AP42 Section:	9.2.1
Reference:	5
Title:	R. J. Haynes and R. R. Sherlock, "Gaseous Losses Of Nitrogen", In Mineral Nitrogen And The Plant-Soil System, Academic Press, San Diego, CA, 1986.

AP 42 #5

Chapter 5

Gaseous Losses of Nitrogen

R. J. HAYNES AND R. R. SHERLOCK

I. INTRODUCTION

An upsurge of interest in gaseous losses of nitrogen from the soil has occurred during the last decade. Much of this research was stimulated by evidence from agronomic nitrogen-balance studies that generally showed an unexplained 10 to 30% loss of applied fertilizer nitrogen (Allison, 1955; Legg and Meisinger, 1982). Experiments involving the use of ^{15}N-labeled fertilizers confirmed that a significant proportion of applied nitrogen is unaccountably lost from soils during cropping (Hauck, 1971; Hauck and Bremner, 1976). A number of processes contribute to gaseous losses of soil nitrogen; these include ammonia volatilization, bacterial denitrification, nitrification, and reactions of NO_2^- with soil components.

Ammonia volatilization may occur whenever free NH_3 is present near the soil surface. The quantities of NH_3 lost are highly variable depending on such factors as rate, type and method of fertilizer nitrogen application, soil pH, and environmental factors including temperature, moisture, and wind (Black *et al.*, 1985a, 1985b). Plants can both absorb and evolve NH_3 from their leaf canopies (Freney *et al.*, 1981) but the major factors that influence the relative magnitude of the two processes are, as yet, unclear.

Denitrification is a major biological process through which N from the soil is returned to the atmosphere (Payne, 1981; Firestone, 1982). The process, which is mediated principally by aerobic bacteria which are capable of anaerobic growth only in the presence of nitrogen oxides, yields nitrous oxide (N_2O) and dinitrogen (N_2) gases. The role of N_2O in stratospheric chemical reactions has generated great interest in the denitrification process. This is because the photochemical breakdown of N_2O in the

stratosphere yields NO, which has a principal role in catalyzing the decomposition of stratospheric ozone (Crutzen and Ehhalt, 1977; McElroy *et al.*, 1977). The stratospheric ozone layer shields the biosphere from harmful exposures to UV radiation.

Nitrous oxide is also released from soil as a by-product of the nitrification pathway (see Chapter 3) although the exact mechanism of N_2O production is unclear (Schmidt, 1982). Under field conditions losses of N_2O through dentrification and nitrification are thought to often occur simultaneously.

Under conditions that favor the accumulation of NO_2^- in soils, chemodenitrification may contribute to gaseous losses of N (Nelson, 1982; Chalk and Smith, 1983). The presence of NO_2^- provides a mechanism for chemodenitrification since NO_2^- tends to react with soil components to form gases (e.g., N_2, N_2O, NO, and NO_2).

In this chapter, the processes involved in gaseous losses of N from the plant–soil system are reviewed and the major factors influencing such losses are discussed. The magnitude and significance of these losses are also considered.

II. AMMONIA VOLATILIZATION

Ammonia volatilization is the term commonly used to describe the process by which gaseous NH_3 is released from the soil surface to the atmosphere. The subject has been reviewed in depth by several workers (Terman, 1979; Freney *et al.*, 1981, 1983; Vlek and Craswell, 1981; Nelson, 1982).

A necessary prerequisite for NH_3 volatilization is a supply of free ammonia (i.e., $NH_{3(aq)}$ and $NH_{3(g)}$) near the soil surface. The source of NH_3 is usually soil NH_4^+. The supply can be from organic nitrogenous sources such as urine or feces of animals, plant residues, or native soil organic matter, all of which decompose to release NH_4^+-N. The factors affecting the decomposition of organic residues and the subsequent release of NH_4^+ are discussed in detail in Chapter 2.

A wide variety of NH_4^+- and NH_4^+-forming compounds are also applied to soils as fertilizers (e.g., $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_2HPO_4$, NH_4Cl, aqua ammonia, and urea). Ammonium-containing fertilizers such as $(NH_4)_2SO_4$ dissolve in soil solution and NH_4^+ ions are produced. In the soil urea, from either animal urine or applied fertilizers, undergoes hydrolysis catalyzed by the enzyme urease to form $(NH_4)_2CO_3$:

$$(NH_2)_2CO + 2H_2O \longrightarrow (NH_4)_2CO_3 \qquad (1)$$

This reaction causes localized areas of high pH close to the site of hydrolysis:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad (2)$$

Ammonium ions interact with the cation exchange complex of the soil resulting in electrostatic binding of NH_4^+ ions to clay and organic colloids. Some of this NH_4^+ may become "fixed" in clay lattices (see Chapter 4). However, NH_4^+ ions in soil solution also enter into equilibrium reactions with NH_3.

Since all of the above-mentioned sources supply N as NH_4^+ rather than NH_3, it is the conversion of NH_4^+ to NH_3 that normally regulates the potential loss of NH_3 through volatilization. Nonetheless, N can also be added to soils as anhydrous NH_3, which is handled as a liquid but changes to a gaseous state during injection.

A. Processes

1. Well Aerated Soils

The basic equilibria that govern ammonia loss are shown in Fig. 1. These equilibria indicate that, in theory, the soil can act as both a source and sink for atmospheric $NH_{3(g)}$. The NH_3 flux (F) into or out of the soil surface may be represented as

$$F = k\,(NH_{3(g)soil} - NH_{3(g)atm}) \quad (3)$$

where $NH_{3(g)soil}$ is the $NH_{3(g)}$ concentration in equilibrium with the soil solution at the soil surface, $NH_{3(g)atm}$ is the $NH_{3(g)}$ concentration of the

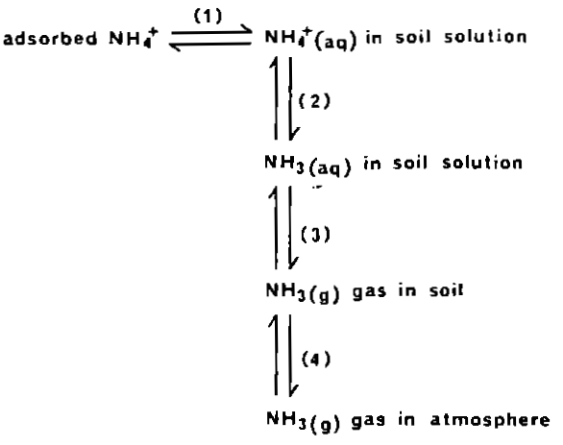

Fig. 1. The various equilibria that govern ammonia loss from soils.

bulk atmosphere, and k is an exchange coefficient whose value may vary with windspeed (Vlek and Craswell, 1981; Freney *et al.*, 1983). Whether $NH_{3(g)}$ is absorbed or volatilized is therefore largely determined by the difference in $NH_{3(g)}$ concentration between the soil surface and the atmosphere.

Atmospheric NH_3 concentrations, although variable, are usually very low, e.g., 2–6 μg NH_3-N m^{-3} (National Research Council, 1979), and there is no evidence that they seriously limit volatilization rates in the field (Vlek and Craswell, 1981; Freney *et al.*, 1983). No direct measurements of equilibrium $NH_{3(g)soil}$ concentrations have been reported but calculations by Vlek and Craswell (1981) show that for $NH_{3(g)atm}$ concentrations of 2–6 ppb, $NH_{3(aq)}$ concentrations of 0.5 ppm or greater are sufficient to promote volatilization. These workers maintained that where NH_3 volatilization is a problem, such levels of $NH_{3(aq)}$ are easily reached. Therefore, under these conditions $NH_{3(g)soil}$ is likely to greatly exceed $NH_{3(g)atm}$, whereupon equation (3) can be simplified to

$$F = k\,(NH_{3(g)soil}) \tag{4}$$

Thus, ammoniacal N added to the soil from whatever source may be subject to loss as $NH_{3(g)}$. Also, the actual magnitude of any loss is likely to depend primarily on the concentration of $NH_{3(g)soil}$, which in turn depends on the total concentration of ammoniacal N species, the values of the individual equilibrium constants (Fig. 1), and the rate of attainment of equilibrium at each stage. Factors such as pH, temperature, etc., which can influence any or all of these separate equilibria, can influence the magnitude of NH_3 loss. Likewise, all strategies designed to limit volatilization losses attempt to manipulate these equilibria either directly or indirectly to reduce the $NH_{3(g)}$ concentration at the soil–air interface.

2. *Flooded Soils*

The fact that NH_3 is the most soluble gas known makes it tempting to suggest that a soil flooded with water would serve as an almost infinite sink for the gas and that any volatilization to the atmosphere would be negligible. This may be so for unfertilized flooded soil but can be demonstrably incorrect for fertilized systems. For example, Vlek and Craswell (1979) showed that up to 50% of urea surface applied to floodwater was lost as NH_3 within 2–3 weeks.

It is now clear that equation (3) and the equilibria described in Fig. 1 apply equally well to flooded and nonflooded soils (Freney *et al.*, 1983). Indeed, since it is relatively easy to measure the ammoniacal N concentration, pH, and temperature within the water overlying a flooded soil and also to obtain values for the exchange coefficient k for the transport of

NH_3 away from the floodwater surface, it has been suggested that the direct application of equation (2) may provide a simple way of predicting NH_3 losses from flooded rice paddies (Leuning *et al.*, 1984). However, in testing this hypothesis Leuning *et al.* (1984) found that because of temperature gradients within the water, the NH_3 concentration at the water–air interface was not generally characteristic of that in equilibrium with the bulk of the floodwater. This implies that for flooded soils transport processes in both the air and water are important in determining the rate of NH_3 volatilization.

Loss of NH_3 from flooded soils is also strongly influenced by wind through a mechanical mixing of the surface water. This and several other factors that influence NH_3 losses from flooded soils are discussed in following sections.

3. *Calcareous Soils*

The presence of $CaCO_3$ in soil is reported to stimulate volatilization of NH_3 from applied ammoniacal fertilizers (Freney *et al.*, 1981). For soils taken from various parts of the world, a strong correlation between NH_3 loss and $CaCO_3$ content has been reported (Lehr and Van Wesemael, 1961; Fenn and Kissel, 1975).

Apart from its effects on the alkalinity and buffering effect on soil pH, $CaCO_3$ also appears to have a more specific effect since when NH_4^+ fertilizers are applied to calcareous soils, the anion associated with the fertilizer can have a large effect on NH_3 loss. Fenn and Kissel (1973) showed that the NH_4^+ salts that produced the highest loss of NH_3 were those that formed insoluble precipitates with Ca (e.g., F^-, SO_4^{2-}, HPO_4^{2-}) whereas other salts having more soluble reaction products with Ca (e.g., NO_3^-, Cl^-, I^-) gave lower losses.

It has been suggested that applications of NH_4^+ compounds to calcareous soils result in the formation of $(NH_4)_2CO_3$ (Fenn and Kissel, 1973). However, NH_4HCO_3 seems a more likely intermediate since the high pH values required for $(NH_4)_2CO_3$ formation in soils are not generally observed (Feagley and Hossner 1978; Nelson, 1982). The sequence of reactions when $(NH_4)_2SO_4$ is added to a calcareous soil suggested by Nelson (1982) follows:

$$CaCO_3 + (NH_4)_2SO_4 \longrightarrow Ca^{2+} + 2OH^- + CaSO_4 + 2NH_4HCO_3 \quad (5)$$

$$2NH_4HCO_3 \longrightarrow 2NH_3 + 2CO_2 + 2H_2O \quad (6)$$

The Ca^{2+} and OH^- ions produced during hydrolysis of $CaCO_3$ may then react with $(NH_4)_2SO_4$ as follows:

$$Ca^{2+} + 2OH^- + (NH_4)_2SO_4 \longrightarrow CaSO_4 + 2NH_3 + 2H_2O \quad (7)$$

The overall reaction (i.e., summation of equations (5), (6), and (7)) can be shown:

$$CaCO_3 + (NH_4)_2SO_4 \longrightarrow 2NH_3 + CO_2 + H_2O + CaSO_4 \quad (8)$$

Thus, the formation of an insoluble Ca salt encourages the dissolution of $CaCO_3$ thereby generating the bases, HCO_3^- and OH^-, that act to deprotonate NH_4^+ to NH_3 and sustain volatilization.

B. Factors Affecting Volatilization

1. pH

The equilibrium between NH_4^+ and NH_3 can be represented as

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \quad (9)$$

Thus, the concentrations of NH_4^+ and NH_3 are determined by the pH of the soil solution. An increase in pH (i.e., an increase in hydroxyl ion concentration) drives the equilibrium to the right thereby producing more NH_3. The proportion of aqueous ammoniacal N ($NH_{4(aq)}^+$ plus $NH_{3(aq)}$) present as $NH_{3(aq)}$ at pH 6, 7, 8, and 9 can be calculated as approximately 0.0004, 0.004, 0.04, and 0.3, respectively (Hales and Drewes, 1979).

Many workers in both laboratory and field experiments have demonstrated that NH_3 losses increase as the soil pH increases (e.g., Wahhab *et al.*, 1956; Volk, 1959; Ernst and Massey, 1960; Watkins *et al.*, 1972; Lyster *et al.*, 1980). Nonetheless, the direct effects of soil pH are difficult to interpret since more often than not the original soil pH has been assumed to characterize the soil pH throughout the duration of NH_3 loss.

Such assumptions are not necessarily correct since equation (9) can also be represented as

$$NH_4^+ \longrightarrow NH_3 + H^+ \quad (10)$$

$$H^+ + OH^- \longrightarrow H_2O \quad (11)$$

Hence, volatilization is accompanied by net acidification of the system (Avnimelech and Laher, 1977), which tends to decrease the rate of volatilization. The original soil pH is, therefore, of prime importance in controlling the extent of volatilization only when the buffering capacity of the soil is high.

