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A simple and easy method to measure ammonia volatilization: Accuracy under field conditions

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ABSTRACT

Field studies on soil ammonia (NH_3) volatilization are restricted in many countries owing to the high costs commonly demanded for accurate quantification. We assessed the accuracy of a simple, open chamber design to capture NH_3 under field conditions, as affected by different chamber placement schemes. Urea-^{15}N was surface applied to lysimeters installed in the spaces between maize rows. Open chambers made from plastic bottles were installed on each lysimeter with variations in i) N rates (3, 8, 13, and 18 g m^{-2}), ii) the height of the chamber above the soil surface (0, 5, and 10 mm), and iii) chamber relocation (static *vs.* dynamic). Reference lysimeters without chambers were used to measure NH_3 losses by ^{15}N-balance. Losses of NH_3-N accounted for more than 50% of the applied N. Relocation of the chambers had no impact on their NH_3-trapping efficiencies, proving to be an unnecessary procedure. Variation in the height of the chambers above the soil surface affected the capture of NH_3, but the results still maintained high linearity with the NH_3 losses quantified by the reference method ($R^2 > 0.98$). When the same placement scheme used in the introductory study describing the chamber was utilized (static and touching the soil surface), we found a trapping efficiency of 60%, which was very similar to that (57%) obtained in the previous study. Our results show that this simple, open chamber design can be used with satisfactory accuracy under field conditions, provided that simple, standardized procedures are warranted.

Key Words: ammonia collector, chamber method, field sampler, gas emission, low-cost chamber, nitrogen cycling

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INTRODUCTION

With the notable exception of soybeans, most important commercial crops are very dependent on the use of high rates of synthetic or organic nitrogen (N)-fertilizers. The use of synthetic organic compounds, such as urea, as fertilizer can generate high N losses through ammonia (NH_3) volatilization, especially when applied on the soil surface. Another primary source of NH_3 volatilization is the deposition of livestock excreta (Nichols *et al*., 2018). After urea hydrolysis into NH_3, some of this gas escapes into the atmosphere, reducing the soil N available to plants. Under propitious soil and weather conditions, more than 50% of the N applied can be lost to the atmosphere as NH_3 (Rochette *et al*., 2013; Martins *et al*., 2017). The emission of this caustic gas can cause significant economic losses and can result in a reaction with acid compounds in the atmosphere forming fine particles of salts less than 2.5 μm, known as PM2.5 (David *et al*., 2019). The humid or dry deposition of these salts on water and land surfaces can contribute to the eutrophication and acidification of ecosystems and indirectly cause the emission of nitrous oxide (N_2O), a potent greenhouse gas (Lam *et al*., 2018). The fine salt particles, approximately the thickness of a blood cell, can be transported long distances and exacerbate air pollution in large cities such as Sao Paulo, Beijing, Cairo, Jakarta, and Los Angeles (Penconek, 2018). Such air pollution is known to cause inflammatory responses in the respiratory system and reduce the resistance of the lungs to infections (Li *et al*., 2019).

To compare practices with the potential to abate NH_3 emissions, it is necessary to use reliable and viable measurement methods. Among the most used methods of quantifying NH_3 volatilization, are micrometeorological techniques (Nelson *et al*., 2019), wind tunnels (Pelster *et al*., 2019), closed static chambers (Rawluk *et al*., 2001), closed dynamic

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chambers (Mariano *et al.*, 2019), and semi-open static chambers (Nômmik, 1973; Rinaldi *et al.*, 2019). Wind tunnels and micrometeorological techniques are expected to cause less disturbance to the environmental conditions near the soil surface, thus, presenting satisfactory accuracy (Sommer and Misselbrook, 2016; Nelson *et al.*, 2019). However, these methods are expensive, require highly-skilled technicians, and demand relatively large plots, which make them nonviable for field studies with multiple treatments and relatively small plots. Because of their viability and convenience, small chambers are very often used to measure NH_3 volatilization. Even so, the construction of some types of chambers, as well as their installation and handling in the field, is sometimes time-consuming and complicated, especially in experiments with more observations (*e.g.*, N rates × sources). Therefore, a chamber type that has received great attention in NH_3 volatilization studies is a simple, open chamber design using an acid trap inside a plastic bottle with the base removed (Jantalia *et al.*, 2012; Nichols *et al.*, 2018). This type of chamber was first described by Araújo *et al.* (2009). The advantages of this type of open chamber are i) easy construction, with the necessary materials available in any region at low cost; ii) easy handling in field experiments, allowing more replication; and iii) free air circulation through the chamber, which minimizes the differences in terms of temperature and humidity between the inside and the outside of the chamber. However, there is a lack of detailed studies on the possible factors affecting the accuracy of this type of chamber under field conditions. This is an intrinsic concern when using techniques of low complexity. The reliability of a method of quantifying gaseous emissions is highly dependent on experimental calibration based on reference methods. Factors related to chamber placement, such as the prolonged deployment of the chamber in one position on the soil surface, could influence its NH_3 trapping efficiency by affecting the microenvironment above the soil surface (Parker *et al.*, 2013). For instance, previous studies showed that an “oasis effect” can affect NH_3 volatilization losses from small-scale measurement areas, causing misinterpretation of the effects of the treatments in a given study (Watt *et al.*, 2016).

The aim of the present study was to assess the influence of the placement scheme of a simply designed open chamber on its NH_3-N trapping efficiency and on its linearity with NH_3-N losses measured by an isotopic reference method to define specific correction factors. The hypothesis is that the observation of simple methodological procedures in the application of this low-cost methodology warrants NH_3 volatilization measurements with an appropriate degree of accuracy.

