

## 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  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ),  $\text{NH}_x$  ( $\text{NH}_3$  and  $\text{NH}_4^+$ ), and  $\text{N}_2\text{O}$ . 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 ( $\text{NH}_3$ ) is the dominant alkaline gas in the atmosphere. It readily reacts with atmospheric acids to form  $\text{NH}_4^+$  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  $\text{NH}_3$ . Ammonia gas is predominantly removed from the atmosphere by dry deposition, while  $\text{NH}_4^+$  aerosols are removed mainly by wet deposition (Asman and Janssen, 1987).

After being deposited,  $\text{NH}_3$  and  $\text{NH}_4^+$  may have serious ecological and environmental effects (Schjoerring et al., 1993). The deposition of  $\text{NH}_3$  and  $\text{NH}_4^+$  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  $\text{NH}_3$  and  $\text{NH}_4^+$  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  $\text{NH}_3$  and  $\text{NH}_4^+$  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

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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  $\text{NH}_3$  and  $\text{NH}_4^+$  contributes to eutrophication, which may lead to algal blooming with subsequent fish kills (Schjoerring et al., 1993).

Major sources of atmospheric  $\text{NH}_3$  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  $\text{NH}_3$  exchange has made the extrapolation of  $\text{NH}_3$  fluxes from short periods of measurements to annual net fluxes a speculative exercise. Also, the large spatial variability in ambient  $\text{NH}_3$  concentration and land use further complicates the interpolation of  $\text{NH}_3$  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 ( $\text{N}_2\text{O}$ ) is radiatively active and thus an important "greenhouse" gas. In the troposphere,  $\text{N}_2\text{O}$  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, 1970). Nitric oxide ( $\text{NO}$ ), on the other hand, is a highly reactive species that contributes to increasing lower tropospheric ozone concentration (Liu et al., 1999).  $\text{NO}_x$  also participates in several reactions in which more stable products such as peroxyacetyl-nitrate, nitric acid, and nitrate aerosol are formed. As a result of these reactions, the atmospheric lifetime of  $\text{NO}_x$  is typically less than 1 d (Derwent et al., 1999).

As a result of its high reactivity,  $\text{NO}$  is usually converted into more stable products before it has time to be dry deposited. However, dry deposition is important for  $\text{NO}_2$  and the secondary products such as peroxyacetyl nitrate, nitric acid, and the nitrates (Derwent et al., 1999). Wet deposition is equally important for nitrate aerosols. Because of the high reactivity of  $\text{NO}_x$ , its emissions strongly influence local and regional atmospheric chemistry, while the long lifetime and spectral properties of  $\text{N}_2\text{O}$  result in it having important atmospheric consequences on a global scale (Derwent et al., 1999).

Microbial denitrification and nitrification are the main sources of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  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  $\text{NO}$  released in the burning of fossil fuels used for various agricultural related activities,  $\text{NO}$  and  $\text{NO}_2$  are also formed in the burning of biomass (Andreae, 1991).

### Ammonia Loss from Soil

Nelson (1982), in *Nitrogen in Agriculture 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.

Study†	Year reported	Soil series or description‡	Classification	N source§	Method	Range of N loss
Al-Kanani et al.	1994	Ste. Rosalie	fine, mixed, nonacid mesic Typic Humaquept	urea	lab incubation 23°C, acid trap ( $\text{H}_3\text{BO}_3$ )	16-21% of urea N applied
Al-Kanani et al.	1991	St. Bernard Ste. Sophie	loamy, mixed, nonacid, frigid Typic Hapludoll; sandy, mixed, nonacid, frigid, Typic Haplorthod	urea, UAN urea, UAN	lab incubation 23.1°C, acid trap ( $\text{H}_3\text{BO}_3$ )	3-55% of urea N applied
Bayrakli and Gezgin	1996	clay loam		urea	field microplots, acid trap ( $\text{H}_3\text{BO}_3$ )	7-24% of urea N applied

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Al-Kanani et al.	1991	St. Bernard Ste. Sophie	loamy, mixed, nonacid, frigid Typic Hapludoll; sandy, mixed, nonacid, frigid, Typic Haplorthod	urea, UAN urea, UAN	lab incubation 23.1°C, acid trap (H <sub>3</sub> BO <sub>3</sub> )	3-55% of urea N applied
Bayrakli and Gezgin	1996	clay loam		urea	field microplots, acid trap (H <sub>3</sub> BO <sub>3</sub> )	7-24% of urea N applied
Clay et al.	1990	Esterville (sl)	coarse, loamy over sandy, mixed mesic Typic Hapludoll	urea	field microplots, acid trap (H <sub>3</sub> BO <sub>3</sub> )	0-175 mg N m <sup>-2</sup> h <sup>-1</sup>
Fox et al.	1996	Hublersburg (sil)	clayey, illitic mesic, Typic Hapludult	urea, UAN	field plots, NH <sub>3</sub> sampler micrometeorological	12-35% of applied N
Harmel et al.	1997	Chillicothe (vgl) Berino (tl)	loamy-skeletal, mixed, thermic, Ustollic Calciorthid; fine, loamy, mixed, thermic Ustollic Haplargid	biosolids	field dynamic NH <sub>3</sub> collectors	8.3-16.6% of applied NH <sub>4</sub> -N
He et al.	1999	Riviera (fs)	loamy, siliceous, hyperthermic, Arenic Glossoqualf	<sup>15</sup> N labeled AN, U, AS, AB	lab incubation 30°C, sponge trap (H <sub>3</sub> PO <sub>4</sub> ), KCL extraction	16-23% of applied N
Jansen and McGinn	1991	sandy loam	fine-silty, mixed, mesic, Aquic Hapludalf	legume green manure	greenhouse pots, acid trap (HCl)	>1-14% of applied N
Larsson et al.	1998	clay		green mulches	field plots closed chambers	2-39% of applied N
Lightner et al.	1990	Xenia (sil)		UUP, AN, urea-KCl, urea-CaCl <sub>2</sub>	field NH <sub>3</sub> collection, acid trap (H <sub>2</sub> SO <sub>4</sub> )	12-41% of applied N
Marshall et al.	1998	State (sil) Pacolet (sl) Lily (l)	fine-loamy, mixed, thermic, Typic Hapludults; clayey, kaolinitic, thermic, Typic Hapludults; fine-loamy, siliceous, mesic, Typic Hapludults	poultry litter	micrometeorological mass balance	2-6% of applied N

Table cont.

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Study†	Year reported	Soil series or description‡	Classification	N source§	Method	Range of N loss
Nathan and Maizer	1994	Estherville (sl)	coarse loamy over sandy, mixed, mesic Typic Hapludoll	urea turkey manure	field microplots, acid trap (H <sub>3</sub> BO <sub>3</sub> )	1-7% of applied N
Ouyang et al.	1998	Ste. Rosalie (c) Ormsdown (scl)	Typic Humaquept Typic Humaquept	urea urea-KCl urea-TSP	field microplots, acid trap (H <sub>2</sub> SO <sub>4</sub> )	1-8% of urea N applied
Ping et al.	2000	loam	Typic Boroll	<sup>15</sup> N urea	field microplots <sup>15</sup> N difference method	avg. 13% of applied N
Quemada et al.	1998	silty clay loam	clayey, carbonatic, calcareous, mesic, Calcixerollic Xerochrept	biosolids (sewage sludge)-DCD	lab incubation 21°C, acid trap (H <sub>3</sub> BO <sub>3</sub> )	5-71% of applied NH <sub>4</sub> <sup>+</sup> -N
Schilke-Gartley and Sims	1993	Kleij (ls)	siliceous, mesic-Aquic Quartzipsamment	poultry litter	lab incubation 23°C, acid trap (H <sub>3</sub> BO <sub>3</sub> )	4-31% of applied N
Shahandeh et al.	1992	Tifton Dothan	fine, loamy, siliceous, thermic, Plinthic Paleudults; fine loamy, siliceous, thermic Typic Hapludults	nutrasweet sludge urea, AS	lab incubation 25°C, acid trap (H <sub>3</sub> PO <sub>4</sub> )	>1-19% of applied N
Sommer et al.	1997	loamy sand		pig slurry	field plots, passive flux and acid trap	4-26% of applied NH <sub>4</sub> <sup>+</sup> -N
Watson and Kilpatrick	1991	Hillsbrough (scl), Loughry (scl), Craigavon (c), Portadown (p)		urea (pellet size)	lab incubation 10°C, acid trap	12-17% of applied N
Whitehead and Raistrick	1990	Batcombe, Hucklesbrook, Frlsham, and Andover		MAP, DAP, AS, AN, urea	lab incubation 20°C, acid trap (H <sub>2</sub> SO <sub>4</sub> )	>1-52% of applied N
Whitehead and Raistrick	1992	Frlsham (sl)		simulated livestock urine	growth chamber 21°C, acid trap (H <sub>2</sub> SO <sub>4</sub> )	23-39% of applied N

† Each study is referenced by the first author.