That factors other than soil pH can influence NH_3 loss is indicated by the fact that substantial NH_3 volatilization can occur from acid soils (e.g., Ernst and Massey, 1960; Blasco and Cornfield, 1966). Indeed, the pH in the solution immediately surrounding a urea or NH_4^+ salt granule may be considerably more important in determining NH_3 losses than the soil pH

itself (Nelson, 1982; Sherlock and Goh, 1984; Black *et al.*, 1984, 1985a, 1985b).

For NH_3 volatilization to occur from flooded soils buffering substances need to be present to prevent acidification of the floodwater caused by the conversion of NH_4^+ to NH_3 (equation (10)). Bicarbonate (HCO_3^-) is the major proton acceptor normally present at typical pH values of floodwater (Vlek and Stumpe, 1978; Vlek and Craswell, 1981) and therefore volatilization in flooded systems can be represented as

$$NH_{4(aq)}^+ + HCO_{3(aq)}^- \longrightarrow NH_{3(g)} + CO_{2(g)} + H_2O \qquad (12)$$

Volatilization can also be greatly influenced by the photosynthetic and respiratory balance of algal growth in the floodwater (Mikkelsen *et al.*, 1978; Vlek and Craswell, 1981). As a result of depletion of CO_2 in the water due to algal photosynthetic activity the pH of the floodwater may rise to 9 or above resulting in large losses of NH_3.

2. *Temperature*

Following applications of urea and NH_4^+ salts, both the instantaneous rate and ultimate extent of NH_3 volatilization increase with increasing temperature (Wahhab *et al.*, 1956; Volk, 1959; Ernst and Massey, 1960; Watkins *et al.*, 1972; Lyster *et al.*, 1980).

The effect of temperature on NH_3 volatilization can be explained at least in part by the temperature dependence of the equilibrium constants (K) for equilibria (2) and (3) (Fig. 1) (Vlek and Stumpe, 1978; Hales and Drewes, 1979; Vlek and Craswell, 1981; Sherlock and Goh, 1984, 1985a). The higher the temperature the greater the proportion of $NH_{3(aq)}$ (equilibrium (2)) present and the greater the proportion of $NH_{3(ag)}$ (equilibrium (3)) present and hence the greater is the potential for NH_3 loss.

Under field conditions the rate of emission of NH_3 follows a marked diurnal cycle that roughly follows that of solar radiation (McGarity and Rajaratnam, 1973; Denmead *et al.*, 1974, 1978; Beauchamp *et al.*, 1978; Freney *et al.*, 1981; Hoff *et al.*, 1981; Vallis *et al.*, 1982; Black *et al.*, 1985a). The diurnal pattern appears to be predominantly related to temperature fluctuations as illustrated clearly in Fig. 2 although the effects of evaporation of water and windspeed cannot be ignored (Denmead *et al.*, 1978).

The extent of losses can also follow a seasonal pattern. Ball and Keeney (1983), for example, found losses of NH_3 from urine patches that averaged 5, 16, and 66% of added urine N under cool moist (winter), warm moist (spring), and warm dry (summer) conditions, respectively.

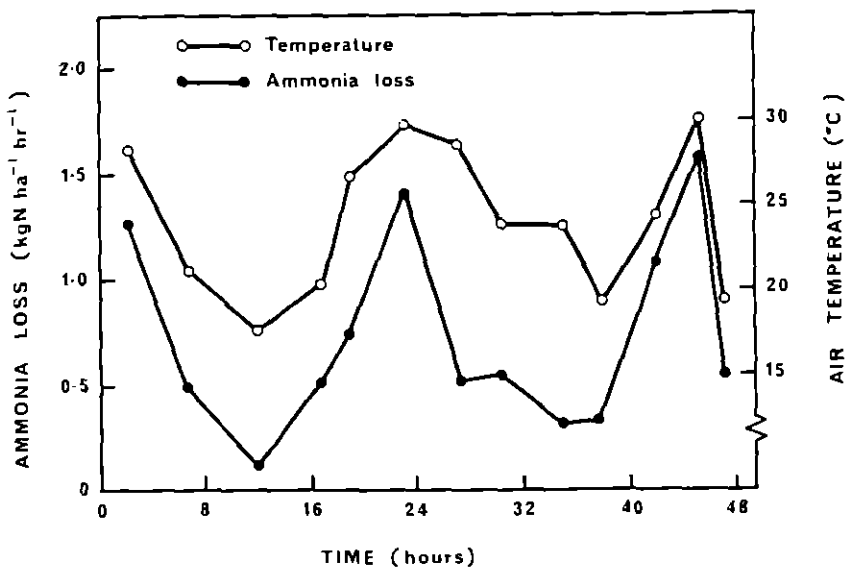

Fig. 2. Diurnal fluctuations in air temperatures and rate of ammonia loss from liquid swine manure. [Redrawn from Hoff *et al.* (1981). Reproduced from *J. Environ. Qual.* **10**, p. 93 by permission of American Society of Agronomy.]

3. *Ammonium Concentration*

The amount of NH_4^+ added to the soil must have a direct effect on the NH_3 evolved as predicted by equation (10) if all other factors are held constant. A linear relationship between the rate of fertilizer application and total NH_3 loss has been shown in a number of studies (Chao and Kroontje, 1964; Hargrove *et al.*, 1977; Hoff *et al.*, 1981). In other studies percentage losses increased as rates of application increased (Wahhab *et al.*, 1956; Volk, 1959; Kresge and Satchell, 1960; Lyster *et al.*, 1980; Black *et al.*, 1985b). Such nonlinear relationships occur mainly from applied urea and are the result of the increasing soil-surface pH induced by urea hydrolysis.

Factors that influence the NH_4^+ concentration in soil solution will also influence the potential for losses of NH_3 through volatilization. Many mechanisms can induce changes in the NH_4^+ concentration and thereby affect the chain of equilibria that determine the extent of NH_3 loss. The more obvious include plant uptake, nitrification, denitrification, leaching, immobilization, and the fixation of NH_4^+ by clay minerals in exchangeable and nonexchangeable forms. All these mechanisms would tend to decrease the NH_4^+ concentration in soil solution and so reduce NH_3 losses.

4. *Soil Characteristics*

Of major importance in determining the soil solution NH_4^+ concentration is the cation exchange capacity (CEC) of the soil. The adsorption of the positively charged NH_4^+ ion onto the exchange complex of soils reduces the amount of NH_4^+ and therefore NH_3 in soil solution at a given pH. Hence, many workers have observed a negative relationship between soil CEC and NH_3 volatilization (Wahhab *et al.*, 1956; Gasser, 1964; Ryan and Keeney, 1975; Fenn and Kissel, 1976; Lyster *et al.*, 1980; Ryan *et al.*, 1981). The effect of increasing CEC in reducing NH_3 volatilization is illustrated in Fig. 3. When other soluble cations are applied along with ammoniacal fertilizer, competition for the exchange sites can result. For example, soluble Ca^{2+} may depress normal adsorption of NH_4^+ on exchange sites leading to enhanced NH_3 losses (Fenn *et al.*, 1982).

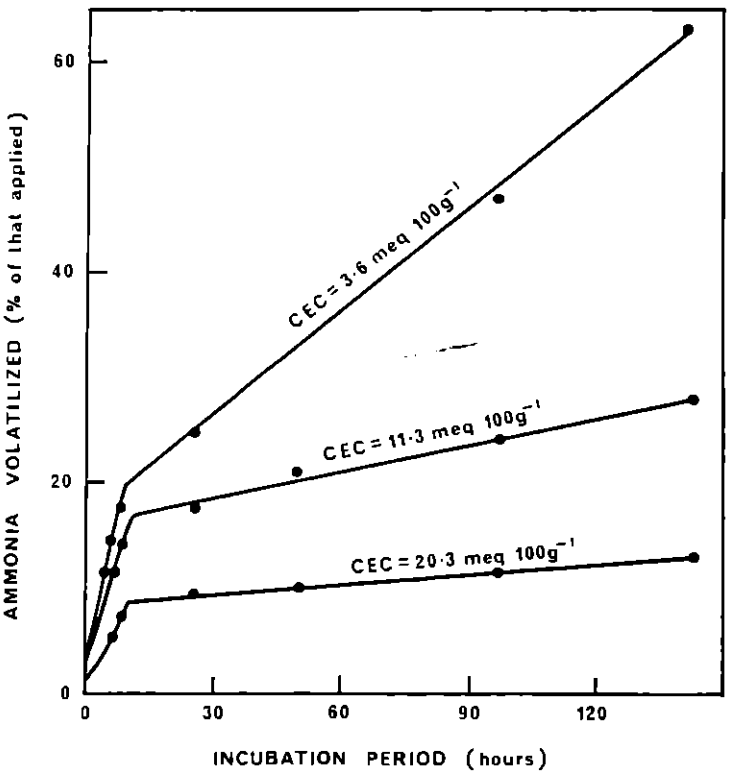

Fig. 3. Rate of ammonia volatilization as influenced by the cation exchange capacity of soil–sand mixtures. [Data from Daftardar and Shinde (1980), by courtesy of Marcel Dekker, Inc.]

As noted earlier when discussing the effect of soil pH, the buffering capacity of the soil can be an important factor influencing NH_3 volatilization because the dissociation of NH_4^+ *ions releases* H^+ *ions as well as* NH_3. Thus, volatilization is normally more prolonged in soils of high base *status where the acidity produced* can be neutralized by carbonate or other forms of alkalinity. Avnimelech and Laher (1977) showed that at a given pH, NH_3 losses increase with increasing buffer capacity. To some extent such an effect may confuse the negative effect of CEC described above since, in general, the higher the CEC of a soil the greater its buffering capacity.

The presence of organic residues has been reported to accelerate (Moe, 1967; Rashid, 1977), decrease (Tripathi, 1958), or not affect (Verma and Sarkar, 1974) NH_3 volatilization from added urea. Such results are not altogether surprising, since while organic matter with a low C : N ratio will be mineralized with the release of NH_4^+, that with a high C : N ratio will immobilize NH_4^+-N from the surrounding soil (Chapter 2). Partially decomposed organic matter will also have a CEC that will influence soil solution NH_4^+ levels.

5. *Soil Moisture Content and Moisture Loss*

Soil moisture content has an important influence on the rate of NH_3 volatilization since it affects the concentration of NH_4^+ and therefore NH_3 in soil solution. Ammoniacal N concentrations in solution at high moisture contents are likely to be lower than those at low moisture contents leading to lower net losses of NH_3 from wetter soils. This has been shown in a number of studies (Martin and Chapman, 1951; Wahhab *et al.*, 1956; Fenn and Escarzaga, 1976).

However, interpretation of results can be confused by simultaneous losses of water. Indeed, the largest amounts of volatilized NH_3 are normally obtained from soils of high moisture content (below saturation) that are allowed to dry (Martin and Chapman, 1951; Wahhab *et al.*, 1956; Fenn and Escarzaga, 1977). Loss of water promotes NH_3 evolution by increasing, or at least maintaining, ammoniacal concentrations in soil solution over time, which leads to greater losses than if no soil drying occurred. Drying also results in the upward movement of water, which helps transport dissolved NH_4^+ and NH_3 to the soil surface (Freney *et al.*, 1981). Some workers have therefore reported that NH_3 losses increase with increasing initial moisture content up to field capacity (Volk, 1959; Ernst and Massey, 1960; Kresge and Satchell, 1960). Although moisture loss promotes NH_3 evolution, the volatilization of NH_3 can occur without concurrent loss of water (Ernst and Massey, 1960; Terry *et al.*, 1978).

In the case of dry fertilizer materials (e.g., urea prills) a low initial soil

moisture content, or rapid drying immediately after application, can slow the rate of fertilizer dissolution and urea hydrolysis and result in small losses of NH_3 (Ernst and Massey, 1960; Volk, 1966). Similarly, when fertilizer solutions or urine are added to very dry soils, losses of NH_3 are often small (Fenn and Escarzaga, 1977; Ball and Keeney, 1983; Vallis *et al.*, 1982). In dry soils, dissolved NH_4^+ may be adsorbed onto soil colloids wherever the solution moves, while in initially wet soils $NH_{4(aq)}^+$ may tend to remain in macropores. Convection to the soil surface would tend to proceed through macropores thus transporting more $NH_{4(aq)}^+$ to the surface of initially wet soils.

Time of rainfall or water application can also be an important factor influencing losses of NH_3. For example, before its hydrolysis urea moves rapidly into the soil when water is applied and losses from surface-applied urea decrease with increasing amounts of applied water (Fenn and Miyamoto, 1981; see Table I). Rainfall immediately after surface applications of urea can significantly reduce losses of NH_3 (Carrier and Bernier, 1971; Morrison and Foster, 1977; Black and Sherlock, 1985). However, as illustrated in Table I, once hydrolysis has proceeded (by 24 hr), the effectiveness of water applications is markedly reduced.

6. *Windspeed*

Estimates of NH_3 volatilization resulting from fertilizer applications have often been carried out in laboratory studies using unrealistically low air exchange rates that fail to simulate field conditions (Nelson, 1982).

Table I

Percentage of Applied Urea N Lost as Ammonia After 7 Days as Affected by the Amount of Water Applied and Its Time of Application[a]

Water applied (mm)	Time of water application (hours after urea application)[b]			
	0–3	8–10	24–26	48–50
0	28	32	31	32
4	8	24	27	n.d.
16	2	10	22	29
48	0.5	n.d.	21	n.d.

[a] Data from Black and Sherlock (1985).

[b] Urea granules were applied to a pasture surface at a rate of 100 kg N ha^{-1}. n.d., not determined.