MATERIALS AND METHODS

Field experiment

A mesocosm experiment was conducted at the Experimental Station of the Brazilian Agricultural Research Corporation, National Agrobiology Research Center, Seropédica, Rio de Janeiro State, Brazil (22°45′ S, 43°40′ W, 33 m above sea level). The climate of the experimental site is tropical (Köppen’s Aw) with a mean annual rainfall of 1 300 mm and a mean annual temperature of 19.8 °C. The wet season occurs from December to March. The experiment simulated a surface broadcasting of urea as a N top-dressing for maize at the six-leaf stage. The soil in the experimental area is a Haplic Acrisol, based on the World Reference Base for Soil Resources (FAO, 2015) or an Ultisol (Typic Hapludult), based on the United States Department of Agriculture (USDA) Soil Taxonomy (Soil Survey Staff, 2018). A square area of 30 m × 30 m was plowed and harrowed to 20 cm depth. A single-cross hybrid of maize (*Zea mays* L., cv. BM207) was sown in this area on January 23, 2018, using a row spacing of 1.0 m (6 plants m^{-1}).

Approximately 5 Mg moist soil was collected from the 0–20 cm layer in an area adjacent to that prepared for maize sowing. The collected soil was mechanically sieved ($<$ 4 mm), transported to a shed, and spread out in a 3-cm layer for air-drying in the shade for 48 h. An aliquot of the collected soil was used for chemical and physical characterization. The soil presented the following properties: pH (H_2O), 5.0; cation exchange capacity, 74 $mmol_c$ kg^{-1}; base saturation, 39%; soil organic carbon (SOC), 12 g kg^{-1}; total N, 1.1 g kg^{-1}; $\delta^{15}N$, 10.7‰; sand, 750 g kg^{-1}; silt, 60 g kg^{-1}; and clay, 190 g kg^{-1}. After that, the soil was amended with lime (2.0 g kg^{-1} soil) and thoroughly homogenized using a concrete mixer. The soil was limed to increase the soil urease activity (van Slyke and Zacharias, 1914) and, therefore, the potential NH_3 volatilization.

After liming, the soil was transferred into small lysimeters made of two stacked plastic boxes (Fig. 1). Each box was 37 cm long, 30 cm wide, and 15.5 cm deep. The upper plastic box was filled with 16.5 kg air-dried soil. The bottom of this box was perforated with 20 holes (8-mm diameter) and covered with a thin layer of fine gravel and a piece of synthetic fabric to allow free drainage. The lower box was used as a reservoir to collect the leachate from the soil. A small plastic tube was connected to the bottom of this box for leachate collection using a vacuum pump (Fig. 1).

Soil moisture was increased to field capacity (24.8%, volume/volume) over a period of 2 d by slowly dripping water through 200-mL disposable plastic cups very finely perforated with a needle. After that, a 2-week pre-incubation was performed to stabilize the microbial activity (Martins *et al.*, 2013) and some natural physical processes (Dexter *et al.*, 1988). Water content was adjusted by weighing every 2 d during pre-incubation. The soil pH rose to 6.3 at the end of this period. After that, the lysimeters were transported to the field and inserted and buried in the pre-excavated

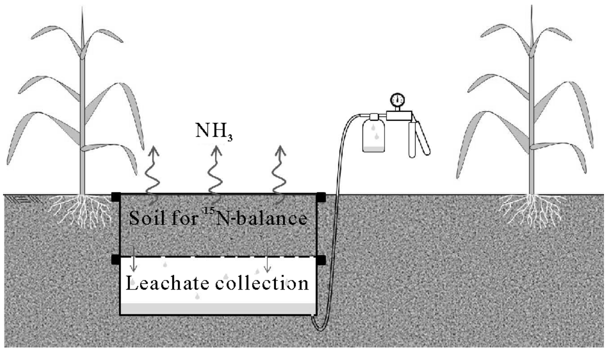

Fig. 1 Schematic representation of the lysimeters used to measure NH_3 volatilization losses based on ^{15}N-balance. This method was used as a reference for calibration of the open chambers based on linear regression.

holes between plant rows. The surface of the soil inside each lysimeter was level with the soil surface in the field (Fig. 1). The lysimeters were spaced evenly, about 2 m apart.

At the end of the experiment (on day 9 after urea application), 500 mL 0.1 mol L^{-1} sulfuric acid solution was carefully and homogeneously spread over the soil surface in each lysimeter to minimize further NH_3-N losses. The lysimeters were immediately transported to a shed. The soil was removed, spread out in 3-cm layers, and air dried in the shade for 48 h over pre-labeled 0.8-m^2 plastic sheets.

Ammonia volatilization measurements using open chambers

Chambers were installed in the lysimeters immediately after application of urea to the soil surface. The design of the chambers was first introduced by Araújo *et al.* (2009). Briefly, the chamber consists of a 2-L plastic soda bottle with the base removed (Fig. 2). A piece of wire (1.24 mm in diameter) was used to install the removed base on top of the bottle, serving as protection against rainwater and dust. The chamber is 0.10 m in diameter; *i.e.*, it traps NH_3 from an area of 0.007 85 m^2. A foam strip (250 mm long, 25 mm wide, and 3 mm thick) presoaked in 10 mL of an acid solution of sulfuric acid (1.0 mol L^{-1}) and glycerol (2.0%, volume/volume) was placed vertically inside the chamber to trap NH_3. The lower end of the foam strip was placed inside a 60-mL plastic pot, which was used to retain the acid solution not absorbed by the foam, thereby avoiding any dripping to the soil surface. A basket made of wire (1.24 mm in diameter) was hung from the top of the bottle and used as a support for the plastic pot and the foam inside the chamber. Further details about this type of chamber were described by Jantalia *et al.* (2012) and Nichols *et al.* (2018).

