AP42 Section:	9.2.1
Background Ch	4
Reference:	60
Title:	R.R. Sharpe and L.A. Harper, "Soil, Plant and Atmospheric Conditions as they Relate to Ammonia Volatilization," *Fertilizer Research,* 42:149-158, 1995.

Fertilizer Research **42**: 149–158, 1995.

Soil, plant and atmospheric conditions as they relate to ammonia volatilization

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Key words: Micrometeorology, N flux, livestock waste, NH_3, ^{15}N

Abstract

Gaseous ammonia (NH_3) transport is an important pathway in the terrestrial N cycle. In the atmosphere NH_3 neutralizes airborne acids and is a major factor determining air quality and acid rain deposition patterns. Redeposition of atmospheric NH_3 plays an important role in the N balance of natural ecosystems and has been implicated in forest decline, plant species change and eutrophication of surface water. Much of the N in soil-plant animal systems can be lost to the atmosphere, particularly with surface applied livestock waste, or urea and anhydrous ammonia fertilizers. Plants can have a significant impact on NH_3 transport because they can both absorb and desorb atmospheric NH_3. Under conditions of low soil N or high atmospheric NH_3 concentrations, plants absorb NH_3. Under conditions of high soil N or low atmospheric NH_3 concentrations, plants volatilize NH_3. This article discusses methods for evaluating NH_3 transport in the filed, the rate of NH_3 volatilized from fertilizer application, and the effects of plants on net NH_3 transport.

Introduction

Ammonia (NH_3) and ammonium (NH_4) are important atmospheric components. Gaseous NH_3 originates in both natural and agricultural systems but the largest fraction comes from livestock waste, fertilizers, and other agricultural sources. Once in the atmosphere, NH_3 is the dominant alkaline gas and is the principal agent for neutralizing airborne acids, such as sulfuric, nitric and hydrochloric acid.

$$2NH_3(g) + H_2SO_4(l) \dashrightarrow (NH_4)SO_4(l, s)$$
$$NH_3(g) + HNO_3(g) \longleftrightarrow NH_4NO_3(s)$$
$$NH_3(g) + HCl(g) \longleftrightarrow NH_4Cl(s)$$

The primary atmospheric reaction is with sulfate (SO_4) because there is a much greater affinity of NH_4 for sulfate than nitrate (NO_3) and little NO_3 will be incorporated into aerosol until the SO_4 is almost completely neutralized [41]. Ammonia thus influences the pH of aerosols and cloudwater and is a major factor in determining air quality and acid rain deposition patterns [28].

From an agricultural viewpoint, NH_3 volatilization is a direct economic loss to the farmer and as much as 40 to 70% of some surface applied N fertilizers can be volatilized [4,6,7,15,35]. In research, if NH_3 losses or gains are not accounted for in N budget studies estimates to evaluate leaching and/or denitrification from agricultural fields can be in serious error [24]. Ammonia released from agricultural systems can also play an important role in the N balance of natural ecosystems.

In northern Europe, it has been estimated that 94% of the NH_3 released from agricultural sources is redeposited into surrounding ecosystems as either NH_3 or NH_4 [1]. Atmospheric NH_3 deposited in natural ecosystems has been implicated in forest decline (12,44) and in plant species change threathening the loss of moors and heathlands [3,40]. Absorption of atmospheric NH_3 by surface water can also accelerate eutrophication. Hutchinson [26] found that surface water can absorb as much as 73 kg NH_3 ha^{-1} y^{-1} from a nearby feedlot.

Comparison of methods

There are inherent difficulties in the measurement of atmospheric NH_3 under both laboratory [36] and field

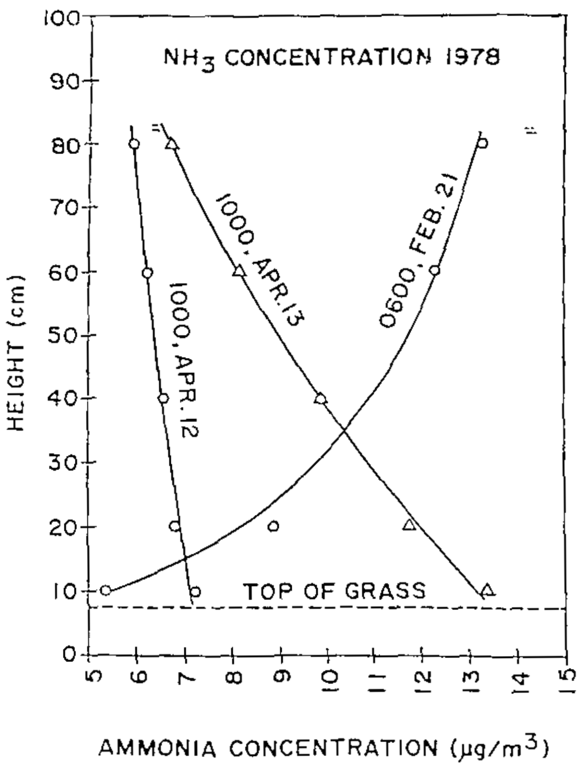

Fig. 1. Ammonia concentration profiles with height obtained over a subtropical pasture.

