

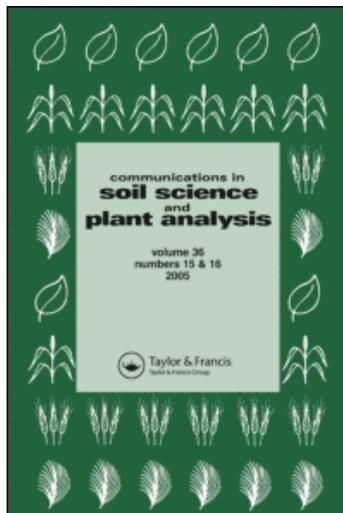
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Improved Method for Field-Scale Measurement of Ammonia Volatilization

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ABSTRACT

We developed a new method for determination of atmospheric ammonia (NH₃) emissions from land-applied nitrogen (N). The new method is a modification of two proven passive flux methods, and is an improvement over these existing methods via reductions in cost, labor and analytical requirements. This new method involves use of one rotating mast placed in the center of a circular plot (15 m radius). The samplers we use are glass tubes (7 mm by 200 mm) that have been coated on the inside with oxalic acid to trap NH₃. This new method was tested against one of the proven methods in a field experiment. A circular plot (15 m radius) was established and urea was applied to supply 200 kg N ha⁻¹. Measurements of NH₃ volatilization were then made for six days after application. A strong linear relationship was evident between our

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new method and the reference method for both horizontal and vertical NH_3 fluxes, as indicated by correlation coefficients of 0.92 and 0.86 for horizontal and vertical fluxes, respectively. The glass tubes that we used consistently absorbed more NH_3 and measured more total NH_3 volatilization than the samplers of the reference method. However, given that micrometeorological methods have underestimated NH_3 volatilization in the past, we feel that our method has improved the accuracy of NH_3 volatilization measurement. In essence, we believe we have developed an improved method for field-scale determination of NH_3 volatilization by reducing initial costs as well as labor and analytical requirements, without sacrificing accuracy of the volatilization measurement.

INTRODUCTION

Ammonia (NH_3) volatilization can be a significant pathway for nitrogen (N) loss from many agricultural systems. In order to improve N budget estimates, accurate measurements of NH_3 volatilization from field-scale studies in typical systems are needed. However, current methods have limited practicality due to either high initial cost or excessive amounts of time and labor required for field and analytical work. We have developed and tested a new passive flux measurement technique for determining NH_3 loss from land-applied animal waste that combines the best attributes of two proven passive flux methods and improves upon them by reducing the cost and labor involved. One of the existing methods was developed by Leuning et al. (1985) and later modified by Sherlock et al. (1989), and centers on a device that requires no power source, flow meters or anemometers. With this device, referred to as an NH_3 sampler, NH_3 loss can be determined without a large labor force (Sherlock et al., 1989). The NH_3 sampler is described in detail by Leuning et al. (1985) and consists of an entrance nozzle and an outer cylinder fitted with mounting pivots and fins to keep the device aligned with the wind. Internal absorbing surfaces consist of a spiral of waffled stainless steel. To collect NH_3 with the device, internal surfaces are coated with a thin layer of oxalic acid (3% w/v in acetone). The interior of the sampler is allowed to dry leaving a deposit of oxalic acid on internal surfaces. To measure NH_3 in the field, a mast is placed in the center of a 25-m radius plot and NH_3 samplers are placed at five heights on the mast (up to 3 m) to measure the horizontal flux density of NH_3 at each height. The samplers are mounted on an arm that allows them to rotate into the prevailing wind. A second mast with samplers at the same heights is placed on the upwind edge of the circular plot to measure background NH_3 . Measurement of wind speed is not necessary because wind speed is integrated into the measurement, i.e., more NH_3 is captured in the sampler as wind speed increases. A radial plot is used to ensure that air flow to the sampler covers the same area of the plot from all directions. A uniform sampling protocol

was accomplished, because the centered sampler is equidistant from any edge of the plot. Several studies have demonstrated the ability of this method to provide relatively accurate estimates of field-scale NH_3 volatilization (Freney et al., 1992; Fox et al., 1996).

