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A comparison of methods of estimating ammonia volatilization in the field*

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Abstract. Accurate estimation of the potential for NH_3 volatilization from urea-based fertilizers is an important step in attaining optimum N-use efficiency from these fertilizers. Published estimates of NH_3 volatilization losses from urea vary widely. Much of this variability may be due to the method of estimation and the degree of influence of the method on NH_3 loss. This study compared two field methods of estimating NH_3 volatilization in the field; a microplot-forced draft method, and a micrometeorogical method. Loss of NH_3 was estimated in three experiments following urea solution application to bare soil, and in two experiments following urea-ammonium nitrate solution application to wheat stubble residue. Both methods were found to be sensitive to soil and climatic variables influencing NH_3 volatilization. Cumulative N loss from the bare soil experiments ranged from 7 to 8 kg N ha^{-1} for the microplot method and from 5 to 20 kg N ha^{-1} for the micrometeorological method. Cumulative loss from wheat stubble residue ranged from 2 to 2.2 kg N ha^{-1} for the microplot method and from 15 to 33 kg N ha^{-1} for the micrometerological method. Loss of NH_3 was especially influenced by soil or residue water content and the influence of water content on the rate of urea hydrolysis. Maximum rates of loss were generally observed near midday, when water content at the soil surface was just beginning to decline and the surface temperature was rapidly rising. The microplot method was found to have a greater potential for affecting the environment and thus influencing NH_3 loss measurements than the micrometeorological method. Windspeed and mixing at the soil surface was influenced by the presence of the microplot cylinder and lid, especially in the wheat residue experiments. It is likely that the micrometeorological method, with its minimal influence on the field environment, more accurately reflects actual levels of ammonia loss. The primary advantage of the microplot-forced draft method is its ability to easily compare relative NH_3 losses from different treatments.

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Introduction

Ammoniacal N fertilizers have the potential to lose significant amounts of ammonia (NH_3) to the atmosphere when applied to the soil surface and not incorporated. Accurate measurement of these losses under field conditions is necessary to assess the severity of NH_3 losses and to improve our understanding of factors controlling these losses. Several methods have been employed to measure NH_3 loss in the field. One common method is the microplot method (Kissel et al. 1977), in which a cover is placed over the microplot periodically (about 10 minutes every 3 hours) and air is drawn through the cover into an acid scrubbing column by a vacuum pump. The rest of the time the plot is open and exposed to normal climatic conditions. By integrating the rates of loss over time, the quantity of loss is determined. The authors found that the rate of NH_3 loss from microplots increased with an increase in airflow up to about 15 changes per minute of the air in the chamber above the soil.

This apparatus has been used to measure NH_3 volatilization from ammonium sulfate (Hargrove et al. 1977), and urea (Hargrove and Kissel 1979), applied to recently cut Coastal bermudagrass (*Cynodon dactylon* L.). With this equipment, good agreement between replicates in NH_3 loss has been found from ammonium sulfate, and with losses of NH_3 from ammonium sulfate in the laboratory, and with loss estimates based on crop response.

A similar microplot system has been used to measure NH_3 loss from liquid swine manure applied to cropland (Hoff et al. 1981). Results showed the system underestimated NH_3 loss on windy days, even though the airflow rate was 30 chamber volumes min^{-1}.

A similar system also has been employed to measure NH_3 loss from urea applied to forest soils (Craig and Wollum 1982). The authors used an air exchange rate of one chamber volume every 37 s. They found in later measurements that the mean windspeed at a height of 5 cm was 1.6 $km\,h^{-1}$, or 80 times the flow rate in the microplot samplers.

Another method to estimate NH_3 volatilization in the field is the micrometeorological mass balance method (Beauchamp et al. 1978, Wilson et al. 1982). The method requires the measurement of the vertical profile of horizontal flux of NH_3 at the center of a circular field of measurement.

Several workers have used this or other micrometeorological methods to measure NH_3 loss from a variety of systems. Many of these studies have been helpful in correlating NH_3 loss with climatic and soil factors. Micrometeorological methods have been used to demonstrate that a crop canopy can absorb NH_3 from the atmosphere (Denmead et al. 1976, 1978; Lemon and Van Houtte 1980); that diurnal patterns of NH_3 flux exist (Beauchamp et al.