conditions [24]. Atmospheric NH_3 concentrations are generally low (5 to 20 ppb) [24] and NH_3 forms strong hydrogen bonds and adheres to any unheated surface, leading to memory effects and sample losses [36]. The three possible approaches to measuring NH_3 volatilization in the field are micrometeorological (MM) methods, enclosure (chambers) methods, and isotopic ^{15}N methods [21].

There is general agreement that MM techniques are to be preferred in principle [9,17]. They do not disturb the soil, plant, or environmental processes which influence NH_3 exchange and they provide a measure of average, integrated flux over a large area, thus minimizing problems associated with point to point variations. Micrometeorological techniques are limited to cropping situations where the air mass has blown over a large homogeneous surface so that profiles of gas concentrations in the air are in equilibrium with the local rate of exchange. Other requirements include high measurement sensitivity, relatively expensive instrumentation, and an understanding of the physics of gas transport under field conditions. Examples of typical NH_3 profiles above a grass pasture are shown in Fig. 1. On April 12 at 1000 h, there was no significant change in atmospheric NH_3 concentrations with height and thus no net transport into or out of the system. Twenty-four hours later on April 13 at 1000 h, there was a decrease in NH_3 concentration with height above the canopy from about 14 to 7 $\mu g\ m^{-3}$ indicating loss from the pasture. On Feb 21 (0600), the NH_3 profile was reversed with an increase in NH_3 concentration with height, indicating absorption of atmospheric NH_3.

Enclosure methods are popular techniques because they are relatively simple, permit replication, are suitable for small experimental plots with different land treatments, and have a lower sensitivity requirement for measuring gas exchange. There are, however, several problems in using enclosures to measure NH_3 fluxes [9]. Ammonia is highly reactive and will readily absorb and desorb from enclosure and pipe walls and any water condensed within the system. Enclosures also modify environmental conditions such as radiation, evaporation, temperature, wind speed and dew formation which can greatly influence NH_3 volatilization. Also, the enclosed surface area in chambers is relatively small and point to point variability of soil gas emissions is often very large. Therefore, accurate measurements of NH_3 fluxes using enclosures are difficult and caution must be taken when interrupting results [9,19,219] although flow-through chambers have shown good results [30,43] when precautions have been taken for NH_3 absorption/desorption.

The ^{15}N balance method estimates NH_3 loss indirectly by measuring all other pathways of N loss from the system and assumes the "unaccounted" for N is lost via NH_3 volatilization. This method allows the soil and/or crop to be open to natural conditions and, with care, the measured amount of NH_3 lost can be determined accurately. Since the ^{15}N method is an indirect measurement, it cannot be used to evaluate NH_3 loss if there are any unaccounted for N losses such as in systems in which denitrification is not measured. Substitution of ^{14}N for ^{15}N in an actively growing canopy may also lead to erroneous results. Plants can absorb and desorb NH_3 [14], and the substitution of ^{14}N from surrounding plants for ^{15}N plants in a microplot can result in an apparent NH_3 loss from the system although the net NH_3 flux from the entire field is zero [24]. This substitution results in a loss of $^{15}NH_3$ from the microplot but no net loss of N from the entire system and thus an overestimation of NH_3 volatilization.

Table 1 gives a listing of accuracies for and comparisons the three methods reported in the literature. Reported accuracies of the MM methods are about 20%

Table 1. Comparison of reported accuracies of microclimate, enclosure and nitrogen isotope methods (after Harper [21]).

