Relaxed Eddy-Accumulation Technique for Measuring Ammonia Volatilization

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Ammonia emissions from fertilized fields not only decrease the fertilizer value but also contribute to environmental pollution in the form of off-site deposition. Quantifying the magnitude of ammonia fluxes is therefore of great interest because of economical and environmental aspects. Two factors make ammonia flux measurements particularly challenging: (i) ammonium in particulate phase often interferes with gas phase ammonia and (ii) ammonia is easily adsorbed on surfaces. Due to the lack of a suitable fast-response ammonia sensor, we decided to explore the feasibility of using denuder tubes with the relaxed eddy-accumulation technique (REA) for measuring ammonia fluxes. In the spring of 1996, the REA technique was successfully used to measure ammonia fluxes over a corn field after urea application. The denuder tubes, coated with oxalic acid, were used at the inlet of the REA system to trap ammonia in air. During the 23 days of measurements, ammonia emission rates ranged from 1 to 1023 ng NH_3 m^{-2} s^{-1}, and deposition rates ranged from 2 to 106 ng NH_3 m^{-2} s^{-1}. As expected, daytime observations show that the ammonia fluxes are highly correlated with solar radiation.

Introduction

The exchange of ammonia (NH_3) between soil, plant, water, and the atmosphere plays an important role in the nitrogen cycle. The loss of NH_3 from agricultural land reduces the fertilizer value for plant production and represents a waste of resources. In the atmosphere, NH_3 is the main neutralizing agent for acids. Ammonia also increases the oxidation rate of SO_2 in cloud droplets. The depositions of NH_3 and NH_4^+ from the atmosphere increase the nitrogen input on vegetated ecosystems. This alteration may also change the composition of the vegetation. Quantifying the magnitude of NH_3 emissions from agricultural fields and deposition to natural ecosystems is therefore of great interest.

Different techniques have been used to study the exchange of NH_3 between terrestrial surfaces and the atmosphere, such as enclosure methods (*2*), isotopic methods (*3*), and techniques based on atmospheric turbulence (e.g., refs *3–6*). The latter techniques are generally preferred, because they do not disturb the soil-plant-atmosphere continuum and provide measurements integrated over a large area.

The gradient method has been used by many researchers to measure NH_3 vertical flux densities over corn field (*3*), forest (*4*), moorland (*5*), and grazed grassland (*6*). In this paper, flux is used as a simplified term for the vertical flux

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density. As an alternative, the relaxed eddy-accumulation (REA) technique is a relatively new method for measuring trace gas flux. It involves the partitioning of the gas sample into two separate reservoirs based on whether the real-time wind-measuring system senses ascending or descending air. The air sampled can later be analyzed using a slow response analyzer such as a gas chromatograph. In the original concept, the air was sampled at a rate proportional to the magnitude of the vertical wind velocity w (*7*). Businger (*8*) suggested a relaxation of this method, in which the valves split the flow strictly on the basis of the sign of w without the proportional sampling. The conceptual simplicity of this technique is appealing because the vertical flux estimate F for a trace gas is a simple function of the standard deviation of the vertical wind velocity σ_w, the difference of the mean concentrations between ascending air $(\overline{c^+})$ and descending air $(\overline{c^-})$, and an empirical coefficient A:

$$F = A\sigma_w(\overline{c^+} - \overline{c^-}) \tag{1}$$

Field experiments have indicated that REA is a suitable alternative for flux measurement of trace gases, such as CO_2, volatile organic compounds, and pesticides (*9–14*). With a suitable design of the sampling system, REA has the potential for measuring NH_3 flux.

Unlike most trace gases in the air, NH_3 can be easily converted to ammonium (NH_4^+) in particulate phase and vice versa. Therefore, special consideration is required during flux measurements to avoid the interference of NH_4^+ in particulate phase with the collection of gas-phase NH_3. The denuder tube is a suitable trap for this purpose (*15*) because, in air, molecules diffuse more quickly than particles. When air is flowing through a tube, the gas-phase NH_3 diffuses from the laminar flow to the coated wall, while particles pass through the tube. The residence time in the denuder tube should be as short as possible ($\sim$ a few seconds) to avoid the interference of NH_3 evaporated from particles and gas–particle and particle–particle reactions. By combining denuder tubes with a REA system, we should be able to measure NH_3 fluxes.