1978, Denmead et al. 1978); that peak NH_3 flux from feedlots is associated with conditions which promote rapid drying (Hutchinson et al. 1982); and that factors most affecting NH_3 flux from urea-fertilized pasture can vary seasonally (Harper et al. 1983).

These studies point out the possible strengths and weaknesses of the two methods of estimating ammonia loss in the field. The microplot method is easily replicated and allows treatment comparisons, but it may not accurately estimate loss under all climatic conditions. Micrometeorological methods permit the measurement of ammonia loss from more complex environments, such as those including a crop canopy, with minimum influence upon the system being measured. These methods are also quite useful in studying loss dynamics on a small time scale. However, because of the large areas required it is more difficult to replicate and apply variable treatments using these methods. Since fertilizers are typically surface applied before the establishment of a crop canopy, the microplot method may describe the losses of NH_3 adequately in some situations, but the method needs more testing over a wide range of environmental conditions, including the presence of surface crop residue. Because the microplots are relatively small, it may be difficult to place crop residue on the microplot surface in a condition representative of the typical field conditions. The objective of this study was to compare the microplot method with a micrometerological method for measuring NH_3 losses from different soils and one soil with and without crop residue.

Materials and methods

The microplot method and micrometerological methods to measure NH_3 volatilization were compared in five experiments carried out in the summer and fall of 1982 and 1983. In all studies, efforts were made to ensure the same soil physical conditions in the adjacent areas used for the two methods. The times of fertilizer application were the same for both methods in all five experiments. Two experiments (Studies 1 and 2) were conducted in the fall of 1982 on a bare Muir silt loam soil (fine-silty, mixed, mesic Pachic Haplustoll). The field was cultivated with a spike-tooth harrow prior to application of fertilizer. The nitrogen source was 20% N urea solution applied at the rate of 120 kg N ha^{-1}. One experiment (Study 3) was conducted in the summer of 1983 on a bare Haynie very fine sandy loam taxadjunct (coarse-silty, mixed, calcareous, mesic Typic Udifluvent) which had been altered through management practices to a non-calcareous surface horizon with a pH of 6.2. The field was cultivated with a rotary cultivator prior to fertilizer application. A 20% N urea solution was applied at the rate of

120 kg N ha^{-1} soon after a light rainfall (< 8 mm) had moistened the upper profile. Two experiments (studies 4 and 5) were conducted in the fall of 1983 on the Muir silt loam soil (same site as the 1982 experiments) covered with 8.7 Mg ha^{-1} wheat straw residue. A 28% N urea-ammonium nitrate solution was applied at the rate of 200 kg N ha^{-1} in Studies 4 and 5.

Microplot method

The microplot sampling system used was the same apparatus developed by Kissel et al. (1977). The basic microplot consisted of a steel cylinder 22 cm dia and 15 cm deep. The microplot cylinder was pushed hydraulically (to minimize soil disturbance) into the soil until it was flush with the soil surface. For the two studies conducted on wheat stubble, the cylinder protruded from the soil approximately 3 cm in order to contain the residue. A weighed amount of stubble residue equivalent to the average amount present in the field was placed inside the cylinder. Fertilizer solutions were broadcast uniformly with a syringe. The microplots were irrigated by applying water with a syringe in amounts equivalent to the rate applied to the adjacent field area for the micrometerological method. Plots were open to rainfall. While sampling, a vacuum system pulled air across the soil surface and through tubing leading to an acid trap containing 150 mL 0.05 M H_2SO_4. An exchange rate of 20 to 25 chamber volumes min^{-1} was used. Air from over the plots was sampled for 10 min every 3 h. Ammonium nitrogen content of the traps was determined colorimetrically using a continuous flow autoanalyzer (Technicon Industrial Systems 1977b). Total loss was estimated by integrating the NH_3 loss rate from a 10 min sampling period over the 90 min both preceeding and following the 10 min sampling period.