Under such conditions NH_3 volatilization can be directly proportional to airflow (Watkins *et al.*, 1972; Kissel *et al.*, 1977) and a number of workers have reported that the rate of NH_3 volatilization increases with an increase in the rate of airflow over the samples (e.g., Overrein and Moe, 1967; Terry *et al.*, 1978; Vlek and Stumpe, 1978).

Increasing windspeed should tend to increase the volatilization rate by promoting more rapid transport of NH_3 away from the air–soil interface. However, when Beauchamp *et al.* (1978, 1982) used an aerodynamic procedure to measure NH_3 losses from surface-applied sewage sludge and liquid dairy manure under field conditions, they found no discernable relationship between windspeed and $NH_{3(g)}$ flux. These workers suggested that volatilization from the soil was diffusion controlled and was limited by depletion of ammoniacal N at sites from which volatilization was possible. Windspeed presumably had little effect on this diffusion process.

It has, however, been clearly demonstrated that increasing windspeed over a flooded soil surface increases the NH_3 volatilization rate (Bouwmeester and Vlek, 1981; Denmead *et al.*, 1982; Moeller and Vlek, 1982). Denmead *et al.* (1982) suggested that there may be considerable resistance to transport of NH_3 in the liquid phase and that the enhanced volatilization in high winds is due to better mechanical mixing of the surface water. Such mixing would also avoid the development at the floodwater surface of a region depleted of NH_3 that might limit the volatilization rate.

7. *Form and Placement of Applied Fertilizer*

Since anhydrous NH_3 is applied to soils as a gas one might expect a tendency for it to escape to the atmosphere. It has generally been shown, however, that regardless of soil type, losses of N during and immediately following injection of anhydrous NH_3 are small if it is applied at an adequate depth (5 to 13 cm) and provided soil moisture conditions and soil physical properties are such that the injection channel is rapidly sealed (Ernst and Massey, 1960; Khan and Haque, 1965; Parr and Papendick, 1966; Nelson, 1982). Thus, anhydrous NH_3 is normally retained in the soil due to its reactions with soil components (see Chapter 4).

As already noted, NH_4^+ salts that produce the largest losses of NH_3 from calcareous soils are those that form insoluble precipitates with Ca (e.g., $(NH_4)_2SO_4$ or $(NH_4)_2HPO_4$). In acidic and moderately acidic soils surface applications of alkaline fertilizers such as NH_4OH or urea generally result in larger losses of NH_3 through volatilization than do applications of neutral or acidic fertilizers such as $NH_4H_2PO_4$ or $(NH_4)_2SO_4$ (Terman *et al.*, 1968; Matocha, 1976). The effect of N form when applied

to a pasture on pH around the fertilizer granules and on NH_3 volatilization from a pasture surface is shown in Fig. 4. The localized rise in pH, due to urea hydrolysis, and the consequently larger loss of NH_3 from urea are obvious.

Several methods have been examined to minimize NH_3 losses from applied urea. Mixing neutral ammonium salts or acidifying agents (e.g., NH_4Cl, $NH_4H_2PO_4$, HNO_3, or H_3PO_4) with urea prior to application can

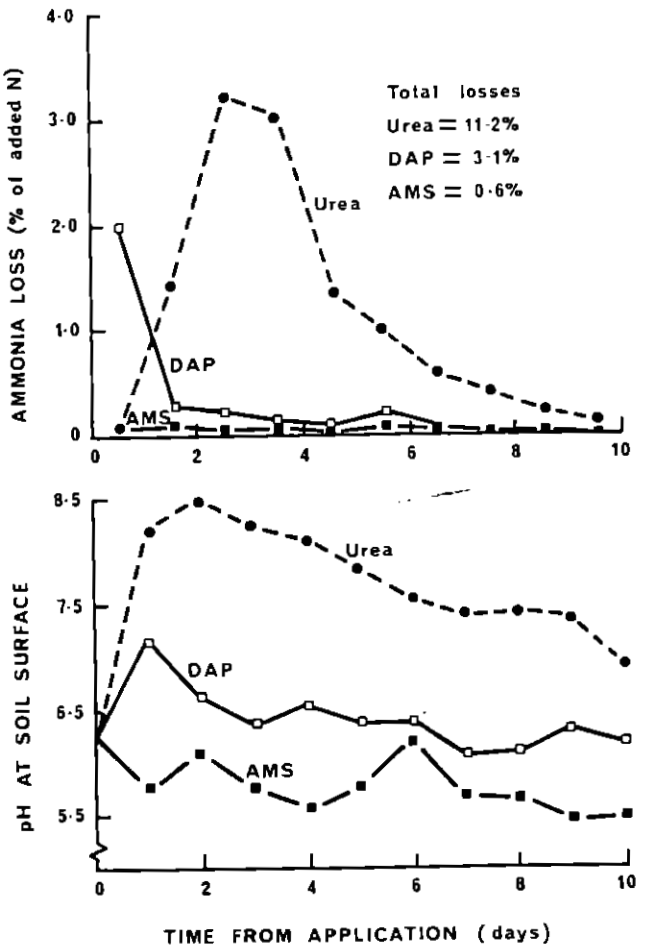

Fig. 4. Effect of form of applied nitrogen (urea, diammonium phosphate (DAP), or ammonium sulfate (AMS)) on daily ammonia volatilization rate from a pasture and pH of the soil surface at the granule site. Rate of applied N = 30 kg N ha^{-1}. [Data from Black, A. S., Sherlock, R. R., and Smith, N. P. (unpublished).]

markedly reduce losses from surface applications (Terman, 1979). Other techniques include the use of slow-release forms of urea (e.g., sulfur-coated urea) (Matocha, 1976; Presad, 1976; Vlek and Craswell, 1979) or urease inhibitors (Moe, 1967; Bremner and Douglas, 1973). Such techniques work by attempting to retard the rate of urea hydrolysis and so prevent the rapid buildup of ammoniacal N.

Another method of reducing losses of NH_3 from applications of NH_4^+ salts or urea is by placement of fertilizers below the soil surface or by thoroughly incorporating them into the topsoil (Ernst and Massey, 1960; Overrein and Moe, 1967; Fenn and Kissel, 1976; Vlek and Craswell, 1979; Hoff *et al.*, 1981). This technique effectively reduces the ammoniacal N concentration of the soil solution at the soil surface thereby reducing losses of NH_3. However, in some circumstances it is common practice to broadcast all fertilizers on the soil surface (e.g., on pastures or under minimum tillage) in which case the opportunity for NH_3 volatilization is enhanced (Black *et al.*, 1984).

As indicated previously, applications of nitrogenous fertilizers to flooded soils can result in considerable losses of NH_3 (Vlek and Craswell, 1979). Placement of fertilizers into soils before flooding can markedly reduce volatilization in comparison with broadcasting the fertilizer over the floodwater (Macrae and Ancajas, 1970; Craswell *et al.*, 1981; Mikkelsen *et al.*, 1978).

8. Presence of Animals

a. Grazing animals. In grazed grassland ecosystems the presence of animals can greatly influence the cycling of N within the system. Indeed it has been estimated that 85 to 95% of N ingested by grazing herbivores is excreted (Henzell and Ross, 1973) and most of this is voided as urine in localized patches on the soil surface (Doak, 1952). Urine is a concentrated N solution (approx. 10 gm N liter^{-1} of which 80–90% is urea) and the effective rate of application within urine patches is often greater than the equivalent of 500 kg N ha^{-1}. Such application rates are considered to be much too high for efficient plant utilization (Ball and Keeney, 1983; Carran *et al.*, 1982). The urea is rapidly hydrolyzed to NH_4^+-N, which results in localized areas with both high pH and high ammoniacal concentrations. It is evident that urine patches provide concentrated focal points within a pasture from which significant NH_3 volatilization will occur. Such losses have been reported to be in the region of 20 to 60% of the urine N (Denmead *et al.*, 1974; Ball *et al.*, 1979; Ball and Keeney, 1983; Carran *et al.*, 1982; Sherlock and Goh, 1984).

b. Feedlots. Modern animal-feeding practices in which large numbers of animals are concentrated in small areas have led to problems in the

disposal of animal wastes (Loehr, 1974; Tunney, 1980). Appreciable NH_3 volatilization may occur during the storage of both heaps of manure and liquid slurries (Tunney, 1980). Apart from the offensive odors produced, the chief concern with such emissions is the reduction in fertilizer value of the materials since losses on the order of 30 to 80% of the N originally present are not uncommon (Vanderholm, 1975). Ammonia volatilization from feedlot areas can be 10 to 30 times that from surrounding areas (Hutchinson and Viets, 1969; Elliott *et al.*, 1971; Luebs *et al.*, 1973).

Volatile aliphatic amines of different molecular weights are also emitted from animal manures. Mosier *et al.* (1973) identified seven basic aliphatic organic nitrogenous compounds, namely, methyl, dimethyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-amyl amines, emanating from a high-density cattle feedlot. It was estimated that these amines constituted only 2 to 6% of the volatilized ammoniacal N with the balance released as NH_3.

Significant losses of NH_3 occur when animal manures are surface-applied to agricultural lands, particularly in the summer months (Lauer *et al.*, 1976; Hoff *et al.*, 1981). Approximately 50% of the added N can be lost as NH_3 in a 3- to 5-day period (Vanderholm, 1975) although incorporation or injection of the manure into the soil immediately following application can markedly reduce losses (Hoff *et al.*, 1981).

9. Presence of Plants

a. Passive role. Crop height and density can be important factors in determining the fraction of applied fertilizer in solution or, in the case of a grazed pasture, the amount of voided urine that reaches the soil surface. Intercepted solution may undergo a number of transformations including direct absorption by foliage (see Chapter 6). Leaf surfaces also possess considerable urease activity and direct volatilization of the hydrolysis products of intercepted aqueous urea and urine has been demonstrated by several workers (Doak, 1952; Volk, 1959; Simpson and Melsted, 1962; McGarity and Hoult, 1971; Watkins *et al.*, 1972). Since leaf surfaces have only a limited CEC and low buffering capacity it seems possible that interception of nitrogenous materials by plant cover may result in increased losses of applied N through NH_3 volatilization (Sherlock and Goh, 1985b).

b. Active role. The absorption and evolution of NH_3 from plants have been reviewed in detail elsewhere (Farquhar *et al.*, 1980, 1983). A finite partial pressure of NH_3 is maintained in the substomatal cavities of plant leaves. When this partial pressure exceeds that of the atmosphere, net evolution of NH_3 occurs. Factors that favor net evolution include high temperatures, low atmospheric partial pressures of NH_3, and high stoma-

tal conductances. Stomatal conductance is greatest under conditions favoring CO_2 assimilation: high light intensity, ample moisture, and high levels of nutrition.

Factors that influence the partial pressure of NH_3 in the substomatal cavity are unclear. Ammonia assimilation in plants is discussed in Chapter 6. Except at high tissue ammonia concentrations, where glutamate dehydrogenase may play a role, the majority of ammonia assimilation occurs through the combined action of the glutamine synthetase and glutamate synthase enzymes. The combined action of these two enzymes is particularly important in the refixation of the massive amounts of ammonia produced during photorespiration. Thus levels of NH_4^+ and NH_3 in plant tissue are normally extremely low. The partial pressure of NH_3 in the substomatal cavities is thought to be maintained by small amounts of NH_4^+ supplied in the transpiration stream plus small amounts present in surrounding leaf cells (Farquhar *et al.*, 1983). During leaf senescence, photorespiration declines but proteolysis (with the release of NH_4^+) increases. Losses of NH_3 from plants may, therefore, be greater during senescence (Farquhar *et al.*, 1983).

A number of workers have measured losses of NH_3 from healthy plant canopies (Martin and Ross, 1968; Stutte and Weiland, 1978; Stutte *et al.*, 1979; Weiland and Stutte, 1979, 1980; Weiland *et al.*, 1979; Farquhar *et al.*, 1980; Lemon and van Houtte, 1980; Hooker *et al.*, 1980) and senescing plants (Farquhar *et al.*, 1979; Hooker *et al.*, 1980). Some circumstantial evidence from N-balance studies also indicates that annual cereal crop plants can lose N when approaching maturity (Wetselaar and Farquhar, 1980). Some of this could be lost as NH_3.

The magnitude of gaseous losses of NH_3 from plants is uncertain and estimates vary greatly. Stutte and co-workers, using pyrochemiluminescent N detection, suggested losses averaging 9 nmol $(m^2$ leaf surface$)^{-1}$ sec^{-1} but losses estimated by other methods are an order of magnitude less (Farquhar *et al.*, 1979; Hooker *et al.*, 1980).

Volatile amines also appear to be liberated from growing plants particularly during flowering (Richardson, 1966; Farquhar *et al.*, 1983).

When the partial pressure of NH_3 in the ambient atmosphere exceeds that in the substomatal cavity then net absorption of NH_3 will occur (Farquhar *et al.*, 1980, 1983). Indeed, NH_3 can be absorbed in the vapor phase through open leaf stomata of leaf canopies and it may also dissolve in water films on the plant leaf surfaces and be subsequently absorbed and metabolized (Denmead *et al.*, 1976). Many workers have demonstrated the uptake of NH_3 by leaves placed in NH_3-enriched atmospheres (Hutchinson *et al.*, 1972; Porter *et al.*, 1972; Rogers and Aneja, 1980; Cowling and Lockyer, 1981). Faller (1972) showed in a long-term experi-

ment that plants can absorb and utilize NH_3 as the only source of N without affecting their normal growth.