Urea [$CO(NH_2)_2$] is one of the most frequently used nitrogen fertilizers. Its global annual consumption (28×10^{12} g N) is more than one-third of the global annual consumption of total nitrogen fertilizers (*16*). After application on the soil, urea is hydrolyzed to NH_4^+ with urease catalysis. The rate of urea hydrolysis is a function of the urea concentration and water content in the soil:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- + OH^-$$
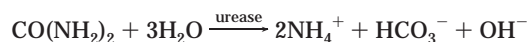
The driving force for NH_3 exchange between the surfaces and the atmosphere is the difference in NH_3 concentration between the soil surface and the ambient atmosphere. In solution, NH_3 concentration exists in equilibrium with NH_4^+. The following thermodynamic equilibrium shows the relationship between NH_3 and NH_4^+:

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

$$\updownarrow$$

$$(NH_3)(g)$$
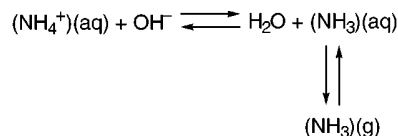
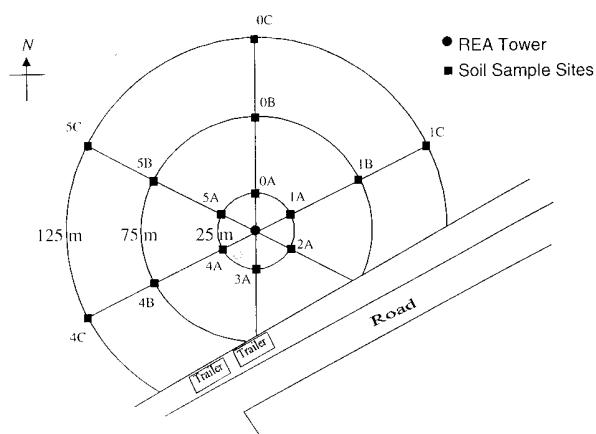Soil properties, such as the cation exchange capacity, pH, buffer capacity, and soil calcium carbonate content, sig-

FIGURE 1. Diagram showing soil sampling sites (labeled as 1A, 1B, etc.) and the tower location.

nificantly influence NH_3 vapor flux. Urea application to soil raises the pH and ammonium concentration, thus providing ideal conditions for NH_3 volatilization. This paper presents a REA/denuder tube system for NH_3 measurement as well as NH_3 daytime fluxes over a corn field fertilized with urea.

Experimental Section

Experimental Site. The experiment was carried out over a 28-ha clay loam field in the Greenbelt Farm of Agriculture and Agri-Food Canada, Ottawa. A micrometeorological tower was erected in the 23-ha field (Figure 1) with eddy-covariance (EC) and REA instrumentation. Broadcast application of urea (46−0−0) at a rate of 138 kg of N ha^{-1} took place on May 22 (DOY 143; DOY, day of year). The field was cultivated to a depth of 6−10 cm when corn was planted on DOY 144. Corn emerged on DOY 153. The field was sprayed with a herbicide on DOY 155. Flux measurements lasted for 23 days (from DOY 146 to DOY 168). The sampling of ammonia with the REA system began at 0700 EST and finished before 1900 EST. The REA technique is based on turbulent transfer and thus depends on effective vertical mixing. Hence accurate measurement of flux is much more difficult to obtain at night than during the daytime due to stable and low wind condition. In addition, NH_3 fluxes are found to be smaller at night than during the daytime. Harper et al. observed that a large NH_3 efflux occurred during the daytime and a small efflux or influx at night on a pasture applied with urea (*17*). Denmead et al. reported that nighttime volatilization rates were only half those observed during the day for similar aqueous NH_3 concentrations (*18*). Therefore, no observations were made between 1900 EST and 0700 EST. On most days data were collected during five sampling periods, except on DOY 153, 154, and 155 when data were collected during only one period. Each sampling period lasted about 2 h.