Micrometeorological method

The micrometeorological method used a mass-balance approach involving the measurement of atmospheric NH_3 concentration and horizontal windspeed at several heights at the center of a circular fertilized plot (Wilson et al. 1983). The plot radius was 20 m except for the first experiment, which used a radius of 49 m. Urea solution or urea-ammonium nitrate solution was applied with a tractor-mounted sprayer. Atmospheric NH_3 concentrations at the center of and outside the plot were determined by collecting NH_3 from the air with gas scrubbing bottles. Details of sampling NH_3 in air and data handling are presented in more detail by McInnes et al (McInnes et al. 1985, 1986a, 1986b).

Hydrolysis rate measurements

Steel cylinders 10 cm diameter and 10 cm deep were pushed into the soil adjacent to the plot used for micrometeorological measurements. Treatments were applied to the soil within each cylinder in the same manner as the microplot cylinders. Treatments were replicated either two or three times depending upon the experiment. Cylinders were periodically removed from the field and the soil within extracted with a 2 M KCl solution containing phenylmercuric acetate. An aliquot of the extract was frozen until later analysis for urea, ammonium and nitrate nitrogen, using colorimetric methods with an autoanalyzer. Urea was determined by the method of Douglas and Bremner (1970). Ammonium and nitrate nitrogen were determined by continuous-flow colorimetric procedures using a Technicon Autoanalyzer II (Technicon Industrial Systems 1977b).

In the two studies conducted on wheat stubble, the soil within the hydrolysis rate cylinders was separated into layers to follow the movement of fertilizer nitrogen with time. The residue above the soil was considered a separate layer.

Results and discussion

The details of NH_3 volatilization rates measured by the micrometerological method and the interaction of NH_3 loss with soil water, soil temperature, and crop residue have been presented elsewhere (McInnes 1986a, 1986b). The results presented here focus on the differences observed between the two methods.

Study 1

The cumulative ammonia-nitrogen loss measured with both methods and the amount of urea remaining unhydrolyzed during Study 1 are shown in Fig. 1. The field received 4.3 mm of rainfall the morning after fertilization. The amount of urea remaining unhydrolyzed declined rapidly following this rainfall. (The second sampling, taken after the rain, indicated that little of the urea had leached out of the depth of soil sampled.) A trace of rain occurred the morning of day 239, 1.3 mm of rain on the morning of day 243, and 0.3 mm of rain on the morning of day 244.

The rate of disappearance was rapid immediately following the first rain, but the amount of urea remaining between the third and fourth measurements was about the same. It appears that the rate of hydrolysis increased

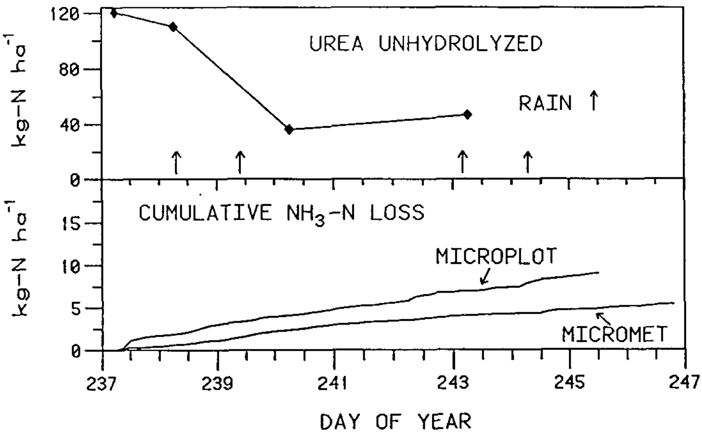

Fig. 1. Urea hydrolysis and cumulative NH_3-N loss, Study 1.

with increasing water content following the rain, then declined as the soil dried. Total amounts of ammonia loss measured by the microplot and micrometeorological methods by day 245 were 8 and 5 kg N ha^{-1}, respectively. The rates of volatilization measured by both methods were slow and fairly steady. We have observed similar loss patterns in laboratory experiments, when urea was leached into the soil by light simulated rain (unpublished data).

