

## Chapter 2. Transformation and Transport Processes of Nitrogen in Agricultural Systems

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This chapter discusses the transformation and transport processes of nitrogen (N) in agricultural systems and provides information on overall reservoir sizes for N. Nitrogen is ubiquitous in the environment and is required for the survival of all living things. It is also one of the most important essential nutrients and is central to the production of all crop plants. The most abundant form of N in the environment is elemental dinitrogen ( $N_2$ ) gas that accounts for 78% of the atmosphere.  $N_2$  gas is inert and is not directly available for plant uptake and metabolism. The atmospheric reservoir is estimated to contain  $\sim 4 \times 10^{19}$  Tg  $N_2$  with a turnover time of  $10^{17}$  year (Reeburgh, 1997). However, some of the most mobile substances found in the soil-plant-atmosphere system contain N and the need to understand N transport and transformations in the environment has been the subject of many reviews and/or books (Keeney, 1982, 1989; Hallberg, 1987, 1989; Follett, 1989; Power and Schepers, 1989; Follett et al., 1991; Galloway et al., 1995; Mosier et al., 1998; Laegreid et al., 1999; Follett and Hatfield, 2001; and SCOPE 2004). "Natural" fixation of atmospheric  $N_2$  is estimated to be  $\sim 100$  TgN/year, globally (Galloway et al., 1995) primarily by lightning and biological processes. Once in fixed or "reactive" form, N can be rapidly incorporated into living tissue. Conversion of relatively inert  $N_2$  gas to biologically available forms is limited by the microbially mediated rate of N-fixation. The estimate of the N contained in the terrestrial biomass reservoir is  $3.5 \times 10^{14}$  TgN with a turnover time of 50 years, while the soil reservoir is estimated at  $9.5 \times 10^{14}$  TgN with a turnover time of 2000 years. The estimated sizes of the global reservoirs of dissolved  $N_2$  and inorganic N in the oceans are  $2.2 \times 10^{17}$  and  $6 \times 10^{15}$  TgN respectively. Sediments are estimated to contain  $4 \times 10^{18}$  TgN and marine biomass is estimated to contain  $4.7 \times 10^{12}$  TgN (Reeburgh, 1997). Estimates of the N in soil show it to contain 2.7 times more N than does aboveground plant biomass, but only a fraction of the amount of N contained in the atmospheric reservoir. Microbially mediated denitrification (i.e., conversion back to  $N_2$  gas) completes the N cycle. Natural terrestrial and ocean denitrification amounts are estimated at 147 and 30 TgN/year, respectively.

## 1. NITROGEN IN AGRICULTURE

To prevent excess losses of N into the surrounding environment it is important to curtail transport processes (leaching, runoff, erosion, and gaseous losses) so that applied and residual N sources within the soil-crop system are not lost but remain where needed for crop use. The objective is to lower the rate and duration of the loss processes themselves. Practices and concepts that lessen the opportunity for the occurrence of loss processes decrease the amount of N that may be lost. Even though the available N supplied from the soil is usually inadequate for optimum crop production, in some cases improved efficiency is achieved by using less added N to decrease the potential for N losses. In other cases it can be achieved by improving the opportunity for N-uptake during key periods of plant growth while using the same amount of N-input. The fate and transport of N from any of the various sources from which it may enter agricultural or terrestrial systems must always be considered in the context of the N cycle. An N-budget, or mass-balance, approach is often needed to understand the options to minimize and/or mitigate the environmental impacts of N that may occur and to improve N-management in these systems.

Commercial fertilizer, manures, and other N sources are generally easily and economically applied. As shown in Figure 1, animal and human wastes were the major fertilizer source of added N before 1960. Nitrogen represents the nutrient

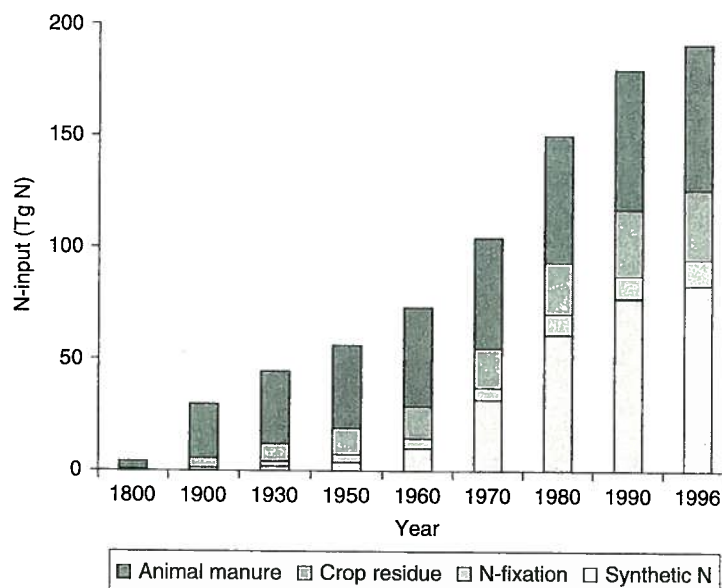
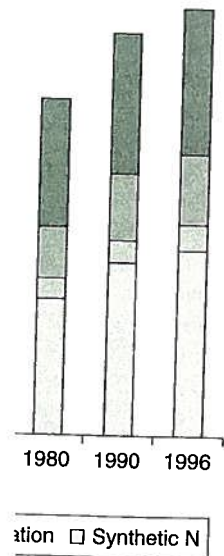


Figure 1. Global annual N-input estimates into crop production from synthetic N, BNF, crop-residue return, and animal manures (Mosier, 2001).

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duction from synthetic N, (2001).

most applied to agricultural land. In 1950 synthetic fertilizer input comprised about 7% of the total N-input of ~56 Tg, but by 1996 synthetic fertilizer N-input comprised ~43% (~82 TgN) of a total input of 190 TgN/year (Kroeze et al., 1999; Mosier, 2001) and through 2002 increased to ~85 teragram of nitrogen (FAO, 2004).

## 2. NITROGEN TRANSFORMATIONS

### 2.1. Biological Nitrogen Fixation

Through the process of biological nitrogen fixation (BNF), symbiotic and non-symbiotic organisms can fix atmospheric  $N_2$  gas into organic N forms (Figure 2). A few living organisms are able to utilize molecular  $N_2$  gas from the atmosphere.

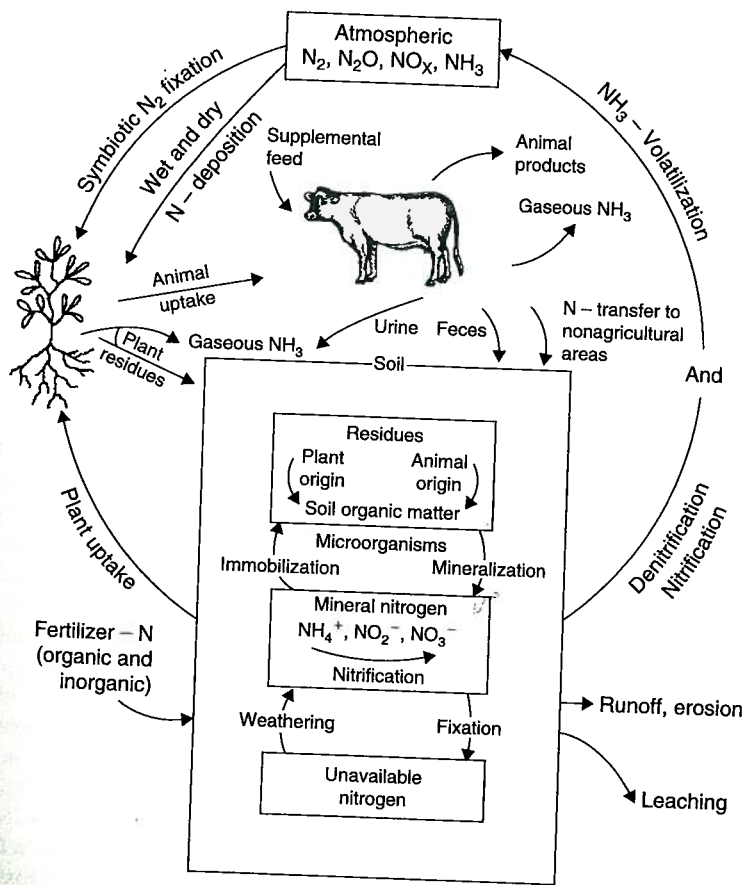


Figure 2. The nitrogen cycle.

The best known of these are the symbiotic Rhizobia (legume bacteria), nonsymbiotic free-living bacteria such as *Azotobacter* and *Clostridium*, and blue-green algae. Generally, in a symbiotic relationship, one organism contains chlorophyll and uses light energy to produce carbohydrates. The other organism receives some of the carbohydrates and uses them as an energy source to enzymatically fix atmospheric  $N_2$  into the ammonia ( $NH_3$ ) form of N and thence into amino acids and other nitrogenous compounds that are nutritionally useful to the chlorophyll containing organism. To agriculture, the most important type of BNF is symbiotic fixation by legumes (i.e., alfalfa, clovers, peas, beans, etc.). An estimate is that leguminous crops return  $\sim 1$  TgN/year of symbiotically fixed N to cropland soils in the United States (Follett et al., 1987; Follett, 2001a) and  $\sim 18$  TgN/year worldwide (Galloway et al., 1995). Even though fixed N resulting from BNF is initially within the nonsymbiotic or symbiotic organism/plant system, the fate, transport and entry of this N into the environment is part of the N cycle.