Reference	Microclimate (MM)	Enclosure (Encl)	^{15}N	Method
Harper(1971)	±20%			*Summation of measurement errors*
Denmead *et al.*, (1996)	+20%			Estimate
Lemon & van Houtte (1980)	±20%			Estimate
Hoff *et al.*, (1981)		-52%		Comparison of NH_3 loss from plastic sheets
Ferguson *et al.*, (1988)	37%>Encl	37%<MM		Comparison over bare soil
Ferguson *et al.*, (1988)	91%>Encl	91%<MM		Comparison over wheat residue
Harper *et al.*, (1993)	7%^{15}N		7%>MM	*Field measurement comparison*
Harper & Sharpe (1994)	83%<^{15}N		83%>MM	Comparison of related experiment

based on estimates or summations of probably measurement errors [10,20,29]. Hoff *et al.* [25] compared NH_3 volatilization from soil applied swine manure and from manure spread on plastic sheets and calculated a −52% error for the losses measured from and enclosure as from plastic sheets. In a comparison of MM and enclosure methods, Ferguson *et al.* [17] showed considerably greater losses with MM methods than with enclosures over both bare soil (37%) and over wheat residue (91%). Harper *et al.* [22] found a 7% difference in loss of NH_3 as measured by MM techniques and by ^{15}N method. This comparison was conducted with a dormant grass sod under dry soil conditions in which denitrification was unlikely and thus no substitutions in the plants of ^{14}N for ^{15}N and NH_3. In a study with irrigated corn, Harper and Sharpe [24] reported an NH_3 volatilization loss of only 3.6 kg N ha^{-1} for the season. In a nearby field under similar environmental conditions and N levels, Francis (personal communication) estimated by the ^{15}N method about 23 kg N ha^{-1} loss as volatile NH_3. Harper and Sharpe [24] attributed the difference in NH_3 losses to substitution of atmospheric $^{14}NH_3$ for $^{15}NH_3$ emitted by the plants.

Catchpoole *et al.* (6) also showed the affects of actively growing plants on NH_3 volatilization as measured by the MM and ^{15}N method (Table 2). During the autumn when there was little plant activity due to heavy grazing and drought conditions, the MM and ^{15}N methods measured similar amounts of NH_3 losses. During the spring and summer when plants were actively growing, the MM method measured less than 50% of the losses by the ^{15}N method.

Table 2. Percentage of N volatilized as ammonia from a subtropical pasture after fertilization with urea.*

Method	Summer	Autumn	Winter	Spring
^{15}N	29	45	23	20
Flux gradient	12	42	13	9

* Fertilized with 94 kg urea ha^{-1} during each season. After Catchpoole *et al.*, [6]

Ammonia volatilization from fertilizer and livestock waste

In addition to excellent reviews which have been published concerning NH_3 volatilization from fertilizers [4,43], NH_3 losses from urea fertilizer is discussed elsewhere in this publication (Freney). Thus this paper will present only a quick overview of the factors affecting NH_3 volatilization from fertilizers.

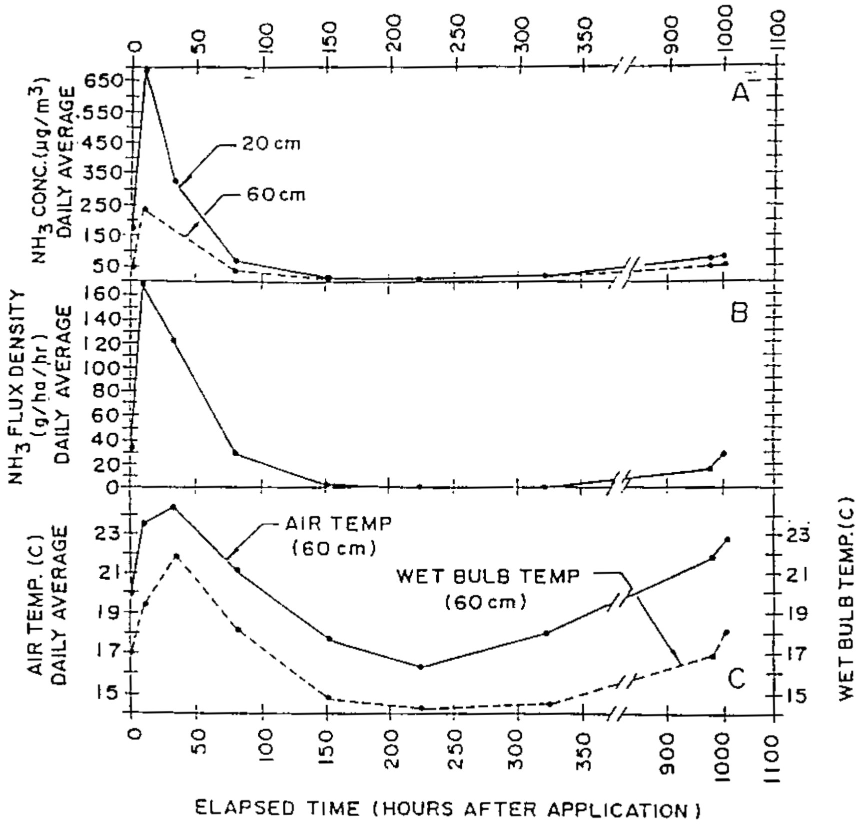

Fig. 2. Aerial NH_3 concentrations and flux densities with average daily air temperatures taken over a subtropical pasture after fertilization with 94 kg urea ha^{-1} in the spring [23].