‡ Letters in parentheses indicate soil texture: c, clay; sil, silt loam; vgl, very gravelly loam; l, loam; lt, loam taxajunct; fs, fine sand; scl, silty clay loam; ls, loamy sand; sl, sandy loam; scd, 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; UUP, urea-urea phosphate; U, urea; DCD, dicyandiamide.

It is estimated that agricultural thropogenic NH<sub>3</sub> released an Livestock production system recognized as the major source (1987) estimated that 81% of the total estimated that livestock accounting practices (handling,

Land application of organic nutrient in question, the major cause for degradation of surface nitrogen on each objective in a given management practices that affect livestock cause increased NH<sub>3</sub> loss reduced disposal. Likewise, emphasis of management practices that affect the organic waste material N.

Although most of the nitrogen from animal excreta, appreciable nitrogen and from decomposing plant material can be emitted into the atmosphere if fertilizers are applied to soil (Demery laboratory conditions conditions can be as great as 90% when N is applied to soils with a buffering capacity (Fenn and others) are generally less, ranging from 10 to 20%. The reason for greater losses in field conditions are typically set to reduce NH<sub>3</sub> loss while these conditions in the field environment (Hargrove,

Ammonia volatilization losses can be grouped into three broad categories: volatilization from unincorporated soils with a pH greater than 7.5; surface-applied, urea-containing

Items affecting the magnitude of ammonia volatilization from organic waste material are environmental conditions, and soil pH (1994). Factors affecting NH<sub>3</sub> loss from agricultural soils are typically also affected by the magnitude of NH<sub>3</sub> volatilization capacity, cation exchange capacity, Ca<sup>2+</sup>, and urease activity (Hargrove 1994). Environmental factors affecting NH<sub>3</sub> loss are temperature, soil moisture (Hargrove 1988). Management

Author	Year	Location	Soil	Urea (pellet size)	Incubation	Losses
Kilpatrick		Loughry (scl), Craigavon (c), Portadown (p)	loamy sand; sl, sandy loam; scl, sandy clay loam; p, peaty	urea (pellet size)	lab incubation 10°C, acid trap	12-17% of applied N
Whitehead and Raistrick	1990	Batcombe, Hucklebrook, Frilsham, and Andover	loamy sand; sl, sandy loam; scl, sandy clay loam; p, peaty	MAP, DAP, AS, AN, urea	lab incubation 20°C, acid trap (H <sub>2</sub> SO <sub>4</sub> )	>1-52% of applied N
Whitehead and Raistrick	1992	Frilsham (sl)	loamy sand; sl, sandy loam; scl, sandy clay loam; p, peaty	simulated livestock urine	growth chamber 21°C, acid trap (H <sub>2</sub> SO <sub>4</sub> )	23-39% of applied N

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It is estimated that agriculture contributes between 55 and >95% of the anthropogenic NH<sub>3</sub> 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 NH<sub>3</sub>. For Europe, Buijsman et al. (1987) estimated that 81% of NH<sub>3</sub> emissions are from livestock while for China, which accounts for 55% of the NH<sub>3</sub> 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 manure 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 NH<sub>3</sub> emissions. Emphasis on the waste disposal objective often utilizes management practices that encourage NH<sub>3</sub> volatilization because increased NH<sub>3</sub> 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 NH<sub>3</sub> and improve plant N use efficiency of the organic waste material N.

Although most of the NH<sub>3</sub> 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 NH<sub>3</sub> when NH<sub>4</sub><sup>+</sup>- or urea-containing fertilizers are applied to soil (Demeyer et al., 1995). The magnitude of NH<sub>3</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub>; (ii) NH<sub>3</sub> volatilization from unincorporated, surface-applied, NH<sub>4</sub><sup>+</sup>-containing fertilizer on soils with a pH greater than 7.2; and (iii) NH<sub>3</sub> volatilization from unincorporated, surface-applied, urea-containing fertilizer (Schepers and Fox, 1989).

Items affecting the magnitude of NH<sub>3</sub> loss from soils include soil factors, environmental conditions, and fertilizer management practices (Nathan and Malzer, 1994). Factors affecting NH<sub>3</sub> volatilization losses from fertilizers applied to agricultural soils are typically also important in controlling NH<sub>3</sub> volatilization losses from organic waste material applications. Important soil factors in determining the magnitude of NH<sub>3</sub> volatilization include texture, initial soil pH, pH buffering capacity, cation exchange capacity (CEC), amount of soluble and exchangeable Ca<sup>2+</sup>, and urease activity (Hargrove 1988; Lightner et al., 1990; Nathan and Malzer, 1994). Environmental factors that are important in determining the magnitude of NH<sub>3</sub> loss are temperature, soil water content, and air exchange at the soil surface (Hargrove 1988). Management factors affecting NH<sub>3</sub> loss include time, rate, form,

and method of application, incorporation, time between application and incorporation, depth of application, irrigation, and amount of surface residue (Demeyer et al., 1995; Lightner et al., 1990; Nathan and Malzer, 1994).

### Effect of pH on Ammonia Loss

Nitrogen sources with greater potential for raising soil pH after application tend to have greater  $\text{NH}_3$  volatilization (He et al., 1999). Ammonia losses increase with higher soil pH because of the increased dissociation of  $\text{NH}_4^+$  to  $\text{NH}_3$ , thus increasing the potential for volatilization (Sharpe and Harper, 1995). The pH in microsites surrounding urea or  $\text{NH}_4^+$  salt granules may be more important in determining  $\text{NH}_3$  loss than the overall soil pH (Nelson, 1982; Stumpe et al., 1984).

With urea,  $\text{NH}_3$  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  $\text{NH}_3$  volatilization to an extent that is influenced by the initial soil pH and CEC (Whitehead and Raistrick, 1990). Hargrove (1988) concluded that the  $\text{H}^+$  buffering capacity of a soil (in this case the resistance to increasing soil pH) is more important than initial soil pH in determining potential  $\text{NH}_3$  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  $\text{NH}_3$  will be volatilized. Ferguson et al. (1984) found that the amount of  $\text{H}^+$  buffering capacity between a soil's initial pH and a pH of around 7.5 would be more directly related to the expected  $\text{NH}_3$  loss than a soil's initial pH when urea is applied.

Buffering capacity can also influence  $\text{NH}_3$  volatilization in the opposite way. Normally,  $\text{H}^+$  ions resulting from the nitrification process will lower the soil pH and reduce the potential for  $\text{NH}_3$  volatilization. If the initial soil pH is sufficiently high for appreciable  $\text{NH}_3$  volatilization to occur ( $>7.5$ ), then the soil's buffering capacity against a decrease in pH influences  $\text{NH}_3$  volatilization by allowing it to occur over a longer period of time before the soil's pH is reduced sufficiently to stop  $\text{NH}_3$  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  $\text{H}^+$  buffering capacity and CEC are related, soil CEC is also important for  $\text{NH}_3$  volatilization because it provides a mechanism by which  $\text{NH}_4^+$  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  $\text{H}^+$  buffering capacity in terms of magnitude of  $\text{NH}_3$  loss (Rachhpal-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  $\text{NH}_3$  loss (Al-Kanani et al., 1991; Hargrove, 1988; Whitehead and Raistrick, 1990). The reduction in  $\text{NH}_3$  loss is usually ascribed to

□ Gaseous Losses other than thro

the relative contribution of the ( Kanani et al., 1991; O'Toole et al. the effect of clay content on N. approached air dryness.

