pH > 7	
Urea or UAN	Broadcast	0–20	2–30	2–40
	Dribble	0–15	2–20	2–30
	Incorporated	0–10	0–10	0–10
Ammonium sulfate	Broadcast	0–40	2–50	5–60
	Incorporated	0–10	0–20	0–30
Ammonium nitrate	Broadcast	0–20	2–25	5–30
	Incorporated	0–10	0–15	0–20
Anhydrous NH_3	Injected	0–2	0–3	0–5
			Soil pH < 7	
Urea	Broadcast	0–5	5–30	5–40
	Dribble	0–5	2–20	2–30
	Incorporated	0	0–2	0–2
UAN	Broadcast	0–5	2–15	2–20
	Dribble	0–5	2–10	2–15
	Incorporated	0	0–2	0–2
Other N sources	Any method	0	0–2	0–2

[1] Adjust estimates for BC, and surface residue by:

low CEC (<10 meq/100 g):	use upper end of range
high CEC (>25 meq/100 g):	use lower end of range
>50% surface residue cover:	use upper end of range
paddy systems:	use values under dry climate & surface broadcast

Source: Meisinger and Randall, 1991. In Managing N for Groundwater Quality and Farm Profitability *(pp. 85–122)*. SSSA, Madison, Wis.

When applied to soil, urea is hydrolyzed by the enzyme urease to NH_4^+, which can be converted to NH_3 at the soil surface by:

$$CO(NH_2)_2 + H^+ + 2H_2O \leftrightarrows 2NH_4^+ + HCO_3^-$$
$$\downarrow$$
$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O$$

Solution pH increases (~8–9 pH) near the dissolving urea granule because of the HCO_3^- produced, increasing volatilization potential.

Urea hydrolysis proceeds rapidly in warm, moist soils, with most of the urea converted to NH_4^+ in several days. Conditions for best performance of surface-applied urea are cold, dry soils at the time of application and/or the occurrence of significant precipitation (0.25–0.5 in.) within the first 3–6 days after application. Movement of soil moisture containing dissolved NH_3 and diffusion of moisture vapor to the soil surface during the drying process contribute to NH_3 volatilization at or near the soil surface.

NH_4^+-containing fertilizers are also subject to volatilization. When $(NH_4)_2SO_4$ is applied to a calcareous soil, the reaction is:

$$(NH_4)_2SO_4 + CaCO_3 + 2H_2O \rightarrow 2NH_4^+ + 2HCO_3^- + 2OH^- + CaSO_4$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O$$

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

Solution pH increases because of the OH^- and HCO_3^- produced. Since $CaSO_4$ is slightly soluble in calcareous soil, the reaction proceeds to the right and NH_3 volatilization is favored due to increasing pH driven by precipitation of insoluble Ca precipitates. Similar reactions occur with other NH_4^+ fertilizers that produce insoluble Ca precipitates (e.g., NH_4HCO_3, $[NH_4]_2HPO_4$). In comparison, volatilization losses are reduced with NH_4^+ fertilizers that produce soluble Ca reaction products (e.g., NH_4NO_3).

Generally, NH_3 volatilization losses in calcareous soils are greatest with urea fertilizers and the NH_4^+ salts that form insoluble Ca precipitates. However, NH_3 losses also occur when N fertilizers are surface applied to acid soils (Table 4-17), especially in pasture, turf, and no-tillage systems with high surface residue cover. NH_3 losses also increase with increasing fertilizer rate and with liquid compared with dry N sources. Urease inhibitors can be added to urea or UAN (urea ammonium nitrate) to reduce volatilization potential (see "N Sources for Crop Production").

Volatilization of N in animal waste can be as high as 40% depending on waste source, N content, and placement (Table 4-18). Immediate incorporation of broadcast manure will reduce volatilization losses (see Chapter 10 for more detail).

N Placement

NH_3 volatilization is much greater with broadcast compared to subsurface or surface band applications (Tables 4-17 and 4-18). Immediate incorporation of broadcast N greatly reduces NH_3 volatilization potential by increasing the volume of soil to retain NH_4^+. With subsurface placement or incorporation of urea or urea-containing N solutions, NH_3 formed must diffuse over greater distances before reaching the atmosphere. If soil and other environmental conditions are favorable

TABLE 4-18
VOLATILIZATION ESTIMATES FROM MANURE APPLIED TO SOILS

		Time after Application	
		Short Term	*Long Term*
Manure Type	**Manure Application Method**	*— % manure N loss —*	
Solid	Broadcast, no incorporation	15–30	25–45
Liquid		10–25	20–40
Solid	Broadcast, immediate incorporation	1–5	1–5
Liquid		1–5	1–5
Liquid	Broadcast	15–35	20–40
	Knifed	0–2	0–2

Source: Meisinger and Randall, 1991. In Managing N for Groundwater Quality and Farm Profitability *(pp. 85–122). SSSA, Madison, Wis.*

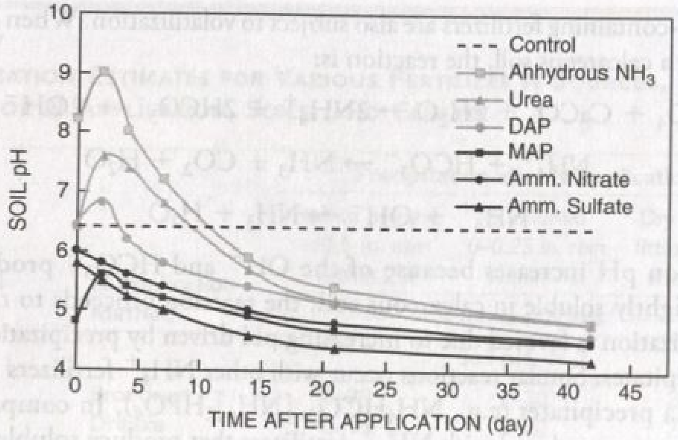


Figure 4-48
Generalized effect of band-applied N fertilizers on soil pH in the band. NH_4^+/NH_3 produced with NH_3, urea, and DAP initially raises soil pH. With time nitrification of added NH_4^+ will decrease pH below the unfertilized soil pH (see nitrification reaction in Table 3-3). Ultimately $(NH_4)_2SO_4$ is more acid forming than any N source (see Table 3-5).
(Adapted from Mulvaney et al., 1997, *Biol. Fert. of Soils, 24:211–220.*)

for NH_3 volatilization, deep incorporation is preferred over shallow surface tillage. Some of the N losses from broadcast UAN with high surface residue cover are due to N immobilization.

Band placement of urea results in soil changes comparable to those produced by applications of anhydrous NH_3 (Fig. 4-48). Diffusion of urea from banded applications can be 2.5 cm (1 in.) within 2 days, while appreciable NH_4^+ can be observed at distances of 3.8 cm (1.5 in.) from the band. After dilution or dispersion of the band by moisture, hydrolysis begins within a few days under favorable temperature conditions.

Agricultural and Environmental Significance of Volatilization Although substantial losses of NH_3 from various N sources have been measured in laboratory studies, their validity should be closely examined. Experimental systems can impose artificial conditions of air movement, temperature, and relative humidity different from those occurring in the field. For example, NH_3 volatilization losses as high as 70% of fertilizer N have been reported from laboratory studies.

Field studies conducted under a wide range of conditions show that volatilization losses with $(NH_4)_2SO_4$ broadcast on a calcareous soil can be about 50% of the fertilizer N applied, while NH_3 volatilization losses can be as high as 30% with urea in field crop systems, and can be much higher in turf systems. In acid soil, NH_3 losses are greater for urea than for $(NH_4)_2SO_4$. Typical NH_3 losses in arable systems are usually <25% in low-pH soils and about double this amount in high-pH soils. In flooded rice systems, NH_3 loss has been reported as high as 75% of applied N.

In general, N source effects on NH_3 loss decrease with $NH_4HCO_3 > (NH_4)_2SO_4 \geq CO(NH_2)_2 > NH_4NO_3$. Increasing N rate significantly increases NH_3 volatilization. Volatilization loss is minimal when soil $pH < 5$, but greatly increases up to pH 8.5. Potential NH_3 volatilization increases with temperature. As temperature approaches 35–45°C, nitrification of NH_4^+ is reduced, which increases availability of NH_4^+ for NH_3 volatilization.

Soil and environmental conditions conducive to maximizing NH_3 losses are high soil pH, low BC, broadcast/unincorporated urea-containing fertilizer or manures, and warm/moist surface soil conditions (Table 4-19). When optimum conditions exist for N volatilization, utilizing urease inhibitors with urea-based products can reduce NH_3 volatilization and increase N use efficiency (see "Urease and Nitrification Inhibitors").

NH_3 Exchange by Plants NH_3 absorption and loss occur in plant leaves. The quantity depends on soil-surface wetness and extent of evaporation, which influence the amount of NH_3 released into the air coming into contact with plant canopies.

TABLE 4-19
SUMMARY OF RELATIVE RISK FACTORS FOR NH_3 VOLATILIZATION

Condition	High Risk	Low Risk
Soil pH	>7	<6
Soil moisture	Moist	Dry
Rainfall, irrigation	Little or none, heavy dew	>0.3 in. after N applied
CEC (meq/100g)	<10	>25
Soil temperature	>20°C (70°F)	<10°C (50°F)
Soil surface	>50% residue cover (turf, pasture, no-till)	Bare
N source[1]	Manure, $(NH_4)_2SO_4$, $CO(NH_2)_2$, UAN, NH_4HCO_3	NH_3, NH_4NO_3 (urea/UAN + inhibitor)[1]
N application	Surface broadcast	Incorporate, subsurface apply

[1] NBPT is a common urease inhibitor (see Table 4-24). If using urea/UAN on high-risk site, consider using a urease inhibitor.

Field crops exposed to air containing normal levels of atmospheric NH_3 may obtain 5–10% of their N requirement by direct absorption of NH_3. Plant seedlings are a natural sink for atmospheric NH_3, absorbing about 40% of the NH_3 from air containing 1 ppm NH_3. NH_3 produced near the ground surface of grass-clover pasture can be completely absorbed by the plant cover. NH_3 volatilization from plant foliage also occurs during ripening and senescence, with values ranging 10–30 lb N/ac/yr.

N SOURCES FOR CROP PRODUCTION

Both organic and inorganic N sources supply the N required for optimum crop growth. Efficient management of N inputs requires understanding N cycling and transformations in soils (Fig. 4-2). Management practices that minimize N losses and maximize the quantity of applied N recovered by the crop will increase production efficiency and reduce potential impacts of N use on the environment. N management technologies are discussed in greater detail in Chapter 10, but the commonly available N sources used in agricultural production systems and their reactions with soil are presented here.