The quantity of NH_3 volatilized from fertilizers is dependent on the type and timing of fertilizer applied, soil type, and environmental conditions at the time of application. The increase in use of N fertilizer worldwide coupled with a trend towards more extensive use of anhydrous ammonia and urea has increased the potential for NH_3 loss from fertilizers.

Soil factors which effect volatilization include cation exchange capacity (CEC), soil pH and moisture. There is a negative correlation between CEC and NH_3 loss [16,32,38]. It appears that a minimum CEC of 25 meq is required to substantially reduce NH_3 volatilization [16,32]. Amonia losses increase with higher soil pH because of the increased dissociation of NH_4 to NH_3, thus increasing the potential for volatilization [8,33,38].

Environmental factors which effect NH_3 volatilization include air temperature, windspeed, and atmospheric NH_3 concentration. Temperature and windspeed are the climatic factors most directly related to NH_3 loss. Increasing temperature increase the NH_3/NH_4 ratio at a given pH, decreases the solubility of NH_3 in water, and increases the diffusion of NH_3 through the soil [5,15]. If a steady supply of NH_3 is available, increasing windspeed would promote more rapid transport of NH_3 away from the soil surface [11,18].

The effect of temperature on NH_3 flux can been seen by comparing Fig 2 and Fig 3. In the spring, NH_3 efflux reached maximum values of about 170 g ha^{-1} h^{-1} within 24 hours after fertilization and declined to near background concentrations after four days (Fig. 2B). During this period daily average temperatures ranged from 20 to 25 °C (Fig. 2C). During the cooler winter measurement period, temperatures were 9 to 15 °C (Fig. 3C) which contributed to a slower flux rate. A moderate efflux began after 24 hours with maximum values of about 70 g ha^{-1} h^{-1} after four days. Flux rates returned to background levels after about four days.

High background NH_3 concentrations can cause a shift in NH_3 transport from efflux to influx (Fig. 4). A

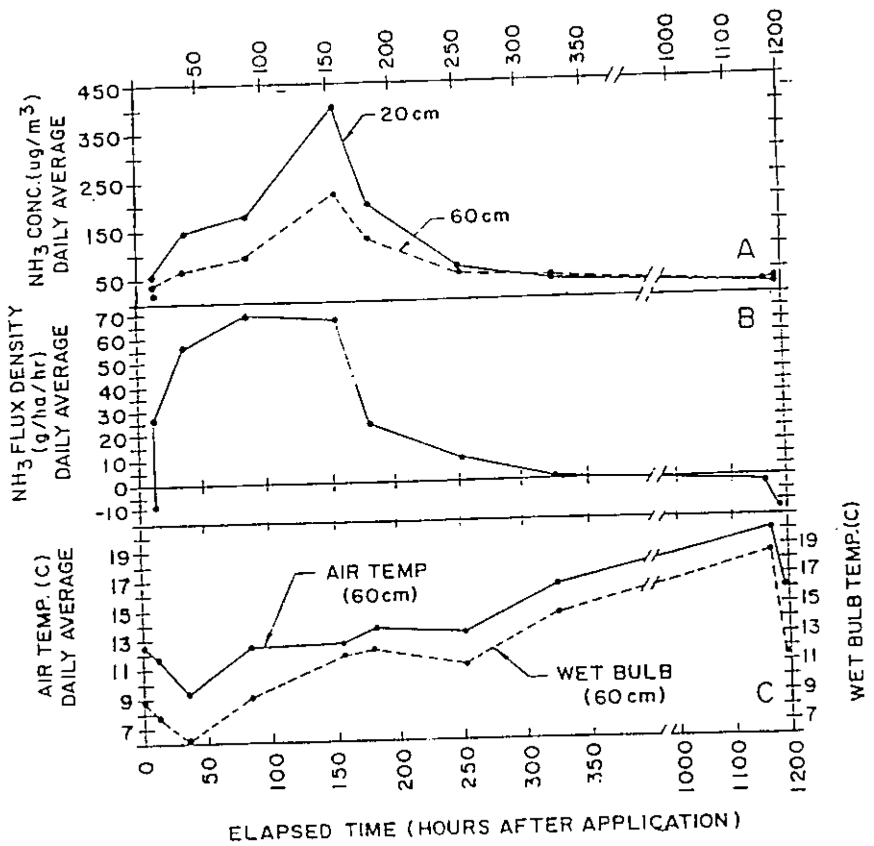

Fig. 3 Aerial NH_3 concentrations and flux densities with average daily air temperatures taken over a subtropical pasture after fertilization with [illegible] kg urea ha^{-1} in the autumn [23].