Metallic supports were used to vertically anchor the chamber inside the area of the lysimeter. To make the supports, wire stakes, 4.2 mm in diameter and 105 cm in length, were shaped to form square U-profiles (35 cm wide and 35 cm high). Two parallel supports were installed 20 cm above the lysimeter by inserting their extremities 15 cm into the soil outside the lysimeter. Rubber bands were placed perpendicularly between the parallel supports to hold the chamber in a vertical position above the lysimeter. A 'blank' chamber was installed in the middle of each experimental block to quantify the "outside NH_3", *i.e.*, the amount of trapped NH_3 not originating from the soil (*e.g.*, NH_3 from the upper opening of the chamber). This 'blank' chamber was the same as those described above except for a 40-cm plastic disc installed to cover the soil surface below the chamber.

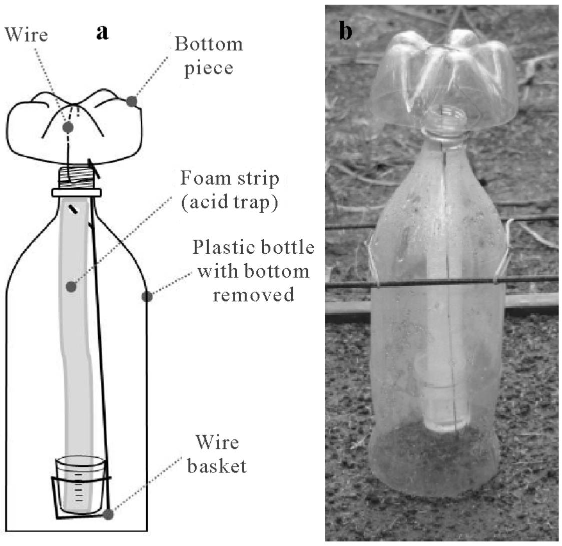

Fig. 2 Schematic representation (a) and a photo (b) of the simple, open chamber used to measure NH_3 volatilization losses in the field.

The foam strips were replaced on days 3 and 6 after N fertilization, with a final collection on day 9. The plastic pots with the collected folded foam strips were hermetically sealed with their lids and transported to the laboratory. The foam strips were then transferred to Erlenmeyer flasks by rinsing the plastic pots with 40 mL of deionized water. The Erlenmeyer flasks were shaken for 20 min at 220 r m^{-1} on an orbital shaker. Then, a 10-mL aliquot of the solution was used for the analysis of NH_4^+ by steam distillation and titration using sulfuric acid solutions with concentrations ranging from 3 to 25 mmol L^{-1}.

Treatments

The experiment adopted a 4 × 3 × 2 factorial arrangement in a randomized complete block design with four replications. The first factor tested in the experiment was N rate, which consisted of 3, 8, 13, and 18 g N m^{-2}. The different rates were applied with the purpose of creating increasing levels of NH_3 volatilization loss. The second factor in the study was the scheme of chamber placement above the soil surface. We tested three different placement schemes: i) the chamber opening just touching the soil surface, which was the scheme used in the introductory study performed by Araújo *et al.* (2009); ii) the chamber opening placed 5 mm above the soil surface; and iii) the chamber opening placed 10 mm above the soil surface. The precise height of the chamber above the emitting soil surface was ensured by three small feet made of 20-mm pieces of a translucent silicone tube (8 mm in diameter) with partial longitudinal cuts. The variation in the height of the chamber above the soil surface was tested with the purpose of simulating situations in which the chamber does not touch the soil surface, such as when there is a layer of plant residue on the soil surface.

The third factor tested in this experiment was the relocation of the chambers to different positions during the period of NH_3 volatilization measurement. Two different schemes were tested: i) static, in which the chamber stayed in the same position from the beginning to the end of the experiment and ii) dynamic, in which the chambers were moved on a daily basis to one of the four predefined positions in the lysimeter (Fig. 3). To standardize this procedure, the area of each lysimeter (0.111 m^2) was split into four virtual quadrants. To facilitate this, the metallic supports of the chambers were placed in such a manner that the chambers could be switched between the four different positions located at the centers of these quadrants. The purpose of testing relocation was to assess if the prolonged presence of the chamber had an effect on the efficiency and linearity of NH_3 trapping.

Urea labeled with 3.5 atom% ^{15}N in excess was surface applied to the soil in the lysimeters when the maize was at the six-leaf stage (30 days after sowing). The urea was evenly distributed across the soil surface of the lysimeter by hand using a 60-mL salt shaker. For each lysimeter, 25 g of washed and dried sand was mixed with the urea to aid in even distribution. Reference lysimeters with no chamber but with the same rates of urea-^{15}N applied (3, 8, 13, and 18 g N m^{-2}) were included in each experimental block. These reference lysimeters were used to determine the NH_3-N volatilization losses based on ^{15}N-balance, which was considered the 'gold standard', that is, a reference method. The NH_3-N losses quantified using these reference lysimeters were used to calibrate the NH_3-trapping efficiency of the chambers. We also used a zero-N control to determine the natural abundance of soil ^{15}N (background soil ^{15}N level) at the end of the experiment.