NH_3 Collection and Analysis. NH_3 in air was collected with denuder tubes, which were 61 cm long glass (Pyrex, Corning) tubes with an internal diameter of 4 mm. The last 40 cm of the tube was coated with 1.5% oxalic acid in acetone, leaving a 21 cm uncoated inlet to establish the laminar flow at a flow rate of 3 L min^{-1}. Laboratory tests showed that, with air flow rates of 1.0, 2.0, 3.0, and 4.0 L min^{-1}, the sorption efficiency of the denuder tube was 99%, 97%, 95%, and 90%, respectively. The standard deviation of three replicate measurements was less than 4% when the flow rate ranged from 1.0 to 3.0 L min^{-1}. When using a denuder system to trap ammonia in the air, it is important to know when the denuder tube begins to lose its sorption efficiency (breakthrough) after a large volume of air has been sampled and a large amount of ammonia has accumulated on the coating layer. Tests show that the breakthrough volume of the denuder

tube was greater than 1.44 m^3, which was four times the sampling volume (0.36 m^3) during field measurements. The denuder tube could trap up to 4.9 μg of NH_3 without losing its sorption efficiency, this value is larger than the maximum amount of NH_3 trapped by the denuder tubes (4.1 μg) during field measurements.

The residence time of the air in a 40 cm long tube (i.d. 4 mm) at a flow rate of 3 L min^{-1} is only 0.10 s. On the basis of the method described by Ferm (*15*), the contribution from particles via evaporation of NH_3 was estimated to be less than 6% of the total observed NH_3. The deposition of particles by gravitation on the tube wall was another source of interference for NH_3 measurement, which was minimized by placing the tubes vertically.

After each measurement period, the samples were immediately extracted with 2.0 mL of deionized water. The potential interference of amines with the concentration analysis of NH_4^+ can be avoided by using ion chromatography. The NH_4^+ concentration in the water was analyzed with an ion chromatograph made from a high-pressure pump (Waters model 510 solvent delivery system, Mississauga, ON, Canada), a sample injector (Rheodyne model 7725, Mississauga, ON, Canada), a chromatographic column (Waters IC-Pak C M/D, Mississauga, ON, Canada), and a conductivity detector (Waters 430, Mississauga, ON, Canada). The eluent used was 1.5 mM nitric acid. Its flow rate was set at 1.2 mL min^{-1}, and the column temperature was kept at 30 °C. Under these conditions, the detection limit of NH_4^+ in water is 3 ppb.

By considering the tube dimension, NH_3 concentration in air, ion chromatographic detection limit, and sampling duration (2 h), the sampling flow rate through the denuder tube was set at 3 L min^{-1}. Under these conditions, the detection limit of NH_3 in air was 0.015 μg of NH_3 m^{-3}.

REA System. The descriptions of the REA sampling system, software, and a data acquisition and control system developed in-house are given by Pattey et al. (*11*, *19*). Wind velocity and temperature fluctuations were measured at 1.75 m above the soil surface with a three-dimensional ultrasonic anemometer/thermometer with 10-cm path length (Kaijo-Denki, DAT-310, Tokyo, Japan). The CO_2 and H_2O mixing ratio fluctuations were measured with a closed-path fast-response infrared gas analyzer (LI6262, LI-COR, Lincoln, NE). An A/D converter (Labmaster card DMA TN-40, Scientific Solutions, Solon, OH) connected to a microcomputer recorded the above signals at a sampling frequency of 20 Hz. The signal of vertical wind velocity w was high-pass-filtered at 0.001 Hz with a digital filter to remove any bias. The filtered w signal was used for controlling the sampling valves and for the flux computations.

NH_3 can easily be adsorbed on surfaces, it is therefore important to position the denuder tubes at the inlet of the sampling system. To have replicate measurements, six denuder tubes were installed on the REA tower at the same level per sampling period (Figure 2), among them, three tubes were for upward moving air and the other three were for downward moving air. Field test confirmed identical flow rates in all tubes. The tubes were installed vertically to avoid the deposition of particles by gravitation. The inlets of these tubes were located 3 cm behind the vertical transducers of the sonic anemometer with the inlets at the midpoint of the 10-cm path.

