Gaseous Losses of Nitrogen other than through Denitrification

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Nitrogen losses from human activities are the major reason behind the growing concerns about the enrichment of the biosphere with reactive N, and crop production is by far the single largest cause of human alteration of the global N cycle (Smil, 1999). Effects of N enrichment range from atmospheric changes to alterations of terrestrial and aquatic ecosystems. Reactive atmospheric N trace gases resulting from agricultural activities include NO, (NO and NO2), NH3 (NH4 and NH4+), and N2O. An accurate quantification of sources and sinks for reactive atmospheric N trace gases constitutes a considerable scientific challenge because of large temporal and spatial variability.

Ammonia (NH3) is the dominant alkaline gas in the atmosphere. It readily reacts with atmospheric acids to form NH4+ that is an important constituent in aerosols and in precipitation (Schjoerring et al., 1993). Dentener and Crutzen (1994) reported that atmospheric aerosols, acting as cloud condensation nuclei, consist in great part as sulfate neutralized to various degrees by NH3. Ammonia gas is predominantly removed from the atmosphere by dry deposition, while NH4+ aerosols are removed mainly by wet deposition (Asman and Janssen, 1987).

After being deposited, NH3 and NH4+ may have serious ecological and environmental effects (Schjoerring et al., 1993). The deposition of NH3 and NH4+ may contribute to soil acidification, eutrophication, foliar leaching of nutrients and increased plant sensitivity to other stress factors such as ozone, drought, frost, and fungal diseases (Yamulki et al., 1996). Nitrification of deposited NH3 and NH4+ enhances the acidification of forest soils as well as the acidification of ecosystems such as heathlands and freshwater lakes (Schjoerring et al., 1993). Deposition of NH3 and NH4+ to N-deficient terrestrial ecosystems represents a major perturbation to ecosystem stability and biodiversity: fertilizing plants with N from the atmosphere initiates changes in the competitive relations among plant species, so
that slow-growing plant species are replaced by fast-growing grass species benefiting from the N enrichment (Heil and Bruggink, 1987). In aquatic ecosystems, deposition of NH₃ and NH₄⁺ contributes to eutrophication, which may lead to algal blooming with subsequent fish kills (Schloesser et al., 1993).

Major sources of atmospheric NH₃ include volatilization from decomposition of animal excrement, fertilized and unfertilized soils, vegetation, oceans, biomass burning, and other combustion processes (Dentener and Crutzen, 1994). Ammonia can be either deposited to soils and plants or emitted from soils and plants (Yamulki et al., 1996). The bidirectional nature of NH₃ exchange has made the extrapolation of NH₃ fluxes from short periods of measurements to annual net fluxes a speculative exercise. Also, the large spatial variability in ambient NH₃ concentration and land use further complicates the interpolation of NH₃ fluxes to landscape scales (Fowler et al., 1998).

Gaseous nitrogen oxides are produced in several ecosystem processes and in turn have a number of critical influences on the chemistry and physics of the atmosphere. For example, nitrous oxide (N₂O) is radiatively active and thus an important "greenhouse" gas. In the troposphere, N₂O has a lifetime of about 120 yr and this long persistence permits transport to the stratosphere where it ultimately is destroyed by photolysis (Liu et al., 1999). This photolytic reaction catalyzes a set of reactions that result in the destruction of stratospheric ozone (Crutzen, 1979). Nitric oxide (NO), on the other hand, is a highly reactive species that contributes to increasing lower tropospheric ozone concentration (Liu et al., 1999). NO also participates in several reactions in which more stable products such as peroxynitrate, nitric acid, and nitrate aerosol are formed. As a result of these reactions, the atmospheric lifetime of NO is typically less than 1 d (Derwent et al., 1999).

As a result of its high reactivity, NO is usually converted to more stable products before it has time to be dry deposited. However, dry deposition is important for NO, and the secondary products such as peroxynitrate, nitric acid, and the nitrates (Derwent et al., 1999). Wet deposition is equally important for nitrate aerosols. Because of the high reactivity of NO, its emissions strongly influence local and regional atmospheric chemistry, while the long lifetime and spectral properties of NO result in it having important atmospheric consequences on a global scale (Derwent et al., 1999).

Microbial denitrification and nitrification are the main sources of NO, and N₂O emitted from soils (Derwent et al., 1999). Chemical denitrification and other kinds of bacterial metabolism involving oxidation or reduction of N also yield trace amounts of the two gases (Smil, 1999). In addition to NO released in the burning of fossil fuels used for various agricultural related activities, NO and N₂O are also formed in the burning of biomass (Andreae, 1991).

Ammonia Loss from Soil

Nelson (1982), in *Nitrogen in Agricultural Soils*, gave an excellent review on gaseous N losses from soil. Rather than reiterating most of this material, we will use this review to mainly provide a research update. Table 8-1 lists some of the characteristics of the studies analyzed. For more detailed information on the principles governing gaseous losses of N from soil, readers are encouraged to examine Nelson’s (1982) text.
Table 8–1. Characteristics of some of the studies analyzed that used various N sources.

<table>
<thead>
<tr>
<th>Study†</th>
<th>Year reported</th>
<th>Soil series or description‡</th>
<th>Classification</th>
<th>N source§</th>
<th>Method</th>
<th>Range of N loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Kanani et al</td>
<td>1994</td>
<td>Ste. Roseale</td>
<td>fine, mixed, nonacidic, Typic Humultedup</td>
<td>urea</td>
<td>lab incubation 23°C, acid trap (H₂SO₄)</td>
<td>16–21% of urea N applied</td>
</tr>
<tr>
<td>Al-Kanani et al</td>
<td>1991</td>
<td>St. Bernard</td>
<td>loamy, mixed, nonacidic, frigid, Typic Hapludult</td>
<td>urea, UAN</td>
<td>lab incubation 23°C, acid trap (H₂SO₄)</td>
<td>3–5% of urea N applied</td>
</tr>
<tr>
<td>Bayrakli and Gezgin</td>
<td>1996</td>
<td>clay loam</td>
<td>coarse, loamy over sandy, mixed mesic, Typic Hapludult</td>
<td>urea</td>
<td>field microplots, acid trap (H₂SO₄)</td>
<td>7–24% of urea N applied</td>
</tr>
<tr>
<td>Clay et al.</td>
<td>1990</td>
<td>Esterville (silt)</td>
<td>clayey, illitic mesic, Typic Hapludult</td>
<td>urea, UAN</td>
<td>field microplots, acid trap (H₂SO₄)</td>
<td>6–175 mg N m⁻² h⁻¹</td>
</tr>
<tr>
<td>Fox et al.</td>
<td>1996</td>
<td>Hublersburg (silt)</td>
<td>loamy-skeletal, mixed, thonic, Ustolic Calciorthid</td>
<td>biosolids</td>
<td>field plots, NH₃ sampler, micrometeorological</td>
<td>12–55% of applied N</td>
</tr>
<tr>
<td>Harmel et al</td>
<td>1997</td>
<td>Chilicotal (vgl) Berno (ft)</td>
<td>fine, loamy, mixed, thonic, Ustolic Hapludult</td>
<td>urea, UAN</td>
<td>field plots, NH₃ sampler, micrometeorological</td>
<td>8.3–18% of applied NH₃</td>
</tr>
<tr>
<td>He et al.</td>
<td>1999</td>
<td>Riviera (fs)</td>
<td>loamy, siliceous, hyperthermic, Arenic Glossaquoll</td>
<td>&quot;N labeled</td>
<td>&quot;N labeled incubation 30°C,</td>
<td>16–22% of applied N</td>
</tr>
<tr>
<td>Jansen and McGinn</td>
<td>1991</td>
<td>sandy loam</td>
<td>fine, silty, mixed, mesic, Aquic Hapludult</td>
<td></td>
<td>greenhouse plots, acid trap (1HCl)</td>
<td>1–14% of applied N</td>
</tr>
<tr>
<td>Larsson et al</td>
<td>1998</td>
<td>clay</td>
<td>line-silty, mixed, mesic, Aquic Hapludult</td>
<td></td>
<td>field plots, closed chambers</td>
<td>2–3% of applied N</td>
</tr>
<tr>
<td>Lightner et al</td>
<td>1990</td>
<td>Xenia (silt)</td>
<td>fine-loamy, mixed, Typic Hapludult, clayey, kaolinitic, thermic, Typic Hapludult, fine-loamy, siliceous, mesic, Typic Hapludult</td>
<td></td>
<td>field NH₃ collection, acid trap (NH₄Cl)</td>
<td>12–41% of applied N</td>
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<tr>
<td>Marshall et al</td>
<td>1998</td>
<td>State (silt) Faciol (silt)</td>
<td>fine-loamy, mixed, Typic Hapludult, clayey, kaolinitic, thermic, Typic Hapludult, fine-loamy, siliceous, mesic, Typic Hapludult</td>
<td></td>
<td>micrometeorological mass balance</td>
<td>2–6% of applied N</td>
</tr>
</tbody>
</table>