Study 2

The cumulative NH_3-N loss with time for the microplot and micrometeorological methods, and the urea present in the soil over time for Study 2 are shown in Fig. 2. The site received 1.0 mm of rain on the morning of day 272,

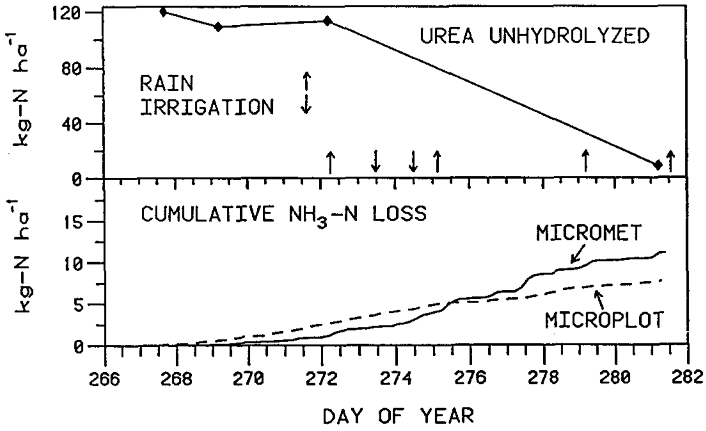

Fig. 2. Urea hydrolysis and cumulative NH_3-N loss, Study 2.

and was irrigated with 1.3 mm of water twice, around noon on days 273 and 274. The site received 8.6 mm of rainfall on the morning of day 275, 3.6 mm of rain on day 279, and 20 mm of rain on day 281. Apparently, soil water content limited urea hydrolysis early in the experiment, since most urea remained unhydrolyzed until the first rain and irrigation. As in Study 1, hydrolysis rate measurements could not be taken frequently enough to separate out the effects of irrigation and rainfall on urea movement and hydrolysis.

As in Study 1, the levels of ammonia loss were fairly small, but steady as measured by both methods. Losses measured from the microplots were higher until day 275, when they were exceeded by total loss measured with the micrometeorological method. The 20 mm rain on day 281 slowed NH_3 loss so that loss measurements were stopped. Cumulative loss to day 281 was estimated by the microplot method to be 7.5 kg N ha^{-1} and by the micrometeorological method to be 11 kg N ha^{-1}.

Study 3

Results from Study 3 are given in Fig. 3. This experiment was conducted in June and July of 1983, a time of the year when potential evaporative demand was high. In order to have adequate moisture for hydrolysis, the fertilizer was applied on day 181 as soon as application equipment could be moved

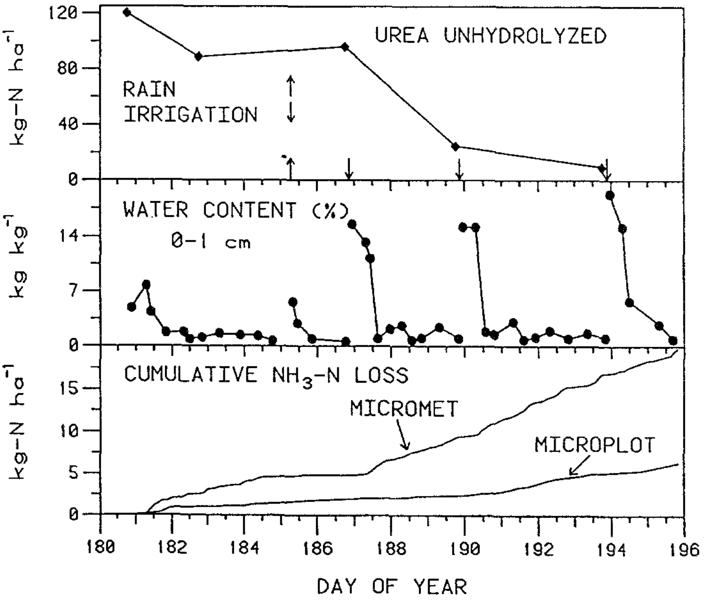

Fig. 3. Urea hydrolysis, soil surface water content, and cumulative NH_3-N loss, Study 3.