## 2.2. Immobilization and Mobilization of Soil Nitrogen

The N taken up by plants from the soil originates from indigenous organic and inorganic forms. Organic N occurs naturally as part of the soil's organic matter fraction; it can also be added to the soil from manure, symbiotic and nonsymbiotic BNF, plant residues, and from other sources. Soil microorganisms and their activities are an integral part of immobilization and mineralization processes in soil (Figure 2); soil-organic N can be transformed to ammonium ( $NH_4^+$ ) by the process of ammonification. Inorganic (mineral) forms of N include  $NH_4^+$  or nitrate ( $NO_3^-$ ), both readily taken up by crops, and nitrite ( $NO_2^-$ ) that occurs as an intermediate form during mineralization of  $NH_4^+$  to  $NO_3^-$ . Even though  $NH_4^+$  is the preferred form, microbes in soil can convert either  $NH_4^+$  or  $NO_3^-$  to satisfy their need for N, a process called immobilization. Immobilization of  $NO_2^-$  and  $NO_3^-$  back to organic forms of N can also occur through enzymatic activities associated with plant or microbial N-uptake and N-utilization processes. Microbes and soil animals use organic matter in soil as food and excrete nutrients in excess of their own needs. When  $NH_4^+$  is released, it is called mineralization. When oxygen is present, microbes in the soil can readily transform  $NH_4^+$  to  $NO_3^-$  with  $NO_2^-$  as an intermediate form, a process called nitrification. This is a fairly rapid process that, under aerobic conditions, can be completed in a few days. Although  $NO_2^-$  can potentially accumulate in soils under some conditions, it usually does not because it is rapidly transformed to  $NH_4^+$  as part of the nitrification process or else it is denitrified.

## 2.3. Gaseous Transformations

### 2.3.1. Ammonia Volatilization

Ammonium ions in the soil solution enter into an equilibrium reaction with  $NH_3$  in the soil solution. The soil-solution  $NH_3$  is, in turn, subject to gaseous loss to the atmosphere. Soil pH and concentration of  $NH_4^+$  in the soil solution are important

egume bacteria), nonsymbiotic diazotrophs, and blue-green algae. Cyanobacteria (blue-green algae) contains chlorophyll *a* and *b* and can enzymatically fix atmospheric nitrogen into amino acids and nucleic acids. The process of BNF is symbiotic (e.g., in legumes) or free-living (e.g., in cyanobacteria). An estimate is that about 18 TgN/year worldwide is fixed by BNF. The fate, transport and entry

from indigenous organic matter, symbiotic and nonsymbiotic microorganisms and their nitrification processes in soil solution ( $\text{NH}_4^+$ ) by the process of nitrification. This includes  $\text{NH}_4^+$  or nitrate that occurs as an intermediate product.  $\text{NH}_4^+$  is the preferred form for most plants.  $\text{NO}_3^-$  to satisfy their need for nitrogen.  $\text{NO}_2^-$  and  $\text{NO}_3^-$  back activities associated with microbes and soil animals in excess of their own needs. Nitrogen is present, microbes as an intermediate form, that, under aerobic conditions, potentially accumulate in soil and is rapidly transformed to nitrate.

Equilibrium reaction with  $\text{NH}_3$  to gaseous loss to the atmosphere are important

factors affecting the amount of  $\text{NH}_3$  loss to the atmosphere. As soil pH increases above 6.0 the  $\text{NH}_3$  form, as a fraction of soil-solution  $\text{NH}_4^+$  plus soil-solution  $\text{NH}_3$ , increases by an order of magnitude; thus, increasing the loss of soil-solution  $\text{NH}_3$  to the atmosphere. As summarized by Stevenson (1986),  $\text{NH}_3$  volatilization:

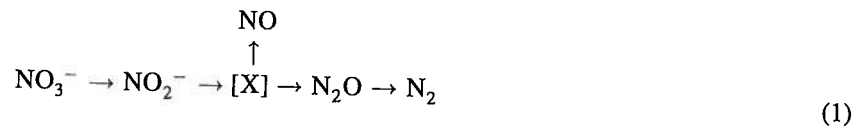
1. Is of most importance on calcareous soils, especially as soil pH exceeds 7.
2. Losses increase with temperature and can be appreciable for neutral or alkaline soil as they dry out.
3. Is greater in soils of low cation exchange capacity (CEC), such as sands.
4. Losses can be high when high N organic wastes, such as manure, are permitted to decompose on the soil surface.
5. Losses are high from urea applied to grass or pasture as a result of hydrolysis of the urea to  $\text{NH}_3$  by indigenous urease enzyme.
6. Losses of soil- and fertilizer-N are decreased by growing plants.

Anhydrous, or gaseous,  $\text{NH}_3$  is a very important direct-application N fertilizer. Gaseous  $\text{NH}_3$  when in contact with moist soil, dissolves in, and reacts with, soil water to form  $\text{NH}_4^+$  and  $\text{OH}^-$  ions. The pH is increased dramatically immediately around the application zone of anhydrous  $\text{NH}_3$ . Therefore, depending on buffering capacity of the soil and the resulting soil pH, equilibrium is approached between soil-solution  $\text{NH}_4^+$  and  $\text{NH}_3$  in the soil solution and gaseous  $\text{NH}_3$ . If anhydrous  $\text{NH}_3$  is placed in dry soil or at too shallow a depth, the  $\text{NH}_3$  is also subject to volatilization. However, the N that is in  $\text{NH}_4^+$  form is readily sorbed to the CEC of the soil.

### 2.3.2. Denitrification

When organic matter in soil decomposes first  $\text{NH}_4^+$ , then  $\text{NO}_2^-$  and finally  $\text{NO}_3^-$  ions form by the process of nitrification (Figure 2). Nitrite usually does not accumulate in soils because it is rapidly transformed to  $\text{NO}_3^-$  or is denitrified to  $\text{N}_2$  gas, nitrous oxide ( $\text{N}_2\text{O}$ ) or nitric oxide (NO). Nitrate can also be lost to the atmosphere through the denitrification processes. Nitrous oxide is a product of incomplete denitrification and is a greenhouse gas identified as contributing to global warming. The importance of  $\text{N}_2\text{O}$  is as a long-lived greenhouse gas whose major anthropogenic source is from agriculture. For example, about 72% of US emissions of  $\text{N}_2\text{O}$  are from agricultural sources (US EPA, 2005). About 5% of the total atmospheric greenhouse effect is attributed to  $\text{N}_2\text{O}$  of which ~70% of the annual global anthropogenic emissions are reported to come from animal and crop production (Mosier, 2001). The climate forcing potential, used to estimate the warming potential of  $\text{N}_2\text{O}$ , is that it is 296 times that of atmospheric carbon dioxide ( $\text{CO}_2$ ) during 100 years (IPCC, 2001). Anthropogenic sources of  $\text{N}_2\text{O}$  were estimated to have been 5.7 and 6.9 TgN/year in 1980 and 1990, respectively (IPCC, 1996; IPCC, 2001). The atmospheric burden of  $\text{N}_2\text{O}$  continues to increase by about 0.25% per year (IPCC, 2001). Following its transport to the stratosphere,  $\text{N}_2\text{O}$  is oxidized to nitric oxide (NO) that in turn catalyzes the destruction of stratospheric ozone ( $\text{O}_3$ ) (Hutchinson, 1995).

Biogenic production in soil is a principle source of atmospheric  $N_2O$ . In addition, several factors affect the ratio of  $N_2O$  to  $N_2$  during denitrification (Table 1). Anaerobic soil processes, rather than nitrification (an aerobic process) are the principle biogenic sources of atmospheric  $N_2O$  (Freney et al., 1979; Goodroad and Keeney, 1984; Klemetsson et al., 1988). Denitrification is a bacterial process, during which  $NO_3^-$  or  $NO_2^-$  are reduced to gaseous N species  $NO$ ,  $N_2O$  or  $N_2$ , and is capable of producing and consuming  $N_2O$  and  $NO$ . Nitrate is reduced first to  $NO_2^-$ , then to  $NO$ , next to  $N_2O$  and finally to  $N_2$  (Eq. 1).



**Table 1.**  
Factors affecting the proportion of  $N_2O$  and  $N_2$  produced during denitrification.

| Factor                   | Will Increase $N_2O/N_2$      |
|--------------------------|-------------------------------|
| $[NO_3^-]$ or $[NO_2^-]$ | Increasing oxidant            |
| $[O_2]$                  | Increasing $O_2$              |
| Carbon                   | Decreasing C availability     |
| pH                       | Decreasing pH                 |
| $[H_2S]$                 | Increasing sulfide            |
| Temperature              | Decreasing temperature        |
| Enzyme status            | Low $N_2O$ reductase activity |

Not only denitrification (a reductive process), but also the oxidative process of nitrification causes emission of a small amount of  $N_2O$  (Tortoso and Hutchinson, 1990). However, denitrification is the route for most losses of gaseous N compounds to the atmosphere. The potential for denitrification is increased as oxygen levels in the soil decreases. Under favorable environmental conditions, *Nitrosomonas* spp. bacteria in the soil readily transform  $NH_4^+$  to  $NO_2^-$  that in turn is transformed by *Nitrobacter* spp. bacteria to  $NO_3^-$  (Figure 2). The small quantity of  $N_2O$  produced during nitrification of  $NH_4^+$  in aerobic soils is a direct metabolic product of chemoautotrophic  $NH_4^+$ -oxidizing bacteria or results from other soil processes dependent on these organisms as a source of  $NO_2^-$  (Tortoso and Hutchinson, 1990).

The general conditions required for denitrification to occur include: (a) presence of bacteria possessing the metabolic capacity; (b) availability of suitable reductants such as organic carbon; (c) restriction of  $O_2$  availability; (d) availability

spheric N<sub>2</sub>O. In addition, nitrification (Table 1). process) are the principal processes (Goodroad and 1979; Goodroad and bacterial process, during denitrification, N<sub>2</sub>O or N<sub>2</sub>, and is reduced first to NO<sub>2</sub><sup>-</sup>,

ing denitrification.

increase N<sub>2</sub>O/N<sub>2</sub>

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oxidative process of nitrification (Goodroad and Hutchinson, 1979). Gaseous N compounds are produced as oxygen levels in the soil decrease, *Nitrosomonas* spp. are transformed by the activity of N<sub>2</sub>O produced as a by-product of chemolithoautotrophic processes dependent on, 1990).

