Pedosphere **31**(2): 243–254, 2021
doi:10.1016/S1002-0160(20)60078-9
ISSN 1002-0160/CN 32-1315/P

Published by Elsevier B.V. and Science Press

PEDOSPHERE
www.elsevier.com/locate/pedosphere

Optimizing the use of open chambers to measure ammonia volatilization in field plots amended with urea

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(Received December 13, 2018; revised January 29, 2019)

ABSTRACT

Measuring ammonia (NH_3) volatilization from urea-fertilized soils is crucial for evaluation of practices that reduce gaseous nitrogen (N) losses in agriculture. The small area of chambers used for NH_3 volatilization measurements compared with the size of field plots may cause significant errors if inadequate sampling strategies are adopted. Our aims were: i) to investigate the effect of using multiple open chambers on the variability in the measurement of NH_3 volatilization in urea-amended field plots and ii) to define the critical period of NH_3-N losses during which the concentration of sampling effort is capable of reducing uncertainty. The use of only one chamber covering 0.015% of the plot (51.84 m^2) generates a value of NH_3-N loss within an expected margin of error of 30% around the true mean. To reduce the error margin by half (15%), 3–7 chambers were required with a mean of 5 chambers per plot. Concentrating the sampling efforts in the first two weeks after urea application, which is usually the most critical period of N losses and associated errors, represents an efficient strategy to lessen uncertainty in the measurements of NH_3 volatilization. This strategy enhances the power of detection of NH_3-N loss abatement in field experiments using chambers.

Key Words: chamber method, experimental error, gas emission, low-cost chamber, nitrogen cycling, nitrogen loss, soil variability

Citation: Martins M R, Sarkis L F, Sant'Anna S A C, Santos C A, Araujo K E, Santos R C, Araújo E S, Alves B J R, Jantalia C P, Boddey R M, Zaman M, Urquiaga S. 2021. Optimizing the use of open chambers to measure ammonia volatilization in field plots amended with urea. *Pedosphere*. **31**(2): 243–254.

INTRODUCTION

The amount of synthetic nitrogen (N) fertilizers used in agriculture globally in 2017 was estimated to be 150 Tg N year^{-1} (USGS, 2018) and may amount to 260 Tg N year^{-1} by 2050 (Mogollón *et al*., 2018). About 50% of the global N output as synthetic fertilizers is represented by urea (Heffer and Prud'homme, 2016). A fundamental problem in using this fertilizer is the potential loss of N to the atmosphere as volatilized ammonia (NH_3). Under favorable conditions for volatilization, the NH_3-N loss can reach more than 50% of the applied urea-N (Martins *et al*., 2017). This process reduces the N-use efficiency of crops and causes air pollution because of the acidifying nature of NH_3 (Eurostat, 2018). These losses also contribute indirectly to the greenhouse effect. Ammonia reacts in the atmosphere forming salts with a consequent redeposition of N to soil, which generates nitrous oxide (N_2O) in the same manner as N fertilization (Klein *et al*., 2007). The evaluation of mitigating techniques to reduce NH_3 volatilization, such as the use of enhanced-efficiency fertilizers, is based on field experiments with frequent use of chambers to trap NH_3 in acid solution (Cantú *et al*., 2017; Afshar *et al*., 2018).

Although the use of chambers to measure NH_3 volatilization in field experiments is common, the area of the plots is invariably much larger than the area covered by the chambers. Therefore, a question that may be raised is: how representative is the sampling of NH_3 trapped by a chamber in field plots? In fact, the first studies on NH_3 volatilization from fertilized soils were not usually performed under field conditions, but under laboratory or greenhouse conditions (Sokoloff, 1938; Jewitt, 1942). The development of chambers for *in situ* measurement of NH_3 volatilization (Volk, 1959; Nômmik, 1973) made possible the conduction of experiments to evaluate N gaseous losses under more realistic field conditions, *e.g.*, with wetting-drying cycles in the soil, small-scale spatial variation in soil parameters, and plant-soil interactions. However, a difficulty that persists even after

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more than 50 years is to assess how much uncertainty is associated with measurements of NH_3 volatilization in field experiments. In statistics, the lower the uncertainty, the lower the probability of making a type II error (β), which is the failure to reject a null hypothesis that is actually false. The lower the β value, the higher the statistical power ($1 - \beta$) of the test to evaluate the effect of treatments (Ellis, 2010). In other words, the lower the uncertainty, the easier the detection of NH_3-N loss abatement. However, decreasing the uncertainty involves increasing the sample size and, consequently, a higher cost of the measurement. Therefore, a rational strategy for field experiments is applying the principle of least effort or least cost required to obtain an estimate within an acceptable margin of error.

The uncertainty of the estimate is owing to the fact that the average value of NH_3 volatilization measured by chambers ($\overline{av}$) is not numerically equal to the real value of NH_3 volatilization (av) in the entire field plot. The uncertainty associated with the measurement is expressed by an error (E).

$$\overline{av} = av + E \tag{1}$$

This error (E) is due to i) the specificity of the measurement method (E_{m}), such as chamber design, ammonia-trapping efficiency, interaction with wind speed, and N quantification in laboratory, and ii) the sampling error (E_{s}), which is usually the most critical factor (Cantarutti *et al.*, 2007). The sampling error depends on the number of sampling points in a given area, that is, the number of chambers per plot. The total error can be described as follows:

$$E = E_{\mathrm{m}} + E_{\mathrm{s}} \tag{2}$$

The E_{s}-type errors are determined by the variability in soil properties that influence N loss through NH_3 volatilization, such as small variation in particle size distribution, microrelief, soil water content, soil chemical properties, presence of organic residues, and urease activity.

Few studies have attempted to assess the uncertainty in NH_3-N loss measurement, especially in small-scale areas, such as plots of field experiments (plots < 100 m^2). Most literature on spatial variability of gaseous emissions in small-scale areas has been focused on CO_2 (Pringle and Lark, 2006; Herbst *et al.*, 2009; Zhao *et al.*, 2018) and N_2O (Chadwick *et al.*, 2014; Liu *et al.*, 2018). The assessment of uncertainty at the field-plot scale can serve as the basis to define the best strategy for the sampling of NH_3 derived from fertilized soils. Considering that the variability may also be time-dependent, concentrating sampling within critical periods of N losses and errors is an efficient approach to decrease the uncertainty in measurement of soil gaseous emissions (Barton *et al.*, 2015).