into the field following a rain. The soil in the 0 to 1 cm layer dried rapidly over the next 4 days, to water contents around 0.01 kg kg^{-1}. This situation is quite similar to an incubation study conducted in our lab (Ferguson and Kissel 1986). In that study, urea was applied to an initially moist sandy loam soil which was subjected to rapid drying conditions. Urea initially diffused into the moist soil, but then moved back towards the soil surface via mass flow because of high evaporative demand. The urea which was concentrated at the dry soil surface was relatively protected from volatile loss of ammonia, since the water content at the soil surface was too low to allow urea hydrolysis. It appears likely that a similar situation occurred in Study 3 following application until the field was irrigated with 5 mm water on the evening of day 186.

The field received 0.4 mm rain the morning of day 185 and was irrigated with 5 mm water on the evening of days 186, 189, and 193. The surface water content increased considerably following each irrigation, but dried rapidly during the day (Fig. 3).

The amount of urea remaining unhydrolyzed (Fig. 3) indicates that around 30 kg of urea-N was hydrolyzed within 2 days after application. It is likely that much of this hydrolysis occurred early in the period, when soil water content was higher. Very little hydrolysis occurred from day 183 to day 187, when the soil surface water content was quite low. Significant amounts of urea were hydrolyzed by the fifth sampling on day 193.

Cumulative ammonia loss measured by both the microplot and micrometeorolgical methods show fairly low levels of loss until the first irrigation. At this point, losses measured by the two methods diverge substantially. Loss rates as high as 5.5 g NH_3m^{-2} s^{-1} were measured by the micrometeorological method soon after irrigation, while the rate of loss did not exceed 2.8 mg NH_3m^{-2}s^{-1} as measured by the microplot method. Periodic increases in the rate of loss were detected from the micrometeorological method at each irrigation, with cumulative loss approaching 20 kg N ha^{-1} on day 195. Measurements from the microplots show a low, steady loss for the entire experiment, with cumulative loss to day 195 of 7 kg N ha^{-1}.

One possible factor influencing the difference in loss measured by the two methods may have been the method of irrigation. The measurement area for the micrometeorological method was irrigated with 5 mm water over a period of 30–40 min using hand-set line sprinklers. The microplots were irrigated by hand using a syringe with the same amount of water, but over a period of approximately 10 min per plot. This rate of water application produced the effect of a more intense rainfall than that from the line sprinklers received. It is possible that more of the urea in the mciroplots was leached to greater depths due to the more intense water application which resulted in ponding in parts of the microplot. The patterns of ammonia loss from the microplots in this experiment were, in fact, similar to those seen in Study 1, where leaching had occurred.

Study 4

Results from this experiment are given in Table 1 and Fig. 4. The fertilizer applied in this experiment was 200 kg N ha^{-1} as 28% N urea-ammonium nitrate solution. Approximately one half of the nitrogen was in the form of urea, one fourth as ammonium and one fourth as nitrate. Because of the heavy wheat stubble residue on the field, little of the nitrogen solution penetrated the residue and reached the soil (Table 2). Initially, 91.9% of the fertilizer N remained on the residue. Much of the fertilizer remained on the residue for the next 5 days following application, until the field was irrigated with 2.5 mm of water on the evening of day 254. The field received 33 mm of rain on the morning of day 255, which served to wash most of the fertilizer

Table 1. Distribution of fertilizer nitrogen with time and depth, Study 4.

Time (h)	Depth (cm)	%				
		Urea	NH_4^+	NO_3^-	Total	Total recovery
0	RES	46.4	22.7	22.8	91.9	
	0–1	0.8	0.3	0.0	1.1	
	1–2	0.1	0.0	0.0	0.1	93.1
24	RES	49.4	21.7	24.6	95.7	
	0–1	0.0	0.2	0.0	0.2	
	1–2	0.0	0.0	0.0	0.0	
	2–3	0.0	0.0	0.0	0.0	
	3–4	0.0	0.0	0.0	0.0	95.9
72	RES	44.4	15.5	20.2	80.1	
	0–1	0.3	0.2	0.2	0.7	
	1–2	0.0	0.0	0.0	0.0	
	2–3	0.0	0.0	0.0	0.0	
	3–4	0.0	0.0	0.0	0.0	80.8
144	RES	0.8	2.5	2.6	5.9	
	0–1	0.3	12.0	0.0	12.3	
	1–2	0.5	7.3	0.1	7.9	
	2–3	0.4	7.1	0.9	8.4	
	3–4	0.1	3.8	0.4	4.3	38.8

Irrigation applied at 105 hours, rain fell at 117 hours after application.