Our results include: (a) presence of suitable soil conditions; (b) availability of suitable soil conditions; (c) availability of suitable soil conditions; (d) availability of suitable soil conditions.

of N oxides, NO<sub>3</sub><sup>-</sup>, NO, or N<sub>2</sub>O (Klemetsson et al., 1988; Firestone and Davidson, 1989; Mosier, 2001). Either the NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> form can potentially contribute to the release of N<sub>2</sub>O to the atmosphere, especially where excess NO<sub>3</sub><sup>-</sup> accumulates in the soil profile and is available for denitrification. Because N<sub>2</sub>O is the greenhouse gas of concern, the proportion of N<sub>2</sub>O produced relative to N<sub>2</sub> under denitrifying conditions becomes of special concern. A number of factors affect the proportion of N<sub>2</sub>O to N<sub>2</sub>. A model by Betlach and Tiedje (1981) predicts accumulation of N<sub>2</sub>O whenever one of the factors shown in Table 1 slows the rate of overall reduction.

### 3. TERRESTRIAL TRANSPORT AND RELATED PROCESSES

#### 3.1. Fertilizer and Manure

The NH<sub>4</sub><sup>+</sup> cation in highly water-soluble compounds that contain NH<sub>4</sub> (Table 2) can be sorbed to the CEC, incorporated (fixed) into clay and other complexes within the soil, released by weathering back into the available mineral pool, or immobilized into organic form by soil-microbial processes. Ammonium that is associated with soil colloids can be transported from its original location and deposited by water and/or wind erosion processes or, under certain conditions, volatilize into the atmosphere as NH<sub>3</sub> gas and be aerially transported across the landscape, including into surface water. Gaseous NH<sub>3</sub> often is returned to the soil-plant system by direct uptake into plant leaves or dissolved in precipitation. Urea and calcium cyanamide (Table 2), are forms of N that, when applied to soil, are acted upon by enzymes in the soil to mineralize the N in them to NH<sub>4</sub><sup>+</sup> ions. Once in the NH<sub>4</sub><sup>+</sup> form and until nitrified to the NO<sub>3</sub><sup>-</sup> ion form, the N in these two fertilizers is also sorbed to the CEC, the negatively charged sites on soil colloids, and is subject to transport by soil

**Table 2.**  
Nitrogen fertilizer materials, their formulas, and chemical analysis

| Material               | Chemical Formula  | Chemical Analysis (%N) |
|------------------------|---|------------------------|
| Anhydrous ammonia      | NH <sub>3</sub>   | 83                     |
| Ammonium nitrate       | NH <sub>4</sub> NO <sub>3</sub>                                     | 33.5                   |
| Ammonium sulfate       | NH <sub>4</sub> SO <sub>4</sub>                                     | 21                     |
| Diammonium phosphate   | (NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> PO <sub>4</sub>      | 18-21                  |
| Monoammonium phosphate | NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>                      | 11                     |
| Calcium nitrate        | Ca(NO <sub>3</sub> ) <sub>2</sub>                                   | 15                     |
| Calcium cyanamide      | CaCN <sub>2</sub>   | 20-22                  |
| Potassium nitrate      | KNO <sub>3</sub>  | 13                     |
| Sodium nitrate         | NaNO <sub>3</sub>   | 16                     |
| Urea                   | CO(NH <sub>2</sub> ) <sub>2</sub>                                   | 45                     |
| Urea-ammonium nitrate  | CO(NH <sub>2</sub> ) <sub>2</sub> + NH <sub>4</sub> NO <sub>3</sub> | 32                     |

erosion. The N in organic materials such as crop residues is also first mineralized to  $\text{NH}_4^+$ , again being subject to sorption to the CEC of the soil until nitrified to the  $\text{NO}_3^-$ . The  $\text{NO}_3^-$  ion, when it is part of the chemical formula in compounds shown in Table 2, does not sorb to the CEC of the soil. Nitrate, a water-soluble anion, is very mobile, and moves readily in dissolved form. The primary transport mechanism for  $\text{NO}_3^-$  ions is by leaching or surface runoff (including return flow). Nitrate that is leached below the crop-root zone often ends up as a pollutant in groundwater supplies. Nitrate can also be dissolved in surface runoff water or in return-flow water that returns to the surface to become part of the runoff. Nitrate and  $\text{NO}_3^-$  ions can also be denitrified and lost to the atmosphere as  $\text{NO}$ ,  $\text{N}_2\text{O}$ , or  $\text{N}_2$  (Eq. 1).

### 3.2. Runoff

Amount and timing of rainfall and soil properties are key factors that influence loss of dissolved N in runoff. Landscape and soil permeability affect infiltration rates. Soils with low runoff potential usually have high infiltration rates, even when wet. They often consist of deep, well- to excessively-drained sands or gravels. Amount of water infiltration will depend on initial soil water content, soil organic matter (SOM), soil structure, and soil texture. In contrast, soils with high runoff potential have one or more of the following characteristics: very slow infiltration rates when thoroughly wetted and containing high clay content possibly of high swelling potential, high water tables, a claypan or clay layer at or near the surface, or are shallow over a nearly impervious subsurface layer. A combination of soil conditions of high runoff potential and high precipitation amounts are especially conducive to surface runoff losses. Steeper slope gradients increase amount and velocity of runoff, while depressions, soil roughness, and presence of vegetative cover or crop residue decrease runoff by improving the infiltration. Williams and Kissel (1991) studied the relationship between soil permeability and surface runoff across several climates. Soils with higher infiltration rates are classified as Hydrology Group A; well- to excessively-drained sands or gravel soils with low runoff potential. Opposite to this is Hydrology Group D that is represented by high-clay; often poorly to very poorly drained soils that have a high runoff potential. Concentration of dissolved N in surface runoff from soils under conservation or no-tillage often is higher than from soil under conventional tillage (Romkens, 1973; McDowell and McGregor, 1984). Reasons may include incomplete incorporation of surface-crop residues, and higher dissolved N concentration in the surface soil because of residue accumulation and decomposition. Also, high concentrations of soluble N can occur when there is a soil horizon barrier (e.g., Fragipan) present in the soil profile that results in return flow of leached N back to the soil surface (Lehman and Ahuja, 1985).

Some of the effects on dissolved nutrients in surface and subsurface water discharges that are associated with agricultural nutrient management for crop production and the use of conservation tillage for erosion control are illustrated (Figure 3) by the work of Alberts and Spomer (1985). Their study site, for this 10-year study, was in the deep loess hills in western Iowa. The loess is underlain by nearly impervious

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is also first mineralized in the soil until nitrified to the nitrate in compounds shown as a water-soluble anion, is the primary transport mechanism (including return flow). Nitrate is a pollutant in groundwater or in return-flow water. Nitrate and  $\text{NO}_3^-$  ions are converted to  $\text{H}_2\text{O}$ , or  $\text{N}_2$  (Eq. 1).

Some key factors that influence infiltration rates, even in drained sands or gravels, are water content, soil organic matter, soils with high runoff rates: very slow infiltration rates, possibly of high water content or near the surface, a combination of soil conditions are especially conducive to amount and velocity of runoff. Vegetative cover or crop residues (Dowell and McGregor, 1985) can occur when there is a high concentration of dissolved nitrogen, which results in return flow.

Subsurface water discharge for crop production is illustrated (Figure 3) by this 10-year study, was high by nearly impervious

glacial till at depths of 4.6 to 24.4 m. Lateral water movement occurs in a saturated soil zone that exists at the loess-till interface. Water from both surface runoff and subsurface flow was sampled. In their study, watershed 2 (WS2) was conventionally tilled (33.5 ha) while watersheds 3 and 4 (WS3 and WS4) were contour-till planted (43.3 ha) and terrace-till planted (60.8 ha), respectively. About 65 head of cattle gleaned the corn stalks from WS3 and WS4 from mid-November to March each year.

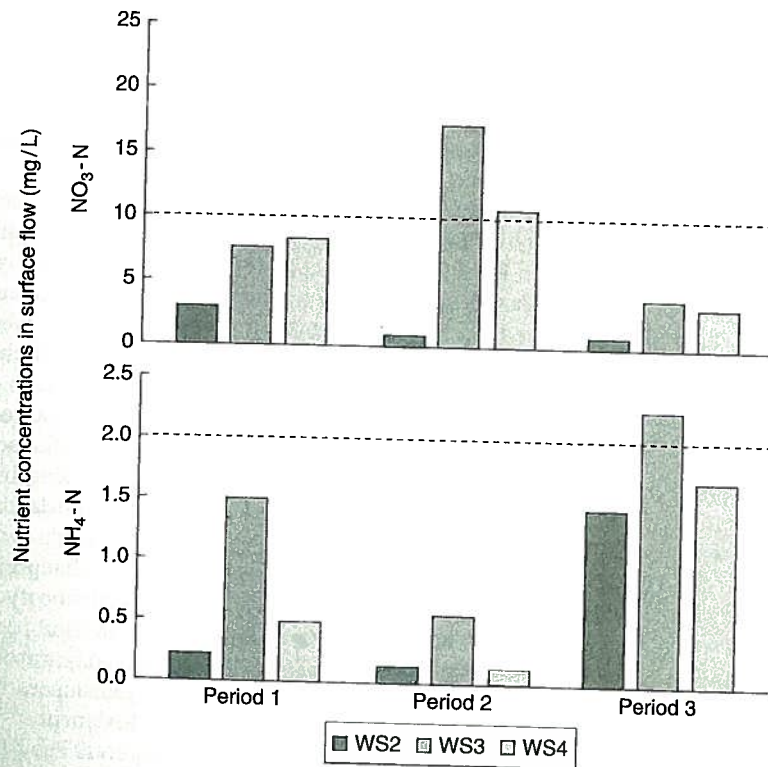


Figure 3. Runoff-weighted concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N in surface flow by seasonal period. Dashed lines represent current water quality standards. (From Alberts and Spomer, 1985).

Figure 3 shows the 10-year, runoff-weighted concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for three time periods; April through June (fertilization, seedbed preparation, and crop establishment period); July through November (crop reproduction and maturation period); and December through March (crop residue period) or periods 1, 2,

and 3 respectively. Water quality criteria for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are shown by dashed lines (US EPA, 1982; Fletcher, 1991) in Figure 3 as 10 and 2 mg/L; respectively. Highest  $\text{NO}_3^-$  concentrations from the till-planted watersheds (WS3 and WS4) occurred during July through November (period 2), perhaps as a result of evaporative drying moving previously applied fertilizer salts to the soil surface. Preplant applications of fertilizer for the conventionally tilled watershed (WS2) had been incorporated with a disk. Ammonium N concentrations were generally from cattle manure and leaching of  $\text{NH}_4^+$  from partially decomposed corn stalks. Issues illustrated by this study include the need to place fertilizer below the soil surface while still maintaining residue cover for soil erosion control. Fall and winter livestock grazing of crop residues likely contributes to N runoff since the manure and urine may be deposited on frozen ground.