Table cont.
| Study† | Year reported | Soil series or description | Classification | N source§ | Method | Range of N loss%
|---|---|---|---|---|---|---|
| Naitian and Maizer | 1994 | Esteville (s) | coarse loamy over sandy, mixed, mesic Typic Hapludoll | urea | field microplots, acid trap (H₂SO₄) | 1–7% of applied N
| Ouyang et al. | 1995 | Ste. Rosalie (c) | Typhic Humaquept | urea | field microplots, acid trap (H₂SO₄) | 1–8% of urea N applied
| Ping et al. | 2000 | clay loam | Typic Boroll | NH₃-N urea | field microplots, ¹⁵N difference method | 12–13% of applied N
| Guernada et al. | 1998 | loamy sand | clayey, calcareous, saline, mesic, Calcaric Argiudoll | biosolids (sewage sludge-DCD | lab incubation 21°C, acid trap (H₂SO₄) | 5–71% of applied N
| Schike-Gartley and Spitz | 1993 | Klej (ls) | Silty clay loam | poultry litter | lab incubation 23°C, acid trap (H₂SO₄) | 4–31% of applied N
| Shatianeh et al. | 1992 | Tifton | fine sandy, loamy, siliceous, thermic | nutrasweet sludge | lab incubation 26°C, acid trap (H₂PO₄) | >1–19% of applied N
| Sumer et al. | 1997 | loamy sand | fine sandy, loamy, siliceous, thermic | urea, AS | pig slurry | 4–26% of applied N
| Watson and Kilpatrick | 1991 | Hillsborough (sid), Lowry (sid), Craigovon (c), Portadown (p) | loamy sand, silt loam, sandy clay loam, p, peaty | urea (pellet, size) | lab incubation 10°C, acid trap | 12–17% of applied N
| Whitehead and Rastie | 1990 | Balcombe | fine sandy loam, silty loam | MAP, DAP, AS, AN, urea | lab incubation 20°C, acid trap (H₂SO₄) | >1–52% of applied N
| Whitehead and Rastie | 1992 | Frisland, and Andover | fine sandy loam | simulated livestock urine | growth chamber 21°C, acid trap (H₂SO₄) | 23–39% of applied N

† Each study is referenced by the first author.
‡ Letters in parentheses indicate soil texture: c, clay; s, silt; ls, loamy sand; sl, sandy loam; sc, sandy clay loam; p, peaty.
§ Capitalized abbreviations indicate N sources: UAN, urea ammonium nitrate; MAP, mono-ammonium phosphate; DAP, diammonium phosphate; AS, ammonium sulfate; AB, ammonia bicarbonates; UUR, urea-urea phosphate; U, urea; DCD, dicyandiamide.
It is estimated that agriculture contributes between 55 and >95% of the anthropogenic NH₃ released annually to the atmosphere (McGinn and Janzen, 1998). Livestock production systems and land application of biosolids are generally recognized as the major sources of atmospheric NH₃. For Europe, Buijsman et al. (1987) estimated that 81% of NH₃ emissions are from livestock while for China, which accounts for 55% of the NH₃ emissions in Asia, Zhao and Wang (1994) estimated that livestock account for 29% of emissions. Total annual emissions are dependent on livestock density, protein intake, animal species, and management practices (handling, storage, and land application).

Land application of organic waste materials usually has two objectives, waste disposal and use of the nutrients for plant growth (Rice et al., 1988). When N is the nutrient in question, the major concern for either objective has been the potential for degradation of surface and groundwater. However, the emphasis that is placed on each objective in a given case can be a primary factor in the selection of management practices that affect NH₃ emissions. Emphasis on the waste disposal objective often utilizes management practices that encourage NH₃ volatilization because increased NH₃ loss reduces land requirements and transportation costs for disposal. Likewise, emphasis on the plant nutrient objective will result in the use of management practices that conserve NH₃ and improve plant N use efficiency of the organic waste material N.

Although most of the NH₃ volatilized from the land surface is derived from animal excreta, appreciable amounts may also be derived directly from fertilizers and from decomposing plant material (Whitehead and Raistrick, 1990). Nitrogen can be emitted into the atmosphere as NH₃ when NH₄⁺ or urea-containing fertilizers are applied to soil (Demeyer et al., 1995). The magnitude of NH₃ losses under laboratory conditions commonly ranged from 20 to 60% of the applied N, but can be as great as 90% when N is applied to the surface of sandy soils with very low buffering capacity (Fenn and Hossner, 1985). However, losses under field conditions are generally less, ranging from 0 to 50% of the applied N (Hargrove, 1988). The reason for greater losses in most reported laboratory studies is that laboratory conditions are typically set to create an optimum environment for high rates of NH₃ loss while these conditions seldom exist for sustained periods in a dynamic field environment (Hargrove, 1988).

Ammonia volatilization losses from fertilizer applied to agricultural soils can be grouped into three broad categories: (i) loss from anhydrous NH₄; (ii) NH₃ volatilization from unincorporated, surface-applied, NH₄⁺-containing fertilizer on soils with a pH greater than 7.2; and (iii) NH₃ volatilization from unincorporated, surface-applied, urea-containing fertilizer (Schepers and Fox, 1989).

Items affecting the magnitude of NH₃ loss from soils include soil factors, environmental conditions, and fertilizer management practices (Nathan and Malzer, 1994). Factors affecting NH₃ volatilization losses from fertilizers applied to agricultural soils are typically also important in controlling NH₃ volatilization losses from organic waste material applications. Important soil factors in determining the magnitude of NH₃ volatilization include texture, initial soil pH, pH buffering capacity, cation exchange capacity (CEC), amount of soluble and exchangeable Ca²⁺, and urease activity (Hargrove 1988; Lightner et al., 1990; Nathan and Malzer, 1994). Environmental factors that are important in determining the magnitude of NH₃ loss are temperature, soil water content, and air exchange at the soil surface (Hargrove 1988). Management factors affecting NH₃ loss include time, rate, form,
Effect of pH on Ammonia Loss

Nitrogen sources with greater potential for raising soil pH after application tend to have greater NH₃ volatilization (He et al., 1999). Ammonia losses increase with higher soil pH because of the increased dissociation of NH₄⁺ to NH₃, thus increasing the potential for volatilization (Sharpe and Harper, 1995). The pH in microsites surrounding urea or NH₄⁺ salt granules may be more important in determining NH₃ loss than the overall soil pH (Nelson, 1982; Stumpe et al., 1984).

With urea, NH₃ volatilization only takes place after hydrolysis to ammonium carbonate by the microbially produced enzyme urease. The optimum pH for soil urease activity is between pH 7.0 to 9.0 (Fan and Mackenzie, 1993). The ammonium carbonate resulting from the hydrolysis of urea generates a localized increase in soil pH, which promotes NH₃ volatilization to an extent that is influenced by the initial soil pH and CEC (Whitehead and Raistrick, 1990). Hargrove (1988) concluded that the H⁺ buffering capacity of a soil (in this case the resistance to increasing soil pH) is more important than initial soil pH in determining potential NH₃ loss under field conditions. If the soil's buffer capacity is high, the pH rise due to urea hydrolysis will be small and only a small amount of NH₃ will be volatilized. Ferguson et al. (1984) found that the amount of H⁺ buffering capacity between a soil's initial pH and a pH of around 7.5 would be more directly related to the expected NH₃ loss than a soil's initial pH when urea is applied.

Buffering capacity can also influence NH₃ volatilization in the opposite way. Normally, H⁺ ions resulting from the nitrification process will lower the soil pH and reduce the potential for NH₃ volatilization. If the initial soil pH is sufficiently high for appreciable NH₃ volatilization to occur (>7.5), then the soil's buffering capacity against a decrease in pH influences NH₃ volatilization by allowing it to occur over a longer period of time before the soil's pH is reduced sufficiently to stop NH₃ volatilization (Ferguson et al., 1984; Hargrove, 1988). As such, the buffering capacity against an increase in pH (from urea hydrolysis) is most important in noncalcareous soils, while the buffering capacity against a decrease in pH (mainly from nitrification) is most important in calcareous soils (Hargrove, 1988).

Effect of Cation Exchange Capacity on Ammonia Loss

Although H⁺ buffering capacity and CEC are related, soil CEC is also important for NH₃ volatilization because it provides a mechanism by which NH₄⁺ ions are removed from soil solution, thereby reducing the total amount of ammoniacal N in the soil solution at any given time that is subject to volatilization (Hargrove, 1988). The influence of CEC is less than that of H⁺ buffering capacity in terms of magnitude of NH₃ loss (Rachipal-Singh and Nye, 1986).

Effect of Soil Texture and Organic Matter on Ammonia Loss

A number of investigators have noted that increased organic matter (OM) and clay content of soil reduced NH₃ loss (Al-Kanani et al., 1991; Hargrove, 1988; Whitehead and Raistrick, 1990). The reduction in NH₃ loss is usually ascribed to the relative contribution of these factors (Al-Kanani et al., 1991; O'Toole, 1993) and the effect of clay content on the water content and its movement within the soil (Bouma et al., 1988).
between application and incorporation of surface residue (Demeyer et al., 1994).

Ammonia Loss

Raising soil pH after application (1999). Ammonia losses increase due to NH₃ volatility. The pH increases may be more important in deserts (1982; Stumpe et al., 1984).