Total N and ^{15}N analyses

At the end of the mesocosm experiment, after air-dried, the soil from each reference lysimeter was sieved through a 2-mm mesh sieve and homogenized for 5 min using a concrete-mixer (30 r min^{-1}). After that, two 25-g subsamples were taken and finely ground (< 150 μm) using a roller-mill apparatus described in detail by Arnold and Schepers (2004) and Sant'Anna *et al.* (2018). Aliquots (40 mg) of the ground soil were weighed into 12.5 mm × 5.0 mm tared tin capsules (D1010, Elemental Microanalysis Ltd., UK). The total N content and ^{15}N enrichment analyses were performed with an Thermo-Finnigan Flash 2000 elemental analyzer coupled to a Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, USA) in the John Day Stable Isotope Laboratory of Embrapa Agrobiology. The amount of urea-N remaining in the soil at the end of the experiment (N_{rem}), in g N m^{-2}, was calculated as follows:

$$N_{\text{rem}} = \frac{\text{SDW}}{A_{\text{lysimeter}}} \times \frac{N_{\text{soil}}}{100} \times \frac{^{15}\text{NAPE}_{\text{soil}}}{^{15}\text{NAPE}_{\text{urea}}} \tag{1}$$

where SDW is the soil dry weight in each lysimeter (g); $A_{\text{lysimiter}}$ is the soil surface area in the lysimeter (0.111 m^2); N_{soil} is the soil total N content at the end of the experiment (%); $^{15}NAPE_{\text{soil}}$ is the ^{15}N atom% excess in the soil at the end of the experiment; and $^{15}NAPE_{\text{urea}}$ is the ^{15}N atom% excess in the fertilizer.

A 100-mL composite sample of the leachate was obtained for each reference lysimeter by mixing weighed volumes according to the daily volume of leachate produced in the experiment. The analysis of the N concentration in the leachate was performed using steam distillation after a pretreatment with Devarda's alloy to reduce nitrate (NO_3^-) and nitrite (NO_2^-) into ammonium (NH_4^+) (Liao, 1981).

For ^{15}N analysis, a predetermined volume of the solution extracted from the foam strips or of the leachate was pipetted into a 50-mL plastic pot containing 500 mg of aluminum oxide powder (Com-Aid, Leco, USA). Each volume was

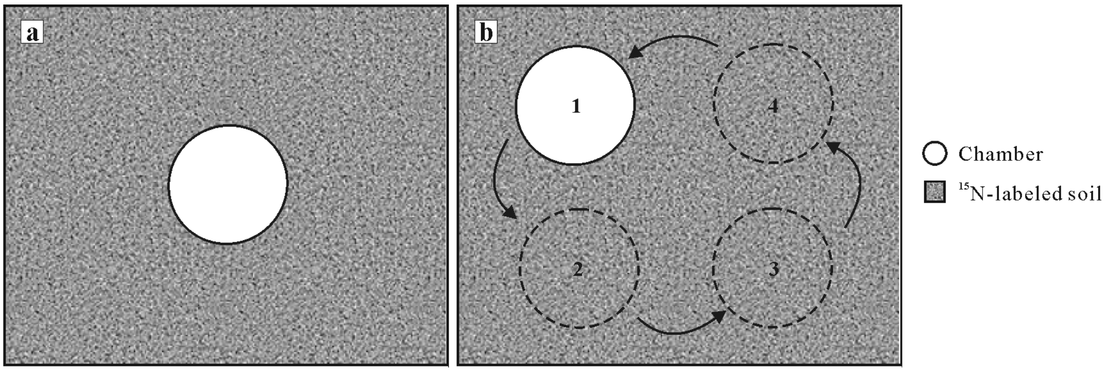

Fig. 3 Schematic representation of the static (a) and dynamic (b) chamber deployment methods tested in the present study.

calculated to obtain 1.0 mg N g^{-1} aluminum oxide powder based on the total N concentration in the solution. Next, the plastic pots were placed in a forced-air oven at 55 °C for 72 h. After drying, 40-mg aliquots of the aluminum oxide powder containing 40 µg N were weighed into tin capsules for ^{15}N analysis following the same procedures described for the soil samples. This aliquot of N (40 µg) was determined to be the best amount for the IRMS in terms of accuracy and precision based on pre-analyses with test samples. To avoid rupture of the tin capsules by oxidation owing to residual sulfuric acid, the IRMS analysis was performed on the same day as the weighing.

The total amount of leached N derived from urea (N_{leach}), in g N m^{-2}, was calculated as follows:

$$\mathrm{N_{leach}} = \frac{V_{\mathrm{leach}}}{A_{\mathrm{lysimeter}}} \times C_{\mathrm{leach}} \times \frac{^{15}\mathrm{NAPE_{leach}}}{^{15}\mathrm{NAPE_{urea}}} \times 10^{-3} \qquad (2)$$

where V_{leach} is the total volume of leached solution collected over 9 d of the experiment, in mL $lysimeter^{-1}$; C_{leach} is the N concentration in the leached solution, in mg mL^{-1}; and $^{15}NAPE_{leach}$ is the ^{15}N atom% excess in the leached solution.

The NH_3-N losses derived from urea measured by ^{15}N-balance ($ANL_{balance}$), in g N m^{-2}, was calculated as follows:

$$\mathrm{ANL_{balance}} = \mathrm{N_{appl}} - \mathrm{N_{rem}} - \mathrm{N_{leach}} \qquad (3)$$

where N_{appl} is the rate of urea applied to the lysimeter, in g N m^{-2}. The losses of urea-derived NH_3-N trapped by chambers ($ANL_{chamber}$), in g N m^{-2}, was calculated as follows:

$$\mathrm{ANL_{chamber}} = \frac{\mathrm{NTC}}{A_{\mathrm{chamber}}} \times \frac{^{15}\mathrm{NAPE_{foam}}}{^{15}\mathrm{NAPE_{urea}}} \qquad (4)$$

where NTC is the amount of NH_3-N trapped in the chamber, in g N; $A_{chamber}$ is the soil surface area covered by the chamber (0.007 85 m^2); and $^{15}NAPE_{foam}$ is the ^{15}N atom% excess in the solution extracted from the NH_3-N-trapping foam strip in the chamber.