### 3.3. Erosion

Detachment of sediments and nutrients from the parent soil is selective for soluble nutrients (such as  $\text{NO}_3^-$ ) and for the fine soil fractions to which nutrients (such as  $\text{NH}_4^+$  and the SOM N) are associated. Therefore, N contained in runoff and/or associated with sediments is present in higher concentrations than in the parent soil. This difference is termed the enrichment ratio. Enrichment of sediment loads is a two-step process: enrichment during particle suspension and enrichment due to re-deposition of coarser particles during overland and channel flows. In order for management practices to decrease the effect of water erosion processes on the production and transport of sediment associated N, they must directly influence the processes involved. Such practices need to protect against soil particle detachment, slow sediment transport, and enhance sediment deposition within the landscape rather than allowing the sediments to move into surface water.

Soil erosion is important to the movement of N into surface water that primarily occurs with soil erosion by water, rather than by wind. Briefly, soil erosion by water includes the processes of detachment, transport, and deposition of the soil particles by raindrops or surface flow (Foster et al., 1985). Some sediment may travel only a few millimeters while other sediment may be transported long distances before either being deposited or reaching a lake, reservoir, or stream. Movement of  $\text{NH}_4^+$  results because it is sorbed to the surfaces of clays and finer sediments. The  $\text{NO}_3^-$  is completely water soluble and thus moves with the water until it re-enters the available soil pool, is utilized by microbes or plants, becomes denitrified, is possibly deposited and buried, or enters and possibly degrades surface and/or groundwaters. A major source of the N that degrades surface water is that which is transported in SOM. A large part of the SOM and soil organic N (SON) contained in it are concentrated near the soil surface and are therefore vulnerable to erosion and oxidative (mineralization/nitrification) processes. Within the United States, about 400 million  $\text{m}^3$  of sediment are dredged each year in the maintenance and establishment of waterways and harbors (Sopper, 1993). Two independent methods of estimating the amount of eroded SON in sediments are to utilize information about river sediment

are shown by dashed 2 mg/L; respectively. eds (WS3 and WS4) is a result of evapora-soil surface. Preplant hed (WS2) had been generally from cattle rn stalks. Issues illus-the soil surface while and winter livestock the manure and urine

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loads or to use estimates of amounts of eroded sediments themselves. To use the sediment load approach for 1991 data collected by Leeden et al. (1991) show the suspended load in 12 major rivers in the United States were 336 Tg/year. Assuming 75% of the suspended load is mostly from soil erosion from cropland the amount of sediment transport attributed to cropland was ~250 Tg/year. Assuming a delivery ratio of 10% and SON content of sediment of 0.25% (Follett et al., 1987; Lal, 1995), the total SON displaced by soil erosion from cropland was about 6.25 Tg/year. Alternatively, (Lal et al., 1998) used an estimate of the amount of eroded sediments to calculate soil organic carbon (SOC) losses. By assuming a SOC:SON of 110:9 in sediment (Follett et al., 1987) the total SON displaced by soil erosion would be about 9.6 Tg/year. Thus considering only the United States, soil erosion serves as an environmental source of 6–9 Tg/year as SON.

Much still needs to be learned about managing cropland soil erosion. For example, Follett et al. (1987) assessed effects of tillage practices and slope on amount of organic N in eroded sediments from cultivated land surfaces in Minnesota (USA) for major land resource areas (MLRAs) 102, 103, 104, and 105. Their estimates using the Universal Soil Loss Equation with average organic matter in topsoil by slope category, dominating slope gradient, and soil series indicates that conservation tillage compared to conventional tillage decreases the amount of organic N associated with eroded sediments by about half with some additional decrease resulting from the use of no-tillage. One can assume that added fertilizer N responds similarly to organic N when it is sorbed to clay surfaces, finer sediments, or to SOM.

### 3.4. Leaching

Nitrate is a negatively charged ion that is repelled by, rather than attracted to the negative charged clay mineral surfaces in soil (i.e., the CEC). It is the primary form of N leached into groundwater, is totally soluble at concentrations found in soil, and moves freely through most soils. Movement of  $\text{NO}_3^-$  through soil is governed by convection of soil solution (i.e., mass-flow) and by diffusion within the soil solution Jury and Nielson (1989). The widespread appearance of  $\text{NO}_3^-$  in groundwater is a consequence of its high solubility, mobility, and easy displacement by water. An extensive literature about N-management, leaching, and groundwater quality includes that by CAST (1985), Follett (1989), Follett et al. (1991), Follett and Wierenga (1995), and Delgado et al. (2005). In addition, it is well documented that  $\text{NO}_3^-$ -N leaching rates will be affected by rain, irrigation, tile drainage, and water table fluctuations during the growing season (Meisinger and Delgado, 2002).

Juergens-Gschwind (1989) reported on leaching losses observed under widely varying conditions (lysimeters, drainage water measurements in field trials, catchment areas, profile and groundwater research in field trials) (Figure 4). The results were made comparable by referencing the N-losses at each site to a ~300 mm drainage level per year. The leaching risk was distinctly higher on arable land than on grassland, and on lighter textured soils than on heavy-textured soils. An upward shift in the data was observed when going from lower nutrition rates obtained by

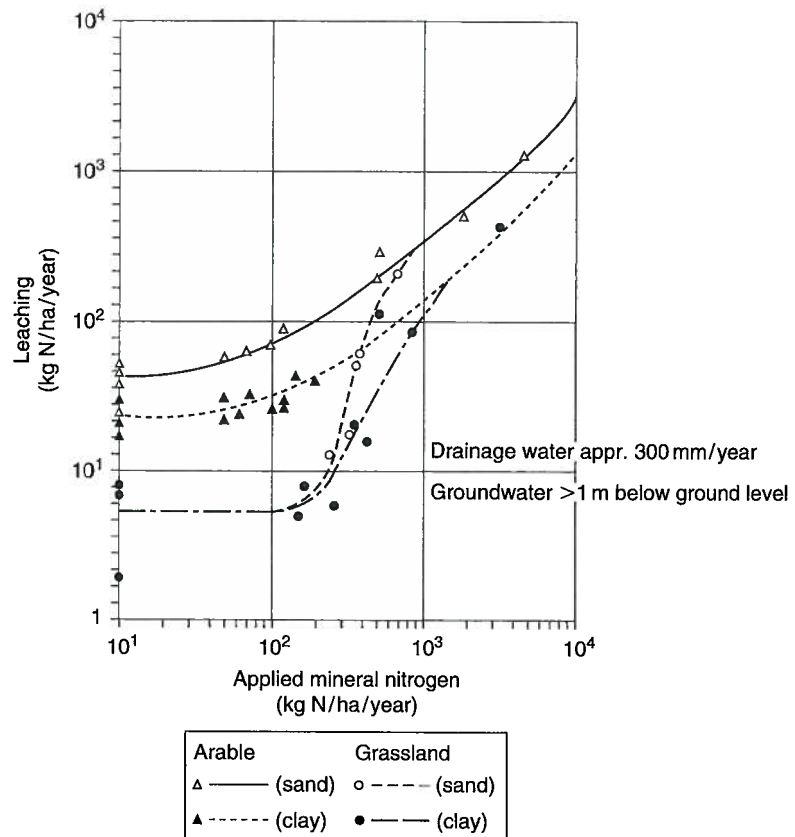


Figure 4. Leaching of nitrogen from arable and grassland systems. (Adapted from Juergens-Gschwind, 1989).

normal fertilization practices to the very high rates that can result from excessive N-fertilization and animal manure disposal (rates in excess of the plant nutrient requirements) on agricultural lands. Soil texture influences how rapidly  $\text{NO}_3^-$  leaching through soil can occur. This influence of soil texture, in sandy soils is documented by Delgado et al. (1999) in which more  $\text{NO}_3^-$  leaching was observed on a loamy sand than on a sandy loam. Also, unless the soil is anaerobic, excess amounts of  $\text{NO}_3^-$  also leach on heavy-textured soils, as illustrated in an N-rate study with irrigated corn (*Zea mays* L.) by Godin (1999). Godin used  $^{15}\text{N}$ -labeled fertilizer on a clay loam soil, he observed that the recommended fertilizer rate (135 kgN/ha) adequately satisfied the crop N requirement and resulted in higher percent recovery of

N than did the excess N rate (200 kg N/ha). At the excess N rate, fertilizer  $^{15}\text{N}$  had leached below the crop root zone (0.9 m) by harvest of the first year and to a depth of over 1.5 m by harvest of the second year.

#### 4. NITROGEN CYCLING IN PASTURE SYSTEMS

Inputs of N into pasture systems include from fertilizer, manure, BNF, wet and dry deposition, supplemental feed to livestock, and mineralization of SOM (Figure 2). Losses may occur through harvest of animal or plant products, transfer of N within the pasture with animal excreta, fixation of N in the soil, soil erosion, surface runoff, leaching, volatilization, and denitrification. The soil compartment includes a pool of available N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) for plant uptake that can exchange with N in residues (organic N) and, for some soils, with fixed  $\text{NH}_4^+$  held between mineral layers of clay. Plant N-uptake is from the available soil pool. The N in the herbage is either harvested and removed from the field, returned to the soil as crop residue and root material, and/or eaten by grazing animals and either utilized by the animal or excreted as feces or urine and returned to the soil.