The following hydrolysis to ammonium. The optimum pH for soil (Mackenzie, 1993). The ammonium content of the affected increase due to an extent that is influenced by pH (Dick, 1990). Hargrove (1988) concluded this resistance to increasing N in determining potential NH₃ volatilization. This way of buffering capacity between a more directly related to the extent applied.

But in the opposite way, the process will lower the soil pH. If the initial soil pH is sufficiently low (less than 7.5), then the soil’s buffering capacity will be reduced sufficiently to prevent volatilization by allowing it to proceed at a high pH (mainly soils (Hargrove, 1988).

Gaseous Losses other than through Denitrification

The relative contribution of the OM and clay components to the CEC of the soil (Al-Kanani et al., 1991; O’Toole et al., 1985). Al-Kanani et al. (1991) also observed that the effect of clay content on NH₃ volatilization became more pronounced as soil approached air dryness.

Effect of Urease Activity on Ammonia Loss

Almost all agricultural soils are considered to have adequate concentrations of urease for a rapid hydrolysis of urea (Hargrove, 1988). However, at higher urease activity, applied urea will be hydrolyzed more rapidly before it can move deeper into the soil (Rachhpal-Singh and Nye, 1986). This will result in higher NH₃ loss potentials because of the increase in ammoniacal N concentrations at the soil surface along with the associated rise in surface soil pH from urea hydrolysis. Vegetation and crop residue are known to increase urease activity (Schilke-Gartley and Sims, 1993). McInnes et al. (1986) reported that urease activity on wheat (Triticum aestivum L.) straw was 20 times that of the soil just below it. Also, the length of time since the soils last received urine or urea may have an effect on initial urease activity (Whitehead and Raistrick, 1990).

Effect of Temperature on Ammonia Loss

He et al. (1999) found that potential maximum NH₃ volatilization increased twofold when the temperature increased from 5 to 25°C and threefold when temperature increased from 25 to 45°C. They concluded that the greatly enhanced NH₃ volatilization at 45°C compared with 25°C was related to the inhibition of nitrification at the high temperature, which increased the availability of ammoniacal N for NH₃ volatilization over a prolonged period of time. Hargrove (1988) reported that temperature influences the magnitude of NH₃ loss in several ways:

- It increases urease activity, thereby increasing urea hydrolysis rate. A faster hydrolysis rate results in higher soil pH and greater NH₃ concentrations near the soil surface.
- It influences the NH₄⁺/NH₃ equilibrium and the equilibrium between NH₃ in solution and NH₃ gas, resulting in a higher proportion of ammoniacal N being present as NH₃ gas.
- It influences the diffusion of urea- and ammoniacal N and bicarbonate ions.
- It increases the solubility of CaCO₃ and of Ca reaction products in calcareous soils.

Effect of Soil Water Content on Ammonia Loss

The influence of soil water content on NH₃ volatilization is generally straightforward for laboratory studies. If the hydrolysis of urea is not inhibited by the lower moisture content, a lower moisture content means a higher NH₃ concentration and a higher pH effect resulting in the largest total NH₃ losses and highest average NH₃ volatilization rates (Demeyer et al., 1995). On the other hand, the influence of soil water content on NH₃ volatilization under dynamic field conditions is very complex and has been difficult for scientists to determine, especially where soil water content fluctuates widely on a daily basis due to the combined effects of upward movement of water in the soil, dew formation, and evaporation (Hargrove, 1988; Bouwmeester et al., 1985) observed that highest total NH₃ losses occurred...
when wet soil conditions were maintained by air humidities between 80 and 95%, with essentially no rainfall. The diurnal pattern of NH$_3$ volatilization loss, with maximum loss near midday, is associated with temperature increases and dew water evaporation that results in increases in NH$_3$-N concentration in the aqueous phase and in the partial pressure gradient of NH$_3$, leading to enhanced NH$_3$ volatilization (Lightner et al., 1990; Nathan and Malzer, 1994).

Hargrove (1988) listed several relationships that have emerged from field studies:

- For maximum NH$_3$ losses, the soil water content must be at or near field capacity at the time of fertilizer application. If the soil is dry, dissolution of dry fertilizer materials is slow and the biological and chemical reactions necessary for volatilization are very slow or do not occur at all.
- On a daily basis, maximum NH$_3$ loss rates occur when the soil surface is drying. As the soil dries, the concentration of NH$_3$ in the soil solution increases resulting in NH$_3$ being lost to the atmosphere to maintain equilibrium with NH$_3$-N. Slow drying of a wet soil results in more NH$_3$ loss than rapid drying.
- If the soil surface dries but is not rewetted by dew or light rainfall, NH$_3$ loss is reduced because of insufficient moisture for the necessary biochemical and chemical reactions.
- If rainfall is sufficient to move the N source into the soil profile, NH$_3$ volatilization ceases.

**Effect of Wind Speed on Ammonia Loss**

If a steady supply of NH$_3$ is available, increasing wind speed would promote more rapid transport of NH$_3$ away from the soil surface by maintaining a lower partial pressure of NH$_3$ over the soil surface (Sharpe and Harper, 1995). However, wind generally has a drying effect on soil that in turn can influence opposite outcomes. Nathan and Malzer (1994) concluded that the drying effect caused by higher wind speeds would result in higher solution concentrations of NH$_3$ at the soil surface, resulting in higher NH$_3$ volatilization. Bouwmeester et al. (1985) noted that wind can impede the volatilization of NH$_3$ by rapidly drying the topsoil and reducing the rate at which underlying urea moves to the soil surface, thus acting as a physical barrier. They further stated that their results indicated that when the relative humidity of the air is high, soil moisture content may remain high enough to promote NH$_3$ losses.

**Effect of Management Practices on Ammonia Loss**

Hargrove (1988) concluded that soil properties largely determine the potential for loss, but environmental conditions determine the actual magnitude of loss under field conditions. Management factors influence the magnitude of loss by modifying the soil properties and/or environmental conditions. As mentioned above, some of the management factors affecting NH$_3$ loss include time, rate, form, and method of application, incorporation, time between application and incorporation, depth of application, irrigation, and amount of surface residue.

Generally, NH$_3$ losses increase with increasing amounts of urea or NH$_3$ added to the soil. Studies have shown that these losses may be linear or exponential such that the relative loss (as percentage of the applied N) may decrease, remain constant, or increase with increasing application rates (Hargrove, 1988). In addition, the NH$_3$ loss potential for urea-ammonium nitrate (UAN) solutions is greater with higher Cu content, with the Cu content of the solution being influenced by the type of fertilizer used.

Gaseous Losses other than the NH$_3$ loss potential for urea-ammonium nitrate (UAN) solutions, but greatest with (g) calcareous soils.

A number of chemical or redox agents used to reduce NH$_3$ volatilization loss include: (i) gaseous loss to that retard hydrolysis of urea and physical and/or chemical changes in the soil solution, leading to enhanced NH$_3$ volatilization (Lightner et al., 1990; Nathan and Malzer, 1994).

These methods have been successful in reducing soil NH$_3$ losses. However, these methods are expensive and may not be practical for use on large-scale commercial farms. Therefore, the development of additives that reduce NH$_3$ losses is important for reducing these losses.

Maximum NH$_3$ losses occur on the soil surface and in the topsoil. Significant reductions in NH$_3$ losses may be expected because bands of fertilizer are exposed to fewer environmental conditions than are broadcast on the soil surface. When NH$_3$ is broadcast on the soil surface, the NH$_3$ loss potential is reduced because of limited moisture for the necessary biochemical and chemical reactions.

Direct injection or incorporation of NH$_3$ fertilizer (Hargrove, 1988). Below 2.5 cm of water was applied to a depth of 2.5 cm. Soils from injected anhydrous ammonia solutions contain a large portion of the injected NH$_3$ that will be lost with upward movement of the water in the soil. It has also been denitrified to a significant extent. The depth to which inorganic materials are applied to the soil surface is from 5 to 10 cm (Hargrove, 1988). In addition, the NH$_3$ loss potential for urea-ammonium nitrate (UAN) solutions is greater with higher Cu content, with the Cu content of the solution being influenced by the type of fertilizer used.
ir humidities between 80 and 95% of NH₃ volatilization loss, with temperature increases and dew point concentration in the aeration of NH₃ leading to enhanced NH₃ loss, 1994).

that have emerged from field content must be at or near field capacity if the soil is dry, dissolution of dry and chemical reactions necessitate occur at all.

occur when the soil surface is dry, NH₃ in the soil solution increases to maintain equilibrium with more NH₃ loss than rapid drying by dew or light rainfall, NH₃ loss require the necessary biochemical reactions into the soil profile, NH₃ volatilization.

Ammonia Loss

sing wind speed would promote surface by maintaining a lower rpe and Harper, 1995). However, turn can influence opposite out the drying effect caused by high concentrations of NH₃ at the soil surface. Bouwmeester et al. (1985) noted that NH₃ rapidly drying the topsoil and is to the soil surface, thus acting as the oxygen that the content may remain high enough.

ons Ammonia Loss

es largely determine the potential the actual magnitude of loss versus the magnitude of loss by incidental conditions. As mentioned NH₃ loss include time, rate, form, steep application and incorporation of surface residue. Amounts of urea or NH₄⁺ addeds may be linear or exponential (added N) may decrease, remain stead (Hargrove, 1988). In addition, the NH₃ loss potential for fertilizers is greatest with urea, intermediate with urea-ammonium nitrate (UAN) solution, and least with NH₄NO₃ salts on noncalcareous soils, but greatest with (NH₄)₂SO₄ and much less with urea or NH₄NO₃ on calcareous soils.