Inorganic N Sources

Manufactured fertilizers are the most important sources of N to plants. Over the last 30 years, world N consumption has increased from 60 to 110 million metric tons (Fig. 4-1).

Anhydrous NH_3 is the basic building block for almost all chemically derived N fertilizer materials (Fig. 4-49). NH_3 is manufactured using the Haber-Bosch reaction with N_2 from the air and H_2 produced from natural gas (CH_4) (Fig. 4-18). Since CH_4 is a limited resource (fossil fuel) and is also used for heating, cooking, and so on, conservation of this vital resource is essential. Increasing demand for CH_4 and decreasing supply increase CH_4 cost, subsequently increasing fertilizer N costs (Chapter 11).

Worldwide about 74% of NH_3 produced is used to manufacture other N fertilizer materials, while 3% is applied directly to soil and the remaining 23% accounts for non-fertilizer uses (Fig. 4-50). In the United States, N solutions, urea, and anhydrous NH_3 account for nearly 90% of total fertilizer N use (Fig. 4-51). The United States

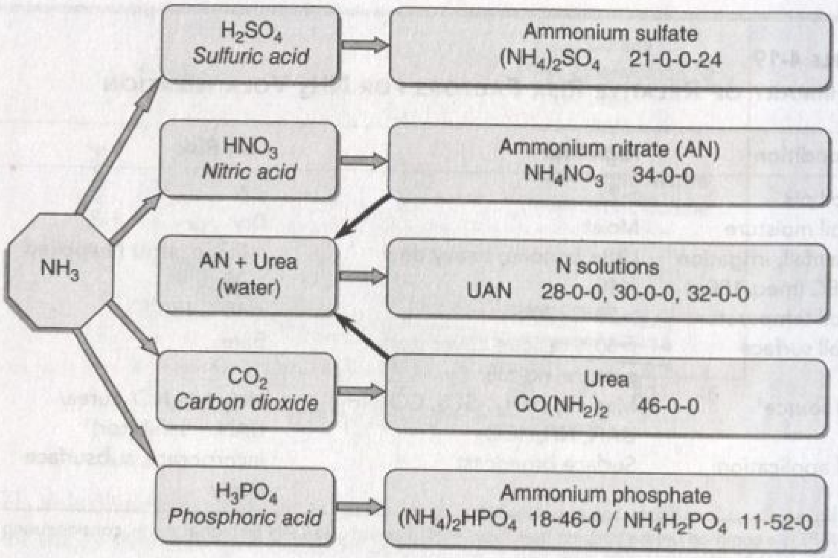


Figure 4-49
Simplified schematic of common N fertilizers manufactured from NH_3.

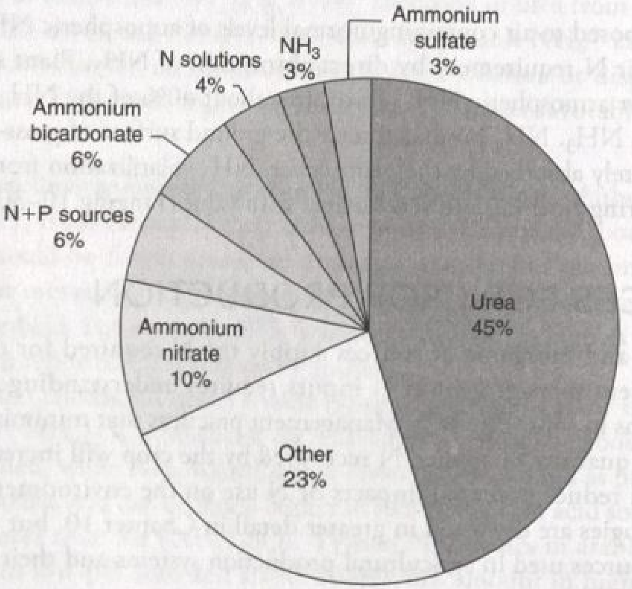


Figure 4-50
Global use of NH_3.

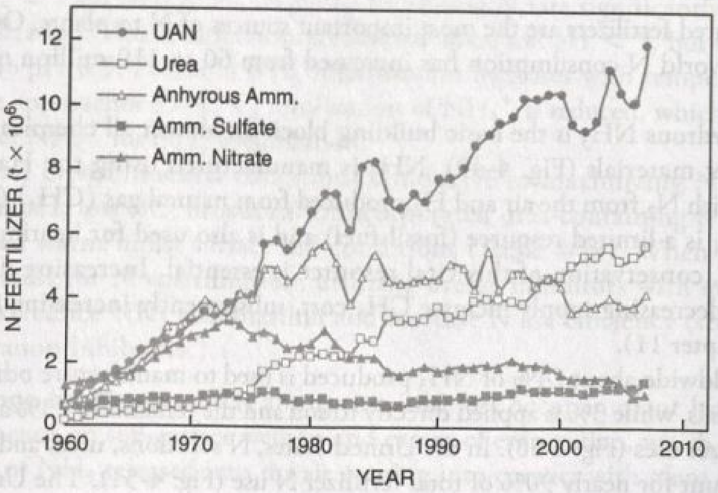


Figure 4-51
Common N sources used in the United States.
(USDA-ERS, 2009.)

and Canada represent nearly all of the direct NH_3 application in agriculture. For convenience, the various N compounds are grouped into three categories: ammoniacal, nitrate, and slowly available (Table 4-20).

NH_4^+ or NH_4^+-Forming Sources

Urea $[CO(NH_2)_2]$

Favorable manufacturing, handling, storage, and transportation economics make urea a competitive N source. It is the most widely used N source in the world. Urea represents ~21% of total fertilizer N use in the United States (Fig. 4-51). Granular urea has noteworthy characteristics, including (1) less tendency to stick and cake than NH_4NO_3, (2) no risk of explosion, and (3) less corrosive to handling and application equipment. Substantial savings in handling, storage, transportation, and application costs are possible because of urea's high N content (Table 4-20).

During manufacturing, biuret (NH_2-CO-NH-CO-NH_2) concentration in urea is kept low due to its phytotoxicity. Biuret levels of 2% can be tolerated in most fertilizers, unless applied to sensitive crops (i.e., citrus, pineapple, and other crops) where $<0.25\%$ is recommended. Solutions made from urea containing $<1.5\%$ biuret are acceptable for foliar application. Urea high in biuret should not be placed near or in the seed row. Biuret is not a problem in most urea products.

As discussed in the previous section (Volatilization of NH_3), careful management of urea and urea-based fertilizers will reduce the potential for NH_3 volatilization losses and increase effectiveness of urea fertilizers. Surface applications of urea are most efficient when they are applied to soils with low volatilization potential. Incorporation with tillage or dissolved into the soil with irrigation or adequate rainfall

TABLE 4-20
COMPOSITION OF SOME COMMON SOLUBLE FERTILIZER N SOURCES

	Nutrient Content (%)							
N Source	*N*	*P_2O_5*	*K_2O*	*Ca*	*Mg*	*S*	*Cl*	Physical State
				NH_4^+ or NH_4^+ forming				
Anhydrous ammonia	82	—	—	—	—	—	—	Gas
Aqua ammonia	20–25	—	—	—	—	—	—	Liquid
Ammonium bicarbonate	21–23	—	—	—	—	—	—	Solid
Ammonium chloride	25–26	—	—	—	—	—	66	Solid
Ammonium nitrate	33–34	—	—	—	—	—	—	Solid
Ammonium sulfate	21	—	—	—	—	24	—	Solid
Ammonium thiosulfate	12	—	—	—	—	26	—	Liquid
Calcium ammonium nitrate	15–27			9–19				Solid or Liquid
Ammonium polyphosphate	10–11	34–37	—	—	—	—	—	Liquid
Diammonium phosphate	18–21	46–54	—	—	—	—	—	Solid
Monoammonium phosphate	11	48–55	—	2	0.5	1–3	—	Solid
Urea	45–46	—	—	—	—	—	—	Solid
Urea-ammonium nitrate	28–32	—	—	—	—	—	—	Liquid
Urea-ammonium phosphate	21–38	13–42	—	—	—	—	—	Solid
Urea phosphate	17	43–44	—	—	—	—	—	Solid
Urea-sulfate	30–40	—	—	—	—	6–11	—	Solid
				NO_3^-				
Calcium nitrate	15	—	—	34	—	—	—	Solid
Potassium nitrate	13	—	44	0.5	0.5	0.2	1.2	Solid
Sodium nitrate	16	—	—	—	—	—	0.6	Solid

TABLE 4-21
NO-TILL CORN GRAIN YIELD AS AFFECTED BY UAN RATE AND METHOD OF APPLICATION

N Rate	Broadcast	Surface Band	
		Unincorporated	*Incorporated*
lb/a	*bu/a*		
80	89	118	125
160	108	133	141
240	114	139	154

Reduced yield with broadcast N is related to both N loss to volatilization and immobilization.

Source: Touchton and Hargrove, 1982, *Agron. J.*, 74:825.

after application will enhance N availability with urea (Table 4-21). Use of coated urea products will also reduce N volatilization losses (see "Controlled and Slow Release Compounds").

Placement of urea with the seed at planting should be carefully controlled because of the toxic effects of free NH_3 on germinating seedlings (see reactions in "Volatilization of NH_3"). The harmful effects of urea placed in the seed row can be eliminated or greatly reduced by banding at least 2.5 cm (1 in.) directly below and/or to the side of the seed row of most crops. Seed-placed urea should not exceed 5–10 lb N/a.

The effect on germination of urea placed near seeds is influenced by available soil moisture. With adequate soil moisture in medium-textured soils, urea at 30 lb N/a can be used without reducing germination and crop emergence. However, in low moisture, coarse-textured soils, urea at 10–20 lb N/a often reduces both germination and crop yields. Seedbed moisture is less critical in fine-textured (clay and clay loam) soils, and urea can usually be drilled in at rates of up to 30 lb N/a.

To summarize, the effectiveness of urea depends on the interaction of many factors, which cause some variability in the crop response to urea. However, if managed properly, urea can be as effective as other N sources (also see "Urease and Nitrification Inhibitors").

N Solutions

Of the liquid N fertilizers used for direct application, N solutions are most common, representing 44% of total N consumption in the United States (Fig. 4-51). Some advantages of N solutions include:

- easier and safer to handle and apply than other N fertilizers (especially NH_3)
- applied more uniformly and accurately than solid N sources
- many pesticides are compatible with N solutions, allowing simultaneous application
- applied through various types of irrigation systems
- excellent source for use in formulation of fluid N, P, K, and S fertilizers

N solutions are usually produced from urea, NH_4NO_3, and water and are referred to as UAN solutions (Fig. 4-49; Table 4-20). Each UAN solution has a specific salting-out temperature, below which dissolved fertilizer salts precipitate. The salting-out temperature determines feasibility of outside winter storage and the time of year for application. Salting-out temperatures vary with N concentration in solution (Table 4-22).

