NEW METHODS TO QUANTIFY NH₃ VOLATILIZATION FROM FERTILIZED SURFACE SOIL WITH UREA

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SUMMARY

Gaseous N losses from soil are considerable, resulting mostly from ammonia volatilization linked to agricultural activities such as pasture fertilization. The use of simple and accessible measurement methods of such losses is fundamental in the evaluation of the N cycle in agricultural systems. The purpose of this study was to evaluate quantification methods of NH₃ volatilization from fertilized surface soil with urea, with minimal influence on the volatilization processes. The greenhouse experiment was arranged in a completely randomized design with 13 treatments and five replications, with the following treatments: (1) Polyurethane foam (density 20 kg m⁻³) with phosphoric acid solution absorber (foam absorber), installed 1, 5, 10 and 20 cm above the soil surface; (2) Paper filter with sulfuric acid solution absorber (paper absorber, 1, 5, 10 and 20 cm above the soil surface); (3) Sulfuric acid solution absorber (1, 5 and 10 cm above the soil surface); (4) Semi-open static collector; (5) ^15N balance (control). The foam absorber placed 1 cm above the soil surface estimated the real daily rate of loss and accumulated loss of NH₃-N and proved efficient in capturing NH₃ volatilized from urea-treated soil. The

(1) Part of first author’s M.S. dissertation. Research funded by FAPESP. Received for publication in October 2009 and approved in October 2010.
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estimates based on acid absorbers 1, 5 and 10 cm above the soil surface and paper absorbers 1 and 5 cm above the soil surface were only realistic for accumulated N-NH₃ losses. Foam absorbers can be indicated to quantify accumulated and daily rates of NH₃ volatilization losses similarly to an open static chamber, making calibration equations or correction factors unnecessary.

Index terms: fertilizer-N, ammonia absorber, ¹⁵N, NH₃-N loss.

INTRODUCTION

Pastures constitute the basis of beef cattle production in Brazil. Economically, production systems that use this feed source are highly competitive in comparison with systems based on agroindustrial by-products, cereal grains and silage (Hodgson, 1990). Fertilization is considered the best alternative to increase beef production, since the possibility of increasing pasture area is limited (Balsalobre, 2002).

For the economic viability of pasture-based beef production it is essential to know how to use fertilizers appropriately to intensify pasture productivity. Nowadays, the maximum efficiency of a fertilizer must be directly related to the lowest environmental impact. Nitrogen fertilizers are the most commonly used, the most expensive and have the greatest potential to damage the environment of all fertilizers.

Gaseous N losses are the main cause of inefficiency of N-fertilizers, contributing to the emission of ammonia, molecular N (N₂) and N oxides, mainly nitrous oxide, into the atmosphere. Such losses must be understood for an appropriate pasture fertilization management and to rationalize fertilizer use. However, methods used to estimate ammonia volatilization losses are expensive and may alter the environmental conditions near the soil surface, by the presence of a collection chamber, and bias the results (Lara-Cabezas & Trivelin, 1999; Araújo et al., 2009). Due to these difficulties and the high cost of NH₃-N losses from pasture systems (Oliveira, 2001; Oliveira et al., 2003, 2007), simple and accessible methods must be developed to evaluate these processes, which are also essential to analyze the N cycle. New methods for the estimation of ammonia volatilization must be calibrated using the ¹⁵N isotope balance technique as reference (Lara Cabeza et al., 1999; Araújo et al., 2009). Thus, the objective of this study was to evaluate and calibrate new quantification methods of N-NH₃ volatilized from urea-treated soil, with minimal disturbance of the volatilization processes.
MATERIAL AND METHODS

The experiment was carried out in a greenhouse of the Department of Animal Science/College of Animal Science and Food Engineering, USP, Pirassununga, SP (21° 59’ S, 47° 26’ W, 634 m asl). Soil was sampled in the 0–20 cm layer of a Typic Hapludox (Embrapa, 1999). Soil bulk density was measured by the volumetric ring method (Machado et al., 2005). Lime analysis was performed according to the saturation base method (Quaggio & Raij, 1996), after which soil samples remained incubated during 90 days. At the end of the incubation period the chemical analysis (Machado et al., 2005) indicated pH (CaCl2) of 6.6; K, Ca and Mg concentrations of 1.7, 39 and 14 mmol dm−3, respectively; CTC of 63 mmol dm−3; and base saturation (V %) of 87 %. Temperature and relative humidity means in the greenhouse are presented in figure 1.