The assessment of uncertainty helps define the sampling strategy that optimizes the experimental efforts for attaining maximum possible precision in the measurements of NH_3 volatilization. The use of simple open chamber (Araújo *et al.*, 2009) enables multiple observations per plot, making it possible to statistically assess the precision of quantification of NH_3 volatilization. The objectives of this study were: i) to investigate the effect of using multiple open chambers on the variability in the measurement of NH_3 volatilization in field plots amended with urea and ii) to define the critical period of NH_3-N losses, wherein the concentration of sampling efforts is capable of reducing uncertainty. This kind of study would help improve the strategy of NH_3 sampling using chambers, with an increased power of detection of significant NH_3-N loss abatement in field experiments.

MATERIALS AND METHODS

Field experiment

To assess the variability in NH_3 emission at the plot scale, an experiment using maize was designed and conducted from February to March 2017, in an experimental field of the Research Center for Agrobiology of the Brazilian Agricultural Research Corporation (Embrapa), in Seropédica, Brazil (22°45′ S, 43°40′ W, altitude of 33 m). The soil of the area is a sandy clay loam, classified as a Haplic Acrisol according to the World Reference Base for Soil Resources (FAO, 2015). The properties of the soil were: pH (H_2O), 5.8; organic carbon (C), 8.5 g kg^{-1}; total N, 0.8 g kg^{-1}; sand, 680 g kg^{-1}; silt, 110 g kg^{-1}; and clay, 210 g kg^{-1}. The area has a tropical climate with dry winter, mean annual temperature of 24 °C, and average annual rainfall of 1 300 mm. The area was deep-ploughed and disc-harrowed prior to the sowing of maize with a row spacing of 0.80 m.

Contrasting urea-based treatments were applied at the five-leaf stage of maize growth, with the purpose of creating contrasting cumulative N losses and different patterns of NH_3 volatilization. The following treatments were applied using side-dress application in a surface band: i) regular urea at 100 kg N ha^{-1} (N100), ii) N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1} (N100 + NBPT), iii) regular urea at 50 kg N ha^{-1} (N50), and iv) control without N fertilizer. The coating of urea granules with NBPT, a urease inhibitor, was performed by adding a commercial solution (Agrotain$^{®}$) at a rate of 530 mg NBPT kg^{-1} urea. The experiment had a randomized complete-block design, with three replicates per treatment. Each plot was 7.2 m × 7.2 m. One replicate plot of the control treatment was considered a missing observation because of poor emergence of maize seedlings, which could affect the NH_3 volatilization (*e.g.*, *via* the effect on soil humidity). To perform the comparison among treatments, we applied the missing data formula technique for randomized complete block design (Gomez and Gomez, 1984).

Measurement of NH_3 volatilization

The NH_3 chambers were installed every 0.8 m along the surface band of urea (Fig. 1). To prevent any edge effect, NH_3 volatilization was not evaluated in an 80-cm strip at either end of the plot and the two outer rows. Therefore, the total number of chambers installed per plot was 49. To guarantee the uniformity of granules on the soil surface, small wood stakes were stuck each 80 cm along the location of the surface band-applied urea, dividing it into 9 segments. A corresponding amount of fertilizer was weighed and evenly spread in each segment, forming a 5-cm surface band at 15 cm distance from the maize stems. Metallic supports made of 4.2-mm diameter wire stakes were inserted 15 cm into the soil in the middle of each segment, forming three adjacent positions where the open chambers were relocated each day. The installation of the open chambers in each segment was performed immediately after urea application. The same scheme was followed in the control plots in the corresponding position to fertilized plots. The relocation of the chambers in three predetermined positions was performed to minimize an "umbrella effect", that is, to avoid prolonged effects of chamber deployment on the soil surface and on the volatilization process itself (Martins *et al*., 2017).

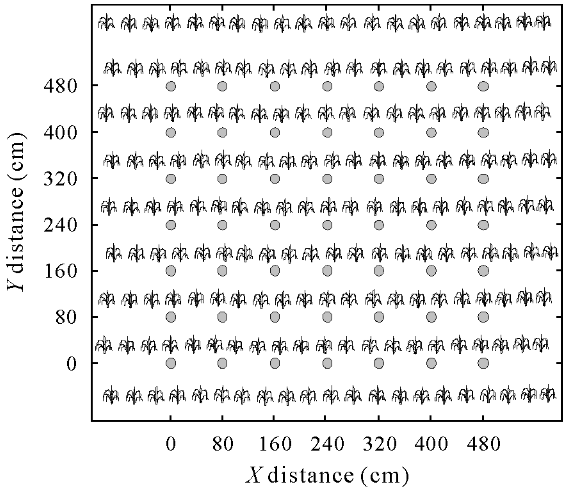

Fig. 1 Scheme of sampling of ammonia (NH_3) volatilized after urea application using open chambers (circles) installed every 80 cm in a plot with maize.

The design of the open chamber was first introduced and calibrated by Araújo *et al*. (2009). A schematic representation of the chamber is shown in Fig. 2. Briefly, the open chamber is made of a 2.0-L transparent polyethylene terephthalate bottle (soda bottle) with its bottom removed and carefully reattached above the top end of the bottle using a wire. This prevents the entry of rainwater and dust. The circular area covered by the open chamber was 78.5 cm^2 (10 cm diameter). A foam strip of 25 mm width, 250 mm length, and 3 mm thickness was attached vertically inside the bottle using a wire with a small hook at the upper end and was hung from the top end of the bottle. The lower end of the foam strip was immersed in a 60-mL plastic pot containing 10 mL acid solution of H_2SO_4 (1.0 mol L^{-1}) and glycerol (2.0%, volume/volume). The foam strip was installed inside the chamber after soaked overnight in the acid solution to ensure a good NH_3-trapping efficiency. During the NH_3 sampling periods, the plastic pot filled with the acid solution was positioned at the lower end of the wire to keep the foam strip moist with the solution. After urea application, the foams were collected and replaced at days 2, 4, 7, 11, 16, 21, and 26. A "blank" chamber was installed in the middle of each plot to quantify the amounts of trapped NH_3 coming from the upper opening of the chamber (outside NH_3). This "blank" chamber was identical to the one described above, except for a 40-cm plastic disc installed to cover the surface area enclosed by the chamber.