study with irrigated corn in central Nebraska showed a net NH_3 efflux from the system except between tasselling and silking (VT to R1 [37]) and the R4 and R5 stages of growth, periods in which NH_3 volatilization would normally be expected [24]. During these periods background NH_3 concentrations increased from 2 to 18 $\mu g\ m^{-3}$ causing the corn to shift from volatilization to absorption.

Management practices that decrease the pH of soil or irrigation water, increase CEC, or move the fertilizer deeper into the soil profile (i.e. injecting fertilizer or irrigation after application) would decrease NH_3 loss. Also, applying fertilizer when it is cooler and less windy would tend to decrease volatilization.

As stated previously, livestock waste is a major source of atmospheric NH_3 [34]. In northern Europe it is estimated that volatilization from animal waste constitutes 50% of the total NH_3 emissions [44]. Injecting or incorporating animal slurry greatly reduces volatilization losses in contrast to surface applications which can result in the loss of 32 [45] to 74% [42] of the applied N (Table 3). Injecting or incorporating the slurry reduced volatilization losses to less than 2% and 7% of the applied N, respectively. Differences in NH_3 losses in the different experiments were attributed to differences in radiation, soil temperature, surface pH, windspeed [45], soil water content [42] or differences in initial composition of the slurry [31].

Volatilization of NH_3 from surface application is very rapid, with most of the loss within the first 24 hours. Ammonia flux rates are highest immediately after application and often decrease 70 to 90% after the first 24 hours [2,42]. Stevens and Logan [39] reported that 24% (37 kg N) of the total N applied to the soil surface was volatilized within seven days, with 76% of this loss coming within 24 hours.

Influence of plants on ammonia flux

Plants play an important role in determining NH_3 flux and a number of studies have shown significant absorp-