The main disadvantage of this method is that each collection device costs approximately US \$250 to build. Using this method, it is common to collect NH_3 at five heights, requiring five samplers. In addition, background measurements are necessary, requiring five more samplers. Thus, 10 devices are required/plot for one measurement time, and a minimum of one replacement set of devices are required for subsequent measurement times, which brings the minimum cost for NH_3 measurement devices on one plot to US \$5,000. With three replications this figure becomes \$15,000, which is cost prohibitive for many research programs.

The other proven passive flux method was developed by Schjoerring et al. (1992) and centers on use of 100 mm long glass tubes coated with oxalic acid on inner surfaces. Two tubes are connected with silicon tubing. To each pair of glass tubes a stainless steel disk with a 1-mm hole in the center is connected to decrease air speed inside the tube and increase NH_3 collection efficiency. The tubes are mounted at five heights on four masts placed at right angles on the periphery of a 15-m radius circular plot. At each height two passive flux sampler units are mounted, one unit having the stainless steel disk facing the plot, and the other unit facing away from the plot. Ammonia coming from the plot is thus collected through the stainless steel disk of the first unit and the open end of the second. Conversely, background NH_3 is collected through the open end of the first unit and through the disk of the second. This method is initially cheaper than the Leuning et al. (1985) method, i.e., glass tubes are much cheaper than the measurement devices developed by Leuning et al. (1985). But, over the long-term the Schjoerring et al. (1992) method is also expensive due to large analytical and labor requirements. For one measurement time on one plot, 80 NH_3 analyses are required (4 masts x 5 heights x 4 tubes/height). With three replications the number of NH_3 analyses becomes 240. With multiple sampling times subsequent to amendment application that generates atmospheric NH_3 (typically a 2-week period), the number of required ammonia analyses can run into the thousands. Associated with the large number of analyses, and the time required to change tubes between measurement periods, is a large labor requirement. The large analytical and labor requirements of the Schjoerring et al. (1992) method may be prohibitive for many research programs.

Gaseous losses of N, such as NH_3 volatilization, can be a big part of the N budget in many situations and must be accurately accounted for. Rates of NH_3 volatilization are typically very rapid immediately following application of animal manures (Sommer et al., 1991; Cabrera et al., 1993; Nathan and Malzer, 1994; Moal et al., 1995). Rates as high as 25.7 kg NH_3 ha⁻¹ d⁻¹ have been reported for studies involving poultry manures (Nathan and Malzer, 1994). Cumulative losses

of N via NH_3 volatilization can amount to a significant portion of applied N. Ammonia losses from animal manures have been found to range from 3.6 to 60% of total N applied (Cabrera et al., 1993; Brinson et al., 1994; Moal et al., 1995). As the demand for food increases around the world, the potential for environmental pollution from N sources increases as well. In the future, N use will have to become more efficient in order to reduce pollution potential. Because NH_3 volatilization from land applied animal manures represents a potential environmental hazard and loss of N fertilizer value to producers, quantification of this N cycle component under field conditions is necessary. Currently, however, there is no method for field-scale measurement of NH_3 volatilization that is user-friendly with respect to initial costs, and time and labor requirements. We have designed a method to remedy that situation.

MATERIALS AND METHODS

Our passive flux NH_3 collection method utilizes the best aspects of the Leuning et al. (1985) and Schjoerring et al. (1992) methods, i.e., low analytical and labor requirements (Leuning et al., 1985) and low initial cost (Schjoerring et al., 1992). We accomplish this by use of a rotating mast which provides for the same mast configuration as utilized in the Leuning et al. (1985) method. As with the Leuning et al. (1985) method, measurement of wind speed is not necessary because wind speed is integrated into the measurement, i.e., more NH_3 is captured in the sampler as wind speed increases. Masts and bases are constructed of aluminum according to the designs shown in Figure 1. Instead of the expensive measurement devices developed by Leuning et al. (1985), we use glass tubes (200 mm long with an inner and outer diameter of 7 and 10 mm, respectively). A stainless steel disk (Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Hoejbjerg, Denmark) with a 1-mm hole in the center is connected to the upwind end of each glass tube. The rotating mast has a windvane mounted at the top so the glass tubes always face the prevailing wind (Figure 1). The rotating mast has holes drilled perpendicular to its height that are fitted with rubber grommets to accept the glass tubes (Figure 1). The mast slides onto a base having a steel rod on which bearings are mounted to ensure that the mast rotates into the slightest prevailing wind (Figure 1). Unlike the Schjoerring et al. (1992) method, only one tube/height is required, because the tubes always face the prevailing wind.