Urea-ammonium nitrate solution originally composed of 50% urea-N, 25% each of ammonium and nitrate-N.

RES = Wheat stubble residue layer.

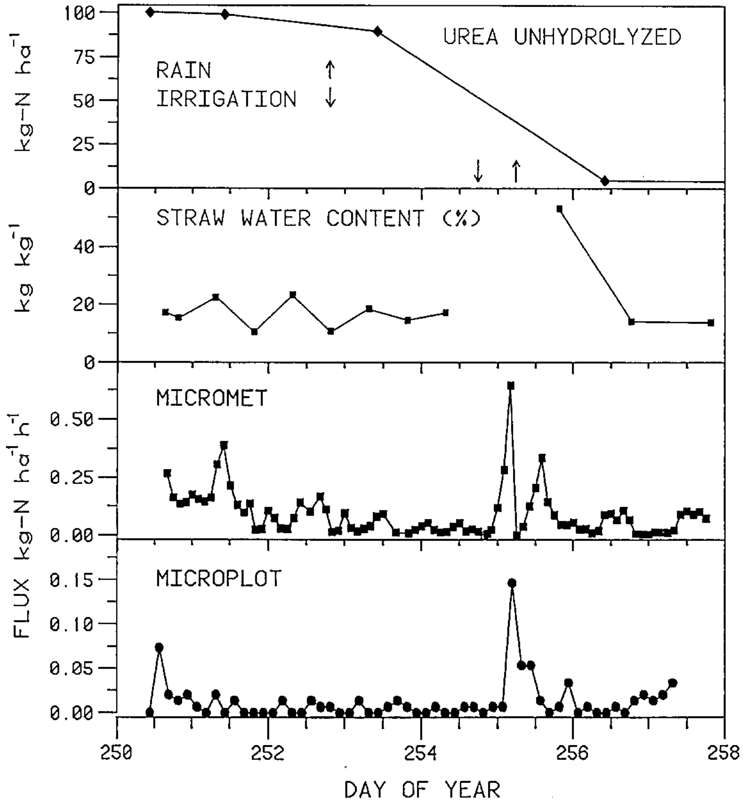

Fig. 4. Urea hydrolysis, straw water content, and NH_3-N flux, Study 4.

off the residue and into the soil (Table 1). At 144 hours (6 days) after application, only 5.9% of the applied nitrogen remained on the residue (Table 1). while significant amounts of ammonium and nitrate-nitrogen were found to a depth of 4 cm. It is likely that the rain leached much of the fertilizer deeper than 4 cm, but that is the maximum depth the cylinders were sampled.

Figure 4 illustrates the amount of urea remaining unhydrolyzed, straw water content, and NH_3 flux for the micrometeorological and microplot methods. The field had been irrigated prior to application of fertilizer, consequently the soil water content was above field capacity beneath the residue layer. The soil water content declined over the next 5 days, but remained quite moist, above 0.122 kg kg^{-1}, corresponding to a negative water potential of 141 J kg^{-1}. The straw water content fluctuated over the same interval, drying during the day and rewetting during the night. Some urea hydrolyzed during this period, as shown by the slightly lower amount remaining unhydrolyzed (Fig. 4). However, most of the fertilizer nitrogen remained on the residue until the irrigation and rainfall.