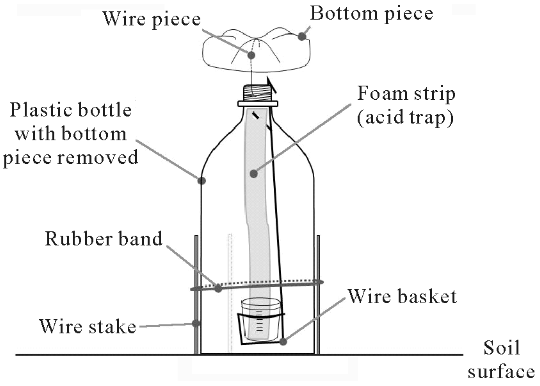

Fig. 2 Scheme of a simple open chamber for NH_3 volatilization measurement under field conditions. Details of the chamber design were first presented by Araújo *et al*. (2009).

To optimize the replacement of the acid traps (foams), plastic pots containing new foams were placed close to their respective chambers before replacement. This operation was performed between 8:00 a.m. and 9:30 a.m., following the same order of chambers, to avoid a time-series variability. The pots containing the foams collected from the field were transported to the laboratory, where the foam and the remaining solution in the pots were transferred to glass conical flasks. A 40-mL volume of deionized water was added to the conical flasks to extract N from the foams by shaking for 20 min on an orbital shaker at 220 r min^{-1}. To determine the N concentration of this solution, a 10-mL aliquot was analyzed by steam distillation (Kjeldahl method) and subsequent titration of the distillate against 15 mmol L^{-1} sulfuric acid.

We calculated the amounts of fertilizer-N applied per chamber based on the formulae for the area of a circular segment (Weisstein, 2019). Considering the diameter of the chamber as 10 cm and that of the fertilizer band as 5 cm centered in the circular area of the chamber, we calculated the area fertilized and enclosed by chamber as 47.82 cm^2. The urea rates in the area specifically covered by the 5-cm surface band was 8 mg N cm^{-2} in the N50 treatment and 16 mg N cm^{-2} in the N100 and N100 + NBPT treatments. Therefore, the amount of N applied per chamber was 382.6 mg for treatment N50 and 765.1 mg for treatments N100 and N100 + NBPT. These N application amounts per chamber were used to calculate the amount of NH_3-N losses as follows:

$$\text{NLDF} = \frac{(\text{NTC} - \text{NTC}_\text{c}) \times 1.74}{\text{NAC}} \times \text{UNR} \tag{3}$$

where NLDF is the NH_3-N loss derived from urea in kg N ha^{-1}, NTC is the NH_3-N trapped in the chamber in fertilized plots in mg N, NTC$_\text{c}$ is the NH_3-N trapped in the chamber in control plots in mg N (background emission), 1.74 is the correction factor for the chamber trapping efficiency (Araújo *et al.*, 2009), NAC is the amount of urea applied per chamber in mg N, and UNR is the equivalent urea-N rate in kg N ha^{-1}. The amount of NH_3-N loss in control plots (NLC) in kg N ha^{-1} was calculated as follows:

$$\text{NLC} = \text{NTC}_\text{c} \times 1.74 \times 10^{-6} \times \frac{10^4}{78.54 \times 10^{-4}} \tag{4}$$

where 10^{-6}, 10^4, and 78.54×10^{-4} are the factors to convert mg N per chamber to kg N ha^{-1}, considering that 1 mg is 10^{-6} kg, 1 ha is 10^4 m^2, and the circular area of the chamber is 78.54×10^{-4} m^2. The amounts of outside NH_3-N trapped in the respective "blank" chambers were subtracted from the total NH_3-N trapped by the chambers to determine the values of NTC and NTC$_\text{c}$.

Supporting variables

During the period of measurement of NH_3 volatilization, the daily precipitation was recorded by an automated pluviometer installed in the experimental area (RainWise Inc., USA). Soil samples were taken from each plot (0–10 cm layer) on a daily basis and were oven dried (105 °C) to determine the gravimetric water content. The volumetric soil water content was determined by multiplying the gravimetric water content by soil bulk density, which was determined using the undisturbed core method (Blake and Hartge, 1986).

Descriptive statistics and determination of required number of chambers per plot

The data obtained from the field experiment were analyzed in order to obtain the basic descriptive statistics parameters, including minimum and maximum values, mean, standard deviation, coefficient of variation (CV), and parameters describing the shape of values distribution (skewness and kurtosis). The normality of the data distribution for each plot was tested by Shapiro-Wilk's test. The number of chambers required to determine the mean within a given margin of error was estimated using the following equation:

$$n = \frac{t^2_{\alpha=0.05} \times s^2}{d^2} \tag{5}$$

where n is the number of chambers required per individual plot, d is the margin of error, $t_{\alpha=0.05}$ is Student's t critical value associated with the confidence level of 5%, and s^2 is the variance of the data set. The statistical analyses were performed using R software (R Development Core Team, 2017).

Literature review on NH_3-N losses from urea

We compiled data from published studies showing results of NH_3 volatilization from soils fertilized with urea in experiments conducted in different regions of the world (Table I). The purpose of this compilation was to obtain an overview of the most critical periods of NH_3-N losses after urea application to soils. From these studies, we extracted the data on localization, soil textural class, soil pH, method of measurement of NH_3 volatilization, treatments tested in the study, and urea-N rates (kg N ha^{-1}). The software GetData Graph Digitizer 2.24 (http://getdata-graph-digitizer.com) was used to obtain the cumulative NH_3-N losses over the measurement period after urea application. Based on these data extracted from the graphs, we determined the total NH_3-N loss as a percent of added N and the period for the occurrence of 70% of the total NH_3-loss.