Gaseous N losses other than NH_3 volatilization

A nitrification inhibitor was added to the ^{15}N-labeled urea to control significant gaseous N losses other than NH_3 volatilization losses, *i.e.*, to minimize gaseous N losses as N_2O and N_2, which are primarily associated with nitrification and denitrification. The compound 2-chloro-6-(trichloromethyl) pyridine, known as nitrapyrin, was used as a nitrification inhibitor and added to the urea at a rate of 1%. The detailed procedures followed when mixing the nitrapyrin with the urea were previously described by Martins *et al.* (2017). To check the effectiveness of nitrapyrin in controlling the gaseous N losses associated with nitrification and denitrification, a parallel experiment was conducted simultaneously to the study described above, to calibrate the NH_3 chambers. In this parallel experiment, we measured daily N_2O fluxes as a general indicator of gaseous N losses due to nitrification and denitrification, based on the fact that this gas is an inherent by-product of both processes (Zhu *et al.*, 2013). Three additional lysimeters were included in each experimental block previously described for the calibration of the NH_3 chambers. Three treatments were tested in this parallel experiment: i) regular urea at 10 g N m^{-2}; ii) urea plus nitrapyrin at 10 g N m^{-2}; and iii) a control (no added N).

The N_2O emissions were measured using non-flow-through, non-steady-state chambers, which consisted of a plastic box, identical to that described for the manufacture of the lysimeters. The chamber was insulated with a 30-mm layer of polyurethane foam (0.018 g cm^{-3}) covered by a self-adhesive bituminous membrane faced with aluminum foil. A sampling port connected to a four-way medical tube, installed at different positions inside the chamber, was used for gas withdrawal. A pressure equilibration vent tube was used following the GraceNet protocol (Parkin *et al.*, 2003). Rubber gaskets and fasteners were used to ensure adequate sealing of the chamber (Clough *et al.*, 2012). Gas sampling was performed daily between 8:30 a.m. and 10:00 a.m., which is the period of day considered to represent the mean daily N_2O flux (Alves *et al.*, 2012). The gas was collected using a 60-mL plastic syringe (polyvinyl chloride syringe). A 35-mL gas sample was taken 0, 20, 40, and 60 min after chamber closure. To purge the system, 10 mL of gas was collected and discarded before each gas sampling. Further details on the procedures of gas collection, analyses of N_2O concentration, and calculation of N_2O fluxes were described by Martins *et al.* (2017).

Auxiliary variables

A rainfall gauge was used to measure daily precipitation (Rainlog Data Logger, Rainwise Inc., USA). Data on temperature, relative air humidity, and wind speed were obtained from a Brazilian National Institute of Meteorology (www.inmet.gov.br) station located 2.0 km southwest of the experimental site. Additionally, for soil moisture monitoring, approximately 10 g of humid soil was sampled daily from an additional lysimeter in each block, using a small auger. These soil samples were oven-dried in aluminum cans for 48 h at 105 °C to determine the gravimetric soil water content. The volumetric water content was obtained by multiplication of the gravimetric water content by the soil bulk density, considering the soil dry mass and the internal dimensions of the lysimeter.

Statistical analyses

The data of the total amount of NH_3-N trapped by the chambers over the nine days of the experiment were subjected to analysis of variance (ANOVA). After that, we tested the statistical significance ($P < 0.05$) of the linear regression $y = a + bx$ to assess the linearity between the amount of volatilized NH_3 trapped by the open chamber (x) and the amount of volatilized NH_3-N measured by ^{15}N-balance in the lysimeters without chambers (y). Statistical analyses were performed using the Sisvar 5.6 software (Ferreira, 2011). All regression analyses were performed only after testing the normality of the errors using the Shapiro-Wilk test and the homogeneity of the variance using Levene's test. When the interception a was not statistically significant ($P > 0.05$), we considered the correction factor for the calibration of the chamber as the slope of the equation (coefficient b) and we calculated the trapping efficiency of the chamber, in percentage, as 100/b.

RESULTS AND DISCUSSION

Ammonia volatilization measured by ^{15}N-balance

The NH_3-N losses measured using the reference method (^{15}N-balance) attained more than 50% of the urea-N applied at 18.0 g N m^{-2} (Table I). These high NH_3-N losses were due to the favorable soil, weather, and fertilizer placement conditions (Fig. 4). The soil pH > 6.0 and soil moisture content almost at field capacity just prior to urea application (Fig. 4a) favored urea dissolution, hydrolysis by urease, and, consequently, NH_3 volatilization (Cabrera *et al.*, 2010). After urea hydrolysis, the NH_3 volatilization process is closely related to soil water evaporation (Al-Kanani *et al.*, 1991), which in turn is a function of wind speed and the partial pressure of water vapor in the atmosphere (Davarzani *et al.*, 2014). Therefore, the drying of the soil over the first few days, which was related to a lowering of the relative air humidity during the afternoon (Fig. 4a, c), as well as the non-limiting air temperatures and wind speeds (Fig. 4b, d) were factors contributing to the high percentages of N lost through NH_3 volatilization.

The results of the parallel experiment to assess gaseous N losses other than NH_3 volatilization showed that cumulative gaseous N loss as N_2O was very low (0.07 g N m^{-2}) from lysimeters receiving regular urea (Fig. 5). The addition of nitrapyrin to the urea further reduced cumulative N_2O emission (0.01 g N m^{-2}), and in these lysimeters the emissions did not differ ($P > 0.05$) from those of the unfertilized control (0.004 g N m^{-2}). This result indicates that nitrapyrin was effective in controlling gaseous N losses through nitrification and denitrification, considering that N_2O is a primary indicator of the occurrence of both processes in soil (Zhu *et al.*, 2013). Therefore, we assumed that gaseous N losses other than NH_3 volatilization were negligible and thus they were not considered in our reference ^{15}N-balance study to measure NH_3 volatilization losses (Table I). The use of nitrapyrin may also have been effective in minimizing losses through N leaching, which were less than 2% of the applied N.