### Effect of Urea

Almost all agricultural soil of urease for fairly rapid hydrolysis of urease activity, applied urea will be deeper into the soil (Rachhpal  $\text{NH}_3$  loss potentials because of soil surface along with the associated vegetation and crop residue are and Sims, 1993). McInnes et al. *cum aestivum* L.) straw was 20 times since the soils last received urease activity (Whitehead and Raistrick).

### Effect of Temperature

He et al. (1999) found that twofold when the temperature increased from 25 to 45°C compared to volatilization at 45°C compared to volatilization over a period of time. Temperature influences the major factors:

- It increases urease activity and hydrolysis rate results in  $\text{NH}_3$  near the soil surface.
- It influences the  $\text{NH}_4^+/\text{N}$  in solution and  $\text{NH}_3$  gas, being present as  $\text{NH}_3$  gas.
- It influences the diffusivity of  $\text{NH}_3$  gas.
- It increases the solubility of  $\text{NH}_3$  in aqueous soils.

### Effect of Soil Water Content

The influence of soil water content on  $\text{NH}_3$  volatilization is forward for laboratory studies. Soil moisture content, a lower moisture content, a higher pH effect resulting in higher  $\text{NH}_3$  volatilization rates (Demeyer et al., 1995). Soil water content on  $\text{NH}_3$  volatilization is complex and has been difficult to study. Soil water content fluctuates widely and has been difficult to control. Forward movement of water in the soil (Whitehead and Raistrick, 1990; Bouwmeester et al. (1988).

between application and incorporation of surface residue (Demeyer et al., 1994).

### Soil pH and Ammonia Loss

Raising soil pH after application (Demeyer et al., 1999). Ammonia losses increase with the dissociation of  $\text{NH}_4^+$  to  $\text{NH}_3$ , thus pH and Harper, 1995). The pH in soils may be more important in determining ammonia loss (Demeyer et al., 1994; Stumpe et al., 1984).

After hydrolysis to ammonium ion, urease. The optimum pH for soil urease activity (Mackenzie, 1993). The ammonium ion generates a localized increase in pH to an extent that is influenced by soil texture (Trick, 1990). Hargrove (1988) concluded that in this case the resistance to increase in pH in determining potential  $\text{NH}_3$  volatilization is high, the pH rise due to the amount of  $\text{NH}_3$  will be volatilized.  $\text{H}^+$  buffering capacity between a soil and a more directly related to the urea is applied.

Volatilization in the opposite way. A process will lower the soil pH if the initial soil pH is sufficiently high (>7.5), then the soil's buffering capacity will allow it to reduce its pH sufficiently to increase urease activity (Hargrove, 1988). As such, the buffering capacity (hydrolysis) is most important in soils against a decrease in pH (mainly in calcareous soils (Hargrove, 1988).

### Soil CEC and Ammonia Loss

As related, soil CEC is also an important mechanism by which  $\text{NH}_4^+$  ions are held. The total amount of ammoniacal N subject to volatilization (Hargrove, 1988; Trick, 1990).  $\text{H}^+$  buffering capacity in terms of soil pH (Trick, 1990).

### Soil OM and Ammonia Loss

Increased organic matter (OM) in soil (Al-Kanani et al., 1991; Hargrove, 1988; Trick, 1990).  $\text{NH}_3$  loss is usually ascribed to

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  $\text{NH}_3$  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 fairly 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  $\text{NH}_3$  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  $\text{NH}_3$  volatilization increased twofold when the temperature increased from 5 to 25°C, and threefold when temperature increased from 25 to 45°C. They concluded the greatly enhanced  $\text{NH}_3$  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  $\text{NH}_3$  volatilization over a prolonged period of time. Hargrove (1988) reported temperature influences the magnitude of  $\text{NH}_3$  loss in several ways:

- It increases urease activity, thereby increasing urea hydrolysis rate. A faster hydrolysis rate results in higher soil pH and greater  $\text{NH}_4^+$  concentrations near the soil surface.
- It influences the  $\text{NH}_4^+/\text{NH}_3$  equilibrium and the equilibrium between  $\text{NH}_3$  in solution and  $\text{NH}_3$  gas, resulting in a higher proportion of ammoniacal N being present as  $\text{NH}_3$  gas.
- It influences the diffusion of urea- and ammoniacal N and bicarbonate ions.
- It increases the solubility of  $\text{CaCO}_3$  and of Ca reaction products in calcareous soils.

### Effect of Soil Water Content on Ammonia Loss

The influence of soil water content on  $\text{NH}_3$  volatilization is generally straightforward for laboratory studies. If the hydrolysis of urea is not inhibited by the low moisture content, a lower moisture content means a higher  $\text{NH}_3$  concentration and a higher pH effect resulting in the largest total  $\text{NH}_3$  losses and highest average  $\text{NH}_3$  volatilization rates (Demeyer et al., 1995). On the other hand, the influence of soil water content on  $\text{NH}_3$  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  $\text{NH}_3$  losses occurred

when wet soil conditions were maintained by air humidities between 80 and 95% with essentially no rainfall. The diurnal pattern of  $\text{NH}_3$  volatilization loss, with maximum loss near midday, is associated with temperature increases and dew water evaporation that results in increases in  $\text{NH}_4^+$ -N concentration in the aqueous phase and in the partial pressure gradient of  $\text{NH}_3$ , leading to enhanced  $\text{NH}_3$  volatilization (Lightner et al., 1990; Nathan and Malzer, 1994).

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

- For maximum  $\text{NH}_3$  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  $\text{NH}_3$  loss rates occur when the soil surface is drying. As the soil dries, the concentration of  $\text{NH}_3$  in the soil solution increases resulting in  $\text{NH}_3$  being lost to the atmosphere to maintain equilibrium with  $\text{NH}_4^+$ . Slow drying of a wet soil results in more  $\text{NH}_3$  loss than rapid drying.
- If the soil surface dries but is not rewetted by dew or light rainfall,  $\text{NH}_3$  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,  $\text{NH}_3$  volatilization ceases.

### Effect of Wind Speed on Ammonia Loss

If a steady supply of  $\text{NH}_3$  is available, increasing wind speed would promote more rapid transport of  $\text{NH}_3$  away from the soil surface by maintaining a lower partial pressure of  $\text{NH}_3$  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  $\text{NH}_3$  at the soil surface, resulting in higher  $\text{NH}_3$  volatilization. Bouwmeester et al. (1985) noted that wind can impede the volatilization of  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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,  $\text{NH}_3$  losses increase with increasing amounts of urea or  $\text{NH}_4^+$  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,

□ Gaseous Losses other than through

tion, the  $\text{NH}_3$  loss potential for fertilizer urea-ammonium nitrate (UAN) is greater in calcareous soils, but greatest with (N) calcareous soils.

A number of chemical or physical methods to reduce  $\text{NH}_3$  volatilization losses have been reported. These methods include: (i) coating urea to slow urea hydrolysis that retard hydrolysis of urea by physical and/or chemical characteristics; (ii) addition of acidifying agents to urea to form soluble salts of Ca, Mg, and/or K carbonates and thereby reduce  $\text{NH}_3$  loss (Buresh and Baanante, 1993; Al-Jarrah et al., 1994). These methods have been successful in the development of additives that are both effective and inexpensive in improving the efficiency of urea.

Maximum  $\text{NH}_3$  losses occur when urea is broadcast on the soil surface. Band application and incorporation reduce  $\text{NH}_3$  losses. Significant reduction in  $\text{NH}_3$  losses may be expected because bands are exposed to fewer environmental conditions than broadcast loss (Black et al., 1987; Watson et al., 1994). Incorporation of animal waste slurries into the soil by tilling (Sommer et al., 1997). One study showed that slurries promotes infiltration.

Direct injection or incorporation of urea reduces  $\text{NH}_3$  loss (Hargrove, 1988). Bouwmeester et al. (1985) reported that if 2.5 cm of water was applied immediately after injecting urea at a depth of 2.5 cm. Soil moisture losses from injected anhydrous ammonia were reduced to a depth of at least 5 cm. The depth to which incorporation is affected completely. The depth to which incorporation is affected depends on soil characteristics; such as texture, soil moisture, and soil temperature. The factor is from 5 to 10 cm (Hargrove, 1988). The factor in  $\text{NH}_3$  volatilization which is affected by injecting with anhydrous ammonia is 50% of the  $\text{NH}_3$  can be lost when a large portion of the injected N is incorporated. Upward movement of the water reduces  $\text{NH}_3$  losses. It has also been demonstrated that slurry injected directly into a core of soil for the same reasons (Sommer and Erskine, 1994).