TABLE 4-22
PHYSICAL AND CHEMICAL CHARACTERISTICS OF UAN

	Fertilizer Grade (% N by weight)		
Composition and Properties	*28%*	*30%*	*32%*
Ammonium nitrate, NH_4NO_3 (%)	40	42	45
Urea, $CO(NH_2)_2$ (%)	30	33	35
Water (%)	30	25	20
Density (lbs/gal) at 15.5°C (60°F)	10.65	10.84	11.06
Salting-out temperature, °C (°F)	−17 (+1)	−10 (+14)	−2 (+28)

Anhydrous NH_3

Anhydrous NH_3 contains 82% N, the highest N content of any fertilizer (Table 4-20). About 16% of all N fertilizer used in the United States is applied as NH_3. Over the last several decades, NH_3 use in the United States has declined as urea and UAN use has increased (Fig. 4-51).

Like H_2O, NH_3 can exist as a solid, liquid, and gas depending on temperature. At room temperature, NH_3 is a colorless, highly irritating gas with a pungent, suffocating odor. NH_3 gas dissolves easily in water to form ammonium hydroxide (NH_4OH), a weak base. NH_3 gas is easily compressed and forms a clear liquid under pressure, which is stored and shipped as a compressed liquid in steel containers. NH_3 is not highly flammable, but can explode when exposed to high heat. When liquid NH_3 is released from a pressurized tank, it expands rapidly, vaporizes, and produces a white cloud of water vapor formed by water condensation in the air surrounding NH_3 as it vaporizes.

Anhydrous NH_3 is hygroscopic and is rapidly absorbed by water. Because NH_3 is very irritating to the eyes, lungs, and skin, safety precautions must be taken with anhydrous NH_3. Safety goggles, rubber gloves, and an NH_3 gas mask are required safety equipment. A large container of water attached to NH_3 application equipment is required for washing skin and eyes exposed to NH_3. Current regulations require certification for anyone applying NH_3.

Because anhydrous NH_3 is a gas at atmospheric pressure, some may be lost to the atmosphere during and after application (Chapter 10). If the soil is hard or full of clods during application, the slit behind the applicator blade will not close or fill, and some NH_3 escapes to the atmosphere.

NH_3 reacts rapidly with soil water and various organic and inorganic soil components through several possible reactions:

- $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
- $NH_3 + H^+ \rightarrow NH_4^+$
- reaction with OH^- groups and tightly bound water of clay minerals
- reaction with water of hydration around exchangeable cations on CEC
- reaction with OM
- NH_4^+ fixation by expanding clay minerals
- adsorption by clay minerals and organic components through H-bonding

Immediately after NH_3 injection, a localized zone high in both NH_3 and NH_4^+ is created (Fig. 4-52). The horizontal, roughly circular- to oval-shaped zone is about 2–5 in. in diameter, depending on several factors influencing NH_3 retention in soil:

> *Soil moisture content* → NH_3 retention increases with soil moisture content, with maximum retention occurring at or near field capacity. As soils become

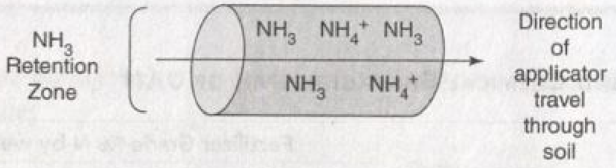


Figure 4-52
Diagram of an NH_3 retention zone.

drier or wetter than field capacity, they lose their ability to hold NH_3. The size of the initial retention zone decreases with increasing soil moisture. Diffusion of NH_3 from the injection zone is impeded by high soil moisture, because of the strong affinity of NH_3 for water.

Clay content → NH_3 retention increases with the clay content. NH_3 diffusion is greater in sandy soils than in clay soils due to larger pores and lower retention capacity of soil colloids.

Injection depth → NH_3 retention increases with increasing depth of injection and varies considerably, depending on soil properties and conditions. Deeper injection depths are required for sandy soils compared to clay soils. In dry soil, NH_3 loss declines with increasing placement depth.

Injection spacing → At a given N rate, NH_3 applied per unit volume of soil decreases with decreasing injection spacing. With the greater retention achieved with narrow spacing, there is less chance of NH_3 loss, especially in sandy soils with limited NH_3 retention capacity.

Soil OM → NH_3 retention increases with increasing soil OM. At least 50% of the NH_3 retention capacity is due to OM.

Temporary changes in soil chemical, biological, and physical conditions occur in the NH_3 retention zone. High NH_3 and NH_4^+ levels ($\approx$1,000–3,000 ppm) produce high soil pH ($\geq$9) and osmotic potential ($\geq$10 bar), resulting in partial and temporary sterilization of soil within the retention zone. NH_3 is toxic to microorganisms, higher plants, and animals. Bacterial activity is probably affected most by free NH_3, while fungi are depressed by the high pH in the retention zone. Partial sterilization in the retention zone can persist for several weeks. As a consequence of reduced microbial activity, nitrification of NH_4^+ will be reduced until conditions return to normal.

The OH^- produced by the reaction of NH_3 with H_2O will dissolve or solubilize soil OM. Most of these effects on OM are only temporary. Solubilization of OM may temporarily increase the availability of nutrients associated with OM.

Contrasting beneficial and harmful effects on soil structure have been reported following use of anhydrous NH_3. Several long-term studies have shown no difference among N sources on soil physical properties. Impairment of soil structure is not expected to be serious or lasting except in situations involving low-OM soils, in which any loss of OM would likely be harmful.

Aqua NH_3

The simplest N solution is aqua NH_3, which is made by forcing compressed NH_3 gas into water, and contains 25–29% NH_3 by weight (Table 4-20). Transportation and delivery costs limit aqua NH_3 production to small, local fluid-fertilizer plants. Aqua NH_3 is used for direct soil applications or to produce other liquid fertilizers. The NH_3 will volatilize quickly at temperatures above 50°F; thus, aqua NH_3 is usually injected into soil to depths of 2–4 in. At temperatures over 50°F, surface applications of aqua NH_3 should be immediately incorporated into the soil.

Ammonium Nitrate (NH_4NO_3)

NH_4NO_3 contains 33–34% N and is manufactured by reacting nitric acid (HNO_3) with NH_3 (Fig. 4-49). Use of NH_4NO_3 in the United States has declined, and for internal security reasons, it is now banned in some countries (Fig. 4-51).

NH_4NO_3 dissolves to NO_3^- and NH_4^+ and is readily available to crops. Several disadvantages of NH_4NO_3 include:

- hygroscopic compound (absorbs water) that results in caking during storage
- high risk of explosion when combined with oxidizable C (oil, diesel fuel, gasoline, etc.)
- less effective for flooded rice than urea or NH_4^+ fertilizers
- more prone to leaching and denitrification than NH_4^+-only products

Ammonium sulfate nitrate (Sulf-N 26) was recently released as an N source that eliminates the explosive properties of NH_4NO_3. The product (26% N, 14% S) is too new in the marketplace to report agronomic responses; however, its behavior in soil would be similar to NH_4NO_3 and $(NH_4)_2SO_4$.

Ammonium Sulfate [$(NH_4)_2SO_4$]

Ammonium sulfate represents only about 5% of total N fertilizer use in the United States (Fig. 4-51). The advantages of $(NH_4)_2SO_4$ include low hygroscopicity and is a source of both N and S. $(NH_4)_2SO_4$ depresses soil pH greater than other N sources (Table 3-5). The main disadvantage of $(NH_4)_2SO_4$ is its relatively low N content (21% N) compared to other sources; however, it can be an economical N source when S is also required.

Ammonium Phosphates

Monoammonium ($NH_4H_2PO_4$) and diammonium [$(NH_4)_2HPO_4$] phosphates are more important P sources than N sources (see Chapter 5).

Ammonium Chloride (NH_4Cl)

NH_4Cl contains 25% N (Table 4-20). The majority of NH_4Cl is used in Japan, China, India, and Southeast Asia. Some of its advantages include higher N concentration than $(NH_4)_2SO_4$ and is superior to $(NH_4)_2SO_4$ for rice. NH_4Cl is an excellent N source for Cl responsive crops (i.e., coconut, oil palm, kiwifruit). NH_4Cl is as acid forming as $(NH_4)_2SO_4$ per unit of N and, thus, is undesirable in acid soils requiring lime. Other shortcomings are its low N content compared to urea or NH_4NO_3, and its high Cl^- content, which limits its use to Cl^- tolerant crops.

Ammonium Bicarbonate (NH_4HCO_3)

This low-analysis N source (19% N) is commonly used in China (25% of total fertilizer N use), but is now being phased out in favor of urea because of its relatively low quality and instability. It is manufactured by passing CO_2 into a concentrated solution saturated with NH_3. At room temperature, NH_4HCO_3 is a white, crystalline powder that dissolves in water to produce a $pH \approx 8$. Applied to warm, moist soils NH_4HCO_3, NH_3 volatilization potential is higher than with urea.

Urea-Based Fertilizers

Urea phosphate [$CO(NH_2)_2H_3PO_4$] is a crystalline product formed by the reaction of urea with phosphoric acid. The common grade is 17-44-0, which is primarily used to produce other grades of lower analysis. Urea phosphates with lower purity standards may be adequate for production of suspension fertilizers and for fertigation. Urea has also been combined with $(NH_4)_2HPO_4$ into a solid 28-28-0.

Granular urea sulfate with grades ranging from 40-0-0-4 to 30-0-0-13 has been produced. The N:S ratio may vary from 3:1 to 7:1, providing enough flexibility to correct N and S deficiencies in crops. Although numerous urea-based fertilizers have been produced in pilot plants, they are not commonly used in North America.

NO_3^- Sources In addition to NH_4NO_3, sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), and calcium nitrate $Ca(NO_3)_2$ should be mentioned because of their importance in certain regions (Table 4-20). NO_3^- sources are soluble and mobile in soil, and therefore susceptible to leaching. Unlike NH_4^+ fertilizers, NO_3^- salts are not acid forming. Because NO_3^- is absorbed by crops more rapidly than the accompanying cation, HCO_3^- and organic anions are exuded from roots, resulting in a slightly higher soil solution pH (Chapter 2). Prolonged use of $NaNO_3$, for example, will maintain or even raise the original soil pH; however, this product should not be used in semi-arid and arid climates because of buildup of exchangeable Na (Chapter 3).

At one time, $NaNO_3$ (16% N) was a major source of N in many countries. Most of it originated in large natural deposits in Chile, where $NaNO_3$ production continues to be a major industry.