Air was drawn through the tubes using a pump at a rate of about 3 L min^{-1} per tube. Depending on w signal, the air sample was directed to the up, down, or dead-band channel by three fast-response two-way solenoid valves (ASCO solenoid two-way valve, Ascoelectric, Brantford, ON, Canada) activated through the control port of the Labmaster card. A dead-band is an interval defined on the w signal, centered at $w = 0$, in which no air sampling takes place. It is used to
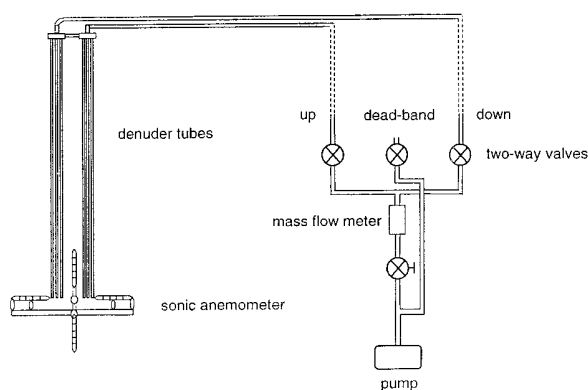
FIGURE 2. Schematic of the relaxed eddy-accumulation/denuder system for measuring ammonia fluxes.

prolong the life of the valves and to increase the difference in trace gas concentration between the updraft and downdraft samples $(c^+ - c^-)$. The volume of the tube holder (64 cm³) and the volume of the tubing (32 cm³) that connected the holder and the valve are much larger than the volume of the denuder tube (8 cm³). The large volumes of the tube holder and the tubing reduced the fluctuation of the flow rate. Meanwhile, it extended the transition time between 0 and 3 L min^{-1}, when valves were closing and opening, to 0.08 s. The transition time was small because the system offers no restriction to the flow. A single fast-response mass flow meter (TSI 8460, TSI Inc., St. Paul, MN) was used to monitor the flow rates in both the up and the down tubes.

Momentum, CO_2, sensible, and latent heat fluxes were measured using the eddy-covariance (EC) technique:

$$F_{EC} = \overline{w'c'} \tag{2}$$

where a prime denotes the fluctuation about the mean value. The coefficient A in eq 1 was calculated for each period using simultaneous computation of the water vapor flux by EC and REA techniques:

$$A = \frac{F_{EC}}{\sigma_w(\overline{c_{H_2O}^+ - c_{H_2O}^-})} \tag{3}$$

When the water vapor flux was too small, CO_2 flux was used to compute the coefficient A. NH_3 flux was not corrected for air density fluctuations because this effect is negligible for the fluxes and concentrations encountered [20].

Soil Samples. Soil samples were collected twice during the experiment. The first set of samples was taken at the beginning of the experiment on DOY 146, 3 days after the urea application. The second set of samples was taken on DOY 163, just before the end of the experiment. On DOY 146 the soil was moderately dry. On DOY 163, the soil was more humid. The sampling sites were distributed along three circles surrounding the REA tower with a radius of 25, 75, and 125 m, respectively (Figure 1). There were six sampling sites on each circle, located at 60° intervals. In two directions, 120° and 180°, there were no sampling sites at 75 and 125 m due to the proximity of the tower to the edge of the field. At each sampling site, 10 cores of soil with 2.5 cm diameter and 15 cm depth were collected into a glass jar. The soil bulk density was 1.32 ± 0.10 g cm^{-3} on DOY 146 and 1.37 ± 0.07 g cm^{-3} on DOY 163. The samples were kept frozen until analysis.

Results and Discussion

The cation exchange capacity (CEC), concentrations of NH_4^+ and NO_3^-, and pH of the soil samples are listed in Table 1.

TABLE 1. Soil Analysis Results for the Ammonia Flux Measurements in Summer 1996[a]

date	CEC (g m^{-2})	pH in CaCl$_2$	NO$_3$−N (g m^{-2})	NH$_4$−N (mg m^{-2})
DOY 146	3.11 ± 0.75	6.0 ± 0.2	8.9 ± 1.1	50 ± 10
DOY 163	3.24 ± 0.75	5.9 ± 0.2	12.4 ± 1.7	44 ± 10

[a] The means and standard deviations are given for 14 sampling sites (see Figure 1).

The CEC and pH measured on DOY 146 show no difference to those measured on DOY 163. The NO_3^- concentration of the soil on DOY 163 was 3.5 g of N m^{-2} higher than that on DOY 146. This increase of NO_3^- in soil indicates that on DOY 163 at least 25% of the urea applied had been converted to NO_3^- through nitrification of NH_4^+. The soil NH_4^+ concentration on DOY 163 was 44 mg of N m^{-2} and was slightly smaller (6 mg of N m^{-2}) than those on DOY 146. The lack of apparent change in NH_4^+ concentration of soil suggested the equilibrium of NH_4^+ in soil.