Ammonia volatilization is a function of soil moisture on the soil surface. However, tillage and soil moisture affect  $\text{NH}_3$  volatilization. Clay and soil moisture daily maximum soil temperature

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## Ammonia Loss

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## Factors on Ammonia Loss

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g amounts of urea or  $\text{NH}_4^+$  add- es may be linear or exponential plied N) may decrease, remain rates (Hargrove, 1988). In addi-

tion, the  $\text{NH}_3$  loss potential for fertilizers is greatest with urea, intermediate with urea-ammonium nitrate (UAN) solution, and least with  $\text{NH}_4^+$  salts on noncalcareous soils, but greatest with  $(\text{NH}_4)_2\text{SO}_4$  and much less with urea or  $\text{NH}_4\text{NO}_3$  on calcareous soils.

A number of chemical or fertilizer modification methods have been used to reduce  $\text{NH}_3$  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 microenvironment with the addition of acidifying agents to decrease  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  losses. Significant reduction in  $\text{NH}_3$  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  $\text{NH}_3$  loss (Black et al., 1987; Watson and Kilpatrick 1991). However, surface band application of animal waste slurries has shown significant reduction in  $\text{NH}_3$  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  $\text{NH}_3$  loss (Hargrove, 1988). Bouwmeester et al. (1985) found no  $\text{NH}_3$  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  $\text{NH}_3$  can be assumed to be minimal if the  $\text{NH}_3$  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  $\text{NH}_3$  volatilization when direct injecting N supplying materials. Working with anhydrous ammonia, Sommer and Christensen (1992) found that up to 50% of the  $\text{NH}_3$  can be lost when injected into a wet soil. They concluded that a large portion of the injected  $\text{NH}_3$  is retained by absorption in the soil water and upward movement of the water due to evaporation may be the cause of the large  $\text{NH}_3$  losses. It has also been demonstrated that  $\text{NH}_3$  loss may be high from animal slurry injected directly into a compressed and excessively wet soil for some of the same reasons (Sommer and Erbsoll, 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  $\text{NH}_3$  volatilization. Clay et al. (1990) reported that residue cover reduced the daily maximum soil temperature and increased the soil water content resulting in

reduced  $\text{NH}_3$  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 urease 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  $\text{NH}_3$  losses in several ways:

- By its associated higher urease 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  $\text{NH}_3$  volatilization by increasing the surface area for urease activity and volatilization to occur. Fenn and Hossner (1985) suggest that higher urease 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 urease degradation.

Living plants can also be great modifiers and significantly influence volatile  $\text{NH}_3$  loss from soils. Actively growing plants influence both the soil's temperature and water regimes and also can have strong effects on the soil-air boundary layer. The plant's ability to both absorb and release atmospheric  $\text{NH}_3$  must be taken into account. Foliar absorption of  $\text{NH}_3$  contributed significantly to the reduction in  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  volatilization under field conditions.

### Ammonia Loss from Plants

Farquhar et al. (1980) were one of the first to report on the existence of an  $\text{NH}_3$  compensation point for plants. The compensation point for  $\text{NH}_3$  is defined as the molar fraction at which the net exchange between plants and the atmosphere is zero. The existence of an  $\text{NH}_3$  compensation point implies that vegetation has a major influence on the transport and budgets of atmospheric  $\text{NH}_3$  (Nielsen and Schjoerring, 1998). The  $\text{NH}_3$  compensation point allows plants to act as both sink and source for atmospheric  $\text{NH}_3$ . At ambient  $\text{NH}_3$  concentrations above the compensation point,  $\text{NH}_3$  is absorbed by leaves, while at concentrations below the compensation point  $\text{NH}_3$  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 (Lea, 1997). As a consequence, substantial concentrations of  $\text{NH}_4^+$  may exist in the leaf and in the apoplastic solution. The concentration of  $\text{NH}_4^+$  and  $\text{H}^+$  in the leaf apoplastic solution determines the size of the  $\text{NH}_3$  compensation point (Husted and Schjoerring, 1996). It is generally accepted that free  $\text{NH}_3$  can diffuse across leaf cell membranes

□ Gaseous Losses other than thr

without the involvement of a nium is constantly generated i as photorespiration, nitrate re (Leegood et al., 1995). For plan  $\text{NH}_4^+$  released during these ca cated directly to the leaves fro

The major pathway of  $\text{NH}_3$  the glutamine synthetase/gluta chloroplast (Schjoerring et al., 1 a transporter with channel-like idly to changes in apoplastic N with mutants of barley (*Hordeu significance of GS in controlling Schjoerring et al. (2000) also re)stantial increase in apoplastic N high  $\text{NH}_3$  compensation points tus, rapid absorption of  $\text{NH}_4^+$  fr  $\text{NH}_4^+$  is constantly generated in ties are critical in controlling N.*

### Factors Influenci

The  $\text{NH}_3$  compensation p of physiological and environm nitide and direction of the  $\text{NH}_3$  scales, depending on environn timing of fertilizer application of the major factors influencing

### Nitrogen Status and pH

Theoretically, the  $\text{NH}_3$  can be determined by knowing the face (apoplast). Husted and Sc trations for oilseed rape plants with plant N status while apop independent of plant N status ; difference in apoplastic pH of 1  $\text{H}^+$  concentrations in the apopl for most plants, a lower pH in will still play an important rol Even under conditions in whic times lower than the extracellu 7.5) and in the chloroplasts (ap plastic solution (approximatel directed toward the apoplast (f

The loss of  $\text{NH}_3$  from the tus of the canopy for wheat (M 1993), oilseed rape (Husted an The concentration of  $\text{NH}_4^+$  in t

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## Plants

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nd that can be used directly as lucts in plants (Lea, 1997). As a may exist in the leaf and in the d  $\text{H}^+$  in the leaf apoplastic solu- point (Husted and Schjoerring, fuse across leaf cell membranes

without the involvement of a membrane translocator (Baron et al., 1994). Ammonium is constantly generated in large quantities in plant leaves by processes such as photorespiration, nitrate reduction, protein turnover, and lignin biosynthesis (Leegood et al., 1995). For plants to efficiently utilize N they must be able to recycle  $\text{NH}_4^+$  released during these catabolic reactions. In addition,  $\text{NH}_4^+$  may be translocated directly to the leaves from the roots (Cramer and Lewis, 1993).

The major pathway of  $\text{NH}_4^+$  assimilation and reassimilation in plant leaves is the glutamine synthetase/glutamate synthase (GS/GOGAT) cycle occurring in the chloroplast (Schjoerring et al., 1998). Ammonium is retrieved by a system involving a transporter with channel-like properties that seem to be able to respond very rapidly to changes in apoplastic  $\text{NH}_4^+$  concentration (Schjoerring 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  $\text{NH}_3$  between plants and the atmosphere. Schjoerring et al. (2000) also reported that inhibition of GS leads to a rapid and substantial increase in apoplastic  $\text{NH}_4^+$  concentration. Schjoerring et al. (1998) noted that high  $\text{NH}_3$  compensation points seemed to always be the result of high tissue N status, rapid absorption of  $\text{NH}_4^+$  from the root medium and/or low activity of GS. Since  $\text{NH}_4^+$  is constantly generated in large amounts in leaf tissues, GS and GOGAT activities are critical in controlling  $\text{NH}_3$  emission from plant leaves.

## Factors Influencing Ammonia Losses from Plants

The  $\text{NH}_3$  compensation point is a variable parameter influenced by a range of physiological and environmental conditions (Schjoerring et al., 1998). The magnitude and direction of the  $\text{NH}_3$  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  $\text{NH}_3$  losses from plants will be covered.

### Nitrogen Status and pH

Theoretically, the  $\text{NH}_3$  compensation point at any given leaf temperature can be determined by knowing the concentration of  $\text{NH}_4^+$  and  $\text{H}^+$  in the aqueous interface (apoplast). Husted and Schjoerring (1996) reported apoplastic  $\text{NH}_4^+$  concentrations 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  $\text{NO}_3^-$  or  $\text{NH}_4^+$  as the N source. If  $\text{H}^+$  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  $\text{NH}_3$  within leaves. Even under conditions in which the intracellular  $\text{NH}_4^+$  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  $\text{NH}_3$  directed toward the apoplast (Nielsen and Schjoerring, 1998).