It is evident that plants can both absorb and release NH_3 from their canopies. Indeed, field measurements of NH_3 flux within and above the canopy of several crops have clearly indicated that NH_3 released at the soil surface can be absorbed within the leaf canopy while some NH_3 may also be simultaneously released from the top of the canopy (Denmead *et al.*, 1976, 1978; Lemon and van Houtte, 1980). The major factors that determine whether net absorption or evolution of NH_3 occurs are, as yet, unclear. Nonetheless, an increase in the height and density of the crop canopy appear to be important factors that tend to reduce NH_3 losses (Denmead *et al.*, 1982).

III. BIOLOGICAL GENERATION OF GASEOUS NITROGENOUS PRODUCTS

Gaseous nitrogenous products can be produced by three groups of organisms: dissimilatory denitrifying bacteria, nondenitrifying fermentative bacteria and fungi, and autotrophic nitrifying bacteria. Denitrifying bacteria are thought to be the most important organisms contributing to losses of nitrogenous gases from soils under anaerobic conditions (Letey *et al.*, 1981; Payne, 1981; Firestone, 1982) but under oxidized conditions nitrifying bacteria could well be important agents (Freney *et al.*, 1979; Bremner *et al.*, 1981).

The organisms and processes involved in the biological production of gaseous N in soils are discussed below and the major factors that are thought to affect such production are reviewed.

A. Processes

1. Dissimilatory Denitrification

Dissimilatory denitrification is a respiratory process that is present in a limited number of aerobic bacteria whereby they can grow in the absence of O_2 while reducing NO_3^- or NO_2^- to N_2 and/or N_2O. The majority of such bacteria are heterotrophs and obtain their energy and cellular C from organic substrates. In the absence of O_2, NO_3^- or oxides derived from it serve as terminal electron acceptors for respiratory electron transport during the oxidation of the organic substrate and a more reduced N oxide or N_2 is produced. The process is described as a dissimilatory reduction since the products of NO_3^- reduction, N_2 and N_2O, are not assimilated but are released to the atmosphere.

a. Denitrifying bacteria. The capacity to use N oxides as electron acceptors in place of O_2 with the evolution of N_2O and/or N_2 has been reported in approximately 20 genera of bacteria (Payne, 1973, 1981; Focht and Verstraete, 1977; Firestone, 1982; Knowles, 1982). These are listed in Table II. The presence of denitrifiers in surface soils may be regarded as ubiquitous (Payne, 1981) since their density frequently exceeds one million per gram of soil (e.g., Jacobsen and Alexander, 1980) and higher concentrations are present in the rhizosphere (Alexander, 1977).

The most common bacteria used for physiological and biochemical studies of denitrification are *Paracoccus denitrificans*, *Pseudomonas denitrificans*, and *Pseudomonas perfectomarinus*. Nevertheless, it is not known which denitrifying organisms are either numerically or functionally most important in soils since laboratory methods of isolating and enumerating these bacteria are likely to favor some organisms to the detriment of others (Firestone, 1982).

Denitrifying bacteria are biochemically as well as taxonomically diverse. Most are chemoheterotrophs: they use carbonaceous compounds as electron donors (reductants) and as sources of cellular C and chemical energy sources. Some grow as chemolithotrophs, oxidizing H_2 (e.g., *Paracoccus denitrificans* and *Alcaligenes* spp.) (John and Whatley, 1975; Thauer *et al.*, 1977) or reduced sulfur compounds (e.g., *Thiobacillus denitrificans*) (Ishaque and Alaem, 1973; Baldensperger and Garcia, 1975). One group is photosynthetic (e.g., *Rhodopseudomonas sphaeroides*) (Satoh, 1977; Sawada *et al.*, 1978).

A few N_2-fixing organisms are known to have the ability to denitrify under anaerobic conditions. These include a considerable number of strains of *Azospirillum brasilense*, which are commonly associated with the roots of many tropical grain and forage grasses (Eskew *et al.*, 1977; Neyra and van Berkum, 1977; Neyra *et al.*, 1977; Scott and Scott, 1978). Several strains of *Rhizobium*, including *R. japonicum*, *R. meliloti*, and

Table II

The Reported Genera of Denitrifying Bacteria

Acinetobacter	*Halobacterium*	*Rhizobium*
Alcaligenes	*Hyphomicrobium*	*Rhodopseudomonas*
Azospirillum	*Micrococcus*	*Spirillum*
Bacillus	*Moraxella*	*Thiobacillus*
Cytophaga	*Paracoccus*	*Vibrio*
Flavobacterium	*Propionobacterium*	*Xanthomonas*
Gluconobacter	*Pseudomonas*	

most of the slow-growing rhizobia, also possess denitrifying capabilities in their free-living state under anaerobic conditions and can produce N_2 or N_2O (Zablotowicz *et al.*, 1978; Zablotowicz and Focht, 1979; Daniel *et al.*, 1980, 1982). Possession of a denitrifying pathway may help free-living bacteria survive anaerobic conditions in the soil (Daniel *et al.*, 1980) and might also be important to rhizobium–legume symbiosis by maintaining nodule integrity under anoxic conditions (Rigaud *et al.*, 1973).

b. Pathways. Detailed discussions of the physiology and biochemistry of the denitrification process have been presented elsewhere (Payne, 1973, 1981; Firestone, 1982; Knowles, 1982; Fillery, 1983) and only the major features are outlined below. The pathway of N oxide reduction is generally represented as

$$\underset{(+5)}{NO_3^-} \longrightarrow \underset{(+3)}{NO_2^-} \longrightarrow \underset{(+2)}{NO} \longrightarrow \underset{(+1)}{N_2O} \longrightarrow \underset{(0)}{N_2}$$

The enzymes responsible for the reductions are NO_3^- reductase, NO_2^- reductase, NO reductase, and N_2O reductase. The obligatory participation of NO and NO reductase in the sequence of reductions is still debatable (see Bryan, 1980; Knowles, 1982) and nitroxyl (NOH) has been suggested as an alternative intermediate (Garber and Hollocher, 1982).

While most denitrifying bacteria possess all the reductase enzyme complexes necessary to reduce NO_3^- to N_2, some lack NO_3^- reductase and are thus "NO_2^- dependent," some lack N_2O reductase and yield N_2O as the terminal product, and others possess N_2O reductase but lack the ability to reduce NO_2^- to N_2O (Knowles, 1981, 1982). Still other groups are sometimes referred to as partial denitrifiers (Ingraham, 1981). These include those lacking NO_2^- reductase and N_2O reductase and can therefore reduce NO_3^- to NO_2^- and NO to N_2O and organisms that lack NO_2^-, NO, and N_2O reductases and are capable of only limited reduction of NO_3^- to NO_2^-.

Characteristics of enzymes involved in the reductions vary depending on the bacterial species involved and the methods of purification used. Some common characteristics can be noted. Dissimilatory nitrate reductase is a membrane-bound enzyme that generally consists of multiple subunits and contains Mo, Fe, and labile sulfide groups (Firestone, 1982; Knowles, 1982). Nitrite reductase catalyzes the reduction of NO_2^- to gaseous products although there is still considerable controversy as to whether NO is the *in vivo* product. There appear to be two main types of nitrite reductase; copper-containing metalloflavoproteins and the apparently more common hemoproteins of cytochrome type *cd* (Knowles, 1982). Nitrite reductase appears to be membrane-associated but readily solubilized (Knowles, 1982). The reactive nature of NO makes isolation and characterization of NO reductase difficult and unequivocal evidence

for its role in denitrification has yet to be provided. Little is known about N_2O reductase although it is thought to be membrane-associated, possibly contains Cu, and is linked to electron transport through cytochromes of types *b* and *c* (Knowles, 1982).

2. *Fermentative Nitrite Dissimilation*

Nitrous oxide can also be produced in soils by the actions of a miscellany of "nondenitrifying" fungi and bacteria (Yoshida and Alexander, 1970; Bollag and Tung, 1972; Smith and Zimmerman, 1981). These nondenitrifying organisms are only able to respire NO_3^- anaerobically as far as NO_2^-, but growing fermentatively they can further dissimilate NO_2^- to NH_4^+ (Sorenson, 1978; Caskey and Tiedje, 1979; Cole and Brown, 1980). Nitrous oxide is produced as a minor product.

The physiological function, if any, of N_2O production by these organisms is not clear. Nitrous oxide production does not appear to be directly related to growth or energy generation (Smith and Zimmerman, 1981) as is the case for the fermentative reduction of NO_2^- to NH_4^+ (Cole and Brown, 1980).

The significance of nondenitrifying NO_3^- reducers as a source of N_2O evolution from soils is unknown. Some research (Smith and Zimmerman, 1981) suggests that these organisms are more numerous in soils than denitrifiers. However, since only a small proportion of the NO_3^- reduced by nondenitrifiers is released as N_2O they are generally thought to be of minor agronomic importance.

3. *Autotrophic Nitrification*

The NH_4^+-oxidizing bacteria *Nitrosomonas*, *Nitrosospira*, and *Nitrosolobus* have the capacity to produce N_2O from NH_4^+ or hydroxylamine (an intermediate in the oxidation of NH_4^+ to NO_2^- by these microorganisms) under most conditions (Yoshida and Alexander, 1970, 1971; Ritchie and Nicholas, 1972, 1974; Bremner and Blackmer, 1980; Blackmer *et al.*, 1980; Goreau *et al.*, 1980). The mechanisms that are thought to be responsible for the production of N_2O by these organisms were outlined in Chapter 3.

Laboratory (Bremner and Blackmer, 1978; Freney *et al.*, 1978; Goodroad and Keeney, 1984) and field evidence (Denmead *et al.*, 1979; Breitenbeck *et al.*, 1980; Mosier *et al.*, 1981, 1982; Smith *et al.*, 1982) has shown that losses of N_2O can occur from soils during nitrification. However, less certain is the significance of these N_2O emissions in comparison with those from denitrification.

It has also been suggested that NO_x emissions may result during nitrification (Verstraete, 1981). Lipschultz *et al.* (1981) showed that cultures of

Nitrosomonas europaea liberated both NO and N_2O during the oxidation of NH_4^+. The ratio of NO produced relative to N_2O rose as the O_2 content within the medium decreased and a mean value of 7.5 mol NO per mole of N_2O produced was observed. Indeed, emissions of NO_x are often observed during nitrification of NH_4^+ fertilizers when applied at high rates (e.g., band applications) although they are thought to occur principally as a result of NO_2^- accumulation and subsequent chemodenitrification (see Section IV).

B. Factors Affecting Biological Gaseous Losses

Most research dealing with factors influencing gaseous losses of N_2O and N_2 from soils has been centered on the process of dissimilatory denitrification. An unknown proportion of N_2O emitted during such experiments is likely to have originated from nitrification of native soil NH_4^+. A detailed discussion of the factors influencing nitrification was presented in Chapter 3. Conditions that favor nitrification will obviously tend to promote N_2O losses from native or applied fertilizer NH_4^+ since the ratio of N_2O evolved to NO_3^- produced during nitrification appears to be reasonably constant (Goodroad and Keeney, 1984). The factors that are generally known to influence denitrification are discussed below and, where appropriate, factors known to influence losses of N_2O through nitrification are also noted.

1. Aeration and Moisture

The activity and synthesis of all the N oxide reductase enzyme systems involved in denitrification are repressed by O_2 (Firestone, 1982; Knowles, 1982). The presence of oxygen also inhibits the activity of preformed reductases (Payne, 1973; Stouthamer, 1976). Indeed, it appears that under aerobic soil conditions the N oxide reductase enzymes are present in repressed form and when O_2 is removed from the soil there are rapid increases in the absolute and relative activities of these enzymes and denitrification commences almost immediately (Smith and Tiedje, 1979a).

Denitrification can probably occur even in well structured aerobic soils due to the occurrence of anaerobic microsites (Firestone, 1982). Anaerobic pockets in soils may often be localized areas of intense respiratory activity where O_2 demand exceeds the supply (Craswell and Martin, 1975; Smith, 1980) rather than areas of passive anaerobiosis. Clearly, factors such as the rate of O_2 consumption and O_2 diffusion rate and structural considerations such as pore geometry and degree of soil compaction are important (Smith, 1977; Ryden and Lund, 1980). In well aerated soils

emissions of N_2O are likely to originate, at least partially, through nitrification (Freney *et al.*, 1978).

Soil moisture is obviously an important factor that influences aeration since with increasing moisture content, air in soil pores is displaced with water. Hence, as illustrated in Fig. 5, with increasing soil moisture contents the rate of denitrification generally increases (Bremner and Shaw, 1958; Pilot and Patrick, 1972; Bailey and Beauchamp, 1973; Craswell and Martin, 1974; Ryden and Lund, 1980). Following periods of intense irrigation or rainfall, soils may become saturated with water at the soil surface for brief periods. During such periods short bursts of intense denitrification occur (Ryden *et al.*, 1979; Ryden and Lund, 1980). Increases in soil moisture content up to about −33 to −10 kPa also increase the rate of nitrification (Chapter 3) and thus the release of N_2O from applied NH_4^+ (Goodroad and Keeney, 1984).