A number of chemical or fertilizer modification methods have been used to reduce NH₃ volatilization losses from urea applications. The most studied methods include: (i) coating urea to slow its rate of dissolution; (ii) use of compounds that retard hydrolysis of urea by reducing the activity of urease; (iii) changing the physical and/or chemical characteristics of the soil environment with the addition of acidifying agents to decrease NH₃ volatilization loss, and (iv) mixing soluble salts of Ca, Mg, and/or K with urea to promote the formation of insoluble carbonates and thereby reduce the rise in pH and concentration of NH₃ in the soil (Buresh and Baanante, 1993; Al-Kanani et al., 1994; Bayrakli and Gezgin, 1996). These methods have been successful to varying degrees and work continues on the development of additives that are economically feasible, environmentally safe, and effective in improving the efficiency of urea fertilizer.

Maximum NH₃ losses occur when N fertilizers and organic waste materials are broadcast on the soil surface (Hargrove, 1988; Nathan and Malzer, 1994). Surface band application and incorporation/injection are often employed to minimize NH₃ losses. Significant reduction in NH₃ losses from surface band applications (including increasing fertilizer granule size) compared with broadcast applications may be expected because banded applications will be in contact with less soil and exposed to fewer environmental factors. Contradictory effects or no effect have been reported for fertilizer granule size with surface applications of urea on NH₃ loss (Black et al., 1987; Watson and Kilpatrick 1991). However, surface band application of animal waste slurries has shown significant reduction in NH₃ volatilization (Sommer et al., 1997). One reason they gave for this is that surface banding of slurries promotes infiltration.

Direct injection or incorporation of N fertilizers results in much reduced or no NH₃ loss (Hargrove, 1988). Bouwmeester et al. (1985) found no NH₃ volatilization if 2.5 cm of water was applied immediately after urea application or when banding urea at a depth of 2.5 cm. Schepers and Fox (1989) conclude that volatilization losses from injected anhydrous NH₃ can be assumed to be minimal if the NH₃ is injected to a depth of at least 5 cm and if the furrow behind the injector seals completely. The depth to which incorporation or injection is necessary depends on the soil characteristics; such as texture, density, CEC, OM content, etc., but for most soils is from 5 to 10 cm (Hargrove, 1988). Soil moisture content is also an important factor in NH₃ volatilization when direct injecting N supplying materials. Working with anhydrous ammonia, Sommer and Christensen (1992) found that up to 50% of the NH₃ can be lost when injected into a wet soil. They concluded that a large portion of the injected NH₃ is retained by absorption in the soil water and upward movement of the water due to evaporation may be the cause of the large NH₃ losses. It has also been demonstrated that NH₃ loss may be high from animal slurry injected directly into a compressed and excessively wet soil for some of the same reasons (Sommer and Erskoll, 1994).

Ammonia volatilization is also affected by the amount of crop residue present on the soil surface. However, there are conflicting reports on how crop residues affect NH₃ volatilization. Clay et al. (1990) reported that residue cover reduced the daily maximum soil temperature and increased the soil water content resulting in
reduced NH$_3$ volatilization losses. Schilke-Gartley and Sims (1993) found either no effect or reduced losses when animal manure was applied to corn (Zea mays L.) and soybean [Glycine max (L.) Merr.] residues in the spring of the year. They suggest one possible reason for their results is reduced ureaase activity in the residues resulting from environmental exposure over the fall and winter months. In contrast, Hargrove (1988) drawing from numerous studies, states that crop residues generally increase NH$_3$ losses in several ways:

- By its associated higher ureaase activity compared with soil;
- By promoting slow drying of the soil surface, thereby maintaining higher loss rates for a longer period of time; and
- By forming a physical barrier between the N source and the soil.

In addition, Whitehead and Raistrick (1990) concluded that leaf litter allows increased NH$_3$ volatilization by increasing the surface area for ureaase activity and volatilization to occur. Fenn and Hossner (1985) suggest that higher ureaase activity may apply only to growing crops and fresh residues rather than older residues that may have been exposed to sunlight, high temperatures, and drying conditions that can result in ureaase degradation.

Living plants can also be great modifiers and significantly influence volatile NH$_3$ loss from soils. Actively growing plants influence both the soil's temperature and water regimes and also have strong effects on the soil-air boundary layer. The plant's ability to both absorb and release atmospheric NH$_3$ must be taken into account. Foliage absorption of NH$_3$ contributed significantly to the reduction in NH$_3$ loss when animal wastes were applied in the spring to a dense and actively growing plant cover (Marshall et al., 1998; Sommer et al., 1997). Effect of growing plants on NH$_3$ loss will be discussed in more detail in the following section.

Our inability to accurately predict environmental factors such as soil temperature, soil water content (especially the thin surface layer), soil water flux, and wind speed on the field or ecosystem level will always limit our ability to accurately predict NH$_3$ volatilization under field conditions.

**Ammonia Loss from Plants**

Farquhar et al. (1980) were one of the first to report on the existence of an NH$_3$ compensation point for plants. The compensation point for NH$_3$ is defined as the molar fraction at which the net exchange between plants and the atmosphere is zero. The existence of an NH$_3$ compensation point implies that vegetation has a major influence on the transport and budgets of atmospheric NH$_3$ (Nielsen and Schjoerring, 1998). The NH$_3$ compensation point allows plants to act as both sink and source for atmospheric NH$_3$. At ambient NH$_3$ concentrations above the compensation point, NH$_3$ is absorbed by leaves, while at concentrations below the compensation point NH$_3$ is lost to the atmosphere.

Ammonium is the only inorganic N compound that can be used directly as a precursor for the biosynthesis of organic N products in plants (Ie, 1997). As a consequence, substantial concentrations of NH$_4^+$ may exist in the leaf and in the apoplastic solution. The concentration of NH$_4^+$ and H$^+$ in the leaf apoplastic solution determines the size of the NH$_3$ compensation point (Husted and Schjoerring, 1996). It is generally accepted that free NH$_3$ can diffuse across leaf cell membranes without the involvement of ammonium is constantly generated as photorespiration, nitrate (Leegood et al., 1995). For plant NH$_3^+$ released during these activities directly to the leaves

The major pathway of N is the glutamine synthetase/glutamate synthetase (Schjoerring et al., a transporter with channel-like to changes in apoplastic with mutants of barley (Harder signification of GS in controlling Schjoerring et al., 2000) also resist the increase in apoplastic high NH$_3$ compensation point, rapid absorption of NH$_3^+$ for NH$_3^+$ is constantly generated activities are critical in controlling N

Factors influencing Nitrogen Status and pH

The NH$_3$ compensation point of physiological and environmental conditions and direction of the NH$_3$ scales, depending on environmental timing of fertilizer application of the major factors influencing Nitrogen Status and pH

Theoretically, the NH$_3$ can be determined by knowing the face (apoplast). Husted and Schjoerring (1996) for oilseed rape plants with plant N status while apoplastic independent of plant N status: difference in apoplastic pH of H$^+$ concentrations in the apoplast for most plants, a lower pH in will still play an important role. Even under conditions in which NH$_3$ times lower than the extracellular 7.5) and in the chloroplasts (apoplastic solution) (approximated) directed toward the apoplast (6)

The loss of NH$_3$ from the canopy for wheat (N 1993), oilseed rape (Husted and Schjoerring, 1996) It is generally accepted that leaf cell membranes...
and Sims (1993) found either as applied to corn (Zea mays L.) or spring of the year. They sug-
lar urease activity in the residues fall and winter months. In con-
trates that crop residues were with soil;
ce, thereby maintaining higher 
source and the soil.
concluded that leaf litter allows face area for urease activity and suggest that higher urease activ-
dues rather than older residues temperatures, and drying condi-
significantly influence volatile once both the soil's tem-
very rapidly to changes in apoplastic NH₄⁺ concentration (Schojoring et al., 2000). Working 
with mutants of barley (Hordeum vulgare L.), Mattsson et al. (1998) demonstrated the 
significance of GS in controlling the flux of NH₄⁺ between plants and the atmosphere.
Schojoring et al. (2000) also reported that inhibition of GS leads to a rapid and sub-
stantial increase in apoplastic NH₄⁺ concentration. Schojoring et al. (1998) noted that 
high NH₄⁺ compensation points seemed to always be the result of high tissue N status, 
rapid absorption of NH₄⁺ from the root medium and/or low activity GS. Since 
NH₄⁺ is constantly generated in large amounts in leaf tissues, GS and GOGAT activities 
are critical in controlling NH₄⁺ emission from plant leaves.

Factors Influencing Ammonia Losses from Plants

The NH₄⁺ compensation point is a variable parameter influenced by a range 
of physiological and environmental conditions (Schojoring et al., 1998). The magnitude 
and direction of the NH₄⁺ fluxes may change on hourly, daily, and seasonal 
scales, depending on environmental conditions, crop growth characteristics, and 
timing of fertilizer application (Sutton et al., 1994). Only a brief discussion of some 
of the major factors influencing NH₄⁺ losses from plants will be covered.