The experiment was arranged in a completely randomized design with 13 treatments and five replications. The factors studied were methods of NH3-loss evaluation and distances between the soil surface and NH3-absorbers, by the following methods: (1) Polyurethane foam (density of 20 kg m−3) with phosphoric acid solution absorber (foam absorber) placed 1, 5, 10 and 20 cm above the soil surface; (2) Paper filter with sulfuric acid solution absorber (paper absorber, 1, 5, 10 and 10 cm above the soil surface); (3) Sulfuric acid solution absorber (1, 5 and 10 cm above the soil surface); (4) Semi-open static collector and (5) 15N balance as reference method.

The experiment lasted from August 26 to September 15, 2005. Plastic pots (17 x 20 cm) without holes for water drainage, to avoid N loss by leaching were filled with 4.4 kg of finely ground air-dried soil. Each pot represented a plot and was fertilized with N at a rate corresponding to 100 kg ha−1 N-urea. The pots for the foam, paper absorber and semi-open static collector treatments were fertilized with normal urea, while those for the 15N balance treatment received enriched urea (5 % 15N). The fertilizer was diluted in water and then applied to the soil surface. Absorbers and collectors were placed above the pots according to the treatments, except for the 15N balance treatment, where no absorber or collector was installed.

The foam and paper filters of the absorbers and collectors were changed every two days to determine the volatilized ammonia, totaling 11 samples in a period of 22 days.

The pots placed on benches were protected by transparent plastic curtains to avoid interference of the air flow from the greenhouse exhaust fans with the capture of volatilized ammonia. Soil moisture was maintained at 50 % of the available water content (AWC), approximately. Pots were daily weighed and watered as required.

The foam absorbers (described in Figure 2) consisted of polyurethane (PU) foams (8.0 x 8.0 cm; density 20 kg m−3) soaked with 11 mL of phosphoric acid solution (0.167 mol L−1). They were placed above PVC plates (10.0 x 10.0 x 0.2 cm) and wrapped in a layer of polytetrafluoroethylene tape (PTFE, density 0.25–0.35 g cm−3, thickness 0.05–0.06 mm), ammonia-permeable and water impermeable. The plates were then installed upside-down above the pots, supported by four plastic rods, maintaining the absorbers at the established distances from the soil surface.

For the paper absorbers, filter paper (8.0 x 8.0 cm) was immersed in 2 mL of H2SO4 solution (5 mol L−1) and the collectors were installed like the foam absorbers.

To prevent contamination with environmental NH3, the absorbers were maintained in plastic bags until installation on the pots. Above each pot one absorber was installed at a specific height, according to the treatment (1, 5, 10 or 20 cm). The PVC plates on the upper side of the absorbers prevented the capture of ammonia present over the collector. After two days, the absorbers were removed, deep-frozen (−18 oC) in plastic bags and immediately replaced by new absorbers.

At the end of the experimental period, the absorbers were disassembled and components washed with deionized or distilled water. For each absorber, the

![Figure 1. Mean temperatures (°C) and relative air humidity (%) during the experimental period (2005).](image-url)
PVC plate and the PTFE tape were washed with approximately 30 mL of water, using a wash bottle, above the PU foam placed in a Bückner funnel attached to a Kitassato and a vacuum pump. For a complete removal of the acid solution, the foam was washed a second time with distilled or deionized water (approximately 300 mL) in the Bückner-Kitassato apparatus. The solution collected in the Kitassato was then transferred to a Backer and the volume recorded for later calculations. To determine N, 50 mL aliquots were analyzed by the steam distillation and titration micro-Kjeldahl procedure (Carmo et al., 2005). For the paper absorbers, each paper filter was finely ground in a mortar and mixed in a Backer with the water used to wash the PVC plate and the PTFE tape (approximately 150 mL). A 50 mL aliquot of the solution produced for each absorber was analyzed for N by the micro-Kjeldahl procedure.

The acid solution absorbers consisted of 35 mL plastic containers (3.5 cm diameter) filled with 5 mL of H₂SO₄ solution (5 mol L⁻¹). The top of each container was sealed with PTFE tape (same type as described before) fixed in place by the container’s lid in which a 3 cm in diameter hole was previously produced. The absorbers were maintained in plastic bags until transference to the plots. The absorbers were fixed upside-down on plastic rods at the established distances from the soil surface. After two days the absorbers were replaced by new ones. The liquid from the containers were placed in sealed and labeled flasks and deep-frozen. To quantify the absorbed N, the flask content was diluted in water to 150 mL. Samples (50 mL) were separated for the micro-Kjeldahl procedure.