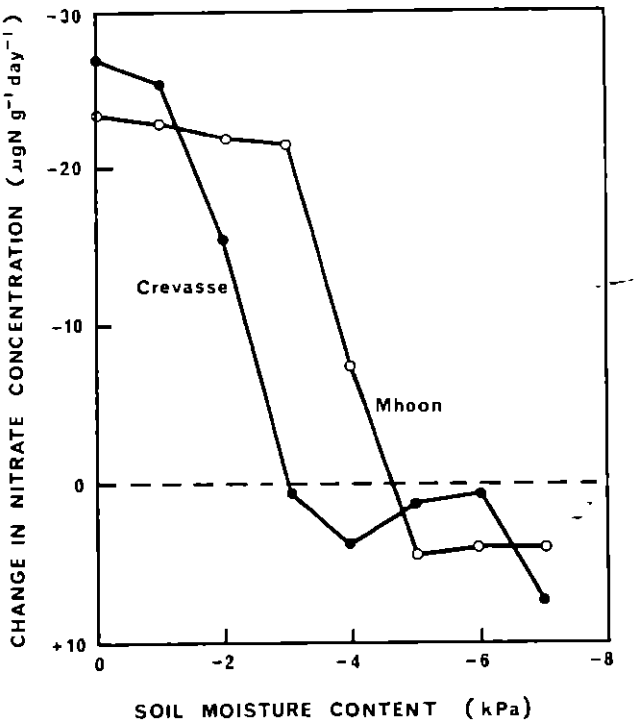

Fig. 5. Rate of nitrate reduction in two soils (Crevasse and Mhoon) as influenced by soil moisture tension. [Redrawn from Pilot and Patrick (1972). Reprinted with permission from The Williams and Wilkins Co., Baltimore.]

Although drainage should reduce denitrification losses by improving soil aeration, it also transfers more dissolved inorganic N from the soil to water courses, ditches, and rivers (Dowdell, 1982). Drainage water can, in fact, contain measurable amounts of dissolved N_2O (Dowdell *et al.*, 1979b, Dowdell, 1984) while NO_3^- transported in water is subject to denitrification during its journey in field drains and within stream courses (e.g., Swank and Caskey, 1982).

The later reductase enzymes in the denitrification sequence appear to be more sensitive to oxygen than are the earlier reductases (Krul and Veeningen, 1977; Betlach and Tiedje, 1981) so that with increasing oxygen concentrations there is an increase in the mole fraction of N_2O emitted (Focht, 1974).

Fluctuating moisture contents can influence the ratio of $N_2O:N_2$ evolved. The mole fraction of N_2O produced is generally high immediately following the onset of anaerobiosis and the proportion of N_2 produced generally increases with time (Rolston *et al.*, 1976, 1978; Letey *et al.*, 1979; Ryden *et al.*, 1979). This effect has been attributed to high concentrations of NO_3^- being initially present in the soil (Rolston, 1981). As noted later, high NO_3^- concentrations tend to inhibit the reduction of N_2O to N_2.

2. *Organic Carbon*

The most abundant denitrifiers are heterotrophs, which require organic compounds as electron donors and as a source of cellular material. Thus the availability of organic matter is an important factor moderating both the rate and total extent of denitrification. High levels of readily decomposable organic matter can also indirectly enhance the potential for denitrification through a general stimulation of microbial respiration, causing rapid O_2 consumption and an acceleration of the onset of anaerobiosis.

A general relationship between total soil organic C or N and denitrification has been observed by several workers (Bremner and Shaw, 1958; McGarity, 1961; Reddy *et al.*, 1982). However, it is the quantity of readily available soil organic carbon that is of particular importance. Thus, rates of denitrification are highly correlated with "available" soil C as evaluated by extractable reducing sugars (Stanford *et al.*, 1975), by water-soluble organic C (Bremner and Shaw, 1958; Burford and Bremner, 1975; Reddy *et al.*, 1982), or by readily mineralizable C (Burford and Bremner, 1975; Reddy *et al.*, 1982). The linear relationship between water-soluble C and the denitrification capacity of 17 soils is shown in Fig. 6. Factors that increase the levels of available C in soils (e.g., drying and rewetting or freezing and thawing) have been shown to increase the capacity of soils to denitrify added NO_3^- (McGarity, 1962; Patten *et al.*, 1980). Denitrification

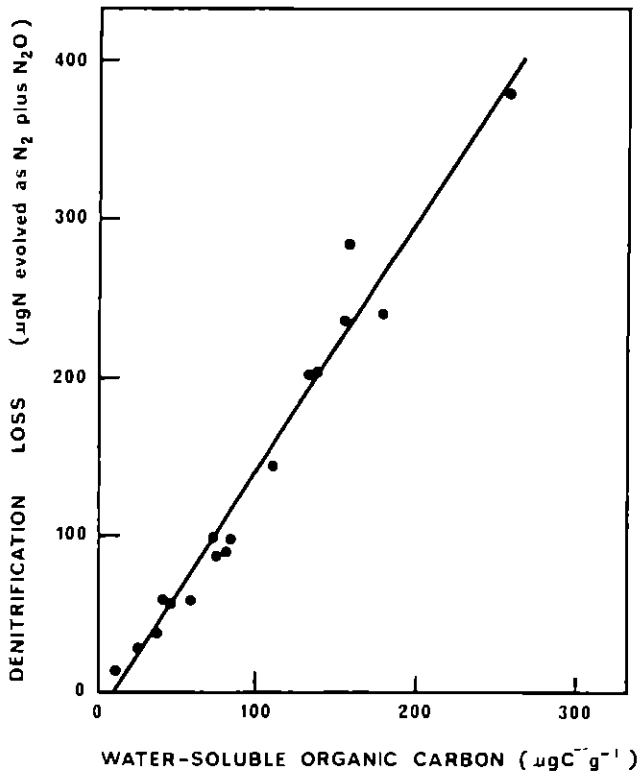

Fig. 6. Relationship between denitrification capacity and water-soluble organic carbon in 17 soils. [Redrawn from Burford and Bremner (1975). Reprinted with permission from Pergamon Press.]

is generally stimulated by additions of organic compounds and residues to soils (Nommik, 1956; Bowman and Focht, 1974; Guenzi *et al.*, 1978; Reddy *et al.*, 1978; Rolston *et al.*, 1982). Indeed, in many situations, the relationship between total soil C and denitrification is only of academic interest since readily available C sources are likely to provide the major C source for denitrification.

The dependence on C availability results in higher denitrification potentials being generally found in surface soils rather than in subsoils (Khan and Moore, 1968). Denitrification activity and populations of denitrifiers generally decrease with soil depth (Bailey and Beauchamp, 1973; Brar *et al.*, 1978; Cho *et al.*, 1979) although significant denitrification can occur down to 60 to 70 cm (Myers and McGarity, 1972; Rolston *et al.*, 1976;

Gilliam *et al.*, 1978). Organic soils generally have high potentials for denitrification (Bartlett *et al.*, 1979; Reddy *et al.*, 1980; Terry *et al.*, 1981).

Carbon availability can also influence the proportion of N_2O and N_2 produced. With increasing available C there is generally a more complete reduction of NO_3^- and therefore less N_2O production in relation to that of N_2 (Delwiche, 1959; Focht and Verstraete, 1977; Rolston *et al.*, 1978; Smith and Tiedje, 1979b).

3. Nitrate Supply

The apparent K_m values (which indicate the NO_3^- concentration required to give half the maximum velocity of denitrification) for the dissimilatory reduction of nitrogen oxides, determined *in vivo* or with purified enzymes, are normally in the range of 5 to 290 μM (see Knowles, 1982). Firestone (1982) noted that a K_m value of 15 μM NO_3^- for denitrifying bacteria would be equivalent to a concentration of 0.04 μg NO_3^--N per gram of soil that had a moisture content of 20%.

Thus it is not surprising that at relatively high concentrations of NO_3^- (greater than 40 to 100 μg N gm^{-1}) the rate of denitrification in soils has been shown to be independent of NO_3^- concentration, i.e., denitrification follows zero-order kinetics (Kohl *et al.*, 1976; Focht and Verstraete, 1977; Blackmer and Bremner, 1978). However, in soils the diffusion of NO_3^- to the sites of denitrification can become an important limiting factor (Phillips *et al.*, 1978; Reddy *et al.*, 1978) so that denitrification reactions are frequently reported to be first order up to 40 to 100 μg N gm^{-1} in soils (Stanford *et al.*, 1975; Starr and Parlange, 1975; Ryzhova, 1979). Indeed, presumably because of the limiting effect of the diffusion of NO_3^-, K_m values for NO_3^- reduction in soil are much higher than those obtained in cultures and range from 130 to 12,000 μM NO_3^- (Bowman and Focht, 1974; Yoshinari *et al.*, 1977).

High levels of NO_3^- can inhibit the reduction of N_2O causing an increase in the ratio of N_2O to N_2 in the product gases (Nommik, 1956; Blackmer and Bremner, 1978: Firestone *et al.*, 1980; Letey *et al.*, 1980; Terry and Tate, 1980; Gaskell *et al.*, 1981). The effect of NO_3^- concentration interacts with soil pH such that the inhibitory effect of NO_3^- on N_2O reduction increases markedly with a decrease in soil pH (Blackmer and Bremner, 1978; Firestone *et al.*, 1980).

4. Nitrifiable N

As already noted, in some studies greater losses of N_2O have accrued from soils after the application of nitrifiable N. In laboratory incubation experiments, soils amended with nitrifiable N (e.g., $(NH_4)_2SO_4$, urea, or the amino acid alanine) yielded more N_2O than similar nonamended or

Table III

Quantities of Nitrous Oxide Released from Well Aerated Soils Treated with Different Forms of Nitrogen[a]

Form	Rate	N_2O-N released (ng gm^{-1} soil) 8 days	30 days
None	0	2	5
$(NH_4)_2SO_4$	50	52	58
Urea	50	58	64
KNO_3	50	4	5
$(NH_4)_2SO_4$	100	146	153
Urea	100	118	124
KNO_3	100	4	7

[a] Data from Bremner and Blackmer (1978).

NO_3^--treated soils (Table III) (Bremner and Blackmer, 1978, 1980, 1981). In these experiments, N_2O production often increased linearly with nitrifiable N and, furthermore, losses were markedly reduced by addition of nitrapyrin (a compound that selectively inhibits autotrophic NH_4^+ oxidation) (Bremner and Blackmer, 1978). Under field conditions, however, the expected relationship between soil NH_4^+ concentrations and N_2O fluxes is frequently complicated by simultaneous denitrification (Mosier *et al.*, 1982; Smith *et al.*, 1982).

5. pH

In pure cultures and in soils, the overall rate of denitrification is often positively related to pH and has an optimum in the range of pH 7.0 to 8.0 (Nommik, 1956; Van Cleemput and Patrick, 1974; Muller *et al.*, 1980). Generally, in the neutral pH range of soils (pH 6 to 8) there is little effect of pH (Burford and Bremner, 1975; Stanford *et al.*, 1975) but at soil pH values below 6.0 denitrification can be strongly inhibited (Klemedtsson *et al.*, 1978; Muller *et al.*, 1980). At pH levels below 5.5, toxic levels of soil Al and Mn could well limit microbial activity. Nevertheless, several workers have reported significant denitrifier activity at soil pH values below 5.0 (e.g., Gilliam and Gambrell, 1978; Muller *et al.*, 1980; Koskinen and Keeney, 1982). In short-term laboratory studies, increasing pH may, to some extent, increase denitrifier activity by temporarily increasing the solubility of soil organic matter (Fillery, 1983).

The lower rates of denitrification often found in acidic soils (Gilliam and Gambrell, 1978; Muller *et al.*, 1980) may be due to a small population of denitrifiers in microsites having a higher pH than the surrounding soil and/or because of denitrifier populations with a low pH optimum or wide pH tolerance (Focht and Joseph, 1974). The optimum pH for nitrification normally appears to be pH 6 to 7 (Chapter 3), and Goodroad and Keeney (1984) observed a greater rate of nitrification of added NH_4^+, and concomitant N_2O emission, from a limed soil (pH 6.7) than from an unlimed control (pH 4.7).

It appears that the N_2O reductase enzyme system is more sensitive than the other reductases to low pH such that, as noted in the previous section, the mole fraction of N_2O produced increases as the pH falls (Blackmer and Bremner, 1978; Tiedje *et al.*, 1981) and at pH 4.0 N_2O may be the major product (Nommik, 1956). Such an effect appears to occur only in the presence of added NO_3^- (Firestone *et al.*, 1980).

6. *Temperature*

Denitrification is markedly influenced by temperature. Below 10°C rates are low and in the range of 10 to 35°C the rate of denitrification is very temperature dependent with a Q_{10} value (the ratio by which denitrification increases for a 10°C rise in temperature) of about 2.0 (Dawson and Murphy, 1972; Bailey and Beauchamp, 1973; Stanford *et al.*, 1975). Rates increase up to a maximum at 60 to 75°C and then rapidly decline (Table IV) (Bremner and Shaw, 1958; Keeney *et al.*, 1979).

The unusually high optimum temperature reported for denitrification may, in part, be the result of the presence of thermophilic *Bacillus* spp. (Focht and Verstraete, 1977). However, above 50°C chemical decomposition reactions of NO_2^- increase in importance (Keeney *et al.*, 1979) so that the high optimum may not be wholly of biological origin. To some extent, indigenous denitrifiers may have temperature optima adapted to their climatic regions (Gamble *et al.*, 1977). The optimum temperature for nitrification is often 25 to 30°C (Chapter 3), and Goodroad and Keeney (1984) showed that N_2O production via nitrification increased as the temperature was raised from 10 to 30°C.

Several workers have observed marked diurnal variability in the rate of N_2O emission from soils that appears to be related to soil temperature (Ryden *et al.*, 1978; Denmead *et al.*, 1979; Blackmer *et al.*, 1982; Lensi and Chalamet, 1982). Maximum rates generally occur in the afternoon and minimum rates during the night. Such results presumably reflect the temperature dependence of both denitrification and nitrification.