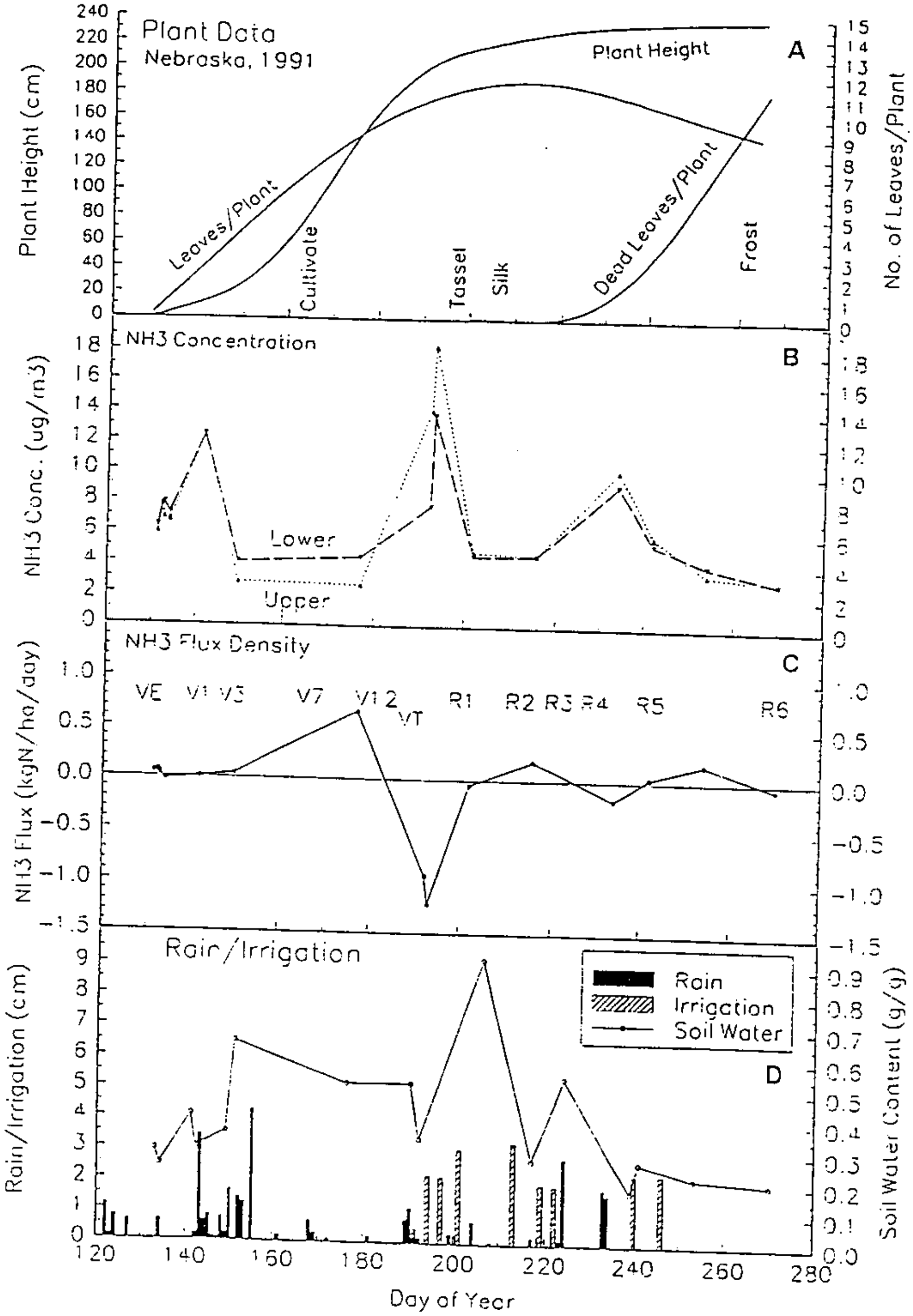

Fig. 4. Average NH_3 concentrations and flux density in corn throughout the measurement season (May–Oct. 1991).