Ammonia trapping by the open chamber

The highest amounts of NH_3-N trapped by the chamber occurred during the first three days after urea application,

TABLE I

Quantification of NH_3 volatilization derived from urea based on ^{15}N-balance

Parameter	Urea application rate (g N m^{-2})				
	0.0	3.0	8.0	13.0	18.0
Total N applied as urea (mg lysimeter^{-1})	0	333	888	1443	1998
Total soil N (g kg^{-1})a)	1.13 ± 0.02b)	1.14 ± 0.01	1.16 ± 0.04	1.21 ± 0.03	1.21 ± 0.03
Total soil N (g lysimeter^{-1})a)	18.7 ± 0.4	18.9 ± 0.2	19.1 ± 0.6	19.9 ± 0.4	20.0 ± 0.5
^{15}N abundance in soil (atom% excess)a)	0.004 ± 0	0.042 ± 0.004	0.090 ± 0.001	0.127 ± 0.005	0.150 ± 0.011
Urea-N remaining in the soil (% of total N)a)	–c)	1.19 ± 0.11	2.49 ± 0.02	3.52 ± 0.16	4.48 ± 0.20
Urea-N remaining in the soil (mg lysimeter^{-1})a)	–	208 ± 22	476 ± 14	701 ± 40	896 ± 40
Urea-N remaining in the soil (% of added N)a)	–	62 ± 7	54 ± 2	49 ± 3	45 ± 4
Total N leaching loss (mg lysimeter^{-1})	61 ± 19	61 ± 4	55 ± 8	54 ± 4	126 ± 50
^{15}N enrichment of leached N (atom% excess)	0.004 ± 0	0.332 ± 0.054	1.040 ± 0.194	1.113 ± 0.178	1.552 ± 0.455
Leached N derived from urea (% in leached N)	–	9 ± 2	28 ± 6	30 ± 5	43 ± 13
Leached N derived from urea (mg lysimeter^{-1})	–	5 ± 1	16 ± 4	16 ± 3	48 ± 23
Fraction of urea-N leached (% of added N)	–	2 ± 0	2 ± 1	1 ± 0	2 ± 1
^{15}N-labeled urea-N lost as NH_3 (mg lysimeter^{-1})d)	–	120 ± 23	396 ± 11	726 ± 43	1 054 ± 59
^{15}N-labeled urea-N lost as NH_3 (g m^{-2})	–	1.1 ± 0.2	3.6 ± 0.1	6.5 ± 0.4	9.5 ± 0.5
Fraction of urea-N lost as NH_3 (% of added N)	–	36 ± 7	45 ± 1	50 ± 3	53 ± 3

a) At the end of the experiment (day 9).

b) Mean ± standard error ($n = 4$).

c) Not applicable.

d) Gaseous N losses derived from fertilizer, other than NH_3 volatilization, were considered to be insignificant based on the auxiliary experiment in which N_2O was measured as an indicator of the occurrence of gaseous N losses caused by nitrification and denitrification (Fig. 4).

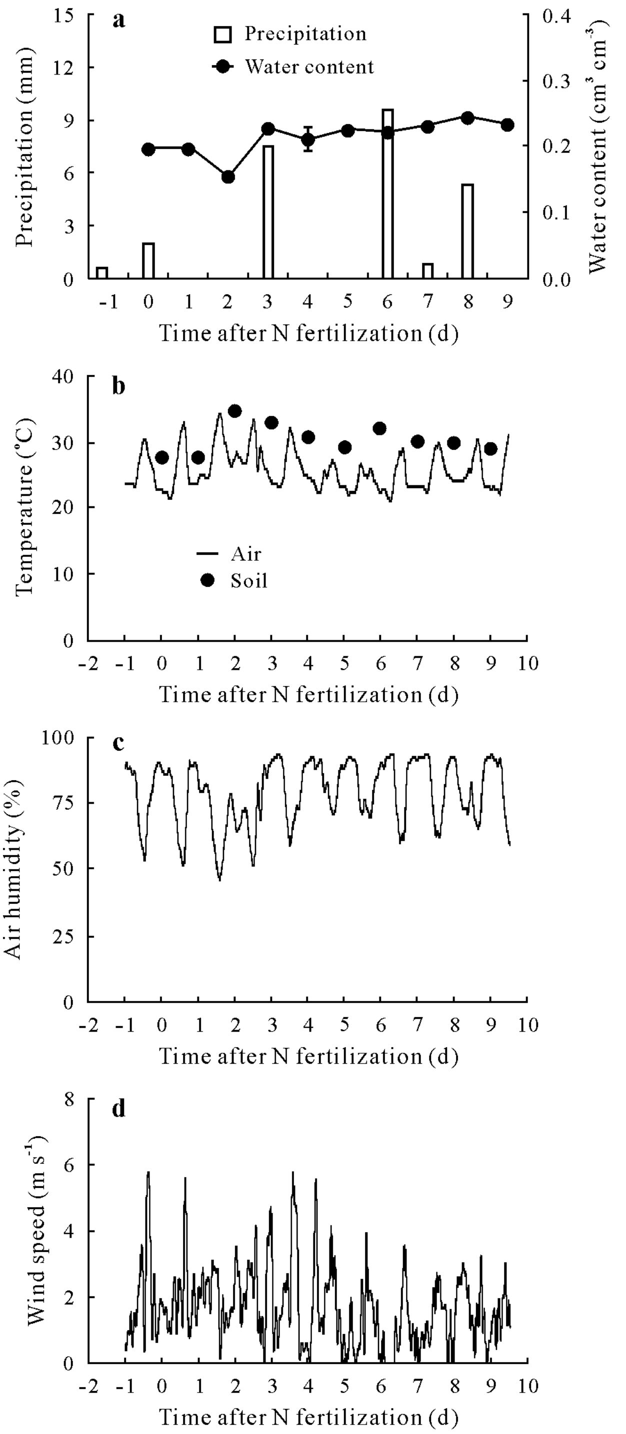

Fig. 4 Precipitation and volumetric soil water content (a), mean daily soil temperature and mean hourly air temperature (b), mean hourly relative air humidity (c), and wind speed (d) during the measurements of NH_3 volatilization for calibration of the chambers. Soil temperature measured at 9:00 am was considered a rough estimate of the mean soil temperature based on the results of the study performed by Alves *et al.* (2012).