Potassium nitrate (KNO_3, 13% N) contains two essential plant nutrients and is a common source in vegetable and tree crops. KNO_3 properties that make it attractive include moderate salt index, rapid NO_3^- uptake, favorable N/K ratio, and negligible Cl^- content.

Calcium Ammonium Nitrate (CAN)

Two commercial products are available that contain different amounts of Ca^{+2} and N (Table 4-20). The most common product in the United States contains $Ca(NO_3)_2 + NH_4NO_3$ (17% N, 8.8% Ca) and is available as a solid or liquid. This product is used on vegetable and tree crops in California, Arizona, and the Pacific Northwest. The value of Ca^{+2} in this material is likely through its positive effect on maintaining the integrity of plant cell membranes (Chapter 2) to enhance cation uptake, referred to as the Viets effect.

Another granular CAN product contains $CaCO_3 + NH_4NO_3$ (27% N, 8% Ca; or 15% N, 19% Ca), helps neutralize acid produced through nitrification of NH_4^+ (Table 3-5), and eliminates potential combustion hazards of NH_4NO_3. This product is commonly used in China and Europe.

Controlled and Slow Release Compounds Because the crop recovery of soluble fertilizer N is $\leq 50\%$, development of N fertilizer products that potentially minimize fertilizer N losses through volatilization, denitrification, and leaching have been developed (Table 4-23). Use of controlled release fertilizer (CRF) or slow release fertilizer (SRF) may improve N use efficiency, while reducing environmental risk of N use. Compared to the major N sources used throughout the world, SRF and CRF use is small, but has nearly doubled in the last decade. North America, Japan, and Europe are the major consumers, primarily in non-agricultural markets (e.g., turf and horticulture) with increasing use in production agriculture.

SRFs represent products where N release is reduced but not well controlled. CRFs are products where the rate and duration of N release is controllable. CRFs or SRFs are classified by:

- organic-N low-solubility compounds → slowly decompose by biological (e.g., urea formaldehyde) or chemical (e.g., isobutylidene diurea) processes
- fertilizer N products with a physical barrier that controls release → fertilizer N coatings include organic polymers, resins, and inorganic materials (e.g., S)
- inorganic low-solubility compounds → fertilizers such as Mg/NH_4 phosphates and partially acidulated phosphates rock (Chapter 5)

TABLE 4-23

CONTROLLED AND SLOW RELEASE N PRODUCTS USED TO REDUCE POTENTIAL N LOSSES BY LEACHING, VOLATILIZATION, AND DENITRIFICATION

			N Content	Inhibition Duration
N Source	**Base Compound**	**Common Name(s)**	— % —	— weeks —
S-coated urea	urea	SCU	30–42	4–12
		Enspan	39	
Polymer/S-coated urea	urea	PolyPlus Poly-S TriKote	38–42	6–16
		XCU	41–43	
Polymer- or resin-coated urea	urea	Polyon, Osmocote,	38–44	8–14
		Meister	25–46	
		Agriform Multicote		
		Escote		
		Prokote		
		ESN		
		Nutrisphere		
Urea formaldehyde	ureaforms	Nitroform	38	10–30+
		FLUF	18	6–10
		Folocron	29	
		GP-4340	30	
	methylene urea	Nutralene	40	7–12
		Hydrolene		
		Nitamin		
	methylol urea	Resi-Grow	30	6–10
	polymethylene urea	CoRoN	12 or 28	7–9
Isobutylidene diurea	isobutylidine urea	IBDU	31	10–16
Triazone	triazone/urea	N-Sure, Nitamin	28–33	6–10
		TriSert, Formolene		
Crotonylidene diurea	urea/crotonaldehyde	Crotodur, CDU, Triabon	34	6–12
Melamine	2,4,6 triamino-1,3,5-triazine	Nitrazine	50–60	6–12

While there is no official differentiation, generally SRFs are microbial degraded N products such as urea formaldehydes, and CRFs are commonly coated or encapsulated products.

SRF → Organic-N Low-Solubility Compounds

These SRF products reduce the rate of N released to soil solution compared to urea or other inorganic N sources. By slowly dissolving during the growing season, NO_3^- will not exceed crop utilization rate, thereby reducing potential N losses predominately through leaching, but reduced denitrification and volatilization losses are also possible.

Urea formaldehyde (UF) is the most common SRF, containing 35–40% N (Table 4-23). Urea is reacted with formaldehyde producing a mixture of UF, unreacted urea, methylol urea, and methylene urea, which can be separated into SRF products of variable solubility or N release rates. For example, methylol urea and methylene urea are more H_2O soluble than UF and, thus, release N faster. The N release rate from UF products is characterized by their solubility in water by determining the activity index (AI) given by:

- cold water (25°C) soluble N (CWSN) contains mostly unreacted urea and exhibits fast N release rate
- hot water (100°C) soluble N (HWSN) contains methylene urea and UF and is slowly released into the soil

- hot water insoluble N (HWIN) contains long-chain UF and has extremely slow N release rate

Once these values are determined, then cold water insoluble N (CWIN) is calculated by:

$$\text{CWIN} = \text{HWSN} - \text{CWSN}$$

Then AI is determined by: AI = (CWIN − HWIN)/CWIN × 100. AI represents the % of relatively long N release (~6 months). Current UF products have ≈50–60% AI values.

Applied to soil, UF products are converted to plant available N through microbial decomposition or hydrolysis. Microbial decomposition is the primary mechanism of N release with the carbon in the methylene urea polymers providing the site for microbial activity. Increasing soil temperature and moisture (up to field capacity) increases the rate of N release.

Another related SRF is *isobutylidene diurea* (IBDU) formed by reacting isobutyraldehyde with urea. IBDU is nearly 90% H_2O soluble and contains 31% N. N release is through chemical decomposition and hydrolysis. Depending on soil moisture and temperature, IBDU can release N for 2–4 months after application (Table 4-23). High soil pH (>7) will reduce N release rate. As a granular material, decreasing particle size will increase exposed surface area and N release rate.

Triazone is a SRF containing 28% N (Table 4-23). Because of the closed-ring structure and strong C-N bonds, N is released slowly. Triazone (N-Sure) is predominately used as a foliar-applied N source, exhibiting excellent absorption properties with no toxicity to plants and commonly used in turf. A new product (Nitamin) is a combination of triazone and methylene urea and contains 22 or 30% N depending on formulation.

Crotonylidene diurea (CDU) contains 32% N, although a commercial product Triabon contains only 16% N.

CRF Coated Fertilizers

These urea-based CRFs are slightly soluble in soil solution, where the N release rate depends on microbial activity and hydrolysis. These products are commonly used in turf, vegetable, and ornamental systems; however, they are increasingly used in cereal grain systems. Like SRF products, CRFs reduce the rate of NH_4^+ and ultimately NO_3^- released to soil solution, thereby reducing leaching, volatilization, and denitrification potential.

Sulfur-coated urea (SCU) is one of the oldest CRFs consisting of a shell of S around each urea granule with 32–38% N and 12–22% S content (Table 4-23). Urea granules are coated with molten S, and then a coating of wax is added to seal cracks in the S coating. An additional layer of conditioner is added to reduce dust and improve handling (Fig. 4-53). Dissolution rate depends on the quality of the S coating. S must be oxidized by soil microorganisms before the urea is exposed and

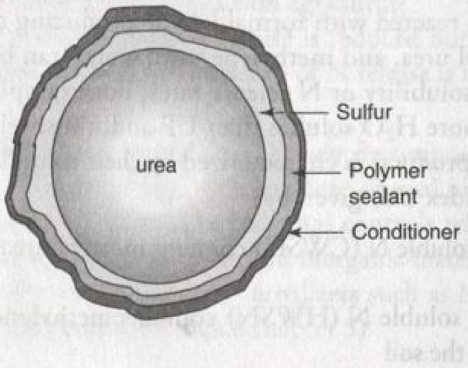


Figure 4-53
Urea coatings used as slow and controlled release N fertilizers. SCU will not contain the polymer coating, whereas PSCU contains all three layers shown. Polymer-coated urea will not contain the S coating.

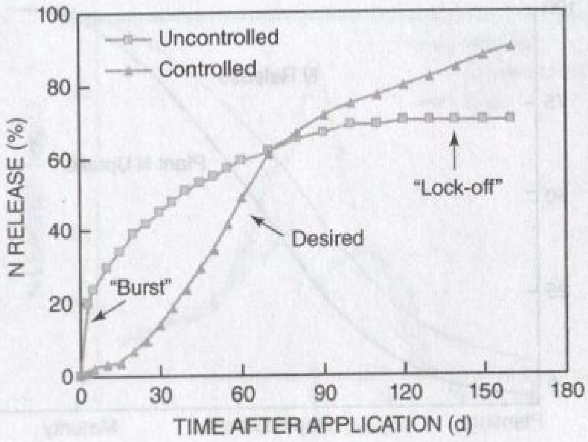


Figure 4-54
Typical N release pattern from selected coated urea products. The controlled N release product releases desired amounts of N at the desired time. The uncontrolled N release product illustrates an initial N "burst" or rapid release, followed by reduced N release or "lock-off" where N release may be insufficient for crop need. Ideally, fertilizer N release occurs just ahead of N uptake demand by the crop (Fig. 4-56).

subsequently hydrolyzed. Only about 30% of SCU granules are perfectly coated, whereas the coating of remaining granules is thin and/or cracked, which accelerates dissolution of the urea granule and N release (Fig. 4-54). If the S coating is too thick, then N release is slowed or "locked-off" (no N release). Therefore, the initial rapid N release could occur too early for recovery by the target plant, and a portion not released or released after the N is needed by the plant. Coating degradation rate will increase with soil temperature and moisture, increasing N release.

Polymer-coated SCU (PSCU) were developed to better control the N release characteristics of SCU (Fig. 4-54). With these products, the SCU is coated with an organic polymer or resin (Fig. 4-53), where the polymer thickness partially controls N release rate. In the soil, H_2O initially diffuses through the polymer layer, into the cracks and defects of the S layer, where urea hydrolysis can begin and NH_4^+ diffuses back through the polymer layer into the soil solution. PSCU products generally provide more uniform N release compared to SCUs.