The semi-open static collectors used in the experiment had been developed by Nönmik (1973), and adapted by Lara Cabezas et al. (1999). The PU foam pieces were soaked in 30 mL of phosphoric acid solution (0.167 mol L⁻¹) with 5 % glycerin and stored in plastic bags before being placed in the collectors. Foams were removed and replaced every two days until the 22nd day. The foams located on the upper part of the collectors were discarded and those located on the lower part were put in plastic bags, identified and deep-frozen until analysis. To quantify N, each foam was washed with water (400 mL, approximately) in a Bückner-Kitassato vacuum pump system and a 50 mL sample was separated for the micro-Kjeldahl procedure. Due to the usual variations in internal conditions in semi-open static collectors (increase in soil moisture and recycling of vaporized water), which interfere with the natural volatilization process (Lara Cabezas & Trivelin, 1990), calibration equations (Lara Cabezas et al., 1999) were used to express N-NH₃ volatilization.

For the ¹⁵N balance treatment, N was applied at a rate of 100 kg ha⁻¹ N of enriched urea (5 atom % ¹⁵N). After 22 days, samples were taken from each pot, from three layers (0–5, 5–10 and 10–15 cm). A H₂SO₄ 5 mol L⁻¹ solution was sprayed on the surface of each sample, to avoid NH₃ volatilization, and the soil dried in a forced-air oven (40 °C/72 h) for posterior analysis by mass spectrometry (ANCA SL) at the CENA/USP laboratory. The non-enriched soil was also evaluated for natural ¹⁵N abundance.

To estimate ammonia volatilization losses, by the ¹⁵N balance method, the following aspects were evaluated:
1. N content (g kg⁻¹) and ¹⁵N content (atom %) in the soil from the plots – quantified in a mass spectrometer attached to an ANCA-SL analyzer (Europa Scientific Ltda.);
2. N percentage originated by the fertilizer (%SNFF) in the soil, according to the equation: %SNFF = \( \frac{a-c}{b-c} \times 100 \), where:
   - a = ¹⁵N abundance in the soil (atoms %)
   - b = ¹⁵N abundance in the labeled fertilizer
   - c = ¹⁵N natural abundance in the control soil (without fertilizer)
3. Amount of soil N derived from the fertilizer (ASNFF), according to the equation:
   \[ \text{ASNFF} (\text{g/pot}) = \frac{\%SNFF}{100} \times N_p \]
   where: Np = accumulated N in the soil from the pots (g);
4. Recovery of N applied to the soil
   \[ \text{Rec} = \frac{\text{ASNFF}}{\text{QAN}} \times 100 \]
   where: QAN = quantity of N applied
5. Volatilization losses
   \[ \text{Losses} = 100 - \text{Rec} \]

Data were analyzed by ANOVA and means compared by Tukey’s test using SAS software (SAS, 1999). For accumulated NH₃-N volatilization the reference method was the ¹⁵N balance method. For NH₃-N daily volatilization rate, daily values were compared using values from the semi-open static collector method as reference.
RESULTS AND DISCUSSION

Estimates of accumulated loss of volatilized NH₃-N based on the semi-open static collector were similar only to estimates obtained by foam absorber 1 cm (FA1) and ¹⁵N balance (¹⁵N) methods (p < 0.01). No calibration equation or correction factor was necessary to estimate the accumulated loss of volatilized NH₃, as occurred with the results obtained by Araújo et al. (2009) and Lara Cabezas et al. (1999). The use of acid absorbers 1, 5 and 10 cm (AA1, AA5 and AA10) and paper absorbers 1 and 5 cm (PA1 and PA5) above the soil resulted in similar values for accumulated NH₃-N compared to ¹⁵N balance (p < 0.01) (Table 1). Therefore, the semi-open collector, FA1, AA1, AA5, AA10, PA1, and PA5 estimated the real accumulated NH₃-N losses. Manzoni & Trivelin (personal communication) compared the paper absorber and the ¹⁵N balance methods observing that the paper absorber 1 cm only estimated real NH₃-N losses by volatilization when volatilization was high.

Foam absorbers at 5, 10 and 20 cm (FA5, FA10 and FA20) and the paper absorbers 10 and 20 cm (PA10 and PA20) underestimated N-NH₃ volatilization losses. It is possible that part of the volatilized NH₃-N was dispersed in the air before reaching the absorbers.

The estimates of accumulated NH₃-N losses were similar for FA1, AA1, AA5, AA10, PA1, PA5 and ¹⁵N balance methods. However, in order to verify if these methods were able to estimate the real NH₃-N volatilization, it would be necessary to compare not only the accumulated values, but the values of the daily NH₃-N loss rate with the reference method (¹⁵N balance), that is, with the curve of ammonia volatilization rates over time. NH₃-N volatilization by the ¹⁵N balance method was only evaluated on the last day of the experimental period, so an estimation of the daily rate of ammonia loss by this method was not possible. Nevertheless, the semi-open collector had already been calibrated by the ¹⁵N balance method by Lara Cabezas et al. (1999). Consequently, the NH₃-N loss values obtained by the semi-open collector were compared statistically with values from the other absorbers for each evaluation day (Figures 3, 4 and 5).