##### 4.1. Role of Soil Organisms

Soil microfauna and microflora have a major role in N cycling. Release of N from plant and animal residue depends on microbial activity. Soil bacteria utilize the more readily available, soluble, or degradable organic fractions. Fungi and actinomycetes decompose the resistant cellulose, hemicellulose, and lignin. Dung beetles, earthworms, and other soil fauna increase the decomposition rates of feces and plant litter by mixing them with soil. Rhizobia and vesicular arbuscular mycorrhizae (VAM) associate with plant roots to fix N and increase nutrient and water scavenging ability, respectively. VAM infection of roots is considered more helpful for tap rooted pasture legume species than for fibrous rooted grasses. At any time, soil-microbial biomass contains much of the actively cycling N of the soil and represents a relatively available N pool, capable of rapid turnover (Bristow and Jarvis, 1991). The energy flux through the soil microbial biomass (SMB) drives the decomposition of organic residues (Smith and Paul, 1990) and SOM. Plant root biomass and soil-microbial processes are intimately linked in grassland systems as described by Reeder et al. (2000). If decomposition exceeds carbon inputs, the SOM will decline. The resulting mineralization of N (and other nutrients) will result in their becoming vulnerable to possible losses into the environment by leaching, denitrification, or other mechanisms (Follett et al., 1995). Because its levels are relatively stable for a particular soil/land-use system, even though the SMB pool is very active for nutrient cycling, SMB can serve as a measure (index) of the effects of agricultural management practices on soil quality. In their study, Follett et al. (1995) utilized  $^{15}\text{N}$  labeled fertilizer and followed the N in the SMB fraction under no-till in a 4-year (winter wheat-sorghum-fallow-winter wheat) cropping sequence. Their conclusion was that, under no-till, biological processes conserved the N by

accumulation of crop residue carbon and N near the soil surface by recycling of N through the crop-SMB system, and maintenance of N in organic forms.

#### 4.2. Role of the Grazing Animal

Grazing animals affect plant growth by defoliation, traffic patterns, herbage fouling, partitioning of ingested N to body weight, feces, and urine, re-distribution of herbage N in excreta, and N turnover rate. Defoliation by grazing animals prevents senescence of plant tissue, removes N in animal products, changes the N pathway from internal plant recycling or leaf fall to return as feces and urine, increases light penetration into the canopy and, through selective grazing, may alter botanical composition by promoting one species over another. Animal traffic may contribute to soil compaction and sometimes contributes to less desirable soil characteristics for plant growth. Herbage fouling by feces reduces its acceptability for grazing, thereby increasing maturity and reducing forage quality and/or consumption by grazers. Urine does not cause herbage to be unacceptable for grazing. Livestock recycle much of the N that they consume from forage back to the soil. The N retention of forage N by livestock, as a percentage of dietary intake, ranges from about 8+% of live weight gain (LWG) (e.g., in steers) to 20% (Follett and Wilkinson, 1995) in high producing animals (e.g., milk cows). For example, a 250 kg steer that ingests 6 kilogram of forage per day (containing 3% of nitrogen in the forage) and gaining 0.8 kg/day may ingest 180 g N/day, retain about 20 g in LWG (12% retention) and excrete the remainder, about 160 gram of nitrogen per day. Excretion as feces and urine both result in volatile losses of  $\text{NH}_3$ . About 74% of the total N excreted is in the urine (Follett and Wilkinson, 1995) and a single urine spot can have an N concentration corresponding to more than 600 kg N/ha (Whitehead, 1995). Some of the N is released to the atmosphere as volatile  $\text{NH}_3$  while the N remaining in the excreta and its associated plant residues return to available nutrient pools in the soil.

Animals on range may utilize more of the forage near watering points. Greater density of dung and increased levels of soil profile  $\text{NO}_3^-$  are frequently observed in areas near watering and shade points (Wilkinson et al., 1989; Haynes and Williams, 1993). Even without transfer of N to unproductive areas such as woods, shade, watering points, fence lines, and paths, consumption and excretion of N by ruminants results in gathering of N from large areas of the pasture, and deposition of the N to smaller areas. This gathering effect results in less efficient re-distribution of N for subsequent uptake by forage plants. On an annual basis, less than 35% of pasture areas receives excretal N and some areas receive one or more applications (overlapping of excreta). Thus some of the pasture area is under fertilized and some over fertilized.

#### 5. PRIMARY AND SECONDARY FLOWS OF NITROGEN

Primary and secondary flows of N are very much a part of the animal/plant N cycling ecosystem as discussed above. The following discussion is focused on

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cropland and surrounding ecosystems but also relates to a livestock system. Figure 5 illustrates some of the flows of N following input of 100kg of fertilizer N. Primary flows are shown as dashed lines. In this example, fifty of the 100kg are harvested in the crop and fifty are lost by the combination of leaching (25 kg), surface runoff (5 kg), and gaseous loss (20kg, primarily denitrification). If 10% of the gaseous N loss is N<sub>2</sub>O, then 2kg N<sub>2</sub>O-N would be generated in the primary cycle. Secondary flows, shown by the solid lines in Figure 5, include feeding of the 50kg of harvested N to animals, which might generate about 45 kg of manure N. The manure is returned to cropland to create a secondary flow of the original fertilizer N. Part of this secondary flow of applied fertilizer N is again removed from the field by the harvested crop; through gaseous losses as NH<sub>3</sub>, N<sub>2</sub>O, NO, and as N<sub>2</sub> gas, surface runoff, and NO<sub>3</sub><sup>-</sup> leaching. However, about half of the manure N is volatilized as NH<sub>3</sub> prior to or during manure application. Volatilized NH<sub>3</sub> is aerially dispersed and eventually can be returned to and cycled through both natural ecosystems and cropland (Duxbury et al., 1993; Mosier, 2001; Nadelhoffer, 2001). Estimates are that, over the course of about 50 years, more than 80% of the N applied to a field will eventually return to the atmosphere through denitrification (Cole et al., 1993). Generally, greater than 95% of this N returns to the atmosphere as N<sub>2</sub> gas but some unknown amount is released as N<sub>2</sub>O.

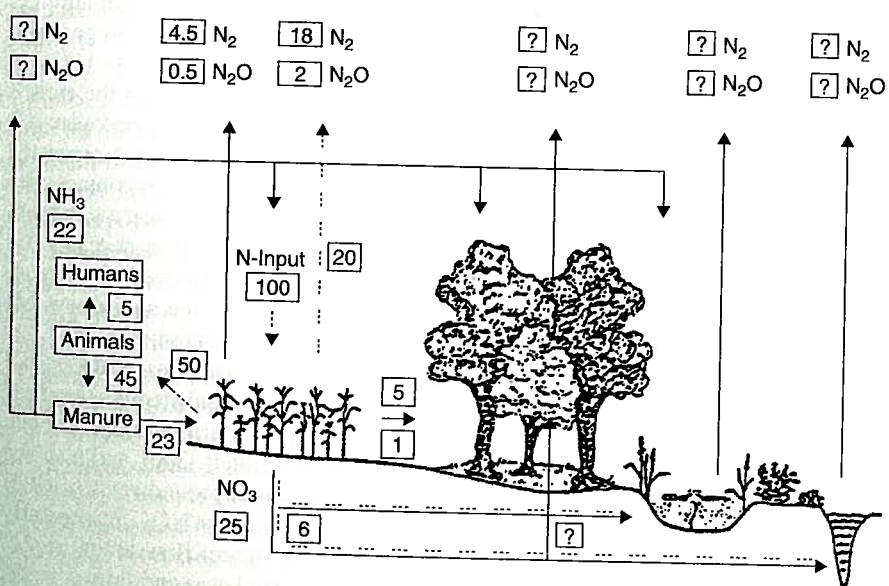


Figure 5. A simplified flow of N fertilizer through the environment. (From Duxbury et al., 1993).

Mosier et al. (1998) evaluated the International Panel on Climate Change (IPCC) methodology (IPCC 1997) as part of an effort to provide a more comprehensive  $N_2O$  emission calculation methodology. Using mid-point values, they recommended that the emission factor relating  $N_2O$  directly from soil to fertilizer-N application should be  $1.25 \pm 1\%$   $N_2O-N$  of the applied fertilizer N. If both direct and indirect-emissions are considered, then about 2.0% of N-input into agricultural system would be emitted as  $N_2O-N$  annually.

## 6. GROUND AND SURFACE WATER

### 6.1. Groundwater

Nitrogen is the nutrient of most concern in the contamination of groundwater, primarily resulting from  $NO_3^-$  leaching. Leaching of  $NH_3^-$  is generally not important since it is strongly adsorbed by soil, except in sands and soils having low retention (CEC) capacities. However,  $NO_3^-$  is readily leached deeper into the soil profile, below the bottom of the root zone, and may eventually leach into groundwater supplies. Nitrate that moves below the crop-root zone is totally soluble and can potentially leach into groundwater. Groundwater flows within permeable geologic formations called aquifers. Aquifers are natural zones beneath the earth's surface that often yield economically important amounts of water. In a very simple system, water and dissolved  $NO_3^-$  percolate below the root zone and through the intermediate vadose zone to an aquifer. From there, these waters can recharge deeper aquifers or discharge to streams or water bodies. Aquifers are subdivided based on geology. A meaningful division, from the perspective of groundwater quality, is between confined and unconfined aquifers. Confined aquifers are separated from the earth's surface by flow-impeding layers that, depending on the degree of impedance, are called aquicludes or aquitards (Figure 6). Unconfined aquifers are not separated from the earth's surface by a flow-impeding layer, and are therefore in contact with the atmosphere through the unsaturated zone. Aquifer systems are often complex. To minimize the amount of  $NO_3^-$  that may enter groundwater, it is necessary to understand the aquifer system and then to identify and apply improved N-management practices to the recharge area of the aquifer. Structure of the aquifer system and subsequent flow patterns affect  $NO_3^-$  dilution, transport, and removal.