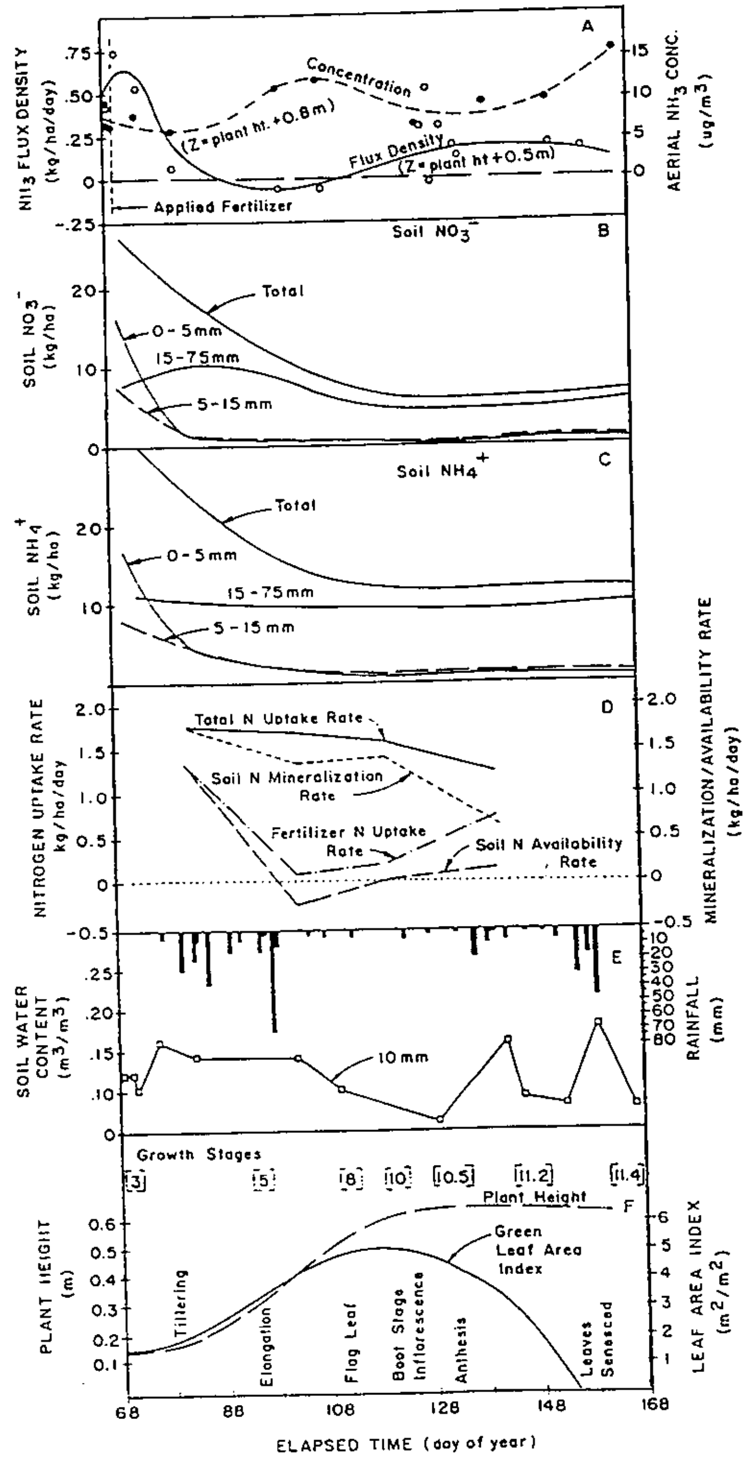

Fig. 5. Comparison of average daily NH_3 concentrations and flux density in wheat with residual soil, plant, and microclimate parameters (March–June, 1983).

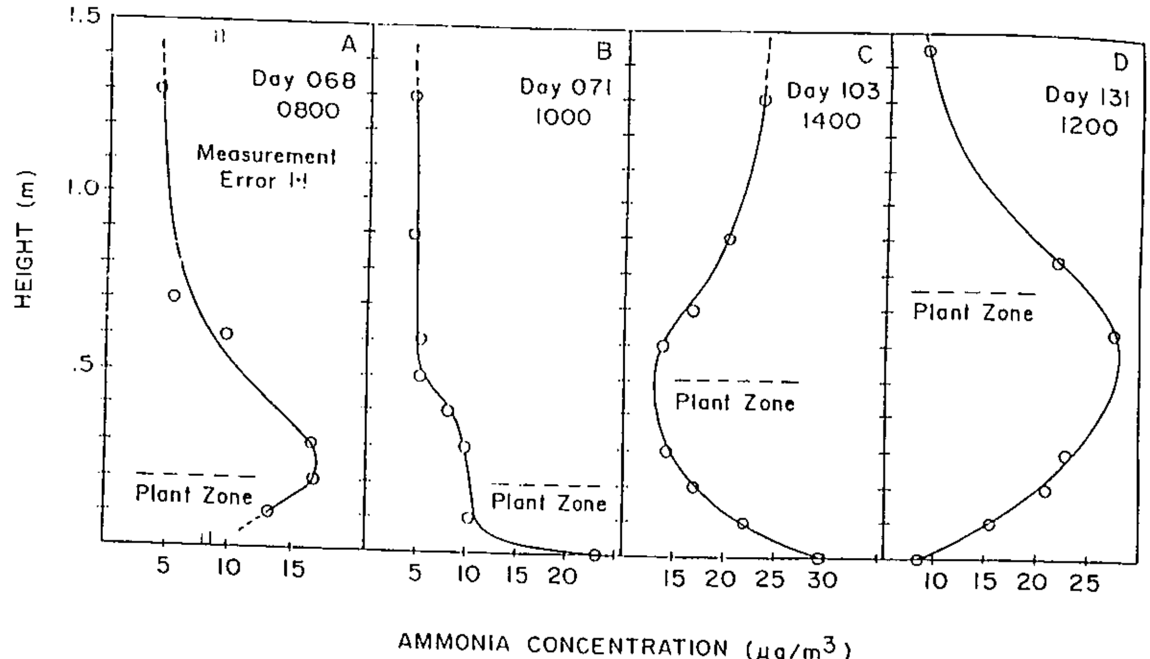

Fig. 6. Ammonia concentration profiles representing efflux (A) before fertilization, (B) after fertilization, (C) influx into plant canopy and (D) efflux from plant canopy.

Table 3. Volatilization of ammonia from animal slurry.

Type of slurry	Appl. method	Total loss (hg N ha^{-1})	% Lost	Reference
Cattle	Surface (w)	77.0	74.0	Thompson
	Injected (w)	2.1	1.9	*et al.*, 1987
	Surface (s)	53.0	48.0	
	Injected (s)	1.5	1.3	
Cattle	Surface	27	32	Vander Molen
	Surface	57	67	*et al.*, 1990
	Incorporated	5	6	
	Incorporated	6	7	
Pig	Surface	48.8	78	Lockyer
Poultry	Surface	27.1	49	*et al.*, 1989
Cattle	Surface	10.3	40	

tion and desorption of NH_3 by plants [22,23,27,36]. The NH_3 compensation point (NH_3CP) is the atmospheric NH_3 concentration at which no net exchange of NH_3 between the plant and atmosphere occurs. It has been found to vary with plant type, temperature, phenological growth stage, time of day, soil and plant N status, and soil water content [13,23,24,36]. In a study

Table 4. Ammonia compensation point (NH_3CP) in irrigated corn.