Polymer-coated CRFs are the most recent technology for controlling N release and reducing N losses by leaching, denitrification, and volatilization (Table 4-23). Similar to PSCUs, N release occurs by the diffusion rate of H_2O (in) and NH_4^+ (out) through the polymer coating (Fig. 4-55). The N release rate is controlled by varying the specific polymer and its thickness. Polymers are alkyd (polyester), polyurethane, or polyolefin coatings. The alkyd-type resin (e.g., Osmocote) is primarily a dicyclopentadiene with a glycerol ester and provides a uniform coating around the fertilizer granule. N release occurs through micropores in the resin. Polyurethane coatings (e.g., Multicote, Polyon) are unique, where the polyurethane reacts with the fertilizer granule and is often referred to

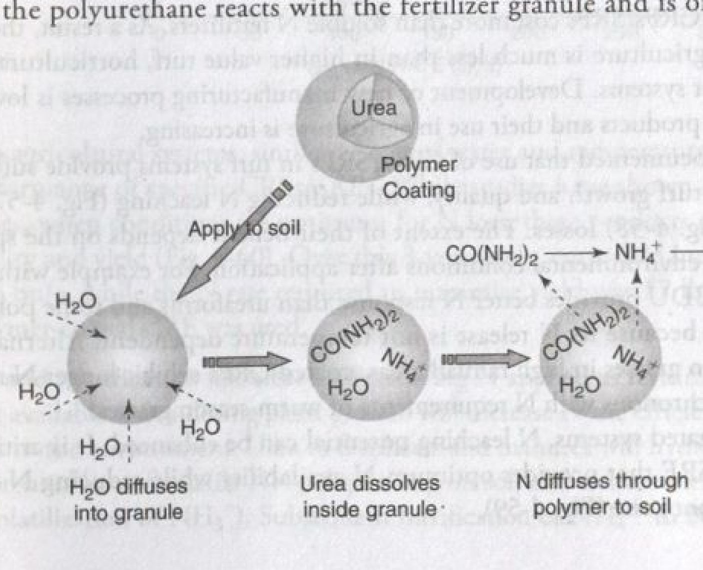
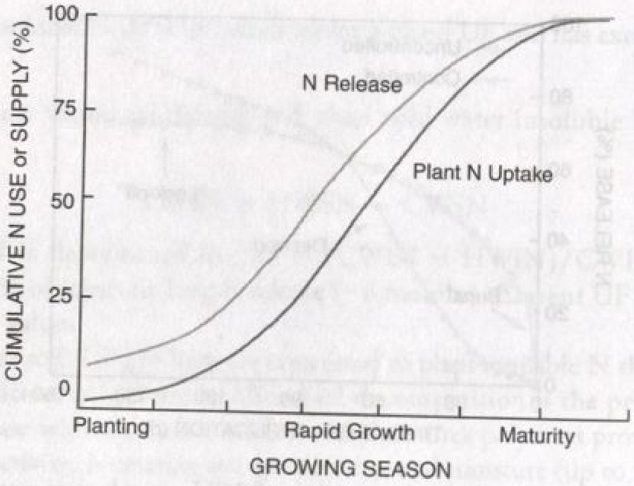


Figure 4-55
Process of controlled N release from a polymer-coated urea granule.

Figure 4-56
Relationship between timing of N released from a CRF or SRF and N demand by the plant.



as a *reacted layer coated fertilizer* (RLCF). RLCF products provide good control of N release, again depending on thickness. Increasing temperature will increase N release, while soil moisture, pH, and microbial activity have little effect. A new product (Nutrisphere) uses a maleic-itaconic polymer that also shows controlled N release characteristics.

Agricultural and Environmental Significance of CRF/SRF The primary purpose of CRF or SRF technology is to provide sufficient N to meet plant requirement, while reducing potential N losses to the environment through leaching, volatilization, and denitrification. In many environments, preplant application of total N needed by the plant will increase N loss potential by any or all of these pathways depending on site-specific conditions. To be classified as a CRF/SRF:

- ≤15% N released in 1 day
- 15–75% N released in 28 days
- at least 75% N released in stated release time

Thus, CRF/SRF technologies are designed to release N throughout the growing season (Fig. 4-56). Ideally, some N must initially release to meet early growth demand; if not, then a low rate of soluble N should be preplant applied. Just ahead of the period of high N demand (maximum vegetative growth rate), sufficient N release must occur. As plant N needs are reduced during maturation, all of the N should have been released. N release without plant N uptake will increase N loss potential.

Generally, CRFs/SRFs cost more than soluble N fertilizers. As a result, their use in production agriculture is much less than in higher value turf, horticultural, and ornamental plant systems. Development of new manufacturing processes is lowering the cost of these products and their use in agriculture is increasing.

It is well documented that use of CRFs/SRFs in turf systems provide sufficient N for optimum turf growth and quality, while reducing N leaching (Fig. 4-57) and volatilization (Fig. 4-58) losses. The extent of their benefit depends on the specific product and the environmental conditions after application. For example with cool-season grasses, IBDU provides better N response than ureaforms and some polymer-coated products because its N release is not temperature dependent. Alternatively with warm-season grasses in high rainfall areas, coated CRFs exhibit longer N release period more synchronous with N requirements of warm-season grasses.

Under irrigated systems, N leaching potential can be enhanced. It is critical to select the CRF/SRF that provides optimum N availability while reducing N transport below the root zone (Fig. 4-59).

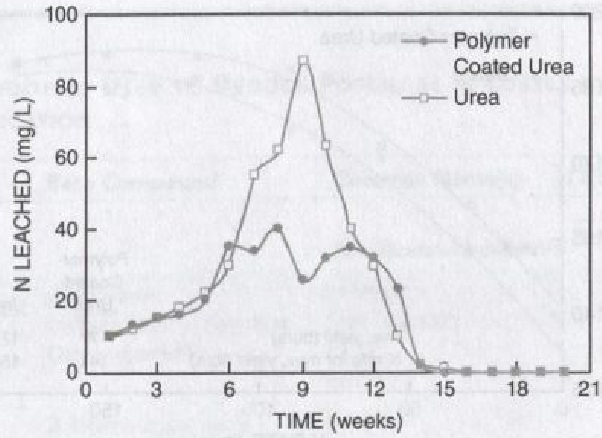


Figure 4-57
Effect of polymer-coated urea on N leached in bermudagrass golf green.
(Shuman, 2001, Proc. Georgia Water Resources Conf. Univ. Georgia, Athens.)

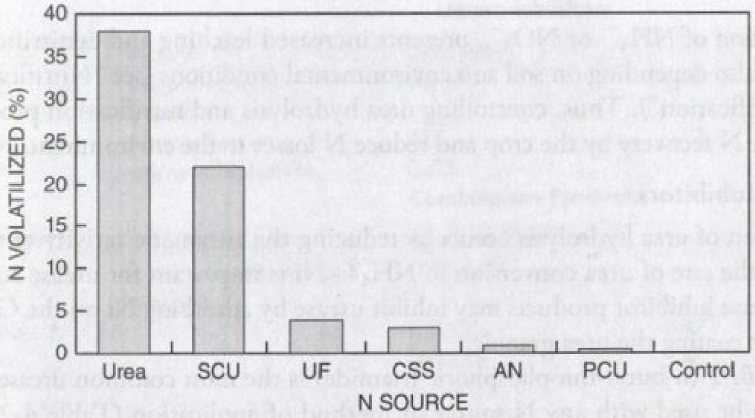


Figure 4-58
Effect of urea products on N volatilization in creeping bentgrass. SCU = sulfur-coated urea; UF = urea formaldehyde; CSS = composted sewage sludge; AN = ammonium nitrate; PCU = polymer-coated urea.
(Knight et al., 2007, Crop Sci., 47:1628–1634.)

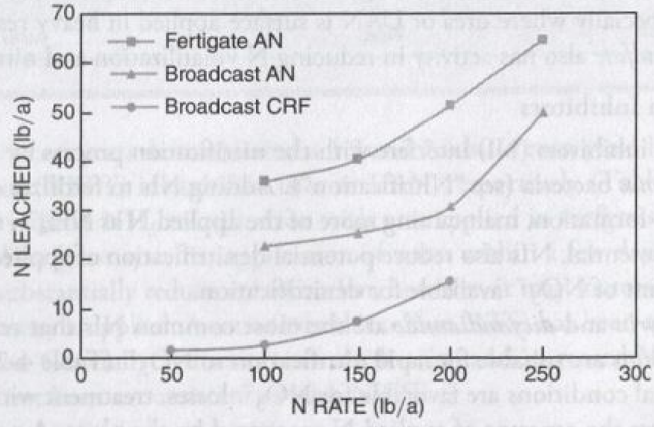


Figure 4-59
Effect of polyolefin resin-coated urea (CRF) compared to ammonium nitrate (AN) on NO_3-N leached in citrus. One application of CRF was compared to same N rate split broadcast (4 split applications) and dissolved in irrigation water (15 applications). Same amount of irrigation water applied to all treatments.
(Paramasivam et al., 2001, SSSAJ, 65:914–921.)

In agricultural systems, similar effects of water and temperature will influence the performance of specific CRFs/SRFs. While studies have shown highly variable responses, when conditions are optimum for N loss, these products can improve N availability and yield (Fig. 4-60). Over this 3-year study, corn yield increased an average of 6 bu/a, while the N rate required to maximize yield was 17 lb N/a less when the polymer-coated CRF was used.

Urease and Nitrification Inhibitors Preserving N applied as fertilizers or manures in plant available forms during plant growth will increase N use efficiency and reduce N losses to the environment. Urea in fertilizers and manures will hydrolyze to NH_4^+ with potential loss of volatile NH_3, depending on soil and environmental conditions (see "Volatilization of NH_3"). Subsequent nitrification of NH_4^+ to NO_3^-, or direct

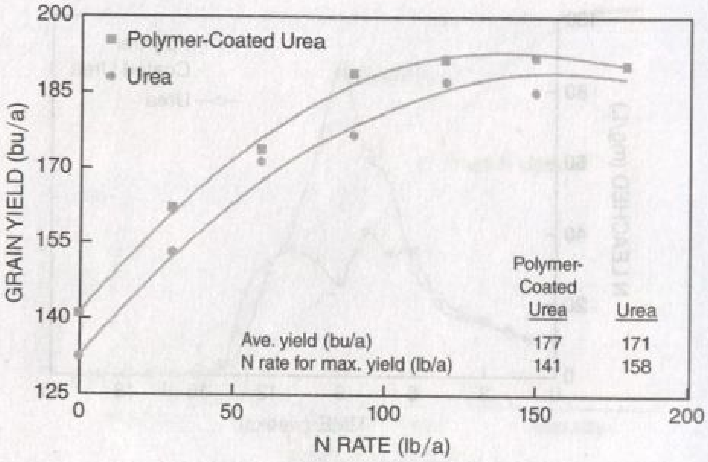


Figure 4-60
Corn yield response to N applied as urea and polymer-coated urea (ESN). Data are averaged over 5 site-years (2003–05). Average yield increase with the CRF was 6 bu/a using 17 lb N/a less N.
(Killorn et al., 2005, Iowa State Univ. ISRF05-29, 31.)

application of NH_4^+ or NO_3^-, presents increased leaching and denitrification potential, also depending on soil and environmental conditions (see "Nitrification" and "Denitrification"). Thus, controlling urea hydrolysis and nitrification processes can improve N recovery by the crop and reduce N losses to the environment.