Our field test was conducted using urea as a N source, applied at a rate of 200 kg N ha⁻¹ in a one-time application. Field tests of our method were conducted at the Turfgrass Research Unit on the campus of Auburn University, Auburn, AL. To prove the efficacy of our method in determining NH_3 flux from land-applied amendments, we compared it directly to the established Leuning et al. (1985) method on the same 15-m radius plot. One mast was placed in the center of the plot, and one NH_3 sampler (Leuning et al., 1985) and one glass tube were mounted

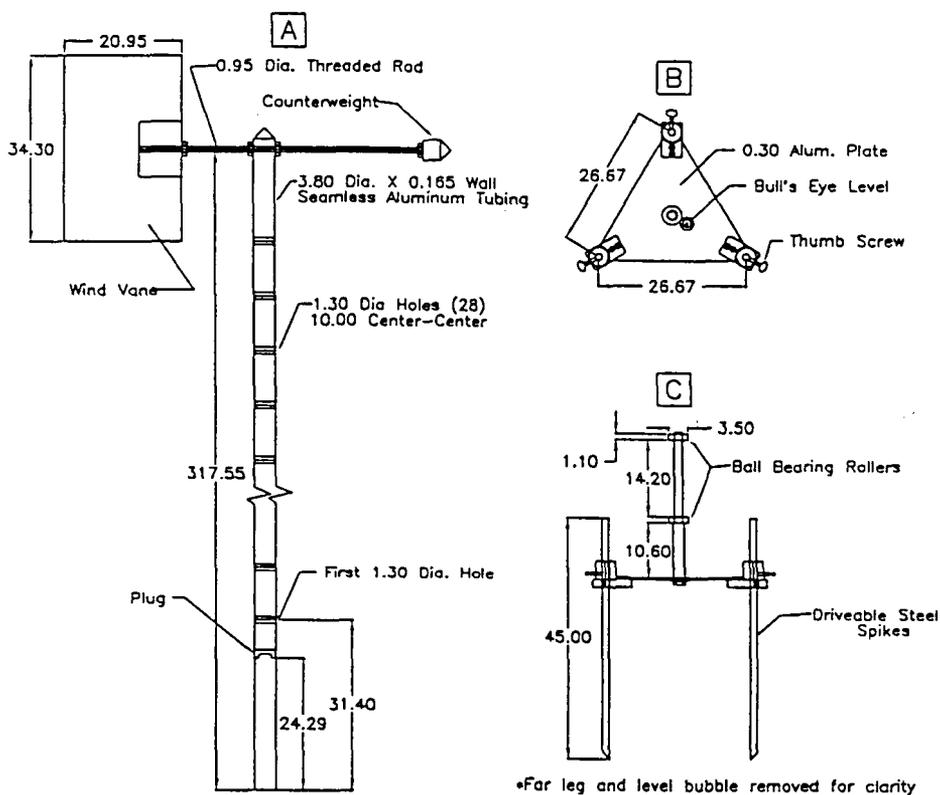


FIGURE 1. Schematic diagram of the rotating mast and base constructed for this study. (A) Side view of the rotating mast and windvane assembly. (B) Top view of the base. (C) Side view of the base. All numbers given are in centimeters.

side by side at each of four heights (0.63, 1.42, 2.21, 3.00 m). Our study did not include a background mast because we did not have the number of NH₃ samplers (Leuning et al., 1985) that would have been required. However, since we were interested in comparing methods, but not interested in the actual amount of N volatilized over the measurement period, background measurements were not necessary. The inside of the NH₃ samplers and glass tubes had previously been coated with oxalic acid (3% w/v in acetone). The NH₃ samplers were attached to the rotating mast with hose clamps. After each exposure period, glass tubes and NH₃ samplers were extracted in 2 and 40 mL deionized water, respectively, and analyzed colorimetrically using a microplate technique for NH₄-N concentration

(Sims et al., 1995). The vertical flux of NH_3 from the plot area was determined by calculating the horizontal flux at each of the four heights and summing the horizontal fluxes from each height. The equations used were modified as follows from Schjoerring et al. (1992):

$$\text{Horizontal flux} = \frac{M}{\pi \times r^2 \times \Delta t}$$

where M =mass of NH_3 captured, r =radius of opening to tube or sampler, and Δt =time length of measurement.

$$\text{Vertical flux} = \frac{1}{2r} \sum_{h=1}^{h=N} (\text{HF}) \Delta h$$

where HF =horizontal flux from each height, h =height of measurement, N =number of measurement heights, Δh =height interval between samples, and r =radius of plot (m).