The loss of  $\text{NH}_3$  from the canopy has been found to increase with the N status of the canopy for wheat (Morgan and Parton, 1989), barley (Schjoerring et al., 1993), oilseed rape (Husted and Schjoerring, 1996), and corn (Francis et al., 1993). The concentration of  $\text{NH}_4^+$  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  $\text{NH}_4^+$  concentration and also increased apoplastic  $\text{NH}_4^+$  concentration at all growth states. Mattsson and Schjoerring (1996) found that plants having access to  $\text{NH}_4^+$  in the root medium had higher apoplastic  $\text{NH}_4^+$  concentrations than plants absorbing  $\text{NO}_3^-$ , and that leaf apoplastic  $\text{NH}_4^+$  concentration increases with  $\text{NH}_4^+$  concentration in the root medium.

### Growth Stage

Bulk tissue  $\text{NH}_4^+$  concentrations change with plant ontogeny. Morgan and Parton (1989) attribute increased potential for  $\text{NH}_3$  volatilization during later developmental stages to genetic changes in plant metabolism that elevated tissue  $\text{NH}_4^+$  concentrations above those occurring in younger, vegetative tissue. They related periods of increased  $\text{NH}_3$  volatilization from anthesis through maturity to changes in the balance between  $\text{NH}_4^+$ -releasing reactions (deamination, senescence-induced proteolysis, and nitrate reduction) and  $\text{NH}_4^+$  uptake reactions (N transport and  $\text{NH}_4^+$  assimilation). As the balance shifts in favor of  $\text{NH}_4^+$ -releasing reactions, there is the establishment of new, higher, steady-state tissue  $\text{NH}_4^+$  concentrations. Schjoerring et al. (1998) also reported that the  $\text{NH}_3$  compensation point depends on plant developmental stage with peaks in  $\text{NH}_3$  emission related to leaf senescence and N remobilization.

### Temperature

The high sensitivity of plant-atmosphere  $\text{NH}_3$  exchange to leaf temperature makes information about temperature very important when data on  $\text{NH}_3$  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 vapors and may constitute a defense mechanism of plants against  $\text{NH}_3$  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  $\text{NH}_3$  to being significant  $\text{NH}_3$  sources. Husted and Schjoerring (1996) reported increasing leaf temperatures from 10 to 35°C caused an exponential increase in  $\text{NH}_3$  emission from plants exposed to low ambient  $\text{NH}_3$  concentrations, indicating that leaf conductance was not the only factor responding to the temperature increase. They noted when simple thermodynamics equations were used in combination with  $\text{NH}_3$  compensation points derived from measurements of apoplastic  $\text{NH}_4^+$  concentrations, increased  $\text{NH}_3$  emissions with increasing temperature could be explained in their study entirely in terms of effects on the equilibrium between gas phase and soluble  $\text{NH}_3$  and  $\text{NH}_4^+$  in the apoplast. The profound influence of temperature on plant-atmosphere  $\text{NH}_3$  exchange is partly via affecting the concentration of atmospheric  $\text{NH}_3$  in equilibrium with  $\text{NH}_3$  in the apoplastic solution, and partly via affecting the physiological processes generating or assimilating  $\text{NH}_4^+$  in the leaf tissues (Schjoerring et al., 1998).

□ Gaseous Losses other than thro

### Wind, Humidity, and Light

In addition to temperature light intensity can influence plant delivery to or removal of  $\text{NH}_3$  from between leaves and air will prevent such a layer will slow down the  $\text{NH}_3$  losses (Holtan-Hartwig and variations in light intensity and a (1996) observed that at low relative humidity at low light intensity of apertures,  $\text{NH}_3$  uptake did not occur in a dry atmosphere compared with a humid atmosphere favored by high light intensities be found under dry atmosphere (Husted and Schjoerring, 1996). control mechanism for the regulation of conductance for  $\text{NH}_3$  d

It is generally reported that  $\text{NH}_3$  emission near midday and Bockman, 1994). Strong diurnal trends in  $\text{NH}_3$  emission have been reported in  $\text{C}_3$  plants. free  $\text{NH}_3$  that must pass out of the leaf via the GAT pathway (Leegood et al., 1992) is very large with rates up to 10 g N m<sup>-2</sup> d<sup>-1</sup> (Joy et al., 1992). Holtan-Hartwig (1996) probably is the effect of light on stomatal conductance on the diurnal trend in  $\text{NH}_3$  exchange. diurnal variations in  $\text{NH}_3$  exchange are strongly temperature along with stomatal conductance.  $\text{NH}_4^+$  and  $\text{H}^+$  in the leaf are absent in  $\text{C}_4$  plants and the major source of  $\text{NH}_3$  in  $\text{C}_4$  plants is generally much less than in  $\text{C}_3$  and  $\text{C}_4$  plants would still be a function of temperature and concentration (Leegood et al., 1992). diurnal trends in  $\text{NH}_3$  emission

### Atmospheric Ammonia Compensation Point

Ambient  $\text{NH}_3$  concentration affects the  $\text{NH}_3$  compensation point in the absence of other factors (Leegood et al., 1992). Increased livestock production has led to increased  $\text{NH}_3$  emissions from agricultural sources and atmospheric  $\text{NH}_3$  concentrations have increased between leaves and ambient air. ApSimon et al. (1992) reported emissions over Europe between 1950 and 1990. Agricultural practices. This would serve as net sinks for atmospheric  $\text{NH}_3$ . ice core data from central Greenland (Leegood et al., 1992).

Schjoerring, 1998). Husted and Schjoerring (1996) reported that plants having access to  $\text{NH}_4^+$  concentrations than plants without access to  $\text{NH}_4^+$  concentration increases with  $\text{NH}_4^+$

with plant ontogeny. Morgan and Schjoerring (1996) reported that elevated tissue  $\text{NH}_3$  volatilization during later development in younger, vegetative tissue. They reported that  $\text{NH}_3$  exchange rates during anthesis through maturity (deamination, senescence) and  $\text{NH}_4^+$  uptake reactions (N assimilation) shifts in favor of  $\text{NH}_4^+$ -release. They reported that the  $\text{NH}_3$  compensation point is higher, steady-state tissue  $\text{NH}_4^+$  concentration is lower, and  $\text{NH}_3$  emission peaks in  $\text{NH}_3$  emission related

$\text{NH}_3$  exchange to leaf temperature is important when data on  $\text{NH}_3$  compensation point are available (Husted and Schjoerring, 1996). In one of the earliest studies, Stutte and da Silva (1981) reported that at 35°C greatly increased the rate of  $\text{NH}_3$  exchange in cultivars tested. Based on their results in conjunction with transpirational cooling, they concluded that stomatal closure of plants against  $\text{NH}_3$  toxicity (Schjoerring et al., 1998) also noted that simply increasing ambient  $\text{NH}_3$  concentrations to switch from being strong  $\text{NH}_3$  sources. Husted and Schjoerring (1996) reported that a 10 to 35°C caused an exponential increase in  $\text{NH}_3$  exchange. At low ambient  $\text{NH}_3$  concentrations, a temperature factor responding to the temperature dependence of  $\text{NH}_3$  exchange was used in conjunction with measurements of stomatal conductance with increasing temperature to predict the effects on the equilibrium  $\text{NH}_3$  concentration in the apoplast. The profound influence of temperature on  $\text{NH}_3$  exchange is partly via affecting the concentration of  $\text{NH}_3$  in the apoplast, and partly via generating or assimilating  $\text{NH}_4^+$

## Wind, Humidity, and Light Intensity

In addition to temperature, various parameters such as wind, humidity, and light intensity can influence plant-atmosphere  $\text{NH}_3$  fluxes. Wind will affect the delivery to or removal of  $\text{NH}_3$  from the exchange surface. A stagnant boundary layer between leaves and air will prevent  $\text{NH}_3$  diffusion, and circumstances that preserve such a layer will slow down the exchange rate while gusty winds may enhance  $\text{NH}_3$  losses (Holtan-Hartwig and Bockman, 1994). Studying the combined effects of variations in light intensity and air humidity on  $\text{NH}_3$  fluxes, Husted and Schjoerring (1996) observed that at low relative humidity (20%)  $\text{NH}_3$  absorption reached a maximum at low light intensity of approximately  $350 \mu\text{mol m}^{-2} \text{s}^{-1}$ , whereas at higher air humidities,  $\text{NH}_3$  uptake did not saturate below  $600 \mu\text{mol m}^{-2} \text{s}^{-1}$ . This reflects that stomata in a dry atmosphere reached full aperture at low light intensity as compared with a humid atmosphere. Under humid conditions  $\text{NH}_3$  exchange would be favored by high light intensities, whereas relatively large  $\text{NH}_3$  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  $\text{NH}_3$  flux into or out of leaves because of its effect on conductance for  $\text{NH}_3$  diffusion (Schjoerring et al., 1998).