Urease Inhibitors

Inhibition of urea hydrolysis occurs by reducing the enzymatic activity of urease, reducing the rate of urea conversion to NH_4^+. Ni is important for urease activity and new urease inhibitor products may inhibit urease by adsorbing Ni on the CEC of the polymer coating the urea granule.

NBPT (n-butyl-thiophosphoric triamide) is the most common urease inhibitor and can be used with any N source or method of application (Table 4-24). These products are more effective in reducing N loss under conditions of high volatilization potential, especially where urea or UAN is surface applied in heavy residue environments. *Thiosulfate* also has activity in reducing N volatilization and nitrification.

Nitrification Inhibitors

Nitrification inhibitors (NI) interfere with the nitrification process by direct toxicity to *Nitrosomonas* bacteria (see "Nitrification"). Adding NIs to fertilizer or manure reduces NO_3^- formation, maintaining more of the applied N as NH_4^+, thus, reducing N leaching potential. NIs also reduce potential denitrification of applied N by reducing the amount of NO_3^- available for denitrification.

Nitrapyrin and *dicyandiamide* are the most common NIs that reduce N losses when conditions are suitable for rapid nitrification to NO_3^- (Table 4-24). If soil and environmental conditions are favorable for NO_3^- losses, treatment with an inhibitor often increases the amount of applied N recovered by the plant. A new NI DMPP has been recently developed.

A tropical forage grass (*Brachiaria humidicola*) has the ability to regulate nitrification in soils by releasing exudates from roots that inhibit nitrification. Current research efforts are evaluating genetic transfer of these mechanisms into grain crops (e.g., rice, wheat, maize, and soybean) and forages.

Agricultural and Environmental Significance of Urease and Nitrification Inhibitors Additives to most solid and liquid N fertilizers have been developed to reduce nitrification, volatilization, and denitrification potential. Improving the effectiveness of urea through subsurface band placement and other N management practices can reduce N volatilization potential without use of urease inhibitors; however, broadcast application may be the only option in certain systems (i.e., no-tillage, turf), where urease inhibitors can substantially reduce N loss. For example, a summary of

TABLE 4-24

FERTILIZER ADDITIVES USED TO REDUCE POTENTIAL N LOSSES BY LEACHING, VOLATILIZATION, AND DENITRIFICATION

Additive	Base Compound	Common Name(s)	N Content	N Process	Inhibition Duration
			— % —		— weeks —
		Nitrification Inhibitors			
Nitrapyrin	2-chloro-6-trichloromethyl pyridine	N-Serve Stay-N 2000	–	Nitrification Denitrification	2–6
DCD	Dicyandiamide	DCD Ensan	1.6		4–8
DMPP	3,4-dimethypyrazole phosphate	DMPP ENTEC	– 12–26		6–8
		Urease Inhibitors			
NBPT	n-butyl-thiophosphoric triamide	Agrotain SuperU	– 46	Volatilization	2–3
Thiosulfate	Ammonium or calcium thiosulfate	ATS CaTS	12	Volatilization nitrification	2–3
		Combination Products			
DCD + NBPT	Dicyandiamide + n-butyl-thiophosphoric triamide	Agrotain Plus HYDREXX	—	Volatilization Nitrification Denitrification	6–8
DCD + NBPT + urea		UMAXX UFLEXX SuperU	47 46		8–12 6–8
Polymer	Maleic-itaconic copolymer	Nutrisphere	—		6–12
Polymer + urea		SSN	46		6–12

78 field trials over 5 years demonstrated a 4.3 and 1.6 bu/a corn yield increase with urease inhibitor (NBPT) included in urea or UAN, respectively (Table 4-25). Use of NBPT also reduces NH_3 volatilization with urea applied in turfgrass (Fig. 4-61). With irrigated turfgrass systems, application of water within a few days of urea application can substantially reduce volatilization; however, it may increase denitrification if excess water is applied. Ammonium thiosulfate (ATS) has been evaluated as a urease inhibitor. Generally, reduction in volatilization and increased N recovery by the crop have not been as consistent as with NBPT.

TABLE 4-25

SUMMARY OF CORN YIELD INCREASES FROM APPLICATION OF NBPT WITH SURFACE-APPLIED UREA AND UAN

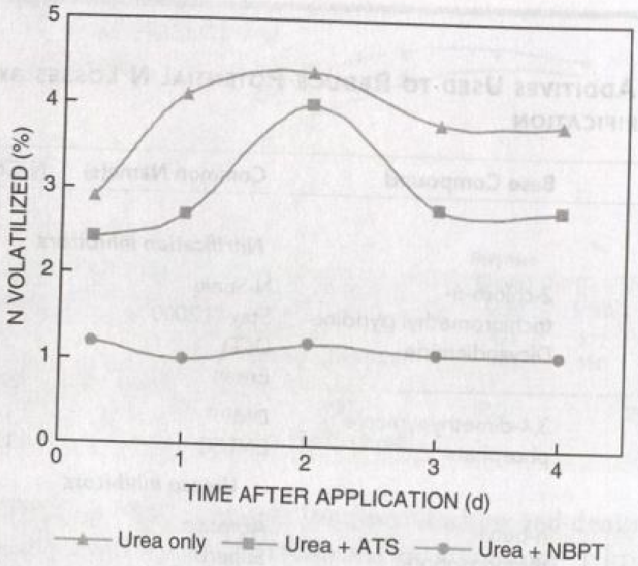
Experimental sites	Number of sites	Yield increase	
		Urea	*UAN*
		bu/a	
All sites	78	4.3	1.6
N responsive	64	5.0	2.8
Significant NH_3 loss	59	6.6	2.7

Source: Hendrickson, 1992, J. Prod. Agric., 5:131–137.

Figure 4-61

Effect of urease inhibitors on N volatilized as a % of urea-N applied (49 kg N/ha) to Kentucky bluegrass.

(Joo et al., 1989, Proc. 6th Inter. Turfgrass Res. Conf.)



The effectiveness of NIs depends on cropping system, climate, soil type, and time of application. NIs can be effective for 2–8 weeks depending on NI and the site-specific conditions. Thus, NIs can help reduce N leaching potential in sandy soils compared to clay soils. In contrast, denitrification in clay soils is generally higher than in coarse-textured soil due to reduced aeration, especially when fertilizer or manure N is applied just prior to irrigation or significant rainfall (Table 4-26). These data illustrate that DCD (dicyandiamide) had a greater effect on reducing N_2O loss as soil H_2O content increased. While ATS also reduced denitrification, it was not as effective as DCD. In contrast, ATS and nitrapyrin were equally effective in increasing fertilizer N availability and N uptake efficiency in spring wheat under wet soil conditions (high winter snowfall) after N application (Table 4-27).

Development of products that contain both urease and nitrification inhibitors has been prompted by studies documenting a positive response when both are included in the fertilizer N (Table 4-28). A summary of field trails throughout the Corn Belt showed 3–30% range in yield increases to NIs included in fertilizer N applied to corn (Table 4-29). For fall-applied N, the primary goal is to maintain applied N as NH_4^+ until soil temperatures decline below 40–50°F; nitrification potential is greatly reduced in cold soils. This is particularly important in cold, wet winter

TABLE 4-26

INFLUENCE OF NITRIFICATION INHIBITORS AND SOIL MOISTURE CONTENT ON TOTAL N_2O-N EMISSION FROM UREA APPLIED (62.5 MG/KG) TO A CLAY SOIL

Treatment	Soil H_2O Content Field Capacity	 80% WHC[1]
	$\mu g\ N_2O - N/kg$ soil	
Control	55	79
Urea	334	744
Urea-DCD	218	416
Urea-ATS	314	655

[1]WHC = water holding capacity.

Source: Kumar et al., 2000, *Current Sci.*, 79:224–228.

TABLE 4-27
INFLUENCE OF NITRIFICATION INHIBITORS ON SPRING WHEAT YIELD, N UPTAKE, AND SOIL N

Fertilizer Treatment	Grain Yield	Grain N Uptake	Total N Uptake	Apparent NUE[1]	N in Fertilizer Band[2] After Application NH_4^+		Before Planting NH_4^+	NO_3^-
					NH_4^+	NO_3^-	NH_4^+	NO_3^-
	bu/a	lb/a		%	ppm			
Control	23.5	25.2	34.6	—	3	1	2	2
Aqua	38.0	40.5	52.9	24	32	21	0	9
Aqua + nitrapyrin	45.4	55.3	72.3	50	65	13	26	11
Aqua + ATS	47.3	58.3	77.0	56	54	17	13	23

[1] NUE = N uptake efficiency.

[2] 75 lb N/a injected 4″ deep on Oct 3. Fertilizer bands sampled 3 weeks after application (Oct 24) and 1 day before planting (May 14).

Source: Goos and Johnson, 1999, *Agron. J.*, 91:1046–1049.

TABLE 4-28
COMBINED EFFECT OF DCD AND NBPT ON SPRING WHEAT

Treatment	Yield	Protein	N Recovery
	g/pot	%	
Urea	8.1	16.4	65.2
Urea + NBPT	8.5	16.8	68.2
Urea + DCD	8.4	16.3	69.4
Urea + NBPT + DCD	10.4	18.0	80.9

Source: Hou et al., *Agric. J.*, 1:109–112.

TABLE 4-29
SUMMARY OF CORN YIELD RESPONSES TO NITRIFICATION INHIBITORS APPLIED WITH UREA OR UAN IN THE U.S. CORN BELT

Region in the Corn Belt	N Application Time	Irrigation	Yield Increase with NI[1] *% of Sites*	*Average %*
Southeast	Fall	No	17	14
GA, MD, NC, SC, TN	Spring		43	15
Eastern	Fall	No	69	9
IL, IN, OH, KY	Spring		51	3
	Spring (no-till)		82	13
Northern	Fall	No	25	5
MI, MN, WI	Spring		17	12
Western (sandy soils) KS, MN, NE	Spring	Yes	52	30
Western (loam & clay soils) KS, NE	Spring	Yes	10	5

[1] Data represent % of sites and average % yield increase to NIs added to fertilizer N.

Source: Nelson and Huber, 1992, *Nat. Corn Handbook*, Iowa State Univ.

climates where denitrification can occur even at soil temperature <40–50°F. For spring preplant applications of N, NIs can retain applied N as NH_4^+ when plant N demand is low and rainfall potential is high. Generally, the highest probability of yield response to NIs is on sandy soils (excessive leaching) and poorly drained fine-textured soils. Under these conditions, potential N loss through leaching and denitrification are the highest, respectively. With any NI, as temperature increases, their effectiveness decreases.