Denitrification appears to follow a seasonal trend with losses of N_2O plus N_2 being markedly higher in summer than in winter (Rolston *et al.*,

Table IV

Effect of Temp Ratio Evolved[a]

Temperature (°C)
7
15
25
40
50
60
65
67
70
75

[a] Data from 43, p. 1126 by
[b] Initial NO_3^-

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Table IV

Effect of Temperature on Gaseous N Loss and the $N_2O/(N_2O + N_2)$ Ratio Evolved[a]

Temperature (°C)	Total incubation time (days)	Gaseous N (% of initial NO_3^--N in system)[b]	$N_2O/(N_2O + N_2)$ (%)
7	16	11	44
15	16	12	49
25	16	44	19
40	4	63	69
50	4	125	0
60	4	134	0
65	4	127	0
67	4	143	0
70	4	109	87
75	4	0	—

[a] Data from Keeney *et al.* (1979). Reproduced from *Soil Sci. Soc. Am. J.* **43**, p. 1126 by permission of the Soil Science Society of America.
[b] Initial NO_3^--N in the soil system = 122 μg N gm^{-1}.

1978). Bremner *et al.* (1980b) observed similar seasonal fluctuations in N_2O fluxes from unfertilized agricultural soils.

In general, increasing temperature tends to increase the proportion of N_2 to N_2O in the products of denitrification (Nommik, 1956; Bailey, 1976; Keeney *et al.*, 1979) although in some cases temperature appears to have little effect (Bailey and Beauchamp, 1973).

7. Plants

Plant roots have several effects on the rhizosphere soil that may influence the potential for denitrification. First, roots release carbonaceous materials (organic substrate for denitrifiers) into the rhizosphere by excretion of soluble compounds, sloughing off root surface and root cap cells, and production of mucigel polysaccharide (Warembourg and Billies, 1979). Thus, large populations of denitrifiers frequently exist in the rhizosphere (Woldendorp, 1963), where they may be 10 to 100 times more numerous than in the root-free soil (Netti, 1955). The metabolism of the carbonaceous material by the rhizosphere microflora will tend to deplete the soil of O_2, as, indeed, will root respiration.

It is evident that if denitrification is limited by O_2 or C supply then the presence of plant roots will tend to stimulate denitrification. Many studies

have confirmed that the presence of plant roots enhances the denitrification of added NO_3^- (Fig. 7) (Woldendrop, 1963; Stefanson, 1972a,b,c; Brar, 1972; Garcia, 1975; Bailey, 1976; Volz *et al.*, 1976) and sometimes causes a decrease in the mole fraction of N_2O produced (Stefanson, 1972a,b). However, Stefanson (1976) observed that while wheat roots stimulated denitrification in soils of low organic matter content they had no effect in soils high in organic matter.

The second major effect of roots is that they absorb NO_3^- and so deplete the soil of substrate for denitrification. Thus, if a supply of NO_3^- is limiting denitrification then plants tend to decrease the rate of denitrification (Guenzi *et al.*, 1978; Buresh *et al.*, 1981). Smith and Tiedje (1979b) confirmed that when soil NO_3^- concentrations are high denitrification rates are increased in the rhizosphere, whereas when NO_3^- concentrations are low denitrification rates are decreased in the presence of roots.

8. Animals

In grassland ecosystems the urine patches formed by grazing animals are recognized as focal points for the loss of N via NH_3 volatilization

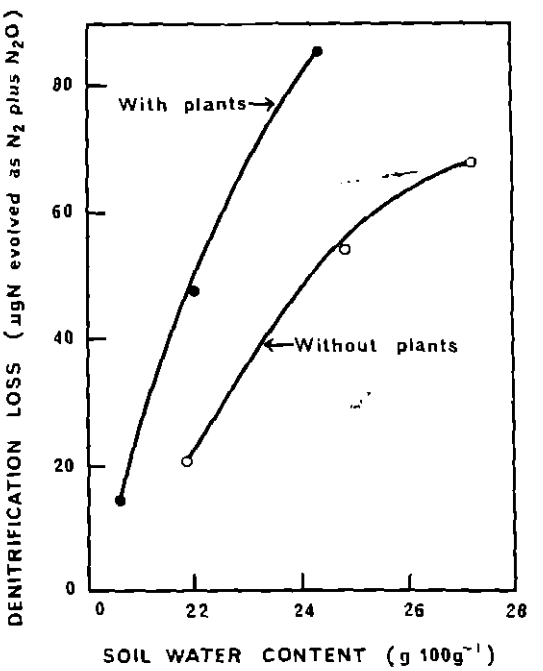

Fig. 7. Effect of plant growth and soil moisture content on the total amount of N (N_2 + N_2O) evolved from a soil. [Redrawn from Stefanson (1972b).]

(Catchpoole *et al.*, 1983; Sherlock and Goh, 1984) and leaching (Ball *et al.*, 1979). However, deposition of urine also results in an immediate release of N_2O, which does not occur from additions of urea of equivalent N content (Sherlock and Goh, 1983). The reason for this rapid production and release of N_2O is unknown although several mechanisms have been suggested (Sherlock and Goh, 1983), including stimulation of denitrification due to rapid onset of anaerobiosis caused by concomitant inputs of readily available C and rapid urea hydrolysis.

9. Tillage Method

In comparison with conventional tillage, the lack of soil disturbance and the presence of a surface mulch under zero tillage result in increased bulk density, a reduction in large pores, reduced aeration, larger but less aerobic aggregates, and a generally higher moisture content in the surface soil (Dowdell *et al.*, 1979a; Lin and Doran, 1984). Levels of water-soluble C can also be higher in surface soils under zero tillage (Lin and Doran, 1984). Such soil conditions obviously tend to favor the activity of denitrifiers and denitrifier populations are generally greater in the surface soil under zero rather than conventional tillage (Aulakh *et al.*, 1984a; Lin and Doran, 1984; Broder *et al.*, 1984). Studies have also shown that losses of N_2O (Burford *et al.*, 1981) or N_2O plus N_2 (Rice and Smith, 1982; Aulakh *et al.*, 1984a,b) are greater from zero tilled rather than conventionally tilled fields although the ratio of $N_2O : N_2$ emitted is not changed measurably. Aulakh *et al.* (1984a) estimated N_2O plus N_2 losses from cropped, conventionally tilled and zero tilled fields as 3–7 and 12–16 kg N ha^{-1} yr^{-1} respectively.

The generally lower rate of mineralization, and therefore nitrification, and the smaller populations of nitrifiers under zero tillage (Rice and Smith, 1983; Broder *et al.*, 1984) suggest that greater losses of N_2O under zero as compared to conventional tillage are the result of greater denitrification rather than nitrification.

IV. CHEMODENITRIFICATION

Chemodenitrification is the term commonly used to describe various chemical reactions of NO_2^- ions within soils that result in the emission of a variety of nitrogenous gases (e.g., N_2, NO, NO_2, and sometimes N_2O). Such gases are of nonbiological origin since they are also evolved from sterilized soil to which NO_2^- has been added. Normally, a higher proportion of added NO_2^--N is converted to (NO plus NO_2)-N than to N_2 (Nelson and Bremner, 1970b; Bollag *et al.*, 1973). Also the [(NO + NO_2)-N : N_2]

ratio usually varies from 2 : 1 at soil pH values of 5.0 to 5.8 to about 1 : 1 at pH values above 5.8 (Nelson, 1982). Small amounts of N_2O are also sometimes evolved from soils following treatment with NO_2^- (Reuss and Smith, 1965; Smith and Clark, 1980a,b).

A. Nitrite Accumulation

Chemodenitrification is likely to be significant only where NO_2^- accumulates in soils. The factors that favor the accumulation of NO_2^- in soils and thus chemodenitrification have been reviewed in detail elsewhere (Nelson, 1982; Chalk and Smith, 1983) and are outlined below.

In well aerated, unfertilized soils autotrophic oxidation of NO_2^- to NO_3^- proceeds at a faster rate than the conversion of NH_4^+ to NO_2^- (see Chapter 3). Consequently, NO_2^- is not normally present in amounts greater than 1 $\mu g\ gm^{-1}$. High concentrations may, however, accumulate when N fertilizers that form alkaline solutions upon hydrolysis are band-applied to soils. Urea, ammonium carbonate, diammonium phosphate, urea ammonium phosphate, and anhydrous ammonia all hydrolyze to produce an alkaline environment. In the fertilizer band of such materials soil pH may reach 10 and the N concentration may be several thousand μg N gm^{-1} (Parr and Papendick, 1966; Chalk *et al.*, 1975). The activity of the NO_2^- oxidizer *Nitrobacter* is more greatly inhibited by high pH and high NH_4^+ levels than is that of the NH_4^+ oxidizers. Thus, in fertilizer bands, NO_2^- can accumulate up to several hundred μg N gm^{-1} (Chalk *et al.*, 1975).

Nitrite has been shown to accumulate during nitrification of urea, NH_4^+ salts, and anhydrous and aqua ammonia (Hauck and Stephenson, 1965; Wetselaar *et al.*, 1972; Pang *et al.*, 1973, 1975; Chalk *et al.*, 1975). Nitrite is particularly reactive under acidic conditions, which may occur around the periphery of fertilizer granules or bands where nitrification of the fertilizer is complete. Nitrite that accumulates in the alkaline fertilizer granule or band may, therefore, be unstable in the peripheral acid portion of the soil environment, leading to gaseous loss of N (Hauck and Stephenson, 1965). Nitrite can also accumulate in alkaline soils treated with acid-hydrolyzing NH_4^+ fertilizers such as $(NH_4)_2SO_4$ (Bezdicek *et al.*, 1971) and in urine patches on grazed pastures (Vallis *et al.*, 1982) where large amounts of urea N are deposited over a small surface area. Accumulation of NO_2^- has also been noted in NO_3^--treated soils during biological denitrification (Cady and Bartholomew, 1960; Doner *et al.*, 1975; Cooper and Smith, 1963; Bailey, 1976; Volz and Starr, 1977). During the freezing of soils, NO_2^- levels can be concentrated in the unfrozen water resulting in a greater potential for chemodenitrification (Christianson and Cho, 1983).

In laboratory studies, a number of workers have observed large deficits during nitrification of urea or NH_4^+ fertilizers in soils and have attributed

such losses to chemical reactions of NO_2^- (Hauck and Stephenson, 1965; Steen and Stojanovic, 1971). It is, however, noted that gaseous losses of N as N_2O, and apparently NO, can occur during autotrophic nitrification of NH_4^+-N (see Section III).

B. Mechanisms

A variety of reactions have been proposed to account for gaseous losses of N by chemodenitrification. The major reactions are discussed below.

1. Decomposition of Nitrous Acid

Nitrous acid is produced when NO_2^- is added to, or formed in, acid soils:

$$NO_2^- + H^+ \longrightarrow HNO_2 \qquad (13)$$

At pH 5, 4, and 3, the proportions of the nitrite N present as undissociated nitrous acid are 1.9, 16, and 74%, respectively (Chalk and Smith, 1983). Nitrous acid can undergo spontaneous decomposition as shown below:

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O \qquad (14)$$

In closed incubation vessels, which are often used to study these reactions in the laboratory, the products actually obtained depend on a number of additional factors. In an aerobic system, NO is usually oxidized to NO_2 and both gases may then be absorbed by the moist soil as HNO_3 (Nelson, 1982). The overall reaction then becomes

$$2HNO_2 + O_2 \longrightarrow 2HNO_3 \qquad (15)$$

In an anaerobic system, NO_2 is normally adsorbed as before but NO appears in the atmosphere. Under these conditions, the overall equation is

$$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O \qquad (16)$$

The proportion of added NO_2^- evolved as (NO plus NO_2)-N is not related to soil organic matter content but increases with decreasing pH because of the large proportion of HNO_2 present at low pH (Bremner and Nelson, 1969; Nelson and Bremner, 1970b; Bollag *et al.*, 1973). Significant amounts of NO and NO_2 are produced when NO_2^- is added to soils of pH greater than 5.5 (Porter, 1969; Nelson and Bremner, 1970a). This may indicate that self-decomposition of HNO_2 occurs at colloid surfaces, where the pH is considerably lower than that of the measured bulk soil pH (Nelson and Bremner, 1970a).

Under field conditions, the extent to which any of these decomposition reactions takes place is not well documented. Several workers have questioned the importance of HNO_2 decomposition in relation to gaseous losses of N from soils (e.g., Broadbent and Clark, 1965; Allison, 1966; Broadbent and Stevenson, 1966). Despite this, a number of workers have recorded emissions of (NO plus NO_2)-N from untreated soils and from soils treated with urea and NH_4^+ fertilizers (Steen and Stojanovic, 1971; Kim, 1973; Galbally and Roy, 1978; Smith and Chalk, 1980a; Johansson and Granat, 1984).

2. *Reactions of Nitrous Acid with Organic Matter*

Several researchers have shown a positive relationship between soil organic matter content and the rate of NO_2^- decomposition, with the concomitant emission of N_2 and N_2O, when NO_2^- is added to soils (e.g., Reuss and Smith, 1965; Nelson and Bremner, 1970b). It is the phenolic constituents of soil organic matter that are largely, if not entirely, responsible for such formation of N_2 and N_2O (Bremner and Nelson, 1969; Stevenson *et al.*, 1970).

The mechanisms involved in the formation of gaseous products by reaction of HNO_2 with phenolic constituents are only partially understood. The reactions are known as nitrosation reactions and involve the addition of the nitroso group (—N=O) to an organic molecule by reaction with nitrous acid. Two possible mechanisms thought to be responsible for the reactions of HNO_2 with phenols are shown in Fig. 8.

Nitrosation reactions also result in fixation of NO_2^- by soil organic matter through the formation of nitroso groups on phenolic rings (Bremner, 1957; Bremner and Fuhr, 1966; Smith and Chalk, 1980b). Bremner and Fuhr (1966) found that when NO_2^- was added to soils with pH values ranging from 3 to 7, part of the N was fixed by organic matter (10–28%) and part was converted to gaseous forms (33–79%). The NO_2^- that is fixed to organic matter is resistant to biological decomposition (mineralization) (Bremner and Fuhr, 1966; Smith and Chalk, 1979).