Nitrogen Status and pH

Theoretically, the NH₄⁺ compensation point at any given leaf temperature can 
be determined by knowing the concentration of NH₄⁺ and H⁺ in the aqueous interface 
apoplast). Husted and Schojoring (1996) reported apoplastic NH₄⁺ concentra-
tions for oilseed rape plants (Brassica napus L.) increased at all growth stages 
with plant N status while apoplastic pH values remained fairly constant and were 
independent of plant N status and plant ontogeny. Dannel et al. (1995) found little 
difference in apoplastic pH of plants grown with NO₃⁻ or NH₄⁺ as the N source. If 
H⁺ concentrations in the apoplastic solution remain fairly constant during growth 
for most plants, a lower pH in the apoplast than in surrounding leaf components 
will still play an important role in the diffusion of dissolved NH₄⁺ within leaves. 
Even under conditions in which the intracellular NH₄⁺ concentration is 10 to 100 
times lower than the extracellular concentration, a high pH in the cytoplasm (7.0– 
7.5) and in the chloroplasts (approximately 8.0 in light) relative to that in the apoplastic 
solution (approximately 6.0) may maintain a gradient of dissolved NH₄⁺ 
directed toward the apoplast (Nielsen and Schojoring, 1998).

The loss of NH₄⁺ from the canopy has been found to increase with the N status 
of the canopy for wheat (Morgan and Parton, 1989), barley (Schojoring et al., 
1993), oilseed rape (Husted and Schojoring, 1996), and corn (Francis et al., 1993). 
The concentration of NH₄⁺ in the leaf apoplastic solution is very sensitive to leaf
N status and external N supply (Nielsen and Schjoerring, 1998). Husted and Schjoerring (1996) reported that increasing plant N status resulted in increased bulk tissue NH$_4^+$ concentration and also increased apoplastic NH$_4^+$ concentration at all growth stages. Mattsson and Schjoerring (1996) found that plants having access to NH$_4^+$ in the root medium had higher apoplastic NH$_4^+$ concentrations than plants absorbing NO$_3^-$, and that leaf apoplastic NH$_4^+$ concentration increases with NH$_4^+$ concentration in the root medium.

Growth Stage

Bulk tissue NH$_4^+$ concentrations change with plant ontogeny. Morgan and Parton (1989) attribute increased potential for NH$_4^+$ volatilization during later developmental stages to genetic changes in plant metabolism that elevated tissue NH$_4^+$ concentrations above those occurring in younger, vegetative tissue. They related periods of increased NH$_4^+$ volatilization from anthesis through maturity to changes in the balance between NH$_4^+$-releasing reactions (deamination, senescence-induced proteolysis, and nitrate reduction) and NH$_4^+$ uptake reactions (N transport and NH$_4^+$ assimilation). As the balance shifts in favor of NH$_4^+$-releasing reactions, there is the establishment of new, higher, steady-state tissue NH$_4^+$ concentrations. Schjoerring et al. (1998) also reported that the NH$_4^+$ compensation point depends on plant developmental stage with peaks in NH$_4^+$ emission related to leaf senescence and N remobilization.

Temperature

The high sensitivity of plant-atmosphere NH$_4^+$ exchange to leaf temperature makes information about temperature very important when data on NH$_4^+$ compensation points are reported (Husted and Schjoerring, 1996). In one of the earliest studies on temperature effects on volatile N loss from plants, Stutte and da Silva (1981) found that increasing air temperature from 30 to 35°C greatly increased the rate of volatile N loss for all eight rice (Oryza sativa L.) cultivars tested. Based on their results, they postulated volatile N losses occurred in conjunction with transpirational water vapor and may constitute a defense mechanism of plants against NH$_4^+$ toxicity under temperature stress. Schjoerring et al. (1998) also noted that simply increasing the temperature from 15 to 30°C can cause plants to switch from being strong sinks for atmospheric NH$_4^+$ to being significant NH$_4^+$ sources. Husted and Schjoerring (1996) reported increasing leaf temperatures from 10 to 35°C caused an exponential increase in NH$_4^+$ emission from plants exposed to low ambient NH$_4^+$ concentrations, indicating that leaf conductance was not the only factor responding to the temperature increase. They noted that when simple thermodynamic equations were used in combination with NH$_4^+$ compensation points derived from measurements of apoplastic NH$_4^+$ concentrations, increased NH$_4^+$ emissions with increasing temperature could be explained in their study entirely in terms of effects on the equilibrium between gas phase and soluble NH$_4^+$ and NH$_4^+$ in the apoplast. The profound influence of temperature on plant-atmosphere NH$_4^+$ exchange is partly via affecting the concentration of atmospheric NH$_4^+$ in equilibrium with NH$_4^+$ in the apoplastic solution, and partly via affecting the physiological processes generating or assimilating NH$_4^+$ in the leaf tissues (Schjoerring et al., 1998).

Wind, Humidity, and Light

In addition to temperature, light intensity can influence pliability to or removal of NH$_4^+$ from between leaves and air will pre such a layer will slow down NH$_4^+$ losses (Holman-Hartwig et al. in variations in light intensity and (1996) observed that at low rela mum at low light intensity of a) humidities, NH$_4^+$ uptake did not occur in a dry atmosphere favored by high light intensities be found under dry atmosphere (Husted and Schjoerring, 1996), control mechanism for the regul affect on conductance for NH$_4^+$.

It is generally reported that emission near midday a and Bockman, 1994). Strong di studies investigating C$_3$ plants, free NH$_4^+$ that must pass out of the GAT pathway (Leegood et al., 1991 is very large with rates up to 10 m$^2$ h$^{-1}$ (Joy et al., 1992). Holman-Hartwig's study found that the diurnal trend in NH$_4^+$ emission showed a clear, significant increase in NH$_4^+$ temperature along with stomata of NH$_4^+$ and H$^+$ in the leaf, absent in C$_3$ plants and the major C$_4$ plants is generally much less between C$_3$ and C$_4$ plants would not temperature and concentration (diurnal trends in NH$_4^+$ emission).

Atmospheric Ammonia Emissions

Ambient NH$_4^+$ concentration measurements point in the absence of livestock production increased NH$_4^+$ emissions from atmospheric NH$_4^+$ concentrations leaves and ambient air. AP-5 emission over Europe between 1990 and 1994, agricultural practices. This would serve as net sinks for atmospheric ice core data from central Green
Husted and Schjoerring, 1998). Husted and Schjoerring (1998) noted that plants having access to NH₄⁺ concentrations at all stages of plant ontogeny. Morgan and Bockman, 1994). Studying the combined effects of variations in light intensity and air humidity on NH₃ fluxes, Husted and Schjoerring, (1996) observed that at low relative humidity (20%), NH₃ absorption reached a maximum at low light intensity of approximately 350 μmol m⁻² s⁻¹, whereas at higher air humidities, NH₃ uptake did not saturate below 600 μmol m⁻² s⁻¹. This reflects that stomata in a dry atmosphere reached full aperture at low light intensity as compared with a humid atmosphere. Under humid conditions NH₃ exchange would be favored by high light intensities, whereas relatively large NH₃ exchange rates may be found under dry atmospheric conditions, even when light intensities are low (Husted and Schjoerring, 1996). Thus, change in stomatal opening is an important control mechanism for the regulation of NH₃ flux into or out of leaves because of its effect on conductance for NH₃ diffusion (Schjoerring et al., 1998).

It is generally reported that NH₃ emission follows a diurnal trend with maximum emission near midday and minimum emission at night (Holtan-Hartwig and Bockman, 1994). Strong diurnal trend reports are typically associated with studies investigating C₃ plants. Each photorespiration cycle in C₃ plants yields a free NH₃ that must pass out of the mitochondria for reassimilation by the GS/GOGAT pathway (Leegood et al., 1995). The rate of NH₃ release by photorespiration is very large with rates up to 10 times that generated by the reduction of nitrate (Joy et al., 1992). Holtan-Hartwig and Bockman (1994) summarized that it probably is the effect of light on stomata opening and on photorespiration that produce the diurnal trend in NH₃ exchange. However, Schjoerring et al. (2000) report that diurnal variations in NH₃ exchange seem to be caused mainly by changes in leaf temperature along with stomatal conductance rather than changes in concentrations of NH₃ and H⁺ in the leaf apoplastic solution. Photorespiration is essentially absent in C₄ plants and the magnitude for diurnal trends in NH₃ emission from C₃ plants is generally much less than for C₄ plants. Comparing NH₃ emissions between C₃ and C₄ plants would suggest that stomatal conductance along with both temperature and concentration (NH₃ release activities) combine to cause the larger diurnal trends in NH₃ emission from C₃ vs. C₄ plants.