Water quality impact zones for N are wells, groundwater supplies, streams, and surface water bodies. Because 95% of rural inhabitants and substantial livestock populations consume groundwater,  $NO_3^-$  concentration is most important and can cause both human and animal health effects (Follett and Follett, 2001 and also see Chapter 4). Those factors that control  $NO_3^-$  concentration in groundwater, such as dilution and well position relative to the primary source areas for  $NO_3^-$ , can greatly affect their impact on groundwater quality. In contrast, stream flow tends to mix groundwater discharge and surface runoff from different land uses and time periods, thus causing generally much lower and more stable  $NO_3^-$  concentrations. Although elevated concentrations of  $NO_3^-$  are most often observed at shallow water table

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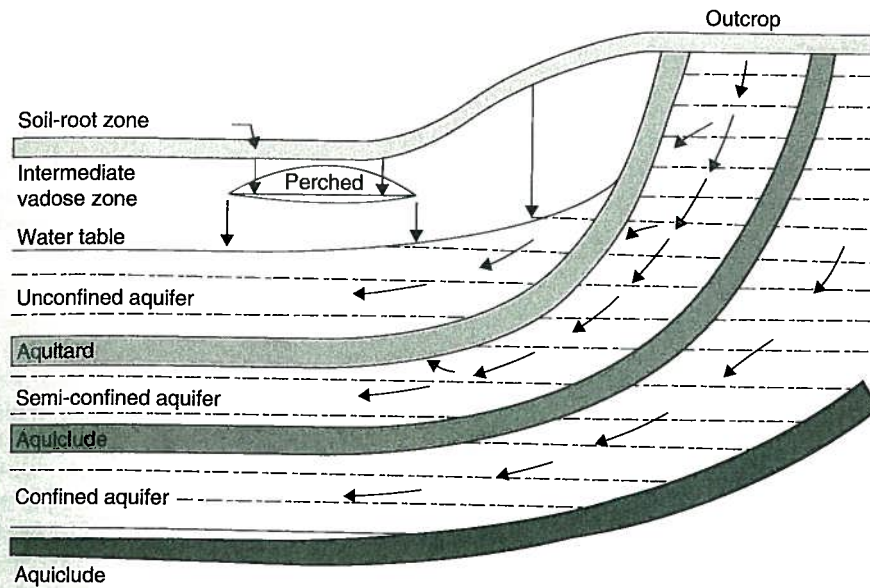


Figure 6. Schematic of vadose zone, aquifer system, and flow direction. (From Pionke and Lowrance, 1991).

depths, long-term increases in deeper wells are possible where deep aquifers are recharged by  $\text{NO}_3^-$ -rich waters. Movement of  $\text{NO}_3^-$  with percolating water, through the unsaturated zone, can be very slow and time required for present-day inputs of  $\text{NO}_3^-$  to reach the groundwater reservoir may be many years. Schuman et al. (1975) observed an average rate of  $\text{NO}_3^-$  movement through silt soils (loess) of about 1 m/year for Iowa. Where 168 kgN/ha (the recommended N rate) was applied, N did not accumulate beneath the crop-root zone. Groundwater flows from areas of high pressure toward areas of low pressure (hydraulic head). Generally movement is slow and there is little mixing of contaminated with uncontaminated groundwater as they flow through the saturated zone, contaminants tend to remain concentrated in zones. Burkart and Stoner (2001) provide a description of shallow aquifer types and an analysis of specific vulnerability to agricultural N sources and management of relatively homogenous agricultural systems in the United States. As described by Johnes and Butterfield (2002), reliable and accurate regional scale N flux modeling is needed to take into account the heterogeneity of landscapes and their impacts on N cycling processes within homogenous landscape units.

Groundwater can re-join the surface of the ground down slope and adjacent to a perennial stream, often along a riparian zone similar to that shown in Figure 7. In a riparian zone, that water table moves progressively toward the land surface and the

intermediate vadose zone is lost as the stream channel is approached. During storms or wet periods, the water table can rise rapidly to intersect the land surface at some distance from the stream – discharge of groundwater to the soil-surface results. The system can be dynamic, with water table levels, extent of the saturated zone, and flow directions changing substantially and rapidly with precipitation (Pionke and Lowrance, 1991). As the groundwater and its dissolved  $\text{NO}_3^-$  move into the more biologically and chemically active soil zones, the  $\text{NO}_3^-$  becomes available for uptake by riparian vegetation. Also, if oxygen levels become limited, activation of soil biological and chemical regimes results in denitrification.

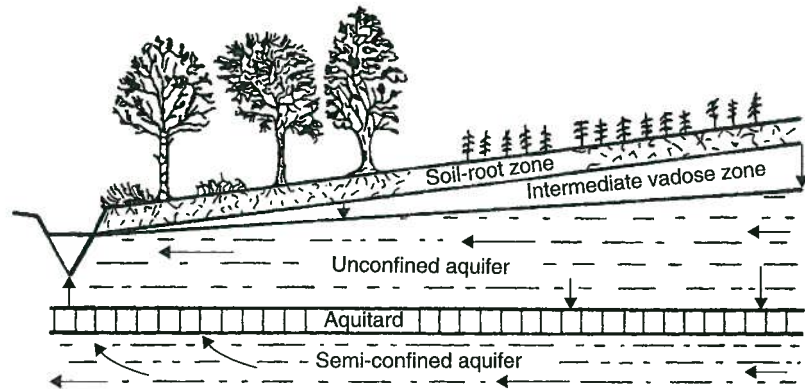
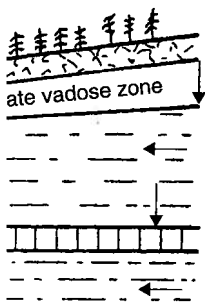


Figure 7. Schematic of the vadose zone, aquifers, and flow directions in a typical riparian zone subject to a humid climate. (From Pionke and Lowrance, 1991).

Many sites of excessive  $\text{NO}_3^-$  accumulation are recognized. Viets and Hageman (1971) conducted a comprehensive review of studies in the United States. Substantial accumulations of  $\text{NO}_3^-$  were found in deep profiles of irrigated Colorado soils, except where alfalfa was the crop (Stewart et al., 1967). Muir et al. (1973) conducted a study of factors influencing  $\text{NO}_3^-$  content of groundwater in Nebraska. Their data indicated that quality of Nebraska water was not being materially influenced by agricultural use of commercial fertilizers previous to that time except on sites of intensively irrigated sandy soils and in valley positions with a shallow underlying water table.

There are numerous sources of N in the environment. Keeney (1989) identified intense land-use activities (e.g., irrigation farming of high value crops, high density of animal operations, or septic tank systems) as causes of excessive  $\text{NO}_3^-$  in groundwater. Irrigation of cropland is widely practiced in the United States, particularly in the more arid west and in the southeast where economic returns are high. The review by Pratt (1984) shows that in situations where roots have access to the entire soil solution,  $\text{NO}_3^-$  is not leached unless excess fertilizer N is added or the soils are over-irrigated.

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As the subsurface system is generally large and not uniform in structure, function, or efficiency, it is much easier to focus on source areas rather than on the whole system. The source area is a bounded area or volume within which one or a set of related processes dominate to provide excessive production (source), permanent removal (sink), detention (storage), or dilution of  $\text{NO}_3^-$ . Source area effects, by definition, are disproportionately large relative to the area or volume occupied. If the source area(s) can be identified, then positioned relative to the generalized flow pattern within the system, a basis is possible for estimating effects on an impact zone.

Systematic data on production practices, input use, and management systems are insufficient to do many of the assessments that are needed. However, quantity and quality of soil-survey data, climate data, and assessments of  $\text{NO}_3^-$  concentrations in various aquifers are increasing. Statistical techniques and simulation models used in conjunction with Geographical Information Systems (GIS) technology show promise in identifying and assessing  $\text{NO}_3^-$  leaching across regions (Christy, 1992; Wylie et al., 1994). Models such as the Nitrate Leaching and Environmental Analysis Package (NLEAP) (Shaffer et al., 1991; Delgado et al., 2000; Shaffer et al., 2001a, 2001b) use farm management, soil, and climate information to estimate  $\text{NO}_3^-$  leaching at a farm or even the soil series level. Such approaches allow the determination of potential landscape  $\text{NO}_3^-$ -leaching hotspots when sufficient information is available. As technology continues to improve it should become possible for decreasing losses of N to the environment by targeting improved practice to those areas, farm enterprises, fields within a farm, or even locations (hot spots) within a field that cause the most damage.

Two approaches to minimize  $\text{NO}_3^-$  leaching into groundwater are: (1) optimum use of the crop's ability to compete with processes whereby plant available N is lost from the soil-plant system. Key elements of the first approach are to assure and N assimilation capacity and vigorous crop growth, and to apply N in phase with crop demand; (2) The second approach might include use of nitrification inhibitors or delayed release forms of N to directly lower potential losses. In addition, realistic crop-yield goals must be selected. Olson (1985) emphasizes that a realistic yield goal would be no more than 10% above recent average yield for a given field or farm. Bock and Hergert (1991) describe a worksheet approach to estimate N-rate requirements. More recently, Kitchen and Goulding (2001) describe estimating N fertilizer requirements and estimating target yields. However, setting yield goals and N-rates are still difficult because of limitations imposed by environmental factors and/or the farmers' own operational skills.

**6.2. Subsurface Drainage**

Still related to the above discussion, high  $\text{NO}_3^-$  flux that often occurs in streams draining agricultural land comes primarily from the groundwater contributions (including tile-drainage effluent) to stream flow. During discharge events, the groundwater and its  $\text{NO}_3^-$  load will include shallow interflow (sometimes referred to as subsurface runoff). However, during the majority of time, deeper baseflow that

re-joins surface water provides the major contribution of  $\text{NO}_3^-$  (Hallberg, 1989). Subsurface drainage is a common water management practice in highly productive areas with poorly drained soils. This practice increases crop yields, reduces risk, and improves economic returns. Substantial amounts of nutrients can be contained in subsurface drainage such as in tile-drainage water (Randall and Goss, 2001). Concern about stream and river water quality and ecological impacts on receiving bodies, that is, lakes and coastal marine areas on the continental shelf have escalated in the last 10 years. Hypoxia, a condition where the concentration of dissolved oxygen is  $<2 \text{ mg/L}$  has been known to exist in portions of the world's oceans and some large lakes for several decades. The cause of hypoxia has been linked indirectly to the load of nutrients, primarily N, delivered to the Gulf via the Mississippi River drainage basin (Turner and Rabalais, 1994; Rabalais et al., 1996). Nitrate concentrations in the Mississippi River are generally highest in the tributaries emanating from Illinois, Iowa, and Minnesota and vary seasonably, usually being higher in winter, spring, and early summer and lower in late summer and early autumn (Antweiler et al., 1995). Burkart and Stoner (2001) determined hydrologic units with the largest residual N contributions available to streams and largest total N loss rates are located in the Upper Mississippi River and the Ohio River basins where row crops, particularly corn and soybean, dominate the landscape. Linkage of subsurface tile drainage of agricultural land,  $\text{NO}_3^-$  in surface water, effect of uncontrollable factors (precipitation and soil mineralization), effects of controllable factors (cropping system, rate and time of N application, nitrification inhibitors, tillage, and drain tile spacing and depth) on losses to subsurface drainage are recently discussed by Randall and Goss (2001 and see also Chapter 6). They report on how long-term field plot research demonstrate effects of crop and nutrient management practices on edge-of-field losses of  $\text{NO}_3^-$  to subsurface drainage water and on research conducted at widely different scales pointing to how agricultural systems affect  $\text{NO}_3^-$  levels in river waters.