RESULTS AND DISCUSSION

Cumulative NH_3 volatilization measured considering the whole set of chambers

The maintenance of volumetric soil water content close to 0.20 cm^3 cm^{-3} in the first few hours after N application was caused by a precipitation of 40 mm prior to fertilization (Fig. 3a), which was a condition favorable for urea hydrolysis and promoted the occurrence of NH_3-N volatilization losses (Fig. 3b). The NH_3 volatilization estimated using data from the whole set of chambers per plot (n = 49) showed that the cumulative NH_3 volatilization amounted to 26.8 kg N ha^{-1} in the N100 treatment, 20.6 kg N ha^{-1} in the N100 + NBPT treatment, 17.8 kg N ha^{-1} in the N50 treatment, and only 0.8 kg N ha^{-1} in the control (Fig. 3c).

Considering the whole set of chambers per plot, the between-block errors indicated by error bars in Fig. 3c were < 1.0 kg N ha^{-1}. By subtracting the NH_3-N volatilized from control, it can be seen that the coating of urea granules with NBPT decreased the NH_3-N loss by approximately

TABLE I

Summary of data from studies on NH_3-N losses from soils amended with urea

Location	Soil texture$^{a)}$	Soil pH	Treatment$^{b)}$	Total NH_3-N loss	Time for 70% of total NH_3-N loss	Method of measurement	Reference
				%	d		
Rio de Janeiro, Brazil	SCL	5.8	N50	34	3	Open chamber (Araújo *et al.*, 2009)	Present study
			N100	26	3		
			N100 + NBPT	20	6		
South Africa	SL	5.3	N224 (Table Mountain sandstone soil)	17	6	Closed chamber (Ernst and Massey, 1960)	Anderson *et al.*, 1962
	S	5.3	N224 (recent red sand soil)	30	7		
	CL	5.3	N224 (Tugela schist soil)	7	8		
	C	5.4	N224 (black dolerite soil)	–$^{c)}$	–		
	CL	5.4	N224 (lower Ecca shale soil)	3	9		
	S	6.8	N224 (recent grey sand soil)	39	7		
	CL	7.7	N224 (middle Ecca shale soil)	6	8		
	SiCL	7.8	N224 (alluvium soil)	6	7		
Canterbury, New Zealand	SiL	6.1	N100 (field capacity)	40	3	Enclosure method (Black *et al.*, 1985)	Black *et al.*, 1987
			N100 (wilting point)	32	4		
			N100 (air dry)	28	17		
Kansas, USA	SiL	6.6	N56	27	9	Plexiglass chamber (Hargrove and Kissel, 1979)	Ferguson *et al.*, 1984
			N56 + hydroxy-Al polymers	12	7		
			N112 + 4.7% strong resins	10	6		
			N112 + 4.3% resin mix	2	9		
			N112 + 3.7% resin mix	1	8		
			N224	42	11		
			N224 + hydroxy-Al polymers	18	12		
Italy	CL	7.9	N120	4	27	Semi-open chamber (Marshall and Debell, 1980)	Gioacchini *et al.*, 2002
			N120 + NBPT	2	29		
			N120 + NBPT + DCD	4	43		
	SL	7.8	N120	10	15		
			N120 + NBPT	1	18		
			N120 + NBPT + DCD	4	30		
São Paulo, Brazil	C	4.6	N50 (open chamber)	13	7	Open chamber (Alves *et al.*, 2011)	Mariano *et al.*, 2012
			N100 (open chamber)	14	15		
			N150 (open chamber)	12	7		
			N200 (open chamber)	16	8		
			N50 (semi-open chamber)	15	8	Semi-open chamber (Nômmik, 1973)	
			N100 (semi-open chamber)	24	7		
			N150 (semi-open chamber)	24	6		
			N200 (semi-open chamber)	24	7		
Bahia, Brazil	SCL	5.1	N120	3	11	Open chamber (Araújo *et al.*, 2009)	Martins *et al.*, 2015
			N120 + zeolite	4	11		
Rio de Janeiro, Brazil	SCL	6.1	N100	54	4	Open chamber (Araújo *et al.*, 2009)	Martins *et al.*, 2017
			N100 + NBPT	37	6		
Stockholm, Sweden	S	4.4	N200 (small pellets)	22	13	Semi-open chamber (Nômmik, 1973)	Nômmik, 1973
			N200 (tablets)	20	15		
			N200 + H_3PO_4	12	19		
			N200 + H_3BO_3	9	21		
Manitoba, Canada	CL	8.1	N100 (in May)	22	8	Semi-open chamber (Nômmik, 1973)	Rawluk *et al.*, 2001
			N100 + 0.05% NBPT (in May)	6	16		
			N100 + 0.10% NBPT (in May)	4	15		
			N100 + 0.15% NBPT (in May)	4	15		
			N100 (in July)	26	5		
			N100 + 0.05% NBPT (in July)	7	10		
			N100 + 0.10% NBPT (in July)	4	13		
			N100 + 0.15% NBPT (in July)	4	12		
	SL	7.9	N100 (in May)	20	8		
			N100 + 0.05% NBPT (in May)	5	18		
			N100 + 0.10% NBPT (in May)	4	17		
			N100 + 0.15% NBPT (in May)	2	18		
			N100 (in July)	50	5		
			N100 + 0.05% NBPT (in July)	23	11		
			N100 + 0.10% NBPT (in July)	19	14		
			N100 + 0.15% NBPT (in July)	21	12		
Quebec, Canada	SiCL	5.4	N140 (banded/incorporated)	27	15	Wind tunnel (Lockyer, 1984)	Rochette *et al.*, 2009
			N140 (broadcasted/incorporated)	16	16		
			N140 (broadcasted)	10	17		
			N140 (polymer-coated)	5	17		

(to be continued)

TABLE I (continued)