Atmospheric Ammonia Concentration

Ambient NH₃ concentrations near the canopy should approach the NH₃ compensation point in the absence of other sources or sinks (Langford and Fehsenfeld, 1992). Increased livestock production and N fertilizer use since 1950 would suggest increased NH₃ emissions from agricultural activities that would produce increased atmospheric NH₃ concentrations resulting in lower concentration gradients between leaves and ambient air. ApSimon et al. (1987) reported a 50% increase in NH₃ emissions over Europe between 1950 and 1980 mainly as the consequence of intensive agricultural practices. This would suggest an increased potential for vegetation to serve as net sinks for atmospheric NH₃ over the last 50 yr. However, in studying ice core data from central Greenland, Laj et al. (1992) concluded that atmospheric
NH$_3$ concentrations have actually decreased over the last 50 yr. Their explanation for decreasing atmospheric NH$_3$ concentrations is the rapid reactions between atmospheric NH$_3$ and acidic aerosols of S and N which themselves have increased in concentrations by three- to fourfold over the last 250 yr. Reactions decreasing atmospheric NH$_3$ concentrations would enhance NH$_3$ losses from crop canopies.

Concentrations of NH$_3$-N in air in rural areas is generally within the range from 1 to 14 µg m$^{-3}$, with about 1 to 6 µg m$^{-3}$ as typical (Holtan-Hartwig and Bockman, 1994). Farquhar et al. (1980) found the NH$_3$ compensation point for young plants of several species to be about 1 to 4 µg NH$_3$-N m$^{-3}$. When the NH$_3$ compensation point exceeds the atmospheric NH$_3$ concentration, NH$_3$ may either be absorbed or emitted by these young plants. Morgan and Parton (1989) reported that the compensation point for wheat increases as plants approach maturity, from about 13 µg NH$_3$-N m$^{-3}$ at early grain filling, to 23 µg NH$_3$-N m$^{-3}$ at late grain filling. Mattsson et al. (1998) showed approximately a 15-fold increase in NH$_3$ compensation point, 2.5 to 26 µg NH$_3$-N m$^{-3}$, for osilage rape when growing from low to high external N supply. The NH$_3$ concentration gradient between the atmosphere and the leaf apoplastic solution stands as the major driving force for NH$_3$ gains and losses in plants.

Carbon Substrates and Plant Stress

Assimilation of NH$_3$ depends on an adequate supply of C in the form of 2-oxoglutarate, an intermediate of the mitochondrial tricarboxylic acid cycle (Schjoerring et al., 2000). The availability of C substrates may also determine how efficiently NH$_3$ is reassimilated in plants. Remobilization of N during the reproductive growth phase combined with nonoptimal photosynthetic conditions (e.g., drought, disease, etc.) may give an excess of N relative to C and result in NH$_3$ losses (Holtan-Hartwig and Bockman, 1994). Papakosta and Gagianas (1991) noted that N losses were related to both N content at anthesis and grain yield for winter wheat (Triticum spp.). Schjoerring et al. (1993) reported similar findings that NH$_3$ losses are related to N harvest index (ratio between grain N content and total shoot N content). High N harvest indices are achieved when favorable climatic conditions produce high grain yields (high C substrates) and effective deposition in the grain of N mobilized from vegetative plant parts. Therefore, NH$_3$ emission will change with year-to-year variations in weather that control C substrate production and crop N economy (Schjoerring et al., 1993).

Emissions from Live Agricultural Plants

Methods used for measuring NH$_3$ exchange between air and crops can be grouped in three main categories and all have problems estimating annual NH$_3$ emissions from plants. Enclosure or chamber methods have difficulty matching natural factors that have important influences on the volatilization of NH$_3$ over the full growth cycle, such as evaporation rate, temperature, wind speed, ambient NH$_3$ concentration and dew formation (Holtan-Hartwig and Bockman, 1994). Conventional micrometeorological methods typically have problems with temporal and spatial variability, short time scales, and the requirement for uniform, level surface sources with long fetches and one-dimensional vertical flux densities (Holtan-Hartwig and Bockman, 1994). Conventional micrometeorological techniques also do not strictly measure NH$_3$ losses from plants, but give a combined

Gaseous Losses other than NH$_3$ flux from plants and a quantity of aboveground plays can be masked by concepts, such that they are not directly measured. If used with standing N methylation and substitution processes contribute to the problem of error in estimation of losses (Holtan-Hartwig and Bockman, 1994).

The bidirectional nature of the large spatial variability of the extrapolation of current landscape scale to a speculative vide a comprehensive list of magnitude of N losses from different plant species and data reported studies are from cereals and Bockman, found NH$_3$-N ha$^{-1}$ d$^{-1}$, but conclude to yearly losses as emissions and plant development stage to for net NH$_3$ losses from kg NH$_3$-N ha$^{-1}$ yr$^{-1}$ if the crop during the grain filling period.

Schjoerring et al. (2000) represent a net source of NH$_3$, below 1 up to 7 kg NH$_3$-N ha$^{-1}$ conditions. They further state that up to 5% of the shoot N content if fertilizer or manure is applied (Holtan-Hartwig and Bockman). With most of the information conducted in northern Europe annual loss values also represent reporting the largest NH$_3$ terranean or midlatitude type location, low humidity and the high N losses from cereals and Gagianas (1991) and 30 kg NH$_3$-N ha$^{-1}$. The large N however the number of studies is a rare phenomenon and that this be substantial. This increases emissions from crops.

Temperature differences and northern Europe would from crops grown in the USA. Temperatures between Spring: 70C, two sites where numerous performed, there is typically o
The last 50 yr. Their explanation for the rapid reactions between those halves have increased in 0 yr. Reactions decreasing atmos- sices from crop canopies.

is generally within the range (Holtan-Hartwig and Bock- compensation point for young H$_2$N m$^{-3}$. When the NH$_3$ con- : NH$_4$ concentration, NH$_4$ may mts. Morgan and Parton (1989) increases as plants approach ma- n filling, to 23 mg NH$_4$N m$^{-3}$ at approximately a 10-fold increase m$^{-3}$, for oilseed rape when going centration gradient between the 1s as the main driving force for

The bidirectional nature of NH$_3$ exchange between plants and air along with the large spatial variability in ambient NH$_3$ concentrations and land use makes the extrapolation of current NH$_3$ exchange data to annual net NH$_3$ exchange on a landscape scale a speculative exercise. Holtan-Hartwig and Bockman, (1994) provide a comprehensive list of 50 references on volatile N losses from plants. The magnitude of N losses found by use of different measuring methods and for different plant species and developmental stages are listed in this review. Most of the reported studies are from cereal crops. In reviewing these studies Holtan-Hartwig and Bockman, (1994) found that emissions mostly fell in the range of 5 to 50 g NH$_3$N ha$^{-1}$ d$^{-1}$, but concluded that daily emissions cannot be directly converted to yearly losses as emissions vary with conditions of temperature, water status and plant development stage. They suggest 1.5 kg NH$_3$N ha$^{-1}$ yr$^{-1}$ as a rough estimate for net NH$_3$ losses from arable crops and that this value may increase to 6 kg NH$_3$N ha$^{-1}$ yr$^{-1}$ if the crop is severely stressed by disease or adverse weather during the grain filling period.

Schoeiring et al. (2000) report that plant communities on arable crop land re- present a net source of NH$_3$ to the atmosphere with net emissions ranging from below 1 up to 7 kg NH$_3$N ha$^{-1}$ season$^{-1}$, depending on plant N status and climatic conditions. They further state that NH$_3$ emissions may lead to a significant loss of up to 5% of the shoot N content. Ammonia emission from crops is also increased if fertilizer or manure is applied in amounts that substantially exceed crop needs (Holtan-Hartwig and Bockman, 1994).

With most of the information on NH$_3$ emissions from crops coming from studies conducted in northern Europe on C$_3$ plants, the question becomes are these annual loss values also representative for warmer climates and C$_4$ plants? Studies reporting the largest NH$_3$ emissions from crops generally tend to have Mediterranean or midlatitude type climates. Above-average temperatures at the study location, low humidity and crops under high N status may have contributed to the high N losses from some of the studies in warmer climates, such as Papakosta and Gagianas (1991) and Francis et al. (1993) with calculated N losses over 75 kg NH$_3$N ha$^{-1}$. The large N losses reported in these studies may be notypical, however the number of studies reporting large N losses indicates that this is not a rare phenomenon and that under certain conditions NH$_3$ loss and exchange can be substantial. This increases the degree of uncertainty in estimating annual NH$_3$ emissions from crops.

Temperature differences during the summer months between central USA and northern Europe would suggest a greater opportunity for NH$_3$ emissions from crops grown in the USA. If one compares June, July, and August ambient air temperatures between Springfield, IL, and Copen hagen, Denmark, or Edinburgh, UK, two sites where numerous studies on NH$_3$ emissions from crops have been performed, there is typically over a 10°C difference in average daily temperatures.
If the higher U.S. temperatures are used in Husted and Schjoerring's (1996) calculations along with parameters that give Schjoerring's et al. (2000) net NH₃ emissions range, the estimated range for Springfield, IL, would be 1 to 25 kg NH₃-N ha⁻¹ yr⁻¹. Estimating annual NH₃ emissions from crops carries a substantial degree of uncertainty and will require considerable work to be done before we fully understand NH₃ exchange between crops and the atmosphere.