Stream water quality data from 904 nonpoint source-type watersheds across the United States were summarized by Omernik (1977). The watersheds ranged in character from forested areas, to urbanized regions, to areas dominated by row-crop agriculture. The data were compared to land use and, as shown in Figure 8, especially the inorganic N concentrations are directly related to the amount of the watershed used for agriculture. The data in Figure 8 are over two decades old now; however, reviews of temporal trends since then also show significant increases in  $\text{NO}_3^-$  (Hallberg, 1989). Referring to Figure 8, long-term environmental concern about the impact may not only need to be the increasing loads of soluble N, but also the dramatic change in the proportion of the particulate and soluble N concentrations. In forest and range systems the major N load was as organic N, much of it in the particulate fraction (related to organic matter); but now the major load in agricultural areas is as soluble  $\text{NO}_3^-$ .

### 6.3. Surface Water

Agricultural production has been identified as a major nonpoint source of pollution in US lakes and rivers that do not meet water quality goals. Nitrogen can be

$\text{NO}_3^-$  (Hallberg, 1989). Nitrate concentrations in highly productive crop yields, reduces risk, nutrients can be contained and land use changes (Randall and Goss, 2001). Land use changes and their impacts on receiving water bodies and the continental shelf have escalated. The concentration of dissolved nitrogen in the world's oceans and the Gulf of Mexico has been linked to land use changes (Gulf via the Mississippi River, et al., 1996). Nitrate concentrations in the tributaries emanating from the Midwest are generally being higher in winter and early autumn (Antweiler et al., 1996). Agricultural units with the largest nitrogen loss rates are located in the Midwest where row crops, particularly corn, and subsurface tile drainage are common. Other controllable factors (precipitation, cropping system, rate and timing of fertilizer, and tile spacing and depth) also influence nitrogen loss (Randall and Goss (2001) plot research demonstrate that field losses of  $\text{NO}_3^-$  to streams vary on different scales point-to-point.

Large watersheds across the United States ranged in characteristics dominated by row-crop agriculture. Figure 8, especially the 90% agriculture watershed, the amount of the watershed used for agriculture is high; however, reviews of nitrogen losses in  $\text{NO}_3^-$  (Hallberg, 1989) demonstrate that the impact may vary. So the dramatic change in nitrogen loss. In forest and range systems, the particulate fraction (related to erosion) is as soluble  $\text{NO}_3^-$ .

Nonpoint source of pollution goals. Nitrogen can be

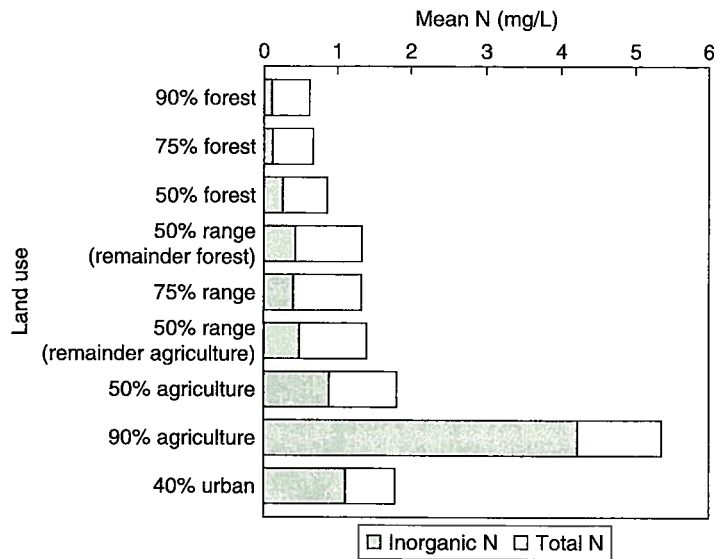


Figure 8. Land use and mean inorganic and total N concentrations from stream data from 904 nonpoint source-type watersheds. (From Omernik, 1977).

transported into aquatic systems from airborne, surface, underground, and *in situ* sources (Table 3). Sediment is the single largest type of pollutant followed by nutrients (NRC, 1993). As discussed above, much of the N that enters lakes and rivers is associated with eroding sediments ( $\text{NH}_3^+$ ), eroding SOM (organic forms of N and  $\text{NH}_4^+$ ), and dissolved in surface runoff (primarily  $\text{NO}_3^-$ ). The water that runs over the soil surface during a rainfall or snowmelt event, by rill or sheet flow, or even high-order channelized flow, may have a relatively high concentration of organic N related to suspended particulate matter, but it is typically quite low in  $\text{NO}_3^-$  concentration.

When waters become too enriched by nutrients, the aquatic environment can become eutrophic – a result of the ensuing luxuriant growth of algae and macrophyte growth to levels that can choke navigable waterways, increase turbidity, and depress dissolved oxygen concentrations. Rapid growth of algae is the greatest and most widespread eutrophication problem. When a large mass of algae dies and begins to decay, the oxygen dissolved in water is depleted and certain toxins are produced, both of which can kill fish. The complexities of eutrophication are that nutrient status of various species of algae can vary from lake to lake or even from different areas and depths of the same lake on the same day. Excess algal growth can create obnoxious conditions in ponded waters, increase water treatment costs by clogging screens and requiring more chemicals, and cause serious taste and odor problems.

Agricultural sources of N can arrive in surface water via airborne dust from wind erosion, through gaseous transport of  $\text{NH}_3$  volatilized from livestock manure

**Table 3.**  
Sources and sinks for the nitrogen budgets of aquatic systems.

| Sources  | Sinks   |
|--|---|
| <i>Airborne</i>                                  |   |
| Rainwater  | Effluent loss                                     |
| Aerosols and dust                                | Ground water recharge                             |
| Leaves and miscellaneous debris                  | Fish harvest                                      |
| <i>Surface</i>                                   |   |
| Agricultural drainage, including tile drainage   | Weed harvest                                      |
| Water erosion of sediment from agricultural land |   |
| Animal waste runoff                              | Insect emergence                                  |
| Marsh drainage                                   |   |
| Runoff and erosion from forest and rangeland     | NH <sub>3</sub> volatilization                    |
| Urban storm water runoff                         |   |
| Domestic waste effluent                          | Evaporation (aerosol formation from surface foam) |
| Industrial waste effluent                        |   |
| Wastes from boating activities                   | Denitrification                                   |
| <i>Underground</i>                               |   |
|  | Sediment deposition of detritus                   |
| Natural ground water                             |   |
| Subsurface agricultural and urban drainage       |   |
| Subsurface drainage from septic tanks            | Sorption of ammonia onto sediments                |
| <i>In situ</i>                                   |   |
| Nitrogen fixation                                |   |
| Sediment leaching                                |   |

or from some fertilizer materials. Surface sources of N from agriculture are perhaps the best understood, and N delivered with eroded soil sediments is a major source.

Groundwater delivery of NO<sub>3</sub><sup>-</sup> to lakes and streams is no doubt very important but difficult to gauge. *In situ* sources include BNF, such as by blue-green algae and the leaching of N from lake sediments. An additional source of N and other nutrients is from wild aquatic birds; however, their role in the nutrient regime of a water body may be more that of cycling agents than of direct sources.

Sawyer (1947) was the first to propose quantitative guidelines for lakes. He suggested that 0.3 mg/L of inorganic N and 0.015 mg/L of inorganic phosphorus

are critical levels above which algal blooms can normally be expected in lakes. However development of nutrient criteria or recommended methodologies for protecting waterbodies from excessive nutrient loading are very much needed. National criteria that are available for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_3$  are generally established to protect human health and aquatic life from toxic eutrophication, or impairments to recreational uses such as swimming, fishing, and boating (Tetra Tech, Inc., 1994).

Under natural conditions,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  occur in moderate concentrations and have little toxicological significance for aquatic life. Because the levels that are toxic to aquatic life are much higher than those expected to occur naturally in surface waters, restrictive water quality criteria for these elements have not been recommended. Two of the main concerns about the impacts of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  on the environment are the primary water quality concern about their potential health effects on humans and ruminant animals associated with contaminated drinking water.

On the other hand,  $\text{NH}_3$  is highly toxic to aquatic organisms. Acute toxicity in fish causes loss of equilibrium, hyperexcitability, increased breathing, cardiac output, convulsions, coma, and death, if concentrations are extreme. Chronic toxic effects include reduced hatching success, growth rates, and developmental or pathological changes in gill, liver, and kidney tissues (US EPA, 1982).

## 7. WITHIN AGRICULTURAL SYSTEMS

### 7.1. Accounting for All Nitrogen Sources

Nitrogen budgets provide a valuable framework to quantify and examine N inputs and losses for agricultural production systems (see Figure 2). Accounting for the major sources of N to cropping systems and into the environment, in general, is especially important. The following are some of the sources that should be considered:

1. Fertilizer N inputs and amounts are easily determined and can be managed.
2. Organic wastes are an important N source. Organic wastes available for use on cropland in the United States include livestock wastes, crop residues, sewage, food processing wastes, industrial organic wastes, logging and wood manufacturing wastes, and municipal refuse. Animal manures and crop residues account for the majority of organic wastes applied to agricultural land.
3. Manure N inputs are uncertain because the N content is related not only to livestock type, age, and health, but also to variations in N content. Once excreted, the N content can change considerably depending on type and amount of bedding, type and time of manure storage, and manure management and placement when being applied. The best way to overcome these uncertainties is through the use of manure analysis and calibration of application equipment. Manure credits are often used to try to account for N that becomes available from applied manure.