Location	Soil texture	Soil pH	Treatment	Total NH_3-N loss	Time for 70% of total NH_3-N loss	Method of measurement	Reference
				%	d		
			N140 + NBPT	4	16		
Madrid, Spain	SL	8.1	N170	10	21	Micrometereo-logical (Misselbrook *et al.*, 2005)	Sanz-Cobeña *et al.*, 2008
			N170 + NBPT	6	19		
Palmerston North, New Zealand	SL	5.7	N100	5	3	Polyvinyl chloride “Sewer-hatch” chamber (Saggar *et al.*, 2004)	Singh *et al.*, 2013
			N100 (Sustain Green)	3	11		
			N100 (Sustain Yellow)	3	10		
			N100 (sulphur-coated)	2	9		
São Paulo, Brazil	SC	5.9	N300	37	11	Closed chamber (Soares *et al.*, 2012)	Soares *et al.*, 2012
			N300 + NBPT	17	13		
			N300 + 10% DCD	44	14		
			N300 + NBPT + 5% DCD	28	5		
			N300 + NBPT + 10% DCD	33	5		
Beijing, China	SL	7.8	N60 (vented chamber)	3	6	Semi-open chamber (Nômmik, 1973)	Wang *et al.*, 2004
			N120 (vented chamber)	6	5		
			N180 (vented chamber)	18	7		
			N60 (closed chamber)	1	4	Closed chamber (Wang *et al.*, 2004)	
			N120 (closed chamber)	1	5		
			N180 (closed chamber)	3	5		

[a] C = clay; CL = clay loam; S = sand; SC = sandy clay; SCL = sandy clay loam; SiCL = silty clay loam; SiL = silt loam; SL = sandy loam.
[b] The number following N in each treatment is the urea application rate in kg N ha^{-1}; NBPT = N-(n-butyl) thiophosphoric triamide; DCD = dicyandiamide.
[c] Not available.

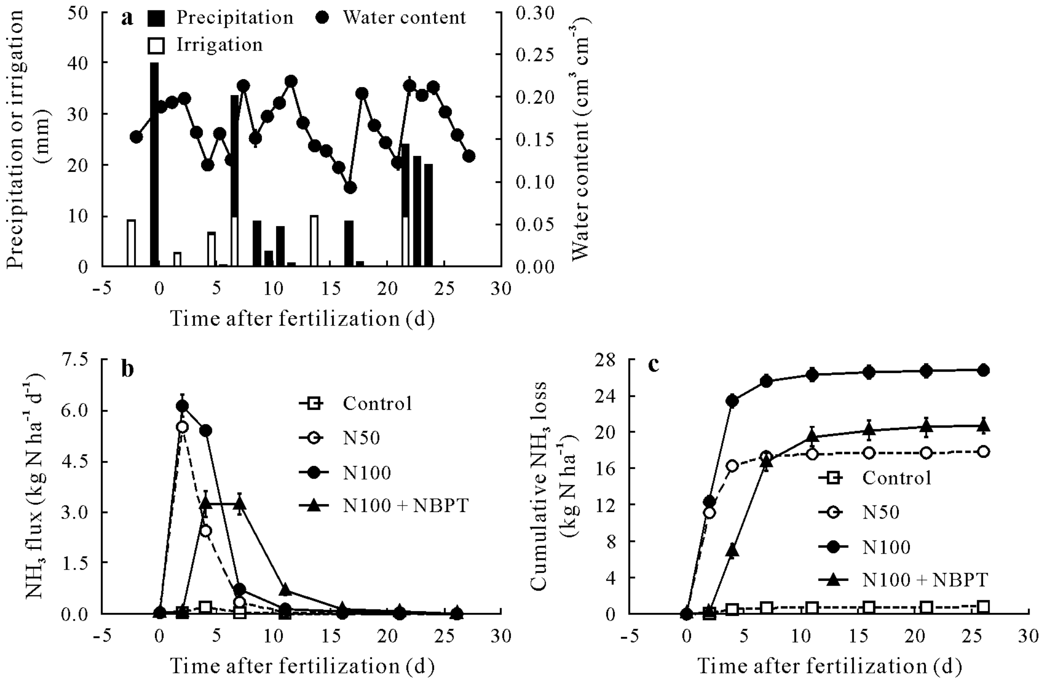

Fig. 3 Precipitation, irrigation, and soil water content (a) and NH_3 flux (b) and cumulative NH_3 loss (c) from the control and urea-applied treatments during the field experiment in Seropédica, Brazil. The estimates were performed considering the mean NH_3 loss of the 49 chambers installed in each plot. Bars are standard errors ($n = 3$). Cumulative NH_3 losses followed by different letters are significantly different based on Tukey's honestly significant difference (HSD) test ($\alpha = 0.05$). Control = without nitrogen (N) fertilizer; N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

25% ($\alpha = 0.05$) (Fig. 3c). The reduction of urea-N rate by half (N50) caused an NH_3-N loss equivalent to 34% of applied N, that is, a higher proportional NH_3-N loss than that observed in the N100 treatment (26% of applied N). A possible explanation of the increase in proportional NH_3-N loss by reduction of N rate is the higher urease efficiency, caused by a lower substrate:enzyme (urea:urease) ratio.

Temporal dynamics and standard errors of NH_3 volatilization

Box plots were used to show the variability in NH_3 losses in each individual fertilized plot across different measurement periods (Fig. 4). It can be clearly seen that the highest mean NH_3-N losses occurred from day 0 to day 7 after application of regular urea (N50 and N100), and from day 2 to day 11 after application of urea granules coated with urease inhibitor (N100 + NBPT). Using the data from the whole set of chambers from each plot, we determined the pattern of temporal variation in standard errors of NH_3 volatilization, in kg N ha^{-1} d^{-1} for each N treatment (Fig. 5). This between-chamber errors peaked during the first 48 h after the fertilizer application in all the evaluated plots. These results indicate that the use of multiple chambers per plot during the first few days after urea application, which was the most critical in terms of mean losses and associated errors (Fig. 5), would be an efficient strategy to reduce the uncertainty. Increasing the number of chambers can increase the reliability of the comparison of N treatments, when it is not possible or not viable to use large number of replicates in experimental fields.