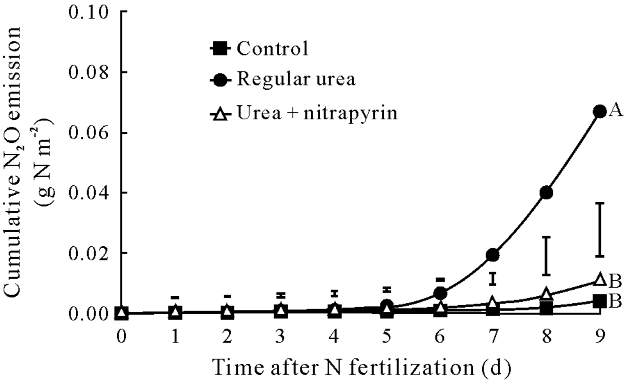

Fig. 5 Cumulative N_2O emission in the treatments during the 9-d experiment. The vertical bars indicate Tukey's least significant differences ($P < 0.05$). The same letters at the end of the lines indicate no significant differences in total cumulative N_2O emission between treatments during the experiment. Control = no N fertilization; regular urea = urea applied at 10 g N m^{-2}; urea + nitrapyrin = regular urea and nitrapyrin at 1% (weight/weight) of urea.

representing, on average, 75% of the total N trapped by the chamber (Table SI, see Supplementary Material for Table SI). The NH_3-N losses in the intermediate period (days 3–6) and in the last period (days 6–9) represented, on average, 17% and 8% of the total N trapped, respectively. High losses in the first few days after the application of urea are usual and have been observed in many experiments with different soil and climatic conditions (Black *et al.*, 1987; Wang *et al.*, 2004; Singh *et al.*, 2013). The amounts of NH_3-N trapped by the blank chambers (outside NH_3) were not detectable and therefore not considered in the final calculations. Only a minor portion of the NH_3 trapped by the chamber was derived from the soil, which contributed to a maximum of 0.3 g N m^{-2} (Table SII, see Supplementary Material for Table SII). The maximum amount of urea-derived N trapped by the chambers was 5.5 g N m^{-2} that occurred when the chamber was kept static and placed touching the soil surface at a N application rate of 18.0 g N m^{-2}.

The relocation of the chamber to different positions in the lysimeter (Fig. 3) had no impact on NH_3 trapping efficiency (Table II). This indicates that the presence of the chamber itself does not affect the process of NH_3 volatilization from soil, which was also shown in previous studies using this type of chamber under different soil and climatic conditions (Araújo *et al.*, 2009; Jantalia *et al.*, 2012). This shows that this chamber does not cause an "oasis" effect as reported in studies

TABLE II

Summary of analysis of variance (ANOVA) of the effects of chamber placement on the capture of NH_3 by a simple, open chamber

Source of variation	F test
Relocation (R)	NS[a)]
Height above soil surface (H)	**
N rate (N)	**
R × H	NS
R × N	NS
H × N	**
R × H × N	NS

**Significant at $P < 0.01$.

[a)] Not significant ($P > 0.05$).

using other methods in which a larger emitting surface is covered, such as when using wind tunnels (Watt *et al.*, 2016). The result of our study is likely due to the small area covered by the chamber (0.007 85 m^2) and to the deployment method which did not use a collar inserted into the soil. Both factors make the homogenization of the soil water content in the area surrounding and enclosed by the chamber easier. This result has a practical consequence for the handling of the chambers in the field. The use of additional metallic supports and the fieldwork involved in daily chamber relocation becomes superfluous because keeping the chamber static does not reduce its NH_3 trapping efficiency (Table II). This is an important advantage when experiments are located at remote sites with many experimental plots and few field assistants. On the other hand, a potential problem associated with the small area of the chamber is the variability in NH_3 emissions caused by the spatial variability of soil properties or by uneven N-fertilizer distribution. This issue was addressed in a recent study testing the use of multiple chambers per plot in a field experiment (Martins *et al.*, 2021). The study showed that the variability of NH_3 volatilization measured by open chambers on a field-plot scale can be significantly reduced by concentrating sampling effort (multiple chambers per plot) to the most critical period of NH_3-N losses, which usually occurs during the first two weeks after N fertilization.

The amount of urea-derived NH_3-N trapped by the chamber was influenced by the interaction between N rate and the height of the chamber above the soil surface ($P <$ 0.01, Table II). The significant effect of this interaction means that the capability of the chamber to trap growing levels of NH_3 derived from growing urea-N rates depended on the height of the chamber above the soil surface (Tables II and SI). At the lowest urea-N rate, no significant differences between the amounts of NH_3 trapped by the chambers were observed (Table SI). In contrast, with increasing urea rate, there was a pronounced effect of chamber height above the soil surface on the capture of NH_3.