To test the precision of denuder tubes for sampling NH_3 in air, three tubes for sampling upward and downward moving air were used for certain sampling periods (all periods on DOY 146−149 and 157 and the first sampling period on DOY 150, 152−155, 160−161, and 163). The mean standard deviation of NH_3 concentration measured with the three tubes was 0.12 μg m^{-3} (no. of observations = 62), while the mean concentration was 2.71 μg m^{-3}.

During the experiment, the NH_3 concentration in air ($[NH_3]$) measured with the REA system ranged from 0 to 34 μg m^{-3}, with a mean of 4.9 μg m^{-3} (no. of observations = 164) (Figure 3). At the same time, the standard deviation of the vertical wind velocity σ_w ranged from 0.19 to 0.52 m s^{-1}, with a mean of 0.34 m s^{-1} (no. of observations = 82). While throughout the measurement σ_w was in the same range, $[NH_3]$ changed significantly. During the first 10 days (DOY 146−155), $[NH_3]$ was very low. It ranged from 0.14 to 4.1 μg m^{-3}, with a mean of 1.2 μg m^{-3} (no. of observations = 64). A significant increase of $[NH_3]$ to 30 μg m^{-3} was observed on DOY 156, when it rained after a period of dry conditions following the application of urea. From DOY 156 to DOY 168, $[NH_3]$ ranged from 0 to 34 μg m^{-3}, with a mean of 7.2 μg m^{-3} (no. of observations = 100).

Equation 1 was used to calculate NH_3 fluxes obtained with the REA system. The coefficient A, based on the water vapor flux simulation for each period, ranged from 0.413 to 0.459 with a mean of 0.447 (no. of observations = 8) on DOY 146 and 147, when the dead-band was initially set at ±10 cm s^{-1}, and ranged from 0.424 to 0.518 with a mean of 0.489 (no. of observations =4) from DOY 148 to DOY 168 when the dead-band was changed to 5 cm s^{-1}.

The daytime 2-h-averaged NH_3 fluxes, latent heat fluxes, and precipitation are illustrated in Figure 3. The mean standard error of NH_3 flux was 33 ± 29 ng m^{-2} s^{-1}, which was estimated solely from the standard deviation of NH_3 concentrations measured with the three tubes. NH_3 fluxes were quite low during the first 10 days, showing the same trend as NH_3 concentration in air. It ranged from −106 to 124 ng m^{-2} s^{-1}, with a mean of 4 ng m^{-2} s^{-1} (no. of observations = 32). The NH_3 fluxes began to increase on DOY 156, when a flux as high as 595 ng m^{-2} s^{-1} was observed. From DOY 156 to DOY 168, the NH_3 fluxes ranged from −55 to 1023 ng m^{-2} s^{-1}, with a mean of 214 ng m^{-2} s^{-1} (no. of observations = 50). The highest flux (1023 ng m^{-2} s^{-1}, 2-h-averaged) was observed on day 161; it is of the same magnitude as the NH_3 fluxes observed by Harper et al. [17] and Freney et al. [21].

On most days, NH_3 fluxes were closely correlated with latent heat fluxes (Figure 3). Mean daytime variations of NH_3 fluxes and latent heat fluxes are shown in Figure 4. These are