As well as N_2 and N_2O, NO and nitromethane (CH_3ONO) have been detected as reaction products of the reactions of NO_2^- with organic matter (Stevenson and Swaby, 1964; Edwards and Bremner, 1966; Stevenson *et al.*, 1970; Steen and Stojanovic, 1971). Several reaction mechanisms have been suggested to explain such emissions (see Chalk and Smith, 1983).

3. *Reactions of Nitrous Acid with Compounds Containing Free Amino Groups*

The reaction between HNO_2 and compounds containing free amino groups (e.g., amino acids, urea, and amines) has long been suggested as a

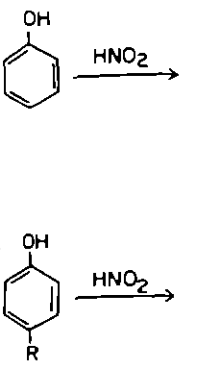

Fig. 8. Two possib
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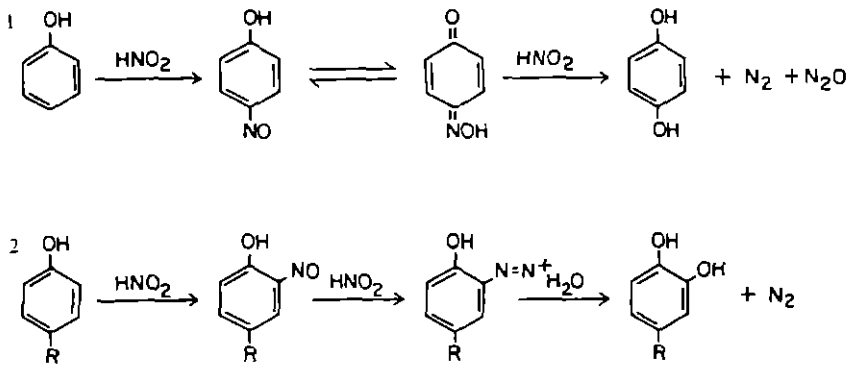

Fig. 8. Two possible reactions of phenols with nitrous acid. Mechanism (1) involves formation of *p*-nitrosophenol, tautomerization of this product to a quinone monoxime, and formation of N_2 and N_2O by reaction of the oxime with HNO_2. Mechanism (2) involves formation of an *o*-nitrosophenol and production of N_2 through decomposition of the diazo group in the diazonium compound formed by reaction of this *o*-nitrosophenol with HNO_2. [After Nelson (1982). Reproduced from "*Nitrogen in Agricultural Soils*" (F. J. Stevenson, ed.) Agronomy Mono. **22**, p. 353 by permission of the American Society of Agronomy. Madison, Wisconsin.]

possible mechanism for gaseous N loss from soil. This "Van Slyke" reaction only takes place at low pH and the N_2 gas evolved is derived in equal quantities from the two reactants:

$$R\text{-}NH_2 + HNO_2 \longrightarrow R\text{-}OH + H_2O + N_2 \qquad (17)$$

Although this reaction is generally considered to be of limited importance as a mechanism for gaseous losses of N from soils (Nelson, 1982), several workers have suggested it as responsible for at least part of the N_2 produced when NO_2^- is added to acid soils (Reuss and Smith, 1965; Stevenson *et al.*, 1970; Smith and Chalk, 1980b). Smith and Chalk (1980b), for instance, found that the ^{15}N enrichment of evolved N_2 from sterilized soils was approximately one-half that of the ^{15}N enrichment of the added NO_2^--N. Christianson *et al.* (1979) observed similar results. Such results suggest that Van Slyke-type reactions were involved since nitrosation reactions alone would result in no isotopic dilution of the evolved N_2.

4. Reaction of Nitrite with Ammonium

Solid ammonium nitrite (NH_4NO_2) explodes on heating to 60 to 70°C to produce N_2 gas (Weast, 1977). The same reaction proceeds much more slowly from concentrated solutions of NH_4NO_2 at low pH (pH < 5.2) (Smith and Clark, 1960). Since applications of NH_4^+ or NH_4^+-forming fer-

tilizers can result in the accumulation of both NH_4^+ and NO_2^- in soils, some workers have suggested that significant gaseous loss of N might occur by chemical decomposition of NH_4NO_2 (e.g., Allison, 1963; Ewing and Bauet, 1966):

$$NH_4^+ + NO_2^- \longrightarrow NH_4NO_2 \longrightarrow N_2 + H_2O \quad (18)$$

In general, NH_4NO_2 decomposition does not occur during incubation or air drying of acidic soils containing NH_4^+ and NO_2^- but some decomposition of NH_4NO_2 can occur when light-textured, neutral, and alkaline soils treated with NH_4^+ and NO_2^- are air dried (Wahhab and Uddin, 1954; Bremner and Nelson, 1969; Jones and Hedlin, 1970).

Thus, it is thought that the reaction is not of general significance in regard to gaseous losses of N from soils (Nelson, 1982) except perhaps when neutral or alkaline soils containing high concentrations of NH_4^+ and NO_2^- are subjected to drying conditions.

5. *Reaction of Nitrous Acid with Hydroxylamine*

A number of workers (e.g., Arnold, 1954; Wijler and Delwiche, 1954; Vine, 1962) have speculated that the chemical reaction of hydroxylamine (NH_2OH) with HNO_2 might generate N_2O:

$$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O \quad (19)$$

Although it has been shown that NH_2OH can be quantitatively decomposed by HNO_2 (Nelson, 1978), Bremner *et al.* (1980a) found that when NH_2OH was added to soils, large amounts of N_2O were formed in the absence of HNO_2. It was suggested by Bremner *et al.* (1980a) that N_2O is formed in soils through other nonbiological transformations of NH_2OH and very little is generated by the reaction of NH_2OH with HNO_2. Such nonbiological transformations were postulated to involve oxidized forms of Mn and Fe (e.g., MnO_2 and Fe_2O_3).

The fact that NH_2OH has not been detected in soils makes the significance of the above reactions questionable (Nelson, 1982). Hydroxylamine is, however, a postulated intermediate of both the biological reduction of NO_3^- to NH_4^+ (Alexander, 1977; Yordy and Ruoff, 1981) and the oxidation of NH_4^+ to NO_3^- (see Chapter 3). The fact that it is not present in soils may be a consequence of its rapid decomposition.

6. *Other Reactions*

Several other reactions have been suggested as possible pathways of chemodenitrification including reactions of HNO_2 with clay minerals and transition metal cations. Such reactions seem unlikely to be significant sources of gaseous N loss from soils although Nelson (1982) suggested

that Fe^{2+} may promote decomposition of NO_2^- formed by microbial reduction of NO_3^- in waterlogged soils. This suggestion deserves further research since significant amounts of Fe^{2+} are often present in anaerobic soils. Indeed, Moraghan and Buresh (1977) showed that chemical decomposition of NO_2^-, with the evolution of N_2 and N_2O, occurred anaerobically in a high Fe^{2+} ion environment while Van Cleemput and Baert (1984) found that soil conditions promoting the formation of Fe^{2+} also promoted NO_2^- decomposition and NO emissions.

V. EXTENT, SIGNIFICANCE, AND FATE OF LOSSES

Global estimates of gaseous losses of N from the plant–soil system were presented in Chapter 1. In this section some recent field measurements of gaseous losses of N are reported and the fate and significance of such emissions are outlined.

A. Ammonia Volatilization

1. Extent of Losses

The amounts of NH_3 volatilized from applications of NH_4^+- or NH_4^+-yielding fertilizers are extremely variable (Terman, 1979) and depend on such factors as type, rate, and method of fertilizer application, soil pH, and environmental factors such as temperature and moisture. Losses of fertilizer N applied to the surface of grassland or bare soil often appear to be in the range of 0 to 25% (Hargrove and Kissel, 1979; Hoff *et al.*, 1981; Craig and Wollum, 1982; Catchpoole *et al.*, 1983; Black *et al.*, 1985b). Significant, but variable, losses of NH_3 can occur following fertilizer applications to flooded soils (Vlek and Craswell, 1981) or when fertilizer is applied in the irrigation water (Denmead *et al.*, 1982).

Volatilization of NH_3 from organic amendments (e.g., animal manures or sewage sludge) applied to soils can be large but also variable (Hoff *et al.*, 1981; Beauchamp *et al.*, 1982; Beauchamp, 1983). Losses are often in the range of 10–60% of applied N. Losses from urine patches on grazed pastures can similarly be relatively high, ranging from 10 to 60% of applied urea N (Harper *et al.*, 1983; Simpson and Steele, 1983; Sherlock and Goh, 1984).

2. Fate of Ammonia Emissions

Ammonia is present in the atmosphere as a gas and in the form of ammonium in water droplets and solid particles. Concentrations of NH_3

and NH_4^+ vary widely in the atmosphere due to inhomogeneity of the sources and sinks (e.g., biological sources and precipitation scavenging). The major removal mechanisms for atmospheric ammonia are by wet and dry deposition. These processes are very rapid and the mean atmospheric lifetime of NH_3 is in the region of 7 to 14 days (Hahn and Crutzen, 1982; Galbally and Roy, 1983).

Gaseous deposition of NH_3 is an important mechanism for the return of volatilized NH_3 to the biosphere since plants, land surfaces, lakes, and oceans can all act as sinks as well as sources for atmospheric NH_3 (Calder, 1972; Dawson, 1977; Georgii and Gravenhorst, 1977; Farquhar *et al.*, 1983). Ammonia volatilized at a particular site can therefore be reabsorbed by direct gaseous uptake nearby. However, the fraction of NH_3 that is converted to an atmospheric aerosol can travel to more distant locations.

Ammonia is extremely soluble in water and once dissolved it ionizes to NH_4^+:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (20)$$

Thus, in the troposphere, NH_3 quickly dissolves in water droplets in clouds with the formation of NH_4^+-containing aerosols. Atmospheric aerosols of H_2SO_4 (often from industrial sources) can be quickly ammoniated to NH_4HSO_4 and $(NH_4)_2SO_4$ under most tropospheric conditions (Huntzicker *et al.*, 1980). Much of the emitted NH_3 is therefore present in the atmosphere as aerosols in the form of NH_4^+ salts (Taylor *et al.*, 1983) such as NH_4NO_3 or $(NH_4)_2SO_4$. It is removed from the atmosphere predominantly by wet deposition. Ammonium found in rainwater can originate from sources hundreds or thousands of kilometers away (Lenhard and Gravenhorst, 1980). Upon evaporation of water, aerosol particles may also be returned by dry deposition.

B. Denitrification and Nitrification

1. Extent of Losses

Few studies have measured directly total losses of applied ^{15}N ($^{15}N_2$ plus $^{15}N_2O$) through denitrification (and nitrification) occurring under field conditions (Rolston, 1978; Rolston and Broadbent, 1977; Rolston *et al.*, 1978, 1982). Rolston *et al.* (1978) measured N_2 plus N_2O losses from plots at two temperatures, two water contents, cropped and uncropped, and manured or unmanured. Losses ranged from zero (for the uncropped driest treatments) to about 75% (for the wettest treatments with manure

added). Rolston and Broadbent (1977) measured N_2 plus N_2O losses over an entire growing season and calculated a loss of about 13 kg N ha^{-1}, which represented approximately 9% of applied fertilizer N.

Several workers (e.g., Ryden *et al.*, 1979; Ryden, 1981; Colbourn *et al.*, 1984) have indirectly measured total denitrification losses by measuring N_2O fluxes in the presence of acetylene (which inhibits further reduction of N_2O to N_2 in the soil). The injection of acetylene into the soil also inhibits nitrification (Hynes and Knowles, 1978; Walter *et al.*, 1979) and thus N_2O emissions from that source. Ryden (1981) estimated denitrification losses of 11 and 29 kg N ha^{-1} yr^{-1} from grassed plots receiving 250 and 500 kg of fertilizer N ha^{-1}, respectively. Other workers (Colbourn and Dowdell, 1984; Colbourn *et al.*, 1984) estimated losses of 18–38 kg N ha^{-1} yr^{-1} from a grassland receiving 210 kg N ha^{-1} and 7–13 kg N ha^{-1} yr^{-1} from winter wheat receiving a fertilizer addition of 70 kg N ha^{-1}.

From the small amount of data available it is evident that gaseous losses can vary considerably. Colbourn and Dowdell (1984), however, generalized that direct and indirect estimates of losses of N_2 plus N_2O from soils range from 0 to 20% of fertilizer N applied to arable soils and 0 to 7% on grassland soils.

While the mole ratio of N_2O produced during denitrification is exceedingly variable (Rolston *et al.*, 1978, 1982; Ryden *et al.*, 1979; Rolston, 1981; Aulakh *et al.*, 1984a), in general, the quantity of N_2 produced during denitrification is much greater than that of N_2O. For example, field experiments have yielded time-averaged N_2O mole fractions of 0.12–0.18 (Ryden *et al.*, 1979) and 0.20–0.30 (Rolston *et al.*, 1982).

The extent of losses of N_2O through the nitrification pathway is not known although field studies have confirmed that significant amounts of N_2O are emitted during nitrification of applied NH_4^+ fertilizers (Hutchinson and Mosier, 1979; Breitenbeck *et al.*, 1980; Bremner *et al.*, 1981; Cochran *et al.*, 1981; Mosier and Hutchinson, 1981; Mosier *et al.*, 1981). Losses of N_2O following applications of urea or NH_4^+ fertilizers have ranged from 0.2 to 0.6% of applied N (Breitenbeck *et al.*, 1980; Mosier *et al.*, 1981) while losses following injection of anhydrous NH_3 have ranged from less than 0.1% (Cochran *et al.*, 1981) to 4.0 to 6.8% of applied N (Bremner *et al.*, 1981). Although losses of N_2O in the above experiments may have originated predominantly from nitrification, emissions caused by denitrification in anoxic microsites cannot be ruled out.