In addition to normal leaf and canopy cycling of NH₃, soils and plant residues can act as sources and sinks for NH₃, thereby increasing the complexity of determining net annual NH₃ exchange between agricultural crops and the atmosphere. Fertilizers and livestock husbandry are typically considered the major contributors of NH₃ to the atmosphere and plants nearly insignificant contributors. However, the sheer number of plants spread across the landscape and the bidirectional nature of NH₃ exchange between plants and air suggest plants play a crucial role in atmospheric NH₃ concentrations. In Hungary, Horvath and Sutton (1998) found no apparent decrease in atmospheric concentrations of NH₃ and NH₄⁺ when pig and cattle numbers were reduced 49 and 47%, respectively, over a 10-yr period. Holten-Hartvig and Bockman (1994) expressed reservations about the possible occurrence of high seasonal emissions of NH₃ from crops, stating a loss of 15 kg NH₃-N ha⁻¹ yr⁻¹ from crops would represent about 30% of total NH₃ emissions from Western Europe. In some cases the assigning of NH₃ source may be just a matter of semantics. As an example, if application of fertilizer or manure exacerbates the loss of NH₃ from plants an argument can be made for either the plant or N supplying material as being the NH₃ source.

Emissions from Dead Agricultural Plants

Decomposing plant material and herbage cut for hay, silage or mulch undoubtedly contributes to the emission of NH₃ to the atmosphere. Crop plants typically start senescence and dropping of lower leaves long before seed maturity is reached. Dropped leaves from crop species like oilseed rape may contain significant amounts of N, and high NH₃ emission can take place from such detached leaves with onset being synchronized with protein and chlorophyll degradation (Schjoerring et al., 1998). Nemitz et al. (2000) found the largest NH₃ concentration at the ground surface for a oilseed rape canopy and determined it was caused by N mineralization from fallen leaf litter that led to release of up to 150 ng NH₃-N m⁻² s⁻¹.

Janzen and McGinn (1991) found as much as 14% of the N in a legume green manure was volatilized as NH₃ within 14 d of application. Incorporation of green manure material into the soil effectively prevented volatile loss of NH₃ but incorporation greatly reduces its effectiveness as a measure to control erosion and conserve moisture (Janzen and McGinn, 1991). Larsson et al. (1998) reported NH₃ losses from herbage rich in N can be substantial with estimated losses ranging from the equivalent of 17% of the applied N for alfalfa (Medicago sativa L.) to 39% for high N grass.

Whitehead et al. (1988) measured the volatilization of NH₃ from cut herbage of perennial ryegrass (Lolium perenne L.) during a 70-d period of investigation for both drying and decomposition. They found NH₃ volatilization during decomposition amounted to 20 to 47% of the herbage N, but NH₃ volatilization during drying amounted to less than 1% of the herbage N. Most of the volatilization of NH₃ during decomposition occurred under moist conditions while the small amount of

Nitrification

NH₄⁺ ———> NH₃ ———> N₂

Nitrosomonas
Nitrosospira
Nitrosococcus

Main Controls
Substrate, O₂, H₂O, T

N₂ ———> N₂

Main Controls
Substrate, available C.

Fig. 8–1. Gaseous emissions (GC temps (Mosier and P. Parkin, 2007).

NH₃ volatilized during dry conditions is unknown (Mosier et al., 1988).

Nitrous Oxide and

Research during the past 10 yr how NOₓ and N₂O are produced, and gas movents of processes involved we are of N that is applied or deposited (C). Del Grosso et al. (2) and Bouman, 1999. Potter et al. presumably similar agricultural in both time and space. The processes involved must be developed (Mosier and B)

We know that NOₓ are processes of nitrification and Firestone. 1982; Hutchinson nitrification, the oxidation of in essentially all terrestrial, logically ubiquitous; a surprise has been identified and consideration that occurs (Schmidt, 1982), water bacteria that oxidize at
ed and Schippering’s (1996) calculation of NH₃ emissions, IL would be 1 to 25 kg NH₃-N crops carries a substantial degree of uncertainty to be done before we fully understand the complexity of determining crops and the atmosphere. In considered the major contributors: The landscape and the bidirectional suggest plants play a crucial role. Horvath and Sutton (1998) found of NH₃ and NH₄⁺ when pig manure is spread, over a 10-yr period. Reservations about the possible impact on crops, stating a loss of 15 kg N or 30% of total NH₃ emissions of NH₄⁺ source may be just a on of fertilizer or manure excretion be made for either the plant or

Cultural Plants

For hay, silage or mulch undisturbed by rain, Crop plants typically may contain significant amounts of NH₃ in detached leaves with on-farm degradation (Schippering et al., 1996) NH₃ concentration at the ground it was caused by N mineralization of NH₃-N m⁻² s⁻¹. 14% of the N in a legume green plication. Incorporation of green material volatilizes loss of NH₃ but in progress to control erosion and soil erosion. For example, Arson et al. (1998) reported NH₃ volatilization with estimated rates ranging from alfalfa (Medicago sativa L.) to 70% volatilization from cut herbage. The 70-d period of investigation for volatilization during decomposition of NH₃ volatilization during dry season, most of the volatilization of NH₃ occurs while the small amount of

Nitrous Oxide and Nitrogen Oxides Biological Sources

Research during the past several decades has improved our understanding of how NO₂ and N₂O are produced, factors that control production, source/sink relationships, and gas movement processes. However, despite extensive knowledge of processes involved we are only beginning to be able to predict the fate of a unit of N that is applied or deposited on a specific agricultural field (e.g., Davidson et al., 2000; Del Grosso et al., 2001a, 2001b; Frolking et al., 1998; Li et al., 1992; Plant and Bouman, 1999; Potter et al., 1998). Studies of emissions of NO₂ and N₂O from presumably similar agricultural and natural systems show highly variable results in both time and space. The complex interaction of the physical and biological processes involved must be understood before reliable predictive capability can be developed (Mosier and Bouwman, 1993; Mosier et al., 1998a).

We know that NO₂ and N₂O are produced primarily from the microbial processes of nitrification and denitrification in soil (Fig. 8–1) (see Schmidt, 1982; Firestone, 1982; Hutchinson and Davidson, 1993, for more detailed reviews). Denitrification, the oxidation of ammonia to nitrate and then nitrates occurs in essentially all terrestrial, aquatic, and sedimentary ecosystems. Although ecologically ubiquitous, a surprisingly few different chemolithotrophic bacteria have been identified and considered to accomplish most of the ammonia oxidation that occurs (Schmidt, 1982). Nitrosomonas and Nitrosospira are the main soil and water bacteria that oxidize ammonia to nitrite while Nitrobacter is the principal ge-

Gaseous Losses other than through Denitrification

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<th>Nitrification</th>
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<tr>
<td>NH₄⁺ → NH₃OH⁻ → [HNO₂] → NO₂⁻ → NO₃⁻</td>
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Denitrification

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Fig. 8–1. Gaseous emissions (CO₂, CH₄, N₂O, and NO) from diverse agricultural production systems (Mosier and T. Parkin, 2007).

NH₃ volatilized during drying implies that hay made in the field under continuous drying conditions is unlikely to release appreciable amounts of NH₃ (Whitehead et al., 1988).
nus of bacteria identified to oxidize nitrate to nitrate (Fig. 8-1; Schmidt, 1982). Denitrification, the microbial reduction of nitrate or nitrite to gaseous N through NO and N₂O (Firestone, 1982) (Fig. 8-1), is performed by a diverse and also widely distributed group of aerobic, heterotrophic bacteria that have the alternative capacity to reduce nitrogen oxides when O₂ becomes limiting. The general requirements for denitrification are: the presence of bacteria possessing the metabolic capacity, suitable electron donors such as organic C compounds, reduced S compounds or molecular hydrogen, anaerobic conditions or restricted oxygen availability, and nitrogen oxides as terminal electron acceptors (Fig. 8-1; Firestone, 1982).

In well-aerated, yet moist conditions, or approximately 60% water-filled pore space (WFPS), N₂O and NO emissions from nitrification of ammonium-based fertilizers can be substantial (Bremner and Blackmer, 1978; Duxbury and McConnaughey, 1986; Hutchinson and Brams, 1992). Other work suggests that N₂O release is a byproduct of nitrification (Yoshida and Alexander, 1970; Ventera and Rolston, 2002) and may occur by denitrification of nitrate by nitrifying organisms under oxygen stress (Poth and Focht, 1985). Nitric oxide emissions are considered to arise from the soil generally from nitrification (Hutchinson and Davidson, 1993) but can arise from abiotic chemical reactions under specific conditions (Nelson, 1982). In wet soils, where aeration is restricted, denitrification is generally the source of N₂O (Smith, 1990). Under these conditions both the rate of denitrification and the N₂O/(N₂ + N₂O) ratio must be known to evaluate NO emissions through denitrification. Typically little NO emissions are observed under such conditions (Hutchinson and Davidson, 1993). According to Smith (1990), soil structure and water content, which affect the balance between diffusive escape of N₂O and its further reduction to N₂, are important in determining the proportions of the two gases as well as NO. Soil WFPS is used to express the interplay of soil water content and microbial activity through most of these discussions, and is the one factor that is generally reflected in the response of trace gas emissions from the soil to changes in soil conditions. Linn and Doran (1984) showed that WFPS is closely related to soil microbial activity. As a result, the activity of soil microbial processes responsible for CH₄ production and consumption (Del Grosso et al., 2000a) and production and consumption of nitrogen oxides can be roughly predicted from WFPS (Davidson, 1991).