It is generally reported that  $\text{NH}_3$  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  $\text{C}_3$  plants. Each photorespiration cycle in  $\text{C}_3$  plants yields a free  $\text{NH}_3$  that must pass out of the mitochondria for reassimilation by the GS/GOGAT pathway (Leegood et al., 1995). The rate of  $\text{NH}_3$  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  $\text{NH}_3$  exchange. However, Schjoerring et al. (2000) report that diurnal variations in  $\text{NH}_3$  exchange seem to be caused mainly by changes in leaf temperature along with stomatal conductance rather than changes in concentrations of  $\text{NH}_4^+$  and  $\text{H}^+$  in the leaf apoplast solution. Photorespiration is essentially absent in  $\text{C}_4$  plants and the magnitude for diurnal trends in  $\text{NH}_3$  emission from  $\text{C}_4$  plants is generally much less than for  $\text{C}_3$  plants. Comparing  $\text{NH}_3$  emissions between  $\text{C}_3$  and  $\text{C}_4$  plants would suggest that stomatal conductance along with both temperature and concentration ( $\text{NH}_3$  release activities) combine to cause the larger diurnal trends in  $\text{NH}_3$  emission from  $\text{C}_3$  vs.  $\text{C}_4$  plants.

## Atmospheric Ammonia Concentration

Ambient  $\text{NH}_3$  concentrations near the canopy should approach the  $\text{NH}_3$  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  $\text{NH}_3$  emissions from agricultural activities that would produce increased atmospheric  $\text{NH}_3$  concentrations resulting in lower concentration gradients between leaves and ambient air. ApSimon et al. (1987) reported a 50% increase in  $\text{NH}_3$  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  $\text{NH}_3$  over the last 50 yr. However, in studying ice core data from central Greenland, Laj et al. (1992) concluded that atmospheric

$\text{NH}_3$  concentrations have actually decreased over the last 50 yr. Their explanation for decreasing atmospheric  $\text{NH}_3$  concentrations is the rapid reactions between atmospheric  $\text{NH}_3$  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  $\text{NH}_3$  concentrations would enhance  $\text{NH}_3$  losses from crop canopies.

Concentrations of  $\text{NH}_3\text{-N}$  in air in rural areas is generally within the range from 1 to 14  $\mu\text{g m}^{-3}$ , with about 1 to 6  $\mu\text{g m}^{-3}$  as typical (Holtan-Hartwig and Bockman, 1994). Farquhar et al. (1980) found the  $\text{NH}_3$  compensation point for young plants of several species to be about 1 to 4  $\mu\text{g NH}_3\text{-N m}^{-3}$ . When the  $\text{NH}_3$  compensation point fluctuates about the atmospheric  $\text{NH}_3$  concentration,  $\text{NH}_3$  may be either 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  $\mu\text{g NH}_3\text{-N m}^{-3}$  at early grain filling, to 23  $\mu\text{g NH}_3\text{-N m}^{-3}$  at late grain filling. Mattsson et al. (1998) showed approximately a 10-fold increase in  $\text{NH}_3$  compensation point, 2.5 to 26  $\mu\text{g NH}_3\text{-N m}^{-3}$ , for oilseed rape when going from low to high external N supply. The  $\text{NH}_3$  concentration gradient between the atmosphere and the leaf apoplastic solution stands as the major driving force for  $\text{NH}_3$  gains and losses in plants.

### Carbon Substrates and Plant Stress

Assimilation of  $\text{NH}_4^+$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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,  $\text{NH}_3$  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  $\text{NH}_3$  exchange between air and crops can be grouped in three main categories and all have problems estimating annual  $\text{NH}_3$  emissions from plants. Enclosure or chamber methods have difficulty matching natural factors that have important influences on the volatilization of  $\text{NH}_3$  over the full growth cycle, such as evaporation rate, temperature, wind speed, ambient  $\text{NH}_3$  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  $\text{NH}_3$  losses from plants, but give a combined

$\text{NH}_3$  flux from plants and soil. The quantity of aboveground plant N losses can be masked by concurrent losses from the soil. This also cannot differentiate if N is lost from the soil or from the plant. Used with standing N methods, the method of substitution occurs and substitution occurs. This is a problematic error in estimation (1997; Harper and Sharpe, 1998).

The bidirectional nature of  $\text{NH}_3$  exchange and the large spatial variability in  $\text{NH}_3$  exchange make the extrapolation of current N losses to a landscape scale a speculative exercise. We provide a comprehensive list of the magnitude of N losses found for different plant species and developmental stages. Reported studies are from cereals and Bockman, (1994) found total  $\text{NH}_3\text{-N ha}^{-1} \text{ d}^{-1}$ , but conclude that yearly losses as emissions are dependent on plant development stage. We estimate for net  $\text{NH}_3$  losses from crops to be 1 to 7 kg  $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  if the crop is harvested during the grain filling period.

Schjoerring et al. (2000) represent a net source of  $\text{NH}_3$  to the atmosphere below 1 up to 7 kg  $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  conditions. They further state that up to 5% of the shoot N content is lost if fertilizer or manure is applied (Holtan-Hartwig and Bockman, 1994).

With most of the informal studies conducted in northern Europe, annual loss values also represent a range of studies reporting the largest  $\text{NH}_3$  losses from northern or midlatitude type of location, low humidity and cold temperatures. The high N losses from some cereals (Papakosta and Gagianas (1991) and Francis et al. (1998)) and from grasses (kg  $\text{NH}_3\text{-N ha}^{-1}$ ). The large N losses from crops are however a rare phenomenon and that it may be substantial. This increases the potential for  $\text{NH}_3$  emissions from crops.

Temperature differences between northern Europe and northern USA would result in higher losses from crops grown in the USA. The temperature differences between Spring and Summer in the UK, two sites where numerous studies have been performed, there is typically a

the last 50 yr. Their explanation is the rapid reactions between each themselves have increased in 10 yr. Reactions decreasing atmospheric losses from crop canopies.

Losses is generally within the range of 10-20% (Holtan-Hartwig and Bockman, 1994). Compensation point for young plants is  $10 \mu\text{g NH}_3\text{-N m}^{-3}$ . When the  $\text{NH}_3$  concentration,  $\text{NH}_3$  may increase as plants approach maturity, to  $23 \mu\text{g NH}_3\text{-N m}^{-3}$  at approximately a 10-fold increase in concentration gradient between the plants as the major driving force for

the supply of C in the form of 2-oxo-tricarboxylic acid cycle (Schroeder) may also determine the utilization of N during the replot photosynthetic conditions (e.g., active to C and result in  $\text{NH}_3$  losses). Papakosta and Gagianas (1991) noted a decrease in grain yield for winter wheat reported similar findings that  $\text{NH}_3$  in grain N content and total shoot N when favorable climatic conditions) and effective deposition in the soil. Therefore,  $\text{NH}_3$  emission will be at control C substrate production

### Cultural Plants

Problems between air and crops can be problems estimating annual  $\text{NH}_3$  losses. Methods have difficulty matching the volatilization of  $\text{NH}_3$  over temperature, wind speed, ambient (Holtan-Hartwig and Bockman, 1994). Methods have problems with temperature and the requirement for uniform, dimensional vertical flux densities. Traditional micrometeorological techniques from plants, but give a combined

$\text{NH}_3$  flux from plants and soil. Standing N methods measure changes in total N quantity of aboveground plant parts at different developmental stages, but N losses can be masked by concurrent uptake of N by the roots. Standing N methods also cannot differentiate if N is lost as  $\text{NH}_3$  or in other ways. Isotopic N has been used with standing N methods to evaluate N loss pathways, but isotope fractionation and substitution occurring during foliar emission and reabsorption cause problematic errors in estimating annual  $\text{NH}_3$  emissions from plants (Francis et al., 1997; Harper and Sharpe, 1998).