Although N_2O is usually assumed to be lost from soil only to the atmosphere, during winter it can also leave the soil dissolved in drainage water. Measured losses range from 0.25 to 4.4 kg N ha^{-1} from agricultural soils (Dowdell *et al.*, 1979b; Harris *et al.*, 1984), which were comparable with gaseous losses of N_2O over the same period.

2. *Nitrous Oxide and Stratospheric Ozone*

Much research on denitrification, and more recently nitrification, has been prompted by a concern that N_2O released into the atmosphere by these processes may increase the rate of reactions in the stratosphere that lead to the destruction of the ozone (O_3) layer (Crutzen and Ehhalt, 1977; McElroy *et al.*, 1977; National Research Council, 1978). The stratospheric ozone layer shields the biosphere from harmful UV radiation and also influences the vertical temperature profile and thus earth surface temperatures (Ramanathan *et al.*, 1976; Wang *et al.*, 1976; Hahn, 1979).

Atmospheric photochemistry in relation to the role of nitrogen oxides has been reviewed in detail elsewhere (Crutzen, 1981, 1983; Hahn and Crutzen, 1982). The low solubility of N_2O in water means that there is no significant removal of atmospheric N_2O from the troposphere by precipitation and it penetrates, almost unimpeded, into the stratosphere. Atmospheric destruction of N_2O occurs through photochemical reactions in the stratosphere:

$$N_2O + h\nu \longrightarrow N_2 + O \quad (21)$$

$$N_2O + O(^1D) \longrightarrow N_2 + O_2 \quad (22)$$

$$N_2O + O(^1D) \longrightarrow 2NO \quad (23)$$

The electronically excited $O(^1D)$ atom is produced by photolysis of ozone in the stratosphere. Approximately 10% of stratospheric N_2O is thought to be converted to NO by reaction (23). Direct transport of NO_x into the stratosphere from the earth's surface is unlikely because of the short atmospheric residence time of NO_x, which is quickly converted to HNO_3 aerosols and thermally unstable organic nitrates (e.g., peroxyacetyl nitrates—PAN) and removed by wet and dry deposition (Crutzen, 1981).

One of the major sinks of O_3 is reaction with NO_x, which catalyzes the destruction of O_3 above 25 km in the stratosphere (Crutzen, 1981, 1983). However, below 25 km, NO_x protects O_3 from destruction (Logan *et al.*, 1978; Zahniser and Howard, 1979). Thus, the major effect of increased production of NO_x in the stratosphere is likely to be a lowering of the center of gravity of the stratospheric ozone by a transfer of mass to altitudes below about 25 km (Crutzen, 1981). Nonetheless, Crutzen (1983) calculated that increasing N_2O emissions will tend to enhance O_3 loss through net catalysis of its destruction in the entire stratosphere; a doubling of atmospheric N_2O abundance might yield a 12% decrease in total O_3.

It is interesting to note that, overall, the global source of N_2O from N fertilizer applications is probably smaller than a few Tg N yr^{-1} (Crutzen

1983). Thus, the impact of the increasing use of N fertilizers on stratospheric ozone is unlikely to be great. Weiss (1981), for example, observed that the global upward trend in atmospheric N_2O concentrations is about 0.2% per year, which can be explained in terms of the 3.5% per year increase in global N_2O emissions caused by fossil fuel combustion.

3. *Fate of N_2 and N_2O*

The quantities of N_2 evolved from the earth's surface during denitrification are extremely small in relation to the atmospheric content. The dinitrogen molecule is very stable and its atmospheric lifetime is of the order of millions of years. N_2 constitutes 79% of the atmospheric mass.

Upon release of N_2O from soils, an unknown portion is believed to be removed by gaseous deposition to vegetation, soil, and water (Rasmussen *et al.*, 1975). However, under conditions of high soil NO_3^- concentrations, when potentially high rates of denitrification may occur, the reduction of N_2O to N_2 is usually inhibited (Firestone *et al.*, 1980) (Table V) and it seems unlikely that the soil will act as a major sink for N_2O (Freney *et al.*, 1978).

The approximate stratospheric lifetime of N_2O is 100 to 150 yr (Galbally and Roy, 1983). The only known photochemical reactions that lead to removal of N_2O from the stratosphere were presented earlier (equations (21), (22), and (23)). Thus, N_2O in the stratosphere is converted to N_2 and NO. More than 90% of the N_2O is thought to be transformed to N_2 in the stratosphere and the remainder is converted to NO (Nicolet and Peetermans, 1972). As discussed in the next section, the NO produced can be

Table V

Effect of Nitrate N Concentration on the Denitrification Rate and the Proportion of Gas Evolved as N_2 and N_2O[a]

Concentration of added NO_3^--N (μg gm^{-1})	Denitrification rate (μg N gm^{-1} hr^{-1})	Percentage of total ^{15}N gas evolved	
		N_2	N_2O
0	—	95.2	4.8
0.5	0.54	93.9	6.1
2.0	0.73	89.8	10.2
20.0	1.15	85.4	14.6

[a] Data from Firestone *et al.* (1979). Reproduced from *Soil Sci. Soc. Am. J.* **43**, p. 1143 by permission of the Soil Science Society of America.

rapidly transformed to NO_2 and thence to HNO_3. These substances are eventually returned to the troposphere and then to the earth's surface by wet and dry deposition.

C. Chemodenitrification

1. Extent of Losses

High rates of chemodenitrification are likely to occur principally as a result of NO_2^- accumulation during nitrification of banded NH_4^+ or NH_4^+-yielding fertilizers, which form alkaline solutions following hydrolysis. Field studies are, however, required to quantify such losses of N_2, N_2O, and NO_x and identify the factors affecting such losses. Emission of N_2O and possibly NO during the nitrification process would tend to confound such results.

Few attempts have been made to directly measure losses of NO_x from soils. Galbally and Roy (1978) measured losses of NO from soils in the range 0.06 to 5×10^{-11} kg N m^{-2} sec^{-1}, which convert to a global source of NO over land of about 1 kg N ha^{-1} yr^{-1} (Galbally and Roy, 1983). Johansson and Granat (1984) measured annual emissions of NO from unfertilized and fertilized arable land of about 0.2 and 0.6 kg N ha^{-1}, respectively.

2. Fate of NO_x Emissions

As discussed in Chapter 1, the two major sources of atmospheric NO_x are emissions from soils through chemodenitrification and combustion sources (automobiles, furnaces, forest fires, etc.). The quantities produced by the two sources are thought to be comparable on a global scale.

Nitric oxide released from the soil surface is quickly converted to NO_2 by O_3 in the lower atmosphere:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (24)$$

This NO_2 can be absorbed by the local plant and soil surface (Galbally, 1974; Rogers *et al.*, 1979; Elkiey and Ormrod, 1981; Galbally and Roy, 1978) or transported long distances in the atmosphere (Galbally and Roy, 1983). Nitric oxide can also be absorbed by plants but much more slowly than NO_2 (Galbally and Roy, 1983).

The major sink identified for NO_x in the troposphere is the dissolution of soluble species in cloud and rain droplets with subsequent removal by precipitation. In the stratosphere NO_2 reacts with OH radicals to yield HNO_3.

Under atmospheric conditions, the conversion of NO_x to HNO_3 occurs

within a few days and the mean atmospheric lifetime of NO_x is thought to be about 1.5 days (Hahn and Crutzen, 1982). Aerosol NO_3^- can readily form since gaseous HNO_3 is attached to, or dissolved in, preexisting aerosol particles (e.g., H_2SO_4, $(NH_4)_2SO_4$, or NH_4HSO_4) through heterogeneous condensation (Taylor *et al.*, 1983). Indeed, SO_4^{2-} and NO_3^- combined with NH_4^+ are usually dominant inorganic species found in atmospheric aerosols (Stevens *et al.*, 1978; Scott and Laulainen, 1979; Huebert and Lazrus, 1980).

The NO_3^--containing aerosols are then removed principally by washout and rainout processes (Fowler, 1978). If vaporization of droplets occurs then the NO_3^- salts may be removed by dry deposition.

VI. CONCLUSIONS

There are several mechanisms that lead to gaseous losses of N from the plant–soil system. These include ammonia volatilization, biological denitrification, nitrification, and chemodenitrification.

Volatilization of NH_3 to the atmosphere is a complex process affected by a combination of physical, chemical, and biological factors. A necessary prerequisite for NH_3 volatilization is a supply of free ammonia (i.e., $NH_{3(aq)}$ and $NH_{3(g)}$) near the soil surface. The conversion of NH_4^+ ions to NH_3 is thus a major process regulating the potential loss of NH_3 from soils. Sources of NH_4^+ in the soil include native soil organic matter, plant residues, animal excretions, added organic materials, or added NH_4^+-containing or -yielding fertilizers. The equilibrium between NH_4^+ and NH_3 is affected by pH, temperature, water loss from the soil, buffering capacity and CEC of the soil, and fixation of NH_3 and NH_4^+ by clay minerals or organic matter.

Most of the NH_3 emitted to the atmosphere from the soil surface is quickly returned to the earth's surface via wet and dry deposition. The lifetime of NH_3 in the atmosphere is only 1 to 2 weeks. Ammonia can be returned to the biosphere via gaseous deposition since plants, land surfaces, and water bodies can all act as sinks for atmospheric NH_3. In the troposphere, the emitted NH_3 quickly dissolves in water droplets in clouds with the formation of NH_4^+ ions. The NH_4^+ is returned via wet deposition as NH_4^+ salts dissolved in rainwater, or the water in the aerosol may evaporate and particles are returned via dry deposition.

Growing plants can act as either sources or sinks for atmospheric NH_3. Absorption of NH_3, emitted from the soil surface, by the leaf canopy above can greatly reduce losses of NH_3 from the plant–soil system.

There are several pathways for the biological generation of gaseous

nitrogenous products. Dissimilatory denitrification is carried out by a limited number of aerobic bacteria that can grow in the absence of molecular oxygen while reducing NO_3^- or NO_2^- to gaseous products (N_2O and N_2). These bacteria are biochemically and taxonomically diverse although most are chemoheterotrophs and use carbonaceous compounds as electron donors and sources of cellular C and chemical compounds as energy sources. The denitrification process is promoted by anaerobic conditions, high levels of soil NO_3^-, and a readily available source of carbon and, in general, is positively related to soil pH and temperature. The quantity of N_2O emitted during denitrification is normally considerably less than that of N_2 although the mole ratio of N_2O produced is influenced by many factors and can vary from 0 to 1.0. The ratio is generally raised under conditions of high NO_3^- levels and low pH and lowered by high temperatures and increasing anoxia.

There is a group of "nondenitrifying" bacteria and fungi that is able to respire NO_3^- anaerobically as far as NO_2^- and when growing fermentatively they can further reduce NO_2^- to NH_4^+ with N_2O being produced as a minor product. The magnitude of the contribution that these organisms make to N_2O evolution from soils is unclear although it is generally thought to be small.

The autotrophic NH_4^+-oxidizing bacteria *Nitrosomonas, Nitrosospira,* and *Nitrosolobus* have the capacity to produce N_2O, and apparently NO, during the oxidation of NH_4^+ to NO_2^-. The exact mechanisms through which these gases are produced are unknown. The potential for losses of N_2O through nitrification is greatest when NH_4^+-containing or -yielding fertilizers are applied to aerobic soils.

The atmospheric lifetime of N_2 is millions of years and that for N_2O is about 150 yr. A major sink of N_2O from the troposphere is diffusion into the stratosphere, where the major part forms N_2 and a small fraction forms NO_x. The nitrogen oxides (NO_x) catalyze destruction of ozone (O_3) in the upper stratosphere but protect it from destruction in the lower stratosphere. Hence, the net result of increased emissions of N_2O from the earth's surface is likely to be a transfer of O_3 mass to lower altitudes rather than destruction of the ozone layer. The NO_x formed in the stratosphere is returned to the lower atmosphere at a low rate and then to the earth's surface through wet and dry deposition.

Chemodenitrification is a term that encompasses the processes responsible for gaseous loss of N from soils through chemical reactions of NO_2^-. Accumulation of NO_2^- does not normally occur except when nitrogenous fertilizers that form alkaline solutions upon hydrolysis (urea, NH_4^+ salts, and anhydrous and aqua NH_3) are band-applied to soils or in NO_3^--treated

soils as an intermediate of denitrification. A variety of gases can be evolved from soils treated with NO_2^- including N_2, N_2O, NO, and NO_2.

Several mechanisms are thought to be involved in chemodenitrification. These include decomposition of nitrous acid with the emission of NO and NO_2, reactions of HNO_2 with phenolic constituents of soil organic matter with the formation of N_2, N_2O, and NO, reactions of HNO_2 with compounds containing free amino groups to liberate N_2, reactions of NO_2^- with NH_4^+ and hydroxylamine with the release of N_2 and N_2O, respectively, and reactions of HNO_2 with metallic cations to form NO and N_2. Although research has established that such reactions can occur, their significance and magnitude under field conditions have yet to be established.

Nitric oxide released from the soil surface can be quickly converted to NO_2 by O_3 in the lower atmosphere. Atmospheric NO_2 can be taken up by the local plant and soil surface or transported into the atmosphere. Nitrogen dioxide is highly soluble in water and reacts with OH radicals to yield HNO_3. The combined atmospheric lifetime of NO, NO_2, and HNO_3 is in the range of 1 to 2 weeks. Heterogeneous aerosol particles are formed in the atmosphere by interaction by gaseous HNO_3 with preformed aerosols and the nitrates are returned to the earth's surface by wet and dry deposition.

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