Organic N Forms

Before 1850, virtually all of the N consumed was primarily animal manure and legume N. Presently these materials account for 40% of the total N use in the United States (Table 4-4). Annually, over 1 billion tons of agricultural, municipal and industrial wastes are generated in the United States. When used as a nutrient source, considerable quantities of N and other nutrients are added, depending on the rate of material applied. This section will provide general information regarding N content of selected organic N sources, while Chapter 10 will provide detailed information on organic nutrient management.

Organic nutrients are classified by their source and effects on the soil and target plant. Source generally refers to animal- or plant-based materials, while effects are characterized by:

- materials that have a stable organic base with a low N content and N mineralization potential (e.g., composts, peat)
- materials with short-term nutrient supply, relatively high N content, and/or readily mineralizable organic N content (e.g., manures, biosolids)

In agricultural cropping systems, the average N content in most organic materials utilized is low (1–12% N) relative to crop N need. Using these materials to meet crop N requirement requires high application rates, which often results in an imbalance of other nutrients (Chapters 10 and 11). To avoid nutrient imbalances and risk to environmental quality, lower rates of organic amendments are supplemented with fertilizer N. In ornamental, turf, and other horticultural systems, plant N requirements can usually be met with appropriate rates of organic N sources.

Non-Manure Sources Many organic materials can be utilized in diverse plant or cropping systems to provide nutrients. The majority used in agricultural and horticultural systems are by-products of animal- or plant-processing facilities and municipal waste treatment plants. About 75% of the sewage handled by municipal treatment plants is of human origin, and the remaining 25% is from industrial sources. The end products of all sewage treatment processes are sewage sludge and sewage effluent. Sewage sludge or biosolids are produced during sewage treatment. Sewage effluent is essentially clear water containing low concentrations of plant nutrients and traces of OM, which may be chlorinated and discharged into surface waters. Biosolids are a heterogeneous material, varying in composition between cities and even from one day to the next in the same city. The United States produces nearly 10 million tons (dry weight) of biosolid waste per year, and about 60% is processed for land application. The remainder is incinerated or buried in landfills.

Biosolids contain 1–6% N (Table 4-30). While there are strict regulations regarding their use in agriculture, they are a valuable nutrient source. Management of biosolids and other organic nutrient sources will be discussed in Chapter 10.

Much of the remaining organic materials used to supply nutrients are waste products from either animal- or plant-processing facilities (Table 4-30). With animal-based materials, the N content is relatively high and the C:N ratio is relatively

Table 4-30
Selected Organic Sources of N and Other Nutrients

Material	C:N	N	P	K	Ca	Mg
		% dry weight				
Animal Based						
Blood meal	2–3	9–13	0.2–1.0	0.2–1.5	1.5–3	0.3–0.4
Bone meal	4–5	4–6	7–12	0.2–0.3	18–25	0.5–0.6
Carcass meal	3–4	6–11	2–7	0.3–0.5	4–10	0.1–0.2
Guano	3–4	8–16	2–7	1–3	18–20	3–5
Plant Based						
Fruit pulp	40–50	0.8–1.4	0.2–0.3	1.2–1.4	0.6–0.9	0.1
Brewers grain	10–12	3–5	0.4–0.7	0.5–1.0	0.2–0.3	0.1–0.2
Distillers pulp	8–10	5–6	0.7–1.0	0.8–6.0	0.2–0.3	0.1–0.2
Compost						
Biogenic waste	15–25	1–2	0.2–0.5	0.5–1.3	1.5–5.0	0.3–1.6
Yard waste	30–50	1–2	0.1–0.3	0.5–0.7	4–6	0.4–0.6
Municipal Sewage						
Biosolids		1–6	1.5–7.0	0.2–0.5	0–12	0.4–0.7

Source: Adapted from Trenkel, 2007, Fertilizers. In *Ullmans Agrochemicals* 1:3–142. Wile-VCH.

low. As a result, N mineralization potential is high making these materials excellent sources of plant available N. In contrast, most plant-based materials (including manures) have low N content and provide little mineralizable N. As a result, plant-based organic wastes are commonly used in ornamental and horticultural systems, where N requirements are lower compared to agricultural cropping systems.

Before using any organic N source, the material should be analyzed for nutrient content by a soil testing laboratory.

Manure Sources The total quantity of manure produced annually in the United States is nearly 150 million tons (dry weight), with about 60% produced and deposited by grazing animals (Table 4-31). The remaining 40% is produced in confined animal feeding operations (CAFO). Approximately 16 million acres (8%) of cropland were fertilized with manure, with the majority (≈60%) applied to corn. Of the total manure produced, 1.3 million tons of N is available for land application (Fig. 4-62). Since the majority of recoverable N is associated with CAFO, many regions in the United States produce more N than can be utilized on-farm. About 60% of recoverable N exceeds that used to meet on-farm crop N requirements, where the majority is related to poultry production (Fig. 4-62). Nutrients in excess of on-farm use must be transported to other areas.

Average annual manure production ranges 6–15 tons per animal unit (Table 4-32). The quantity of N in manure and the availability to plants vary greatly and depend on (1) nutrient content of the animal feed, (2) method of manure handling and storage, (3) quantity of added materials (i.e., bedding, water), (4) method and time of application, and (5) soil properties. Most wastes exiting the animal contain 75–90% water. Storage and handling usually reduce water content in solid-storage systems and increase water content in liquid systems, such as the lagoon storage common with swine production (see Chapter 10).

TABLE 4-31
ANIMAL MANURE PRODUCTION IN THE UNITED STATES, WITH TOTAL N AND P EXCRETED AND RECOVERABLE (USABLE) AS A NUTRIENT SOURCE

				N		
Manure source	No. Animals	Dry manure	*Excreted*	*Recoverable*	*Total*	*Organic*
	# × 10^6	t × 10^6			%	
Dairy	12.3	27.0	1.00	0.32	2–3	1.0–1.5
Beef	68.4	91.5	3.87	0.26	1–2	0.7–1.5
Swine	8.5	9.3	0.60	0.14	3–5	1.5–2.5
Poultry	6.1	17.9	0.99	0.58	4–6	2.4–3.6
Total	95.3	145.7	6.45	1.29		

Source: USDA-ERS, http://www.ers.usda.gov/Data/manure/default.asp?ERSTab=2.

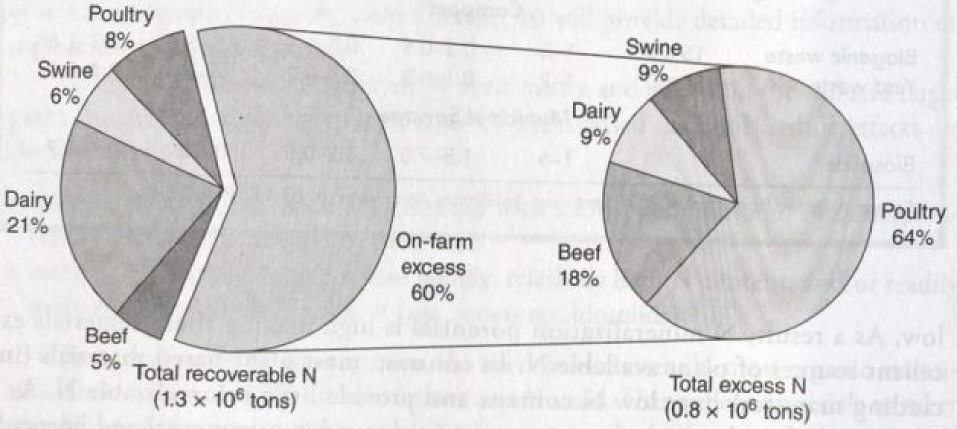


Figure 4-62
Total manure N available and the proportion in excess for on-farm utilization.
(Gollehon et al., 2001. USDA-ERS. Agric. Information Bull. No. 771).

TABLE 4-32
TYPICAL ANNUAL MANURE AND N PRODUCTION PER ANIMAL UNIT (AU) FOR COMMON ANIMAL TYPES

Animal Type	Animals per AU[1]	Manure Production (as excreted)	N (as excreted)	N (after losses[2])
		tons/AU	*lb/t*	
Beef cows	1	11.5	11.0	3.3
Dairy cows	0.74	15.2	10.7	4.3
Heifers, dairy calves	1.82	12.1	6.1	1.8
Steers, calves, bulls	1.64	10.6	11.0	3.3
Swine, breeders	2.67	6.1	13.3	3.3
Swine, slaughters	9.09	14.7	11.3	2.8
Hens & pullets	250	11.5	26.9	18.5
Broilers	455	15.0	26.8	16.1
Turkeys for slaughter	67	8.2	30.4	16.2
Turkeys hens for breeding	50	9.1	22.4	11.2

[1] AU = 1,000 lb animal weight.
[2] Volatilization and denitrification.
Source: Kellogg et al., 2000, USDA-NRCS, ERS, Report No. nps 00-0579.

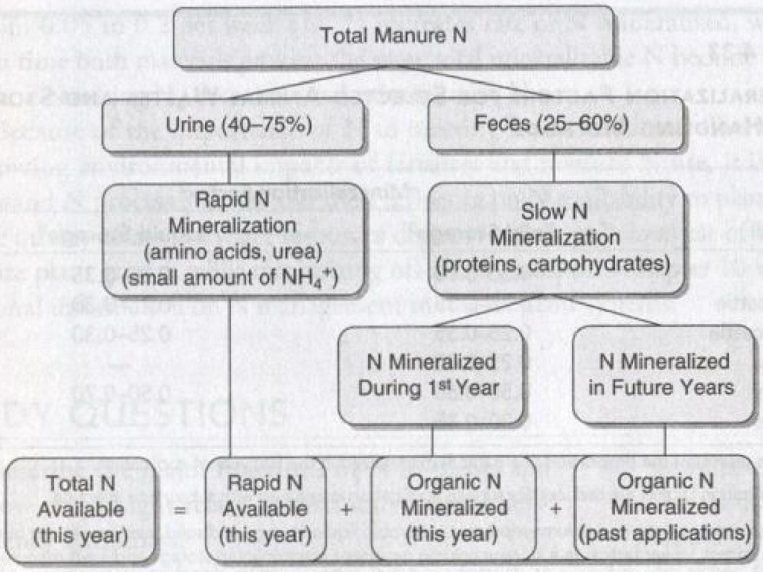


Figure 4-63
Form and relative N availability in land-applied manure.