Based on our estimates, 70% of the total NH_3-N losses occurred in the first 3 d after urea application in the N50 and N100 treatments and in the first 6 d after NBPT-coated urea application in N100 + NBPT (Fig. 1). Taking into consideration this same threshold level of cumulative losses (70% of total loss), we analyzed the results of NH_3 volatilization from urea-based fertilizers in studies conducted in different regions of the world (Table I). This analysis revealed that the major part of NH_3-N losses usually occurs during the first two weeks after urea-N application, especially in studies showing high total NH_3-N losses (> 10% of applied N). This is consistent with the idea that the use of multiple chambers during the initial period following urea application, when the peak of emission and associated error is expected, represents a strategy to improve the precision of NH_3 volatilization measurements. This is a common temporal pattern for the NH_3 emission after urea amendment to soil (Table I), and it is significantly less variable than the temporal pattern of emission of other gases from soil (Barton *et al*., 2015; Zhao *et al*., 2018). For example, the prediction of the most critical periods of soil N_2O or CO_2 emissions is relatively complex because of their high temporal variability (Barton *et al*., 2015; Zhao *et al*., 2018).

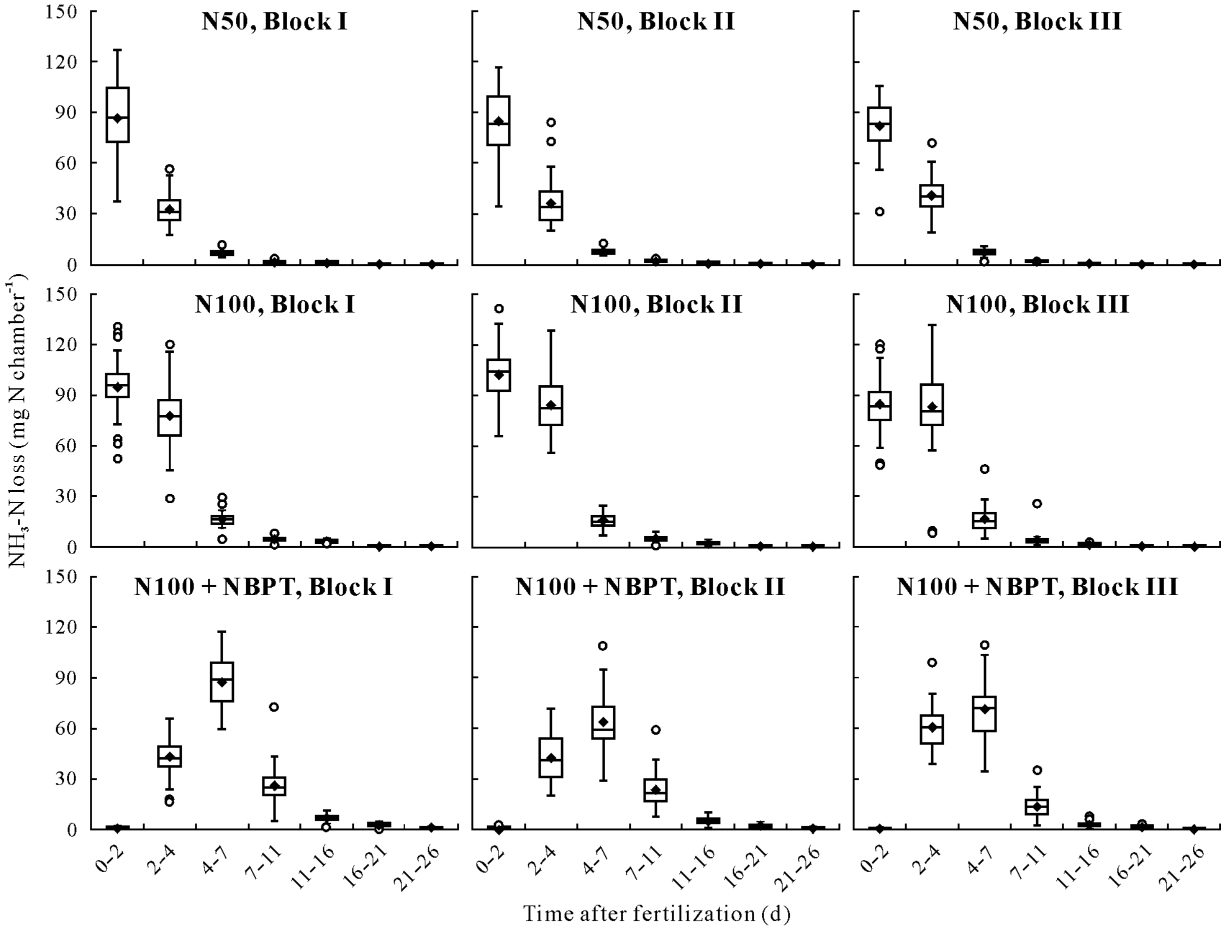

Fig. 4 Box plots of NH_3-N loss from individual field plots. The boxes indicate the range from the first to the third quartile. The median is indicated by horizontal line within the box. Diamonds indicate mean values (n = 49). Whiskers show the upper and lower extremes. Circles indicate outliers. N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

Descriptive statistics

Considering the total NH_3-N losses from each sampling point of each plot, it is apparent that, even with the level of between-chamber variability, there is an evident effect of the N rate and that of the urease inhibitor (Fig. 6). The mean NH_3-N loss per plot ($n = 49$), in mg N chamber^{-1}, ranged 0.3–0.9 in the control, 129–133 in the N50 treatment, 139–168 in the N100 + NBPT treatment, and 191–210 in the N100 treatment (Table II). The magnitude of the between-chamber CV was similar for the different fertilized treatments. The CV ranged 13%–17% in the N100 treatment, 14%–