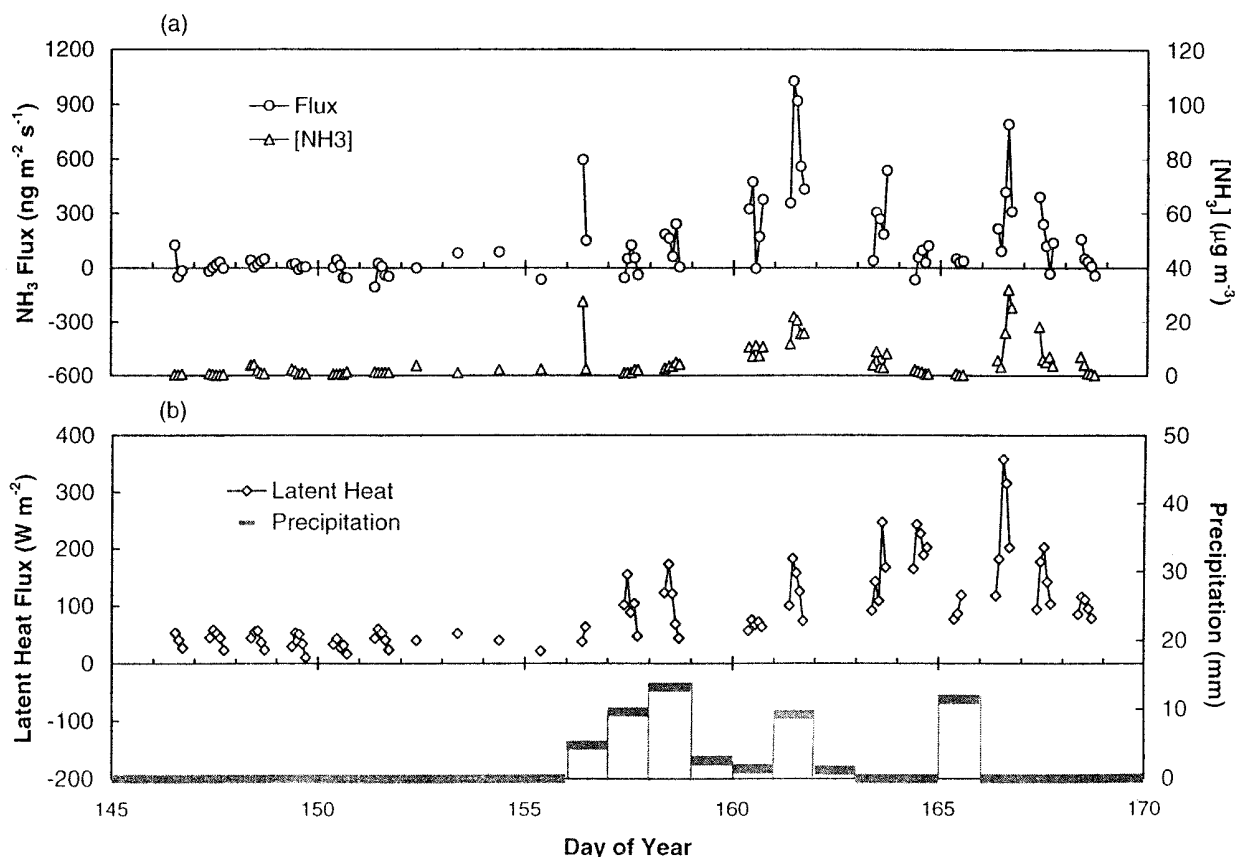FIGURE 3. Time course of ammonia concentrations ([NH₃]), ammonia fluxes, latent heat fluxes, and precipitation.

the mean NH₃ and latent heat fluxes measured on days when five consecutive observations were taken from 0700 to 1700 EST. The large error ranges in Figure 4 are caused by the large variations of NH₃ and latent heat fluxes between different days. Figure 4 shows that from 0700 to 1700 EST, NH₃ and latent heat fluxes had the lowest values during the period 0700−0900. The highest values of both fluxes were observed during the period 0900−1100. After 1100, NH₃ and latent heat fluxes decreased gradually.

As expected, significant increases in both NH₃ concentrations and fluxes were observed with precipitation (Figure 3a,b). During the first 10 days there was no precipitation and the soil was dry; both NH₃ concentrations and fluxes were low. This is consistent with the observation of Sommer and Jensen that, during periods with low air humidity and dry conditions, NH₃ losses from urea were negligible (22). On DOY 156, the first precipitation (5 mm) after the application of urea caused both NH₃ concentrations and fluxes to increase significantly. Throughout the rainy weather, which lasted from DOY 156 to DOY 165, relatively high NH₃ concentrations and fluxes were observed. The effect of soil water availability on NH₃ fluxes has also been observed by Harper et al. (17). NH₃ efflux increased to high rates when the soil was wet during urea application and increased slowly to moderate levels when urea was applied to a dry soil surface.

The corresponding increase of NH₃ concentrations and fluxes with precipitation suggests that NH₃ was mostly from local source and that soil water content is an important factor in controlling the production and emission of NH₃. The hydrolysis of urea leads to the formation of NH_4^+. The low soil moisture before DOY 156 limited the hydrolysis rate of urea and, thus, the amount of NH_4^+ available for NH₃ emission. The precipitation on and after DOY 156 increased soil moisture and, thus, the hydrolysis rate of urea as well

as NH₃ fluxes. In addition, the high soil moisture provided the possibility for high evaporation rates from the soil. The movement of moisture to the surface helped to bring NH_4^+/ NH₃ to the surface, thus increasing NH₃ fluxes. This was most likely the reason that NH₃ fluxes were well correlated with latent heat fluxes (Figure 4).