The bidirectional nature of  $\text{NH}_3$  exchange between plants and air along with the large spatial variability in ambient  $\text{NH}_3$  concentrations and land use makes the extrapolation of current  $\text{NH}_3$  exchange data to annual net  $\text{NH}_3$  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  $\text{g NH}_3\text{-N ha}^{-1} \text{d}^{-1}$ , 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  $1.5 \text{ kg NH}_3\text{-N ha}^{-1} \text{yr}^{-1}$  as a rough estimate for net  $\text{NH}_3$  losses from arable crops and that this value may increase to  $6 \text{ kg NH}_3\text{-N ha}^{-1} \text{yr}^{-1}$  if the crop is severely stressed by disease or adverse weather during the grain filling period.

Schjoerring et al. (2000) report that plant communities on arable cropland represent a net source of  $\text{NH}_3$  to the atmosphere with net emissions ranging from below 1 up to  $7 \text{ kg NH}_3\text{-N ha}^{-1} \text{season}^{-1}$ , depending on plant N status and climatic conditions. They further state that  $\text{NH}_3$  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  $\text{NH}_3$  emissions from crops coming from studies conducted in northern Europe on  $\text{C}_3$  plants, the question becomes are these annual loss values also representative for warmer climates and  $\text{C}_4$  plants? Studies reporting the largest  $\text{NH}_3$  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  $75 \text{ kg NH}_3\text{-N ha}^{-1}$ . The large N losses reported in these studies may be nontypical, however the number of studies reporting large N losses indicates that this is not a rare phenomenon and that under certain conditions  $\text{NH}_3$  loss and exchange can be substantial. This increases the degree of uncertainty in estimating annual  $\text{NH}_3$  emissions from crops.

Temperature differences during the summer months between central USA and northern Europe would suggest a greater opportunity for  $\text{NH}_3$  emissions from crops grown in the USA. If one compares June, July, and August ambient air temperatures between Springfield, IL, and Copenhagen, Denmark, or Edinburgh, UK, two sites where numerous studies on  $\text{NH}_3$  emissions from crops have been performed, there is typically over a  $10^\circ\text{C}$  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  $\text{NH}_3$  emissions range, the estimated range for Springfield, IL, would be 1 to 25 kg  $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ . Estimating annual  $\text{NH}_3$  emissions from crops carries a substantial degree of uncertainty and will require considerable work to be done before we fully understand  $\text{NH}_3$  exchange between crops and the atmosphere.

In addition to normal leaf and canopy cycling of  $\text{NH}_3$ , soils and plant residues can act as sources and sinks for  $\text{NH}_3$ , thereby increasing the complexity of determining net annual  $\text{NH}_3$  exchange between agricultural crops and the atmosphere. Fertilizers and livestock husbandry are typically considered the major contributors of  $\text{NH}_3$  to the atmosphere and plants nearly insignificant contributors. However, the sheer number of plants spread across the landscape and the bidirectional nature of  $\text{NH}_3$  exchange between plants and air suggests plants play a crucial role in atmospheric  $\text{NH}_3$  concentrations. In Hungary, Horvath and Sutton (1998) found no apparent decrease in atmospheric concentrations of  $\text{NH}_3$  and  $\text{NH}_4^+$  when pig and cattle numbers were reduced 49 and 47%, respectively, over a 10-yr period. Holtan-Hartwig and Bockman, (1994) expressed reservations about the possible occurrence of high seasonal emissions of  $\text{NH}_3$  from crops, stating a loss of 15 kg  $\text{NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  from crops would represent about 30% of total  $\text{NH}_3$  emissions from Western Europe. In some cases the assigning of  $\text{NH}_3$  source may be just a matter of semantics. As an example, if application of fertilizer or manure exacerbates the loss of  $\text{NH}_3$  from plants an argument can be made for either the plant or N supplying material as being the  $\text{NH}_3$  source.

### Emissions from Dead Agricultural Plants

Decomposing plant material and herbage cut for hay, silage or mulch undoubtedly contributes to the emission of  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3\text{-N m}^{-2} \text{ s}^{-1}$ .

Janzen and McGinn (1991) found as much as 14% of the N in a legume green manure was volatilized as  $\text{NH}_3$  within 14 d of application. Incorporation of green manure material into the soil effectively prevented volatile loss of  $\text{NH}_3$ , but incorporation greatly reduces its effectiveness as a measure to control erosion and conserve moisture (Janzen and McGinn, 1991). Larsson et al. (1998) reported  $\text{NH}_3$  losses from herbage mulch 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  $\text{NH}_3$  from cut herbage of perennial ryegrass (*Lolium perenne* L.) during a 70-d period of investigation for both drying and decomposition. They found  $\text{NH}_3$  volatilization during decomposition amounted to 20 to 47% of the herbage N, but  $\text{NH}_3$  volatilization during drying amounted to less than 1% of the herbage N. Most of the volatilization of  $\text{NH}_3$  during decomposition occurred under moist conditions while the small amount of

□ Gaseous Losses other than

### Nitrification



**Main Controls**  
Substrate,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , T



**Main Controls**  
Substrate, available C, T

Fig. 8-1. Gaseous emissions (CC terms) (Mosier and T. Parkin, 2007).

$\text{NH}_3$  volatilized during dry conditions is unhead et al., 1988).

### Nitrous Oxide and

Research during the past few decades has shown how  $\text{NO}_x$  and  $\text{N}_2\text{O}$  are produced in agricultural systems, the relationships, and gas movement. The identification of processes involved were a major focus of N that is applied or deposited (Mosier et al., 2000; Del Grosso et al., 2000; Bouman, 1999; Potter et al., 1999). Presumably similar agricultural processes in both time and space. The identification of processes involved must be a major focus (Mosier and Bouman, 1999).

We know that  $\text{NO}_x$  and  $\text{N}_2\text{O}$  are produced in essentially all terrestrial, biologically ubiquitous, a surprising discovery that has been identified and considered (Schmidt, 1982). The identification of water bacteria that oxidize an

ed and Schjoerring's (1996) calculating's et al. (2000) net  $\text{NH}_3$  emissions, IL, would be 1 to 25 kg  $\text{NH}_3\text{-N}$  crops carries a substantial degree risk to be done before we fully understand the atmosphere.

g of  $\text{NH}_3$ , soils and plant residues are increasing the complexity of determining agricultural crops and the atmosphere. It is primarily considered the major contributors, but other insignificant contributors. However, the landscape and the bidirectional exchange suggests plants play a crucial role. Horvath and Sutton (1998) found emissions of  $\text{NH}_3$  and  $\text{NH}_4^+$  when pig manure was applied, respectively, over a 10-yr period. There are still reservations about the possible contribution from crops, stating a loss of 15 kg  $\text{NH}_3$  about 30% of total  $\text{NH}_3$  emissions from pig manure. The source may be just a combination of fertilizer or manure excretion. It can be made for either the plant or

### Cultural Plants

For hay, silage or mulch undoubtedly contribute to the atmosphere. Crop plants typically release  $\text{NH}_3$  before seed maturity is reached. Hay may contain significant amounts of  $\text{NH}_3$  in such detached leaves with on-plant degradation (Schjoerring et al., 1998).  $\text{NH}_3$  concentration at the ground level was caused by N mineralization of 10 ng  $\text{NH}_3\text{-N m}^{-2} \text{s}^{-1}$ .

As much as 14% of the N in a legume green manure is lost during application. Incorporation of green manure reduces the volatile loss of  $\text{NH}_3$ , but is not a measure to control erosion and sedimentation. Larsson et al. (1998) reported  $\text{NH}_3$  emissions from alfalfa (*Medicago sativa* L.) to be 1.5 kg  $\text{NH}_3\text{-N m}^{-2} \text{yr}^{-1}$ .