Linear regression between the NH_3 trapped by the chamber and the NH_3 volatilization measured by ^{15}N-balance

Because the relocation of the chamber did not affect the capture of NH_3 (Table II), the linear regressions between the NH_3 trapped by the chamber and the amounts of volatilized NH_3 measured by the reference method were performed for each height of chamber above the soil surface. The significant interaction between the height of the chamber above the soil surface and the urea-N rate ($P < 0.01$, Table II) implies that the regression lines for each height have significantly different slopes (Fuchs, 2011). This is clearly shown in Fig. 6. The linear regression presented a good fit to the data obtained from different schemes of chamber placement, as denoted by $R^2 > 0.98$ ($P < 0.01$, Fig. 6). The close approximation to linearity exhibited by the regression lines show that the variance in the amounts of NH_3 measured by the reference method is highly predictable from the amounts of NH_3 trapped by the open chamber. This type of assessment under real conditions of measurement is essential to establish the reliability of a method (Almeida *et al.*, 2002).

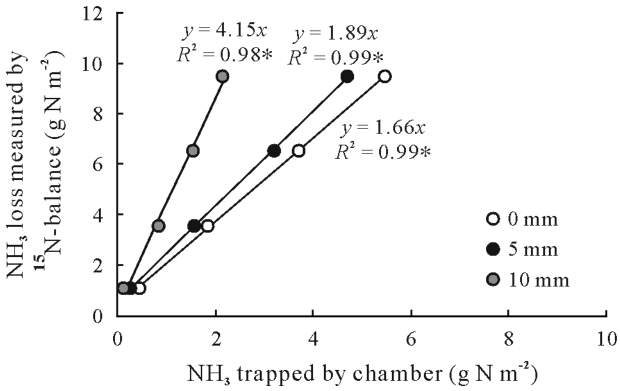

Fig. 6 Linear regression between the NH_3-N loss determined by ^{15}N-balance (no chamber deployment) and the NH_3-N loss trapped by open chambers with three placement schemes (*i.e.*, 0, 5, and 10 mm above the soil surface). The significance of the parameters of regression (slope and intercept) was tested for each treatment. The *P*-values for the y-intercept in the regression models were greater than 0.05, and hence this constant was not considered in the equations.*Significant at $P < 0.05$. 0 mm = 0 mm above (or touching) the soil surface; 5 mm = 5 mm above the soil surface; 10 mm = 10 mm above the soil surface.

The values of y-intercept (coefficient a) estimated for the linear regressions were not significantly different from zero ($P > 0.05$, Fig. 6). Therefore, the slopes of the regression lines were taken as the correction factors for calibration of the chamber. In other words, the coefficient b of the linear regression was used to convert the amount of NH_3 trapped by the chamber into the total amount of NH_3 lost through volatilization (Fig. 6). It is interesting to note that when the chamber was positioned following the scheme described in the introductory study of Araújo *et al.* (2009) (touching the soil surface) the correction factor was 1.66. This value is close to the 1.74 obtained by those authors. The NH_3 trapping efficiency of the chamber, in percentage, was obtained by dividing 100 by the coefficient b. The efficiency was 60% when the chamber was placed touching the soil surface. This efficiency was reduced to 53% and 24%, respectively, when the chamber was placed 5 and 10 mm above the soil surface. Although the NH_3 trapping efficiency of the chamber dropped significantly with increasing height, the linearity of the fit continued to be high, showing a good capability of predicting real NH_3-N losses using the chamber.

The good fit of the regression lines in Fig. 6 shows that the chamber can be used reliably to assess NH_3 volatilization in field experiments, provided that i) the height of the chamber above the soil surface is standardized, and ii) the correction factor for NH_3 trapping efficiency is adjusted if the chamber is placed not touching the soil surface. Overall, the most practical and reliable manner of using the chamber is to keep it static and touching the soil surface. Our results indicate that if this scheme of placement is correctly followed, the correction factor of 1.74 proposed by Araújo *et al.* (2009) has a good possibility of producing an accurate measurement of NH_3 volatilization using the chamber. When the strict application of this scheme of placement is not possible due to the presence of short plants (*e.g.*, grass), plant residue on the soil surface, or the microrelief of the soil, a standardized height should be applied considering a specific correction factor, as presented in our study. It is also important to notice that heights < 5 mm would not cause considerable variation in the NH_3 trapping efficiency of the chamber. Therefore, if the chamber is placed < 5 mm above the soil surface, the use of a correction factor of 1.74 (Araújo *et al.*, 2009) would not cause a significant reduction in the accuracy of this method (Fig. 6).

As a final remark, we stress that use of sophisticated methods, such as micrometeorological mass balance, offers indisputable advantages, including measurements over large areas with high representativeness. However, when the use of such techniques is not possible for financial or technical reasons, the plastic bottle chamber can be a viable option to reliably quantify NH_3 volatilization. Each sampler costs less than two US dollars (Shigaki and Dell, 2015) and can be used with satisfactory accuracy in the field, provided that some simple, standardized methodological procedures are warranted.

CONCLUSIONS

The relocation of the chamber had no impact on its NH_3 trapping efficiency, proving it to be an unnecessary procedure. In contrast, variation in the height of the chamber above the soil surface affected the capture of NH_3 by the chamber, but the results still maintained high linearity with the NH_3 losses quantified using an isotopic reference method ($R^2 > 0.98$). When we applied the same scheme of placement used in the study describing the chamber (Araújo *et al.*, 2009), static and touching the soil surface, we observed a trapping efficiency of 60% (correction factor of 1.66). This result is very similar to the NH_3 trapping efficiency of 57% obtained in that previous study (correction factor of 1.74), showing that satisfactory accuracy is ensured if simple, standardized procedures are followed. The use of this simple, low-cost open chamber was shown to be a suitable and reliable approach to quantifying NH_3 volatilization losses from agricultural soils.

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SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version.

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