The NH_3 flux measured by both the micrometeorological and microplot methods began soon after application (Fig. 4). Some of this early loss was enhanced by the free NH_3 in the fertilizer solution, but loss was largely from the ammonium fraction of the fertilizer because of the high pH of the staw (McInnes et al. 1986b). This early flux of NH_3 from the field was followed by several days of low levels of loss until the first irrigation. Following irrigation, rapid NH_3 evolution was observed with both methods until the rain the next morning. It is likely that much of this ammonia loss occurred because of an increase in the rate of urea hydrolysis caused by an increase in available moisture. Following the rainfall, loss rates measured by both methods returned to low values, similar to those prior to the irrigation and rain.

In comparing NH_3 flux measured by both methods, we found greater NH_3 loss with the micrometeorological method. Ammonia flux measured by the microplot method prior to the irrigation averaged 0.01 kg N ha^{-1} h^{-1}, while the micrometeorological method averaged 0.1 kg N ha^{-1} h^{-1} for the same period. Total $NH_3{}^{-}N$ loss measured by the micrometeorological method over the course of the experiment was 15 kg N ha^{-1}, while the microplot method measured a loss of 2.2 kg N ha^{-1}. The peak level of loss measured by the micrometeorological method following the irrigation was over 0.6 kg N ha^{-1} h^{-1}, while the microplot peak flux was four times less. One explanation for this discrepancy may have been the placement of the microplot cylinders. The cylinders were left protruding out of the soil approximately 3 cm in order to contain the wheat straw layer. When the lid was closed over the cylinder and air was drawn in through ports around the lid, the air flowing over the straw may not have mixed well throughout the space inside the lid and cylinder. This may have resulted in increased diffusion resistance of the chamber and decreased the NH_3 flux. The protrusion of the cylinder above the soil surface would affect airflow across the soil and residue inside the chamber between loss measurements as well, with associated influences on residue and soil water content, urea hydrolysis rate, and total NH_3 loss.

The micrometeorological method also showed a relatively large flux of ammonia following the rainfall, while the microplot method showed a smaller, slightly displaced peak in flux (the morning of day 256). This difference in flux may have been due to the sensitivity of the micrometeorological method to windspeed. Although atmospheric ammonia concentrations were lower than during the previous peak in flux, the windspeed increased following the rain, resulting in a fairly high rate of loss. The microplot method, with the possible dead airspace around the wheat straw, may have been less sensitive to this increase in windspeed.

Study 5

Results from this experiment are shown in Table 2 and Fig. 5. The experiment was basically a repeat of Study 4, but with two light irrigations to stimulate urea hydrolysis. The field was irrigated with 2.5 mm of water on the evening of days 261 and 262. The straw water content fluctuated considerably due to irrigation followed by drying. Soil water content in the surface cm remained high throughout the experiment. Table 2 illustrates that much of the fertilizer nitrogen remained on the residue, although the amount varied, as seen in the differences in total recovery at 9, 23, and 45 hours after application. The amount of urea remaining unhydrolyzed declined rapidly as the straw was moistened by successive irrigations. (Table 2 and Fig. 5).

Table 2. Distribution of fertilizer nitrogen with depth and time, Study 5.

Time (h)	Depth (cm)	%				
		Urea	NH_4^+	NO_3^-	Total	Total recovery
9	RES	44.6	18.1	20.3	83.0	
	0–1	0.2	0.2	0.0	0.2	83.4
23	RES	20.3	9.2	0.6	39.1	
	0–1	11.6	5.9	2.6	20.1	59.2
45	RES	11.6	12.1	13.8	37.5	
	0–1	1.7	16.6	4.6	22.9	
	1–2	1.0	9.1	1.8	11.9	72.3
72	RES	0.1	0.9	0.0	1.0	
	0–1	0.1	12.6	1.1	13.8	
	1–2	0.1	11.5	1.5	13.1	
	2–3	0.0	8.0	0.9	8.9	
	3–4	0.0	4.9	1.0	5.9	42.7
96	RES	0.1	0.7	0.3	1.1	
	0–1	0.1	12.9	0.0	13.0	
	1–2	0.0	16.1	0.0	13.0	
	2–3	0.0	5.0	0.0	5.0	
	3–4	0.0	4.2	0.0	4.2	39.4

Irrigation applied at 22 and 46 hours, rain fell at 62 hours after application.