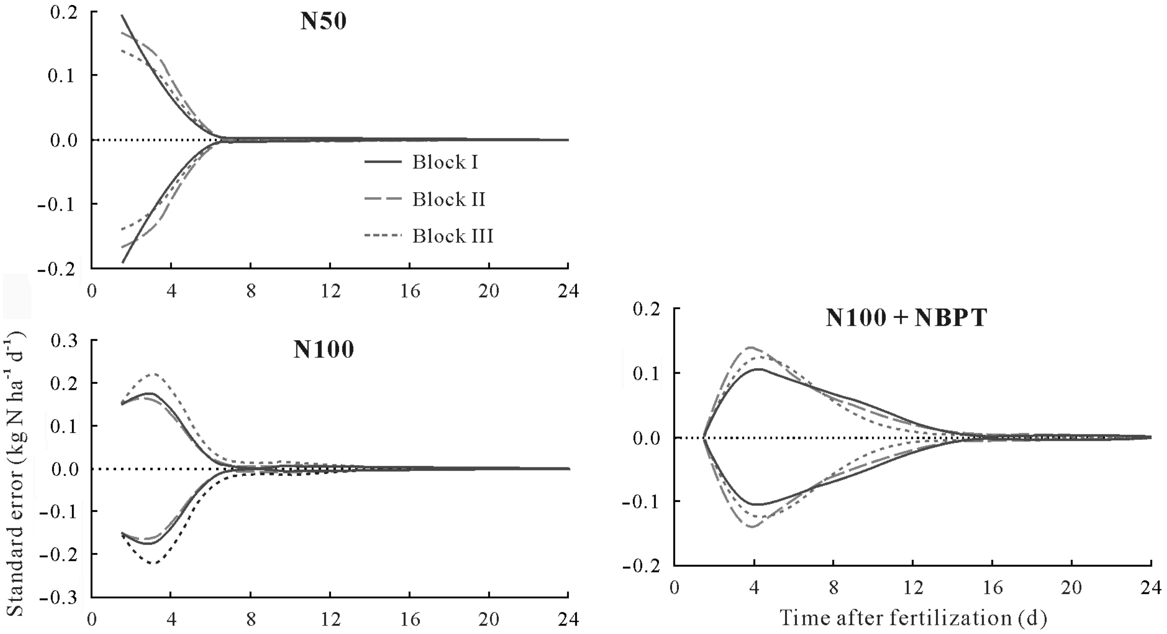

Fig. 5 Standard error of the mean of NH_3 volatilization for each individual plot as a function of the time after urea application to soil. N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = *N*-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

TABLE II

Statistical summary of the cumulative NH_3-N loss after the surface application of urea to maize crop at the five-leaf growth stage in the experimental field plots, where open chambers (49 in each plot) were used for the measurements

Experimental plot[a)]	Mean	Minimum	Maximum	SD[b)]	CV[c)]	Skewness	Kurtosis (excess)	*P* value[d)]
	mg N chamber^{-1}				%			
Control[e)]								
Block I	0.3	0.2	0.8	0.1	33	2.09	6.61	< 0.001
Block III	0.9	0.4	1.9	0.4	40	1.02	0.44	< 0.001
Mean	0.6	0.3	1.4	0.2	36			
N50								
Block I	129	63	173	25	19	−0.57	0.32	0.259
Block II	131	68	179	23	18	−0.23	−0.13	0.278
Block III	133	85	163	20	15	−0.39	−0.67	0.078
Mean	131	100	222	25	17			
N100								
Block I	197	142	247	25	13	−0.14	−0.22	0.488
Block II	210	162	292	28	13	0.56	0.49	0.335
Block III	191	115	250	32	17	−0.16	−0.19	0.535
Mean	200	72	172	23	17			
N100 + NBPT								
Block I	168	115	230	24	14	−0.05	0.00	0.862
Block II	139	83	223	27	20	0.61	0.68	0.167
Block III	150	104	212	25	16	0.47	−0.06	0.489
Mean	152	140	263	28	14			

[a)] Control = without N fertilizer; N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = *N*-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

[b)] Standard deviation.

[c)] Coefficient of variation.

[d)] According to Shapiro-Wilk test.

[e)] One replicate plot of the control treatment was considered a missing observation because of poor emergence of maize seedlings.