Depending on soil and environmental conditions and method of fertilizer application etc., losses of urea by NH₃ volatilization can vary widely [e.g., from negligible with dry soil (22) to as high as 50% of the applied urea within 2 weeks from a flooded rice field (23)]. Apparently, for this study, the availability of water for the hydrolysis of urea is one of the most important factors controlling NH₃ emissions from fields applied with urea. Using the NH₃ fluxes measured with the REA technique, it was estimated that, during the field experiment, 1.1 kg of N ha⁻¹ was lost through the daytime volatilization of NH₃, which is about 0.8% of the urea applied to the field. This value is quite small but comparable with the results of Freney et al. (21), where about 1.7% N was lost as NH₃ during the first 23 days after irrigating a cracking clay soil with urea solution. The observed low N loss is not surprising if we consider the relatively dry condition of the soil during the measurement period and the fact that the measurements were not continuous. Only the daytime NH₃ fluxes were measured. Higher value of N lost through volatilization of NH₃ could have been observed had we extended the measurement period. The denuder sampling was manually operated and was labor intensive, hence the length of the measurements of NH₃ fluxes was limited by the lack of resources. For the second half of the measurements, after corn emerged, absorption of NH₃ by plant could also be a factor that resulted in the low net NH₃ fluxes (24).

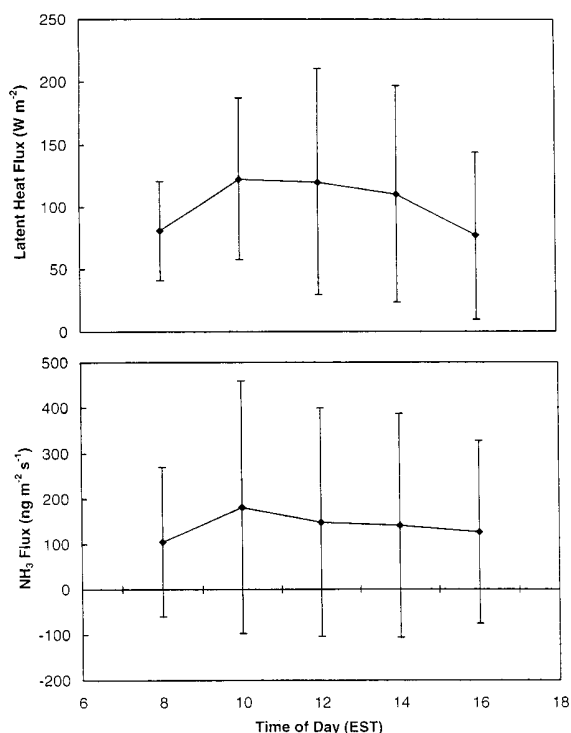In summary, daytime NH₃ emission rates ranged from 1 to 1023 ng m⁻² s⁻¹, and deposition rates ranged from −2 to

FIGURE 4. Daytime variation of the latent heat fluxes and the NH₃ fluxes measured with the REA technique. The error bars are based on one standard deviation of NH₃ and latent heat fluxes measured on days when five consecutive observations were taken between 0700 and 1700 EST.

-106 ng m^{-2} s^{-1}. The observations show that NH$_3$ fluxes and evaporation rates are closely correlated with incoming radiation. Relatively low NH$_3$ fluxes were observed during the first 10 days measurements, which was due to the dry soil conditions. After the first rainfall on DOY 156, NH$_3$ fluxes increased considerably. On DOY 161, NH$_3$ fluxes as high as 1023 ng m^{-2} s^{-1} were observed. During the 23 days of field measurements, 1.1 kg of N ha^{-1} were lost through the daytime volatilization of NH$_3$, which is about 0.8% of the urea applied to the field. To our knowledge, this is the first field experiment using REA technique to measure NH$_3$ fluxes. The results showed that REA is a suitable method for quantifying NH$_3$ emission and deposition between the terrestrial biosphere and the atmosphere.

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