RESULTS AND DISCUSSION

The glass tubes consistently measured more NH_3 volatilization than did the NH_3 samplers, as reflected in measurements of both horizontal and vertical fluxes. However, both sampling devices recorded the same pattern of horizontal flux in response to differences in height and length of exposure time (Table 1). As was expected, NH_3 absorption decreased with increasing height and increased as exposure times increased (Table 1). Both sampling devices also followed a similar trend for vertical fluxes (Table 2). Although the total amount of NH_3 volatilization measured by the glass tubes was higher than that measured by the NH_3 samplers, the values were relatively close (Table 2). Although not a true continuous measurement, cumulative losses of NH_3 from the fertilized area over the periods during which comparisons of the glass tubes and the NH_3 samplers were made amounted to 18.4% and 15.1% of applied N, respectively. There was a strong linear relationship between the two methods for both horizontal and vertical fluxes. Simple linear regression of the horizontal flux data revealed a coefficient of determination of 0.92 for the two methods (Figure 2). Similarly, simple linear regression of the vertical flux data revealed a coefficient of determination of 0.86 for the two methods (Figure 3). These numbers indicate that these methods responded to variability in NH_3 flux the same way, but they do not explain why the glass tubes recorded more volatilization nor which method is more accurate.

One reason the tubes indicate more NH_3 volatilization may be that they are much simpler in design. The tubes are simply one piece of glass tubing with little chance for leaks. The NH_3 samplers are three piece units that could possibly lead to leaks. Also, the glass tubes, being a simple cylinder in shape, can more easily be completely extracted. The NH_3 samplers on the other hand, while also

TABLE 1. Horizontal flux measured in glass tubes and NH₃ samplers at each height and exposed for various lengths of time the first six days after urea application.

Days after application	Exposure time (hr)	Height (m)	Glass tube ----- mg NH ₃ m ⁻² hr ⁻¹ -----	NH ₃ sampler
1	6.5	0.63	692	554
1	6.5	1.42	290	317
1	6.5	2.21	213	136
1	6.5	3.00	186	191
2	24.2	0.63	341	324
2	24.2	1.42	180	148
2	24.2	2.21	119	78
2	24.2	3.00	97	77
3	22.6	0.63	733	486
3	22.6	1.42	181	124
3	22.6	2.21	91	66
3	22.6	3.00	126	56
4	29.5	0.63	543	401
4	29.5	1.42	129	96
4	29.5	2.21	88	48
4	29.5	3.00	108	41
5	15.4	0.63	623	419
5	15.4	1.42	245	105
5	15.4	2.21	122	61
5	15.4	3.00	127	65
6	22.3	0.63	421	379
6	22.3	1.42	216	93
6	22.3	2.21	102	61
6	22.3	3.00	125	43

TABLE 2. Vertical NH₃ flux and total NH₃ volatilization measured in glass tubes and NH₃ samplers during the six days after urea application.

Days after application	Exposure time (hr)	Glass tube ----- kg NH ₃ ha ⁻¹ -----	NH ₃ sampler
1	6.5	2.71	2.33
2	24.2	5.35	4.62
3	22.6	8.05	5.23
4	29.5	8.02	5.49
5	15.4	5.31	3.16
6	22.3	5.84	4.05
Total NH ₃ volatilization:		36.8	30.1