Time	Environ.* Variable	r^2	NH_3CP ($\mu g\ m^{-3}$)	Highest correlation
All day	All	0.62	7.7	NH_3
(0000–2400)	NH_3	0.61	6.6	–
Daytime	All	0.86	8.2	NH_3
(0800–1000)	NH_3	0.85	8.2	–
Nighttime	All	0.64	5.8	T
(0000–2400)	NH_3	0.14	6.5	–
Dawn	All	0.99	6.7	Plant N
(0000–2400)	NH_3	0.0	6.9	–
Morning	All	0.98	7.3	NH_3
(0000–2400)	NH_3	0.90	6.6	–
Afternoon	All	0.99	8.5	u
(0000–2400)	NH_3	0.23	7.9	
Evening	All	0.97	7.3	Ri
(0000–2400)	NH_3	0.39	7.8	
Dusk	All	0.99	3.0	NH_3
(0000–2400)	NH_3	0.99	3.4	

*All variables include radiation (Ri), temperature (T), windspeed (μ), Plant N and soil water content. After Harper & Sharpe [25].

with irrigated corn, Harper and Sharpe [24] found the NH_3 CP to range from 6 to 9 $\mu g\ m^{-3}$ except at dusk when it dropped to about 3 $\mu g\ m^{-3}$ (Table 4). In their study, there appeared to be a sufficient supply of N throughout the season and NH_3 flux was most closely associated with atmospheric NH_3 concentrations than with other measured variables (Table 4). Plants absorbed NH_3 when atmospheric concentrations were greater than 9 $\mu g\ m^{-3}$ and volatilized NH_3 when atmospheric concentrations were less than 6 $\mu g\ m^{-3}$.

Absorption or volatilization of NH_3 is strongly influenced by plant and soil N status. Fig. 5 presents soil, plant and atmospheric N transport for a wheat crop fertilized with NH_4NO_3. Ammonia loss prior to fertilization on day 69 was primarily from the plants since there was little free NH_4 in the soil. The increase in net NH_3 efflux after fertilization was due to higher plant N (and NH_4) concentrations and increased soil NH_4 concentrations at the soil surface (Figs 5A and 5C). When soil NH_4 and NO_3 concentrations in the upper layers decreased to about background levels (Figs 5B and 5C), net NH_3 transport to the atmosphere decreased to zero. Simultaneously, during this early vegetative period (days 78–108), fertilizer availability decreased due to immobilization of fertilizer N (as measured by ^{15}N; Fig. 5D) but plant N content increased. These decreases in soil N and fertilizer uptake resulted in a short term N deficiency during which time the plants absorbed atmospheric NH_3 (days 90–110; Fig. 5A). After day 110, soil N availability increased due to remineralization of fertilizer N and plant growth rate decreased due to the start of senescence (Fig. 5F) and the plants volatilized excess N.

Ammonia concentration profiles above the wheat canopy are shown in Fig. 6. On days 68 (before fertilization) and 131, the greatest NH_3 concentrations were at the top of the canopy indicating that the plants were an NH_3 source causing an efflux out of the system (Fig. 6A and 6D). After fertilization, NH_3 volatilized both from the soil and plants (Fig. 6B). During the period of N deficiency, plants were a sink for atmospheric NH_3 as indicated be the reduced NH_3 concentrations within the plant zone (Fig. 6C).

Agriculture is a major source of atmospheric NH_3 and volatilization of NH_3 from surface applied manure and fertilizer represents a direct economic loss to the farmer.

Micrometeorological techniques are usually the preferred method for measuring NH_3 transport but under certain conditions enclosure methods and ^{15}N isotopic measurement techniques have been used successfully. Plants can play an important role in net NH_3 transport. Under conditions of low soil N availability or high atmospheric NH_3 concentrations, plants can absorb atmospheric NH_3. Under conditions of high soil N availability or low atmospheric NH_3, plants can volatilize NH_3. In the atmosphere, NH_3 is important in neutralizing acidic species such as H_2SO_4, HNO_3 and HCl. Neutralizatian of acidic species results in the formation of NH_4 salts in cloud droplets and precipitation which can contribute to forest decline, plant species change and eutrophication of surface water.

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