Linn and Doran (1984) demonstrated that aerobic microbial reactions, nitrification and respiration, peaked at WFPS of approximately 60% while responses that are sensitive to oxygen, i.e., denitrification, increased greatly above 80% WFPS. Firestone and Davidson (1989) developed the relationships of WFPS and soil microbial activity to NO and N₂O emissions. Their conceptual model, the hole-in-the-pipe (HIP) model, relates the sum of NO + N₂O emissions to indices of N availability and relates the ratio of NO/N₂O emissions to soil water content. The rates of nitrification and denitrification are described as being analogous to the flow of N through a pipe, while the sizes of the holes in the pipe determine the relative fractions of NO and N₂O that leak out. In fertile soils the flow through the pipe is large, and emissions of one or both gases are also large. In dry soils, NO is the dominant gas that leaks out of the pipe while in wetter soils N₂O is the more important endproduct (Davidson and Verchot, 2000; Davidson et al., 2000). Davidson (1991) observed that the largest NO emissions could be expected at WFPS values of 30 to 60% and the highest N₂O emissions at 50 to 80% WFPS.

Under wetter soil conditions from the soil.

The interplay of substrates demonstrated by Parton et al. (1982) in N₂O emissions from soils. The CENTURY ecosystem model (De Vries, 1982) with feedbacks of nitrification and denitrification that NO₃ emissions are due to nitrification are proporcional to the modeled soil NH₄ (N₂O) oxidase (N₂O) emission compensation, WFPS, heterotrophic calculated by multiplying the calculated as a function of soil microbial activity. Why is driven by nitrification with nitrification. When diffusivity is low, denitrification is less than to less than one. The NO₃ sub by rain events onto dry soils.

Using the IPCC/UNEP/UN (1996) that the anthropogenic N₂O emissions totaled 0.86 Tg in 1990 and biological N fixation residues. Anthropogenic NO₃ emissions on Davidson and Kingerlee (1990).

Nitrogen Emissions

Most anthropogenic nitrogen estimates that nearly 87% of g in the Tropics. Biomass burning in the economy (Andreae, 1991):

- Clearing of forest and br
- Control of brush, weedy lands;
- Nutrient regeneration in
- Control of fuel accumulates
- Production of charcoal for
- Energy production for a

In living plants the nutrient that are most easily burned, so before burning much plant tissue and carbon of the nutrients (Carbon contents of dry plant biomass are: 0.3% C, 0.5 to 3.4% C).
Under wetter soil conditions $N_{2}$ should be the dominant gaseous N product emitted from the soil.

The interplay of substrate availability, oxygen supply, and gas diffusion are demonstrated by Parton et al. (2002) who describe a model to simulate $NO_{x}$ and $N_{2}O$ emissions from soils. They have developed N gas flux modules for the DAYCENT ecosystem model (Del Grosso et al., 2006) and have tested the model extensively with observations from different soils. The N gas flux model assumes that nitrification and denitrification both contribute to $N_{2}O$ and $NO_{x}$ gas emissions but that $NO_{x}$ emissions are due mainly to nitrification. Nitrous oxide ($N_{2}O$) emissions from nitrification are proportional to nitrification rates, which are calculated as a function of modeled soil NH$_4$ concentration, WFPS, temperature, pH, and texture. Nitrous oxide ($N_{2}O$) emissions from denitrification are a function of soil $NO_{x}$ concentration, WFPS, heterotrophic respiration, and texture. The $NO_{x}$ emissions are calculated by multiplying total $N_{2}O$ emissions by a NO/C ratio function that is calculated as a function of soil parameters (bulk density, field capacity, WFPS) that influence gas diffusivity. When soil gas diffusivity is high most of the N gas flux is driven by nitrification with a correspondingly high NO/$N_{2}O$ (maximum of 25). When diffusivity is low, denitrification dominates and the ratio of NO/$N_{2}O$ drops to less than one. The NO$_x$ submodel also simulates $NO_{x}$ emission pulses initiated by rain events onto dry soils.

Using the IPCC/UNEP/OECD/IEA (1997) guidelines, USEPA (2001) estimated that the anthropogenic $N_{2}O$ emissions from U.S. soils due to agricultural soil management totaled 0.96 Tg in 1993. This estimate is based on N input from synthetic fertilizer and biological N fixation as well as N recycled in livestock manure and crop residue. Anthropogenic $NO_{x}$ emissions due to agricultural soil management, based on Davidson and Kingerlee (1997), were an estimated 0.2 Tg of NO$_x$-N in 1999.

Nitrogen Emissions from Burning Agricultural Biomass

Most anthropogenic biomass burning occurs in the Tropics. Andreea (1991) estimates that nearly 87% of global emissions from biomass burning takes place in the Tropics. Biomass burning serves a variety of purposes in agriculture and economy (Andreea, 1991):

- Clearing of forest and brush land for agricultural use;
- Control of brush, weeds, and litter accumulation on grazing and crop lands;
- Nutrient regeneration in grazing and crop lands;
- Control of fuel accumulation in forests;
- Production of charcoal for industrial and domestic use; and
- Energy production for cooking and heating.

In living plants the nutrients N and S are mainly concentrated in those parts that are most easily burned, such as leaves, small twigs and bark, but fortunately before burning much plant tissue is dry and dead and has actually lost a major portion of its nutrients (Crutzen et al., 1979). On a mass basis, the nutrient element contents of dry plant biomass are relatively low: about 0.3 to 3.8% N, 0.1 to 0.9% S, 0.01 to 0.3% P, and 0.5 to 3.4% K (Andreea, 1991).
Fires in diverse ecosystems are very different in the production of gaseous and particulate emissions (Levine et al., 1995). The chemical composition of emissions from burning biomass depends primarily on the rate of energy release (intensity) or combustion (Cofer et al., 1991a). Combustion is strongly coupled to fuel moisture, fuel type, fuel size, fuel array, ignition pattern, terrain, and weather. Flaming combustion produces more highly oxidized products such as \( \text{CO}_2 \) and \( \text{NO}_x \) while smoldering leads to increased emissions of more reduced species such as \( \text{CO}, \text{CH}_4 \), and \( \text{NH}_3 \) (Griffith et al., 1991). In open burning of biomass, temperatures are fairly low and the high temperatures necessary for the oxidation of atmospheric \( \text{N}_2 \) seldom exists (Gerstle and Kemitz, 1967).

Nitrogen is present in plant biomass mostly as amino groups (R-\( \text{NH}_2 \)) in the amino acids of proteins (Andreæ, 1991). During combustion it is released by pyrolytic decomposition of the OM and then partially or completely oxidized to various volatile N compounds. On average approximately 90% of the biomass N is volatilized during a burn (Lobert et al., 1990). Nitric oxide is the single most abundant species emitted, but it represents only 10 to 20% of the N initially contained in the fuel (Andreæ, 1991). Clements and McMahon (1980) reported a similar amount with a rough average of about 30% total yield for all \( \text{NO}_x \) species. Nitrogen compounds other than NO (\( \text{NO}, \text{NO}_2, \text{NH}_3, \text{HCN}, \text{organic nitrates}, \text{and nitrates} \)) account for another 10 to 20% of the fuel N (Andreæ, 1991). Average emission values reported by Lobert et al. (1990) for percentage of biomass N released as \( \text{NH}_3 \), HCN, and nitrates of 4, 2.4, and 1% respectively, lie well within this range. Emission of molecular N is not monitored because of its high atmospheric content, and the majority of any unaccounted-for N is possibly released as \( \text{N}_2 \) (Andreæ, 1991). Lobert et al. (1991) using a burning apparatus with an artificial atmosphere for simulating open fires reported 41 to 46% of the fuel N was emitted as \( \text{N}_2 \). They concluded \( \text{N}_2 \) emissions belonged to the flaming stage rather than to the smoldering stage.

LeBel et al. (1991) estimated \( \text{NH}_3 \) emissions from biomass burning would account for 14% of the total global atmospheric \( \text{NH}_3 \) budget. This is much higher than the Lobert et al. (1991) estimate that shows biomass burning on average accounting for about 5% of the total \( \text{NH}_3 \) source. In nearly all of their experiments, Lobert et al. (1991) found \( \text{NO}_x \), to be the most important reactive N emission product from biomass burning and from their calculations of source strength yields estimated an average contribution of 12% to the global budget. This falls in the range of 10 to 20% of the global \( \text{NO}_x \) budget estimated by Granier et al. (2000) for \( \text{NO}_x \) from biomass burning. For \( \text{NO}_x \), Cofer et al. (1991b) concluded that more than 7% (and probably less) of the global source of \( \text{NO}_x \) can be attributed directly to biomass burning. Similarly, Lobert et al. (1991) estimated biomass burning contributing only about 3% to the global source of \( \text{N}_2 \). Lobert et al. (1991) reported that HCN and CH\(_3\)CN, two of the most important nitrates emitted by biomass burning, together released 3.6% of the fuel \( \text{N} \) and in some experiments, HCN emissions can be as high as \( \text{NO}_x \) emissions when incomplete combustion was predominant. Data on global sources of nitrates is lacking, however biomass burning may well be the major source for the release of these gases into the atmosphere Lobert et al. (1991).
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McMahon (1981) reported a simi-
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