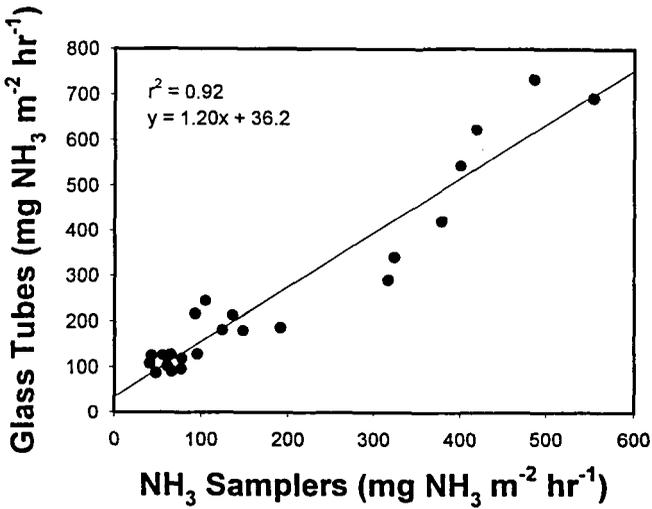


FIGURE 2. Regression of horizontal NH₃ flux measured in glass tubes vs. horizontal NH₃ flux measured in NH₃ samplers.

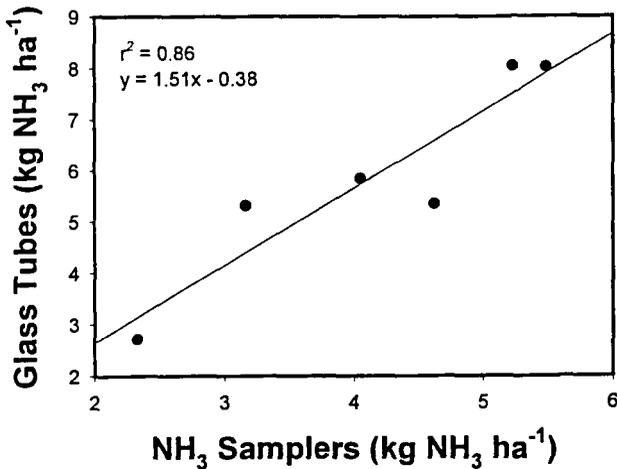


FIGURE 3. Regression of cumulative vertical NH₃ flux measured in glass tubes vs. cumulative vertical NH₃ flux measured in NH₃ samplers.

cylindrical, are filled on the inside with spirals of waffled stainless steel. This material on the inside can make it more difficult to get complete extraction of the absorbed NH₃.

Schjoerring et al. (1992) compared the mean NH₃ flux from two micrometeorological methods to the actual amount of NH₃ lost from beakers containing NH₄HCO₃. They found that mean NH₃ flux from micrometeorological methods was always less than the actual amount of NH₃ lost from the beakers. The micrometeorological methods Schjoerring et al. (1992) looked at underestimated actual NH₃ loss by an average of 45%. They claimed underestimation of NH₃ volatilization recorded in their study was most likely caused by deposition of NH₃ and subsequent absorption of NH₃ to the soil surface, which are processes that would affect any micrometeorological method. Based on their findings, it would appear that micrometeorological methods may underestimate actual NH₃ volatilization. If this is true, then both methods in our study likely underestimated actual amounts of NH₃ loss. The NH₃ loss measured by our method was 18% higher than that measured by the micrometeorological method we used as a reference. Therefore, since it appears that micrometeorological methods may underestimate actual NH₃ volatilization, and our method using glass tubes, absorbed more NH₃, we conclude that our method is likely to give a more accurate measure of NH₃ volatilization compared to NH₃ samplers of the reference method.

CONCLUSIONS

Our method is an improvement over the Leuning et al. (1985) and Schjoerring et al. (1992) methods in terms of initial cost, and analytical and labor requirements. Each of our collection devices (glass tubes) costs a maximum of US \$1.35 to fabricate (less if the researcher's laboratory has the capacity to cut and fire-polish the tubes), which is 185X less than the cost of the device described by Leuning et al. (1985). Also, our rotating mast costs no more to build than the masts constructed for the other methods. Our method also results in 8X less NH₃ analyses/plot/measurement time than the Schjoerring et al. (1992) method. Our new method reduces these cost and labor requirements without sacrificing accuracy of NH₃ volatilization estimates. In fact, we believe our method yields a more accurate measure of NH₃ volatilization because it is less likely to underestimate true NH₃ volatilization. In summary, we have devised and tested a new method of measuring field-scale NH₃ volatilization from land-applied N that is less expensive, less complex, and more accurate than methods previously available.

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