From the 4th to the 10th day after urea application the losses estimated by FA1 were similar to those estimated by the semi-open collector (Figure 3). Losses are considered more relevant during this period. On the 14th and 22nd day, losses estimated by both methods were equal again (p < 0.01).

With FA1 it was possible to obtain the real estimates of the accumulated NH₃-N loss by volatilization and the daily rate ammonia loss by volatilization.

Although curves for results by FA5, FA10 and FA20 methods indicated lower NH₃-N volatilization values when compared to the semi-open collector, the pattern was the same, with a peak for NH₃-N loss on the sixth day. The similarity of these curves indicated that the calibration of these methods with ¹⁵N may be possible, as similary done in the case of the semi-open collector by Lara Cabezas & Trivelin (1999) and Araújo et al., 2009.

Losses estimated by PA1 and PA5 were the same as by the semi-open collector, from the 6th to the 10th day and on the 14th and 22nd day after urea application (Figure 4).

On the 6th, 10th and from the 14th to the 18th day after urea application, the amount of volatilized NH₃-N estimated by the semi-open collector method was equal to the AA1 method. Volatilization estimated by AA5 and the semi-open collector was similar from the 8th to the 10th day and from the 14th to the 18th day after urea application (Figure 5). Ammonia

Table 1. Accumulated losses of volatilized NH₃-N estimated by the tested experimental methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Height above the soil surface</th>
<th>Accumulated losses of volatilized N-NH₃</th>
<th>mg/plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-open static collector</td>
<td>.</td>
<td>69.88 a</td>
<td></td>
</tr>
<tr>
<td>Foam absorber</td>
<td>1</td>
<td>53.89 ab</td>
<td></td>
</tr>
<tr>
<td>¹⁵N balance (reference method)</td>
<td>.</td>
<td>46.96 abc</td>
<td></td>
</tr>
<tr>
<td>Acid absorber</td>
<td>1</td>
<td>44.01 bed</td>
<td></td>
</tr>
<tr>
<td>Acid absorber</td>
<td>5</td>
<td>35.53 bed</td>
<td></td>
</tr>
<tr>
<td>Acid absorber</td>
<td>10</td>
<td>34.03 bed</td>
<td></td>
</tr>
<tr>
<td>Paper absorber</td>
<td>1</td>
<td>27.88 cde</td>
<td></td>
</tr>
<tr>
<td>Paper absorber</td>
<td>5</td>
<td>25.87 cde</td>
<td></td>
</tr>
<tr>
<td>Foam absorber</td>
<td>10</td>
<td>21.96 de</td>
<td></td>
</tr>
<tr>
<td>Foam absorber</td>
<td>5</td>
<td>21.32 de</td>
<td></td>
</tr>
<tr>
<td>Paper absorber</td>
<td>10</td>
<td>13.33 e</td>
<td></td>
</tr>
<tr>
<td>Foam absorber</td>
<td>20</td>
<td>13.33 e</td>
<td></td>
</tr>
<tr>
<td>Paper absorber</td>
<td>20</td>
<td>12.14 e</td>
<td></td>
</tr>
<tr>
<td>CV (%)</td>
<td>.</td>
<td>34.70</td>
<td></td>
</tr>
</tbody>
</table>

Means followed by different letters are different (P ≤ 0.01) by Turkey’s test.
volatilization reached maximum values between the 4th and 6th day after urea application, as reported by Lara Cabezas & Trivelin (1990) and Costa et al. (2003). It was observed that the amounts of lost and captured NH3-N detected by FA1 were most similar to those of the semi-open collector, in the 22 days of
evaluation. Since estimates of NH$_3$-N volatilization by FA1 and semi-open collector were equal to estimates by the $^{15}$N balance method, it is possible to indicate FA1 as an advantageous alternative to the other two methods, mainly because it is less expensive and does not interfere with the natural process of NH$_3$ volatilization from the soil either, as verified by Lara Cabezas & Trivelin (1990) for the semi-open collector.

The evaluation of the FA1 method under field conditions is under way, with a view to quantify ammonia volatilization and foliar emission in pastures.

**CONCLUSION**

Polyurethane foam with phosphoric acid solution absorber (foam absorber) installed 1 cm above the soil surface is efficient in capturing N-NH$_3$ volatilized from urea-treated soil, estimating the daily and accumulated loss rates of N-NH$_3$ correctly.

**ACKNOWLEDGEMENT**

The authors gratefully acknowledge funding support of this research by the Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP.

**LITERATURE CITED**