Urea-ammonium nitrate solution originally composed of 50% urea-N, 25% each of ammonium and nitrate-N.

RES = Wheat stubble residue layer.

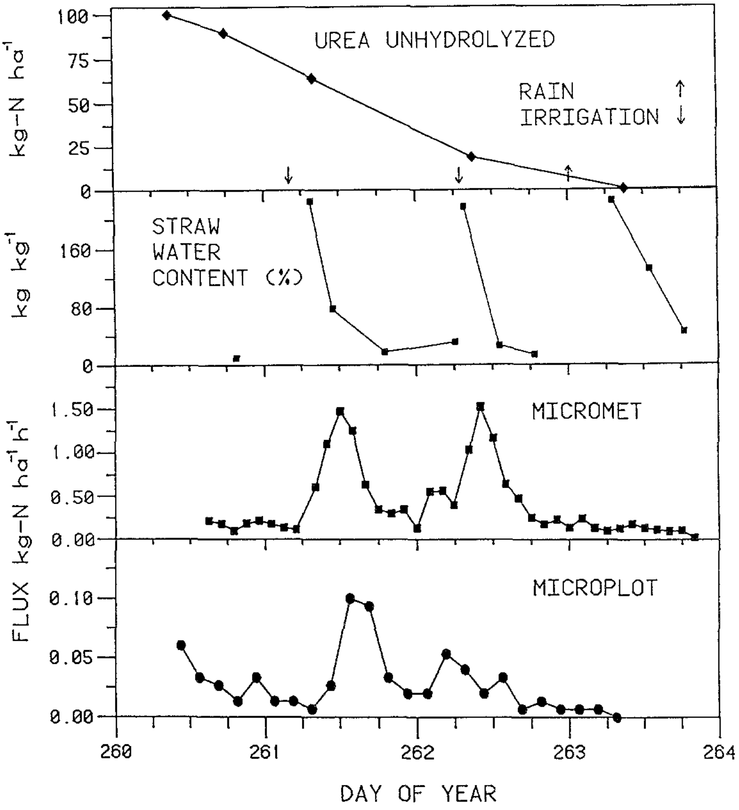

Fig. 5. Urea hydrolysis, straw water content, and NH_3-N flux, Study 5.

The rates of NH_3 loss measured by both methods peaked and then declined as the straw was moistened by irrigation and then dried. The field received 28 mm rainfall on day 263, which greatly reduced volatilization rates. The NH_3 flux, as in Study 4, differed greatly between the two methods. Peak levels of loss measured by the micrometeorological method reached 1.5 kg N ha^{-1} h^{-1}, while the loss measured by the microplot method never exceeded 0.1 kg N ha^{-1} h^{-1}, a 15-fold difference. Again, as in Study 4, the difference in loss measurement may have been due to the air flowing across the residue in the microplots and not mixing with the air down in the residue. Total loss measured by the micrometeorological and microplot methods was 33 and 2 kg N ha^{-1}, respectively.

Summary

In five field experiments comparing the micrometeorological and microplot methods of measuring NH_3 loss, we found that both methods measured similar patterns in the rates of NH_3 loss on a daily basis. Both methods indicated consistently that the greatest diurnal flux of ammonia from the soil or straw surface occurred when moisture was relatively high and surface temperature was increasing rapidly and approaching its daily maximum. These conditions occurred typically around late morning or early afternoon. Both methods indicated that the major factor controlling NH_3 loss between days was soil or residue water content, with wetter conditions enhancing loss. The amount of total NH_3 loss measured was similar in both methods on the bare Muir silt loam soil, but in the other experiments the agreement was not as good. The agreement was especially poor for Experiments 4 and 5 on the Muir silt loam with surface crop residue.

Because the microplot method requires that a cylinder be pressed into the soil, the chances of modifying the environment at the soil surface is much greater than with the micrometeorological method. The microplot cylinders were allowed to protrude 3 cm above the soil surface to allow room for wheat straw in Experiments 4 and 5, and this apparently created an environment for NH_3 loss that was much different from that in the adjacent field area.

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