4. BNF, especially by legumes, can be an especially important source of N. Although the importance of BNF has been known for centuries, there are few quantitative methods for estimation of BNF. Currently, the method most used is that of recognizing BNF by legumes with legume credits.
5. Nitrate contained in irrigation water is available to the crop and should be considered when making fertilizer recommendations. Crop utilization of  $\text{NO}_3^-$  from irrigation water is greatest when plant-N requirement is greatest and other N sources are not excessive.
6. Atmospheric additions, including volatilized  $\text{NH}_3$  from livestock operations, are another source of N to agricultural systems and to the environment. The mechanisms of additions that are identified include N dissolved in precipitation, dry deposition, and direct plant absorption of gaseous  $\text{NH}_3$ .
7. Contributions of residual soil N require soil testing for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  within the root zone and will be discussed below.
8. Nitrogen mineralization is the term given to biological decomposition of organic material in soils and their conversion and contribution to inorganic forms is significant.

#### 7.1.1. Soil Nitrogen Availability Tests

Available soil N represents residual N in the soil profile, plus N mineralized from the SOM during the growing season. While residual N has proven to be a useful index in certain regions of the United States, no generally accepted index exists for N mineralization. Obviously, such a development would represent a major advance for avoidance of excessive fertilizer N applications. A complement to a soil N test may be a plant tissue N test. An attractive feature of tissue tests is that the plant root system tends to integrate spatial variability of soil N supplying power over a relatively large field volume.

#### 7.1.2. Soil Organic Nitrogen Availability

A significant part of plant-N requirements are supplied by mineralization of SOM during the growing season. Various N availability indexes exist, but they typically provide qualitative rather than quantitative measures of SON availability. Early concepts of an N availability index have been modified; but to date, no SON availability procedure has received general acceptance from a soil test standpoint. Ultimately, a systems-type, mass-balance N approach may be the best alternative. The present recommendation is to follow pertinent N fertilizer guides that have been developed locally for specific crop needs and soil areas.

### 7.2. Agricultural Practices

#### 7.2.1. Nitrification Inhibitors

The  $\text{NH}_3^+$  ion is sorbed to the CEC of the soil; whereas,  $\text{NO}_3^-$  ion is not and can be readily leached or denitrified. Both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are readily available to



important source of N. In recent centuries, there are few methods, the method most used is redits.

the crop and should be considered. Crop utilization of N requirement is greatest

from livestock operations, to the environment. The N dissolved in precipitation as  $\text{NH}_3$ .

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is,  $\text{NO}_3^-$  ion is not and are readily available to

crops. Nitrification inhibitors include chemicals added to soils to stabilize fertilizer applied as  $\text{NH}_3$  or in the  $\text{NH}_4^+$  form by inhibiting the activity of the *Nitrosomonas* bacteria in the first step of the nitrification process.

### 7.2.2. Control/slow Release Fertilizer

The method used to alter the release of N from soluble materials has been to coat water-soluble N fertilizer with less water-soluble materials and thus retard entry of water into the particle and the movement of N out. Coatings applied to soluble N materials generally have been of three types: (1) Impermeable coatings with small pores that allow slow entrance of water and slow passage of soluble N out of the encapsulated area; (2) Impermeable coatings that require breakage by physical, chemical, or biological action before the N is dissolved; and (3) Semi-permeable coatings through which water diffuses and creates internal pressures sufficient to disrupt the coating. Sulfur-coated urea (SCU) has been developed for a number of years as a product with characteristics of slow-N release. Elemental sulfur (S) was chosen because of its relatively low cost and ease of handling. Newer control-release N fertilizer materials are also being developed and marketed (Shaji and Gandeza, 1992). These newer materials have polyolefin resin coatings. The coatings can be tailored to provide a range of N release rates that are suitable for a variety of cropping systems. However, further field research is needed to insure the utility of these newer materials for cropping systems.

### 7.2.3. Conservation Tillage

Use of conservation or reduced tillage (including no-till) continues to increase as an alternative for nearly all forms of crop production. Management systems which maintain crop residues at or near the soil surface have several attractive features, including less on-farm fuel use and its associated  $\text{CO}_2$  emissions (Follett, 2001b), more available soil water, and reduced soil erosion. However, adoption of conservation tillage practices may result in some N moving from the soil-plant systems into the environment under certain conditions.

There is no question that conservation tillage is effective in decreasing particulate N losses associated with soil erosion and surface water runoff as discussed above. However, effects of conservation tillage on leachable N are not as well delineated as are surface losses. Generally, conservation tillage provides a wetter, cooler, more acidic, less oxidative soil environment. Under such conditions, processes of ammonification and denitrification may be favored over nitrification. Conversely, for  $\text{NO}_3^-$  that is already present, the leaching potential may be greater under conservation tillage. This is because more undisturbed soil-macropores exist for  $\text{NO}_3^-$  and water movement. Increased water flow, into and through the root zone, has been observed under no-till compared to conventional-tillage soils. This higher flow has been attributed to decreased water evaporation because of surface residues and increased numbers of undisturbed channels (e.g., earthworm and old roots) continuous to the soil surface. The surface mulch enhances the environment for earthworms and the lack of tillage preserves existing channels for several years.

#### 7.2.4. Rotations, Cover Crops, and Nitrogen-Scavenging Crops

Rotations and cover crops, historically used as a means of conserving soil and/or providing an organic N source, have received renewed interest as an aid in avoiding excessive N losses to the environment. Whereas monocultures of grain crops (e.g., corn and wheat) require high inputs of fertilizer N, such inputs can be decreased with crop rotations that require less, or fix atmospheric N. Because less excess profile N may be expected with a rotation, there should be less potential for N-leaching. An exception may be under certain rotation-fallow conditions designed to conserve water in drier areas. "Cover crops" protect the soil from erosion and losses of nutrients via leaching and runoff. The term "winter cover crop" is used for a cover crop grown to protect the soil during the winter fallow period. Despite its acceptance, a winter cover crop does not necessarily need to be used during winter and can be used even during summer (Delgado et al., 2004). If a legume is used, it can also potentially fix atmospheric  $N_2$ , and enhance soil N reserves (Power et al., 1983). Thus, the definition of "winter cover crops" can thus be expanded to those crops that are grown for improving soil, air, and water conservation and quality; nutrient scavenging, cycling and management; increasing beneficial insects in integrated pest; and/or for short-term (e.g., over-winter) for animal-cropping grazing systems (Reeves, 1994; Delgado et al., 2004).

Winter cover crops can be effective in absorbing both  $NO_3^-$  and available water during the fall, winter, and spring, thereby decreasing the N-leaching potential. When the cover crop is returned to the soil, some of the absorbed N is then available to the following crop (Delgado et al., 2004). Both legumes and nonlegumes are used from a strictly N-leaching standpoint. While an annual crop such as rye can be effective in scavenging excess available N from within crop rooting zones, deep-rooted perennials should be considered for  $NO_3^-$  accumulation below normal rooting depths. Alfalfa, with a potential rooting depth in excess of 15 feet, is a crop that merits particular attention.

#### 7.2.5. Filter Strips

Vegetative filter strips, also referred to as buffer strips and riparian zones, remove sediment, organic matter, and other pollutants from runoff and waste waters. Under field conditions, excess runoff from terraces is frequently diverted to a strip. Upon entering the strip, both the flow velocity and transport capacity of the runoff are reduced. The sediment and its associated pollutants are then removed from the runoff by filtration, deposition, infiltration sorption, decomposition, and volatilization processes. The effectiveness of filter strips in removing sediment and particulate N is well established. Less certain is the effectiveness of filter strips for removing soluble N in runoff. Uptake by filter strip vegetation of mineral N transported by runoff water may occur during times of active growth but less during other times of the year. Also, some denitrification may be occurring. Scavenging of N from underground water and the vertical horizon by riparian vegetation, especially by deeper rooted plants, also may be important for removing dissolved N in surface and subsurface flows before the N is transported into streams and lakes.

### Crops

of conserving soil and/or forest as an aid in avoidance of grain crops (e.g., losses can be decreased with less excess profile N available for N-leaching. An option to conserve water and reduce losses of nutrients via a cover crop grown to fix nitrogen, a winter cover crop can be used even during periods when crops are not growing. Thus, the definition of cover crops for improving soil health, cycling and managing nutrients (e.g., over-planting, etc., 2004).

$\text{NO}_3^-$  and available water capacity. N-leaching potential. Sorbed N is then available to plants and nonlegume annual crop such as rye in crop rooting zones, and denitrification below normal depth of 15 feet, is a crop

losses and riparian zones, from runoff and waste water is frequently diverted to treatment. The limited transport capacity of streams and rivers means that nutrients are then removed through denitrification, decomposition, and sedimentation. Removing sediment and nutrients from streams through the use of filter strips for denitrification and removal of mineral N through denitrification but less during periods when crops are not growing. Scavenging by riparian vegetation, especially removing dissolved N in streams and lakes.

## 8. SUMMARY

Nitrogen (N) is ubiquitous in the environment. It is also one of the most important nutrients and is central to the growth of all crops and other plants. However, N also forms some of the most mobile compounds in the soil-plant-atmosphere system; and there is mounting concern about agriculture's role in N delivery into the environment. Nitrogen represents the mineral fertilizer most applied to agricultural land. This is because available soil-N supplies are often inadequate for optimum crop production. This chapter reviews the fate and transport of N from the various sources used to supply the N-requirements of crops in the context of the N cycle. Use of N budgets or a mass-balance approach is needed to understand the options for improving management of N in farming and livestock systems and for mitigating the environmental impacts of N. Fertilizing crops for crop N-uptake that will be near the point of maximum yield generally is an economically and environmentally acceptable practice. The objective is to lower the rate and duration of the loss processes themselves. Practices and concepts that lessen the opportunity for loss processes to occur and that help decrease the amount of N that may be lost to the environment are considered. In some cases improved efficiency is achieved by using less nutrients and in other cases it can be achieved by increasing the yield while using the same amount of N-input. In either case, the goal is to decrease the total residual mass of N in the soil. Another approach is to keep the residual N in the soil-crop system by curtailing the transport processes (leaching, runoff, erosion, and gaseous losses) that carry pollutants out of the soil crop system.

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