N Availability with Organic Nutrient Sources With any organic N source, N availability to a plant will depend on the quantity of organic or mineralizable N (Table 4-31). With manure, total N contents range from 1 to 6%, 50 to 75% of the total N is organic N, while the remaining 25 to 50% is NH_4^+. A large proportion of the initial N excreted is volatilized during storage and handling (Table 4-32). Thus, manure N availability to plants depends on mineralization of the organic N. The mineralization process is the same as described previously for soil OM.

Organic N in manure is composed of stable and unstable forms (Fig. 4-63). Depending on the animal, a large proportion of the waste is urine, which contains some NH_4^+ and readily mineralizable organic N compounds (e.g., urea, amino acid, uric acid). If not volatilized during or after application (see Chapter 10), these N sources are immediately plant available.

Since NH_4^+ can be converted to NH_3 under optimum soil and environmental conditions, significant volatilization losses of manure N are possible, ranging from 15 to 40% of total N. In lagoon systems, 60–90% of total manure N can be lost through denitrification and volatilization during storage and land application.

The remaining stable organic N will mineralize in the first and subsequent years after application (Table 4-33). The less-resistant stable organic N will generally mineralize in the year of application. This fraction represents 30–60% of total manure N, depending on manure source. The more-resistant stable organic N mineralizes slowly over the next several years, where about 30, 15, and 5% of the N mineralized in the first year is mineralized in the second, third, and fourth years, respectively. N mineralization rates vary between manure sources (Fig. 4-64). These data show that total N mineralized is much greater with poultry waste compared to beef and swine waste. The initial N mineralization rate is also much higher with poultry waste.

The kinetics of N mineralization from manure, legume, or native soil OM can often be described by a first-order rate equation:

$$N_{min} = N_o\left(1 - e^{-kt}\right)$$

where N_{min} = amount of N mineralized at time, t
N_o = the total mineralizable N pool
k = mineralization rate constant (t^{-1})

This equation indicates that when "k" increases, larger quantities of N mineralize initially, with decreasing N mineralized with time (Fig. 4-65). In this example, increasing

TABLE 4-33

MINERALIZATION FACTORS FOR SELECTED ANIMAL WASTES AND STORAGE/HANDLING METHODS[1]

	Mineralization Factor[2]	
Animal	Solid Storage[3]	Liquid Storage[3]
Swine	0.50–0.60	0.30–0.35
Beef cattle	0.25–0.35	0.25–0.30
Dairy cattle	0.25–0.35	0.25–0.30
Sheep	0.25–0.35	—
Poultry	0.50–0.60	0.50–0.70
Horses	0.20–0.35	—

[1] Factors represent the proportion of organic N mineralized in the first year of application.

[2] Mineralization factors are reduced for surface application compared with subsurface injection.

[3] Higher factors in a storage column represent anaerobic liquid storage and solid manure without bedding or litter added. Lower factors in a storage column represent aerobic liquid storage and solid manure with bedding or litter added.

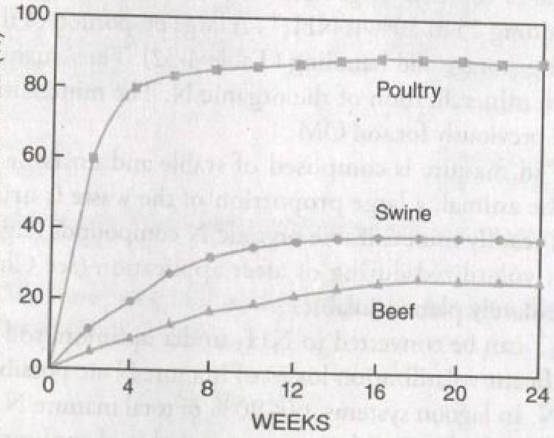


Figure 4-64
N mineralization of organic N in selected liquid animal manures applied to a sandy soil.
(Van Faassen, 1987, Netherlands. In V. D. Meer [Ed.], Animal Manure on Grassland and Fodder Crops, Martinus Nijhoff Publ. Dordrecht, Netherlands.)

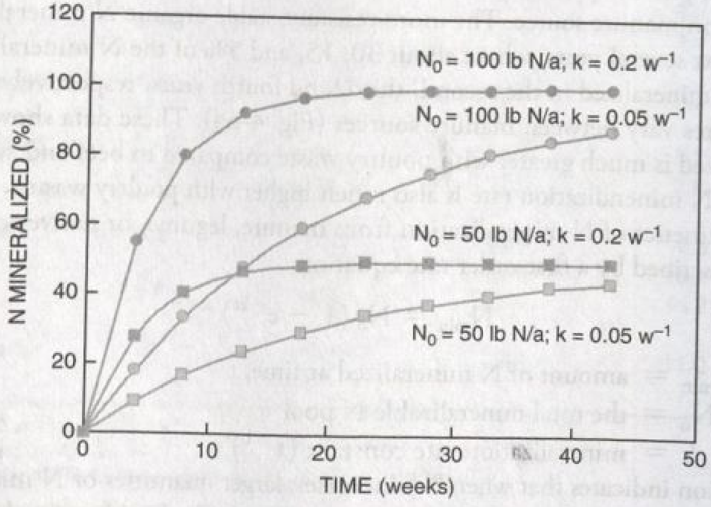


Figure 4-65
General first-order kinetics of N mineralization. Two manure sources with different total mineralizable N (N_o = 100 lb N vs. N_o = 50 lb N). The N mineralization rate constant (k) is varied between 0.05 and 0.2 per week (w^{-1}). Higher "k" represents manures that mineralize N at a faster rate.

"k" from 0.05 to 0.2 per week (w^{-1}) increases rate of N mineralized, where given enough time both materials provide the same total mineralizable N because $N_o = 100$ in both. Decreasing N_o decreases total mineralizable N.

Because of the importance of N to meeting future food and fiber needs, and the growing environmental impacts of fertilizer and manure N use, it is critical to understand N processes in soil and their influence on N availability to plants. Protecting the quality of air and water resources depends on our judicious use of N inputs to optimize plant growth while minimizing off-site N transport. Chapter 10 will provide additional information on N management in diverse plant systems.

STUDY QUESTIONS

1. Describe the major functions of N in plants and how they might relate to distinctive visual deficiency symptoms.
2. Do crops utilize both NH_4^+ and NO_3^-; which is preferred and why? Does the stage of growth influence crop uptake of either NH_4^+ or NO_3^-?
3. Identify an important soil property that can be altered by uptake of NH_4^+ or NO_3^-.
4. How is atmospheric N made usable to higher plants (exclude synthetic N fixation)? What microorganisms are responsible for N fixation?
5. What soil property can exercise considerable influence on the survival and growth of *Rhizobia* in soil? Describe at least two practical ways of improving the effectiveness of *Rhizobia*.
6. Define ammonification and nitrification. What factors affect these reactions in soils?
7. Why does intensive cultivation of land lead to a rapid decomposition of OM? How does this influence N availability in both the short and long term?
8. What is the difference between N fixation and nitrification?
9. Nitrification is a two-step reaction. What are the two steps and what organisms are responsible for each? Why is nitrification important and a mixed blessing?
10. If leaching losses of N are to be minimized after fall application of NH_4-N, soil temperatures during winter months should not rise above what point? As a general rule, is fall application of NO_3-N fertilizers to a spring-planted crop a sound practice? Why or why not?
11. What is NH_4^+ fixation? What are the soil conditions under which it occurs? How important is NH_4^+ fixation to N availability?
12. Barley straw was incorporated a week before planting fall wheat. At planting, you applied 20 lb N/a, 10 lb P/a, and 30 lb K/a fertilizer. The wheat germinates and turns yellow. Tests show low N in the tissue. What is wrong with the wheat? What would you advise?
13. In what forms may N gas be lost from soil? Discuss the conditions under which each form is lost, and write the reactions involved. Can there be large losses of N gases from soil? How would you prevent or minimize the various gaseous losses of N?
14. Classify the various forms of N fertilizers. What are the most important sources of N?
15. What developments have resulted in the great increase in urea use?
16. List changes in soil properties influenced in the injection zone of anhydrous NH_3.
17. What conditions favor NO_2^- accumulation? Describe the harmful effects of NO_2^- on crops.
18. Ammonium volatilization of urea in soils can be an important N loss mechanism. The reaction is $NH_2\text{-}C\text{-}NH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$
    a. Volatilization losses of urea fertilizer applied to the soil can occur if not properly managed. List the factors/conditions that would maximize the potential for NH_3 volatilization.
    b. What urea management recommendations would you make to minimize NH_3 volatilization?
    c. What other source of urea (besides urea in fertilizer or manure) is subject to volatilization?
19. What is urease and why is it important? How do urease inhibitors reduce N loss?
20. What are the important factors governing the selection of fertilizer N source?
21. Why does NH_4-N have an acidifying effect on the soil?
22. Describe the conditions in which nitrification inhibitors have the greatest potential for increasing the efficiency of N fertilizer management.

23. A crop consultant recommends 80 lb N/a to a sorghum crop in a soybean-sorghum rotation. The following data are available:

Previous Soybean Crop	Sorghum Crop	Soil Data
30 bu/a grain yield	100 bu/a yield goal	2% OM
40 lb residue/bu	56 lb/bu test weight	1% OM degradation rate
40% residue C	75 lb residue/bu	20 lb/a profile N content
30:1 C:N ratio	1.8% grain N	30 lb N/a soybean credit
	0.6% residue N	

Is the recommendation accurate? Show all work.

24. A turf specialist annually applies 100 lb N/a as $(NH_4)_2SO_4$ to turfgrass. Initial soil pH was 6.8 and the CEC = 14 meq/100 g. After 20 years, would the soil pH drop below 6.8 if 1 ton/a $CaCO_3$ were applied every 4 years? If so, by how much (use Table 3-3)?

25. A farmer wants to increase the OM from 1.5% to 2.0%. How many years will he take, if he produces 6000 lb/yr crop residue (60:1 C:N, 40% C, 80% of residue N used to make OM)? The annual decomposition rate of the soil is 1%.

26. For 3000 lb/a residue (40% c) and C:N = 60, calculate the quantity of inorganic soil N immobilized by micro lies.

27. A soil contains 2% OM with an annual decomposition rate of 1%. The producer wants to increase OM to 3%. How many years will it take if he produces 10,000 lb crop residue/yr (residue contains 40% C and C:N is 80:1). Assume 80% of residue N ends up as N in soil OM, ultimately.

28. With a neat diagram, explain the N cycle.

29. How nitrogen supply influences the utilization of carbohydrates? Explain.

30. Mention the economically important microorganisms involved in biological N_2 fixation. What are their general properties and agricultural importance?

31. Discuss the steps involved in the industrial synthesis of NH_3. Write the chemical reactions.

32. What are green house gases?

33. What is C:N ratio? What is it's effect on mineralization?

34. Classify the organic nutrients by their source and effects on soil.

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