Volatilization of  $\text{NH}_3$  from cut herbage was measured over a 70-d period of investigation for alfalfa.  $\text{NH}_3$  volatilization during decomposition was 1.5 kg  $\text{NH}_3\text{-N m}^{-2} \text{yr}^{-1}$ . Most of the volatilization of  $\text{NH}_3$  occurred during the first 10 days while the small amount of

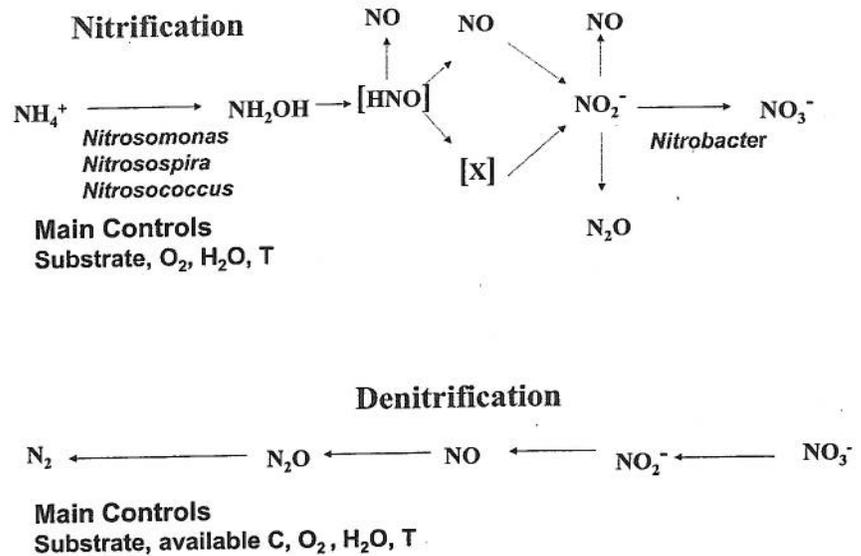


Fig. 8-1. Gaseous emissions ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}$ ) from diverse agricultural production systems (Mosler and T. Parkin, 2007).

$\text{NH}_3$  volatilized during drying implies that hay made in the field under continuous drying conditions is unlikely to release appreciable amounts of  $\text{NH}_3$  (Whitehead et al., 1988).

### Nitrous Oxide and Nitrogen Oxides Biological Sources

Research during the past several decades has improved our understanding of how  $\text{NO}_x$  and  $\text{N}_2\text{O}$  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; Frohling et al., 1998; Li et al., 1992; Plant and Bouman, 1999; Potter et al., 1998). Studies of emissions of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  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  $\text{NO}_x$  and  $\text{N}_2\text{O}$  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). Nitrification, the oxidation of ammonia to nitrite and then nitrate (Fig. 8-1) occurs in essentially all terrestrial, aquatic and sedimentary ecosystems. Although ecologically ubiquitous, a surprisingly few different chemoautotrophic bacteria have been identified and considered to accomplish most of the ammonium oxidation that occurs (Schmidt, 1982). *Nitrosomonas* and *Nitrospira* are the main soil and water bacteria that oxidize ammonia to nitrite while *Nitrobacter* is the principal ge-

nus of bacteria identified to oxidize nitrite to nitrate (Fig. 8-1; Schmidt, 1982). Denitrification, the microbial reduction of nitrate or nitrite to gaseous N through NO and N<sub>2</sub>O (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 O<sub>2</sub> 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), N<sub>2</sub>O and NO<sub>x</sub> emissions from nitrification of ammonium-based fertilizers can be substantial (Bremner and Blackmer, 1978; Duxbury and McConaughy, 1986; Hutchinson and Brans, 1992). Other work suggests that N<sub>2</sub>O release is a byproduct of nitrification (Yoshida and Alexander, 1970; Venterea and Rolston, 2002) and may occur by denitrification of nitrite 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 N<sub>2</sub>O (Smith, 1990). Under these conditions both the rate of denitrification and the N<sub>2</sub>O/(N<sub>2</sub> + N<sub>2</sub>O) ratio must be known to evaluate N<sub>2</sub>O emissions through denitrification. Typically little NO<sub>x</sub> 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 N<sub>2</sub>O and its further reduction to N<sub>2</sub>, are important in determining the proportions of the two gases as well as NO<sub>x</sub>. 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 CH<sub>4</sub> 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 describe NO and N<sub>2</sub>O emissions. Their conceptual model, the hole-in-the-pipe (HIP) model, relates the sum of NO + N<sub>2</sub>O emissions to indices of N availability and relates the ratio of NO/N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O emissions at 50 to 80% WFPS.

□ Gaseous Losses other than thr

Under wetter soil conditions l  
ted from the soil.

The interplay of substrate demonstrated by Parton et al. N<sub>2</sub>O emissions from soils. The CENT ecosystem model (Del G sively with observations from nitrification and denitrification that NO<sub>x</sub> emissions are due m from nitrification are proporti function of modeled soil NH<sub>4</sub><sup>+</sup>. Nitrous oxide (N<sub>2</sub>O) emission: centration, WFPS, heterotroph calculated by multiplying tota calculated as a function of soil influence gas diffusivity. Whe is driven by nitrification with . When diffusivity is low, denitr to less than one. The NO<sub>x</sub> sub by rain events onto dry soils.

Using the IPCC/UNEP/OI that the anthropogenic N<sub>2</sub>O en agement totaled 0.96 Tg in 199 fertilizer and biological N fixati residue. Anthropogenic NO<sub>x</sub> er on Davidson and Kinglerlee (19

## Nitrogen Emissions

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

- Clearing of forest and br
- Control of brush, weed lands;
- Nutrient regeneration in
- Control of fuel accumula
- Production of charcoal fo
- Energy production for cc

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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 CO<sub>2</sub> and NO, while smoldering leads to increased emissions of more reduced species such as CO, CH<sub>4</sub>, and NH<sub>3</sub> (Griffith et al., 1991). In open burning of biomass, temperatures are fairly low and the high temperatures necessary for the oxidation of atmospheric N seldom exists (Gerstle and Kemnitz, 1967).

Nitrogen is present in plant biomass mostly as amino groups (R-NH<sub>2</sub>) in the amino acids of proteins (Andreae, 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 (Andreae, 1991). Clements and McMahon (1980) reported a similar amount with a rough average of about 30% total yield for all NO<sub>x</sub> species. Nitrogen compounds other than NO (NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, HCN, organic nitriles, and nitrates) account for another 10 to 20% of the fuel N (Andreae, 1991). Average emission values reported by Lobert et al. (1990) for percentage of biomass N released as NH<sub>3</sub>, HCN, and nitriles of 4, 2.4, and 1% respectively, lie well within this range. Emission of molecular N usually is not monitored because of its high atmospheric content, and the majority of any unaccounted-for N is possibly released as N<sub>2</sub> (Andreae, 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 N<sub>2</sub>. They concluded N<sub>2</sub> emissions belonged to the flaming stage rather than to the smoldering stage.

LeBel et al. (1991) estimated NH<sub>3</sub> emissions from biomass burning would account for 14% of the total global atmospheric NH<sub>3</sub> 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 NH<sub>3</sub> source. In nearly all of their experiments, Lobert et al. (1991) found NO<sub>x</sub> 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 NO<sub>x</sub> budget estimated by Granier et al. (2000) for NO<sub>x</sub> from biomass burning. For N<sub>2</sub>O, Cofer et al. (1991b) concluded that no more than 7% (and probably less) of the global source of N<sub>2</sub>O can be attributed directly to biomass burning. Similarly, Lobert et al. (1991) estimated biomass burning contributing only about 3% to the global source of N<sub>2</sub>O. Lobert et al. (1991) reported that HCN and CH<sub>3</sub>CN, two of the most important nitriles emitted by biomass burning, together released 3.6% of the fuel N and in some experiments, HCN emissions can be as high as NO<sub>x</sub> emissions when incomplete combustion was predominant. Data on global sources of nitriles 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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from biomass burning would account budget. This is much higher than biomass burning on average accounting all of their experiments, Lobert et al. reactive N emission product from source strength yields estimated as. This falls in the range of 10 to 20% (Cramer et al. (2000) for NO<sub>x</sub> from biomass that no more than 7% (and probably contributed directly to biomass burning, biomass burning contributing only about 1) reported that HCN and CH<sub>3</sub>CN, biomass burning, together released N emissions can be as high as NO<sub>x</sub> dominant. Data on global sources may well be the major source for the (Cramer et al. (1991).

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