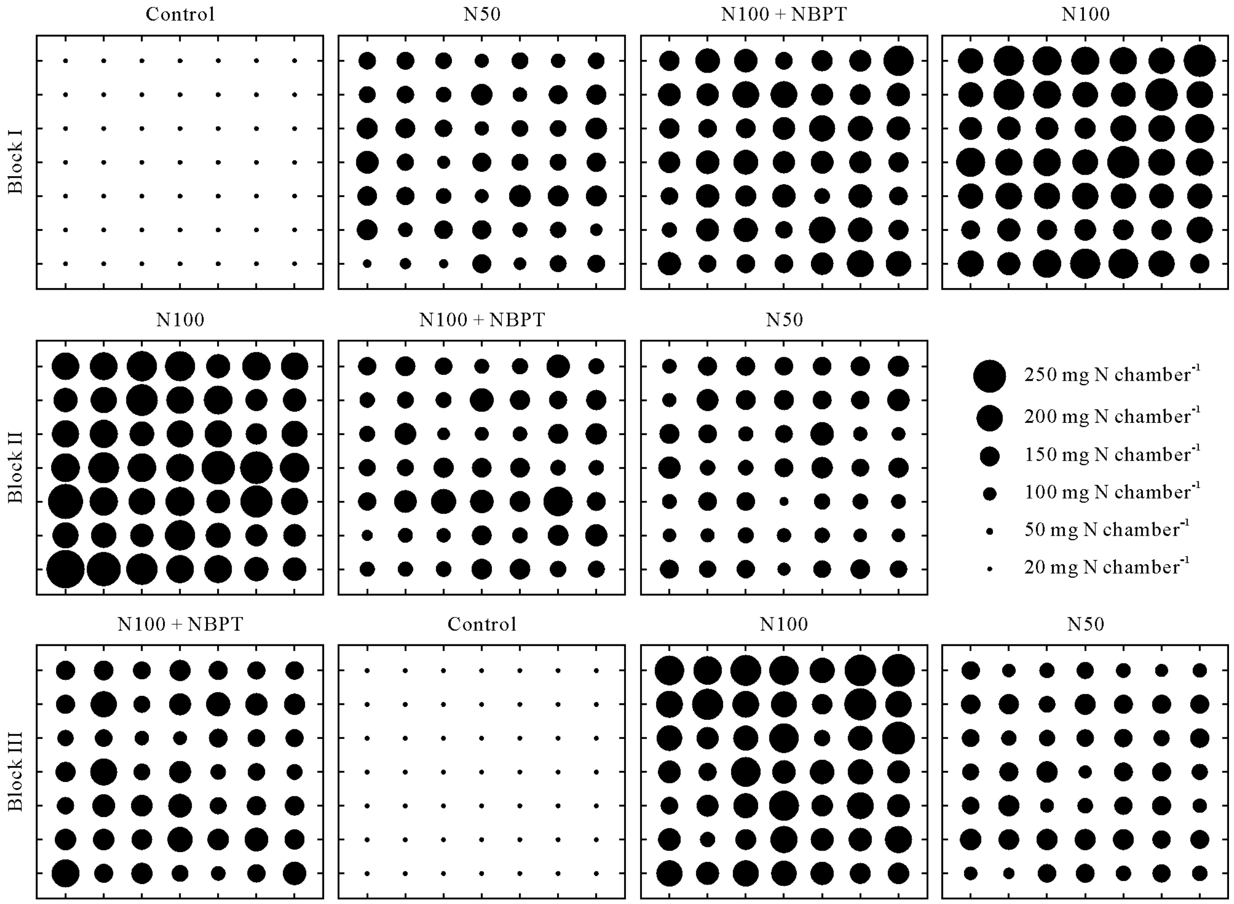

Fig. 6 Variation in cumulative NH_3-N loss measured by plastic bottle chambers placed on a 0.80-m^2 grid after urea-N was surface applied to maize crop at the five-leaf growth stage in the four treatments of a field experiment in Seropédica, Brazil. Forty-nine chambers were used in each plot. One replicate plot of the control treatment was considered a missing observation because of poor emergence of maize seedlings. Control = without N fertilizer; N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

20% in the N100 + NBPT treatment, and 15%–19% in the N50 treatment. The values of skewness, kurtosis, and the significance of Shapiro-Wilk test showed that the NH_3 volatilization from different chambers in each fertilized plot followed a normal distribution. On the other hand, the observations in the control plots presented a higher CV than the fertilized plots (33%–40%) and did not follow a normal distribution. However, even with a higher CV and non-normal distribution of observations in the control plots, it was not expected that the background emissions of NH_3 significantly affected the overall variability of the experiment, considering that the NH_3-N losses in the control plots and their associated errors were very low compared to values for the fertilized plots (Fig. 6, Table II). For example, the maximum value of NH_3-N loss observed in the chambers from the control plots (1.9 mg N $chamber^{-1}$, block III) was only 3% of the minimum NH_3-N loss observed in the chambers from the fertilized plots (63 mg N $chamber^{-1}$, block I of N50).

The level of between-chamber variability observed in the present study (Table II) was significantly higher than the variability obtained from N analysis in laboratory (Kjeldahl method) for the quantification of NH_3-N trapped in foams (Table III). The variability in the N analysis is a part of E_m-type error. The precision of the analyses was very high in samples representing losses higher than 1.0 mg N $chamber^{-1}$. Above this threshold, the CV of the N analysis ranged 0.3%–2.3%, which was very low compared with the between-chamber CV of the fertilized plots (13%–20%, Table II).

Required number of observations

Using a classical statistical approach based on the standard deviation of the observations, we estimated the required number of chambers per plot as a function of the expected margin of error (Table IV). The required number of chambers per plot did not vary significantly with the treatment applied. It was shown that the use of only one chamber per plot generated a value of NH_3-N loss within an expected margin of error of 30% of the true mean. To have a value of NH_3-N loss within a margin of error reduced by half (15%), 3–7 chambers were required, with a mean of 5 chambers per plot. For a 12.5% margin of error, Herbst *et al.* (2009) estimated that 5–123 (31 on average) observations were required for

TABLE III

Test-retest reliability of the Kjeldahl method for NH_3-N determination in randomly selected solutions extracted from the foams used to trap NH_3 in the open chambers installed in the field

Sample No.	Number of measurements	Mean	Minimum	Maximum	Standard deviation	Coefficient of variation
		mg N chamber^{-1}				%
1	4	133	130	135	2.2	1.7
2	5	118	117	120	1.3	1.1
3	5	113	113	114	0.5	0.4
4	5	108	105	111	2.0	1.9
5	4	107	106	108	0.5	0.5
6	5	105	104	106	0.6	0.6
7	5	90	89	91	1.0	1.1
8	5	89	87	90	1.3	1.5
9	5	87	85	88	1.2	1.3
10	5	85	84	85	0.7	0.9
11	5	70	70	70	0.2	0.3
12	5	55	54	57	1.1	2.0
13	5	52	51	53	0.6	1.2
14	5	44	43	45	1.0	2.4
15	5	39	38	40	0.5	1.2
16	5	39	38	39	0.4	1.0
17	5	27	26	27	0.4	1.4
18	5	25	25	26	0.4	1.4
19	4	17	17	18	0.5	2.8
20	5	11	11	11	0.3	2.3
21	5	7.1	6.9	7.3	0.20	2.8
22	5	6.6	6.5	6.7	0.06	0.9
23	5	2.2	2.2	2.3	0.06	2.9
24	5	0.74	0.72	0.76	0.02	2.5
25	5	0.60	0.58	0.62	0.02	3.3
26	5	0.55	0.51	0.59	0.03	6.3
27	5	0.51	0.49	0.53	0.01	2.6
28	5	0.29	0.27	0.31	0.02	6.0
29	5	0.14	0.13	0.17	0.02	11.6
30	6	0.11	0.09	0.14	0.02	18.1
31	5	0.07	0.04	0.08	0.02	29.8
32	5	0.06	0.05	0.08	0.01	18.5
33	4	0.05	0.04	0.05	0.01	13.9
34	5	0.04	0.03	0.05	0.01	17.6

TABLE IV

Required number of chambers per plot as a function of the expected margin of error in the measurement of NH_3 volatilization in some urea-fertilized plots, considering $\alpha = 0.05$, degrees of freedom = 48, and Student's $t = 2.011$

Margin of error	Required number of chambers per plot[a)]									Mean
	N50			N100			N100 + NBPT			
	Block I	Block II	Block III	Block I	Block II	Block III	Block I	Block II	Block III	
30%	2	1	1	1	1	1	1	1	1	1
25%	2	2	1	1	1	2	1	2	2	2
20%	4	3	2	2	2	3	2	4	3	3
15%	7	6	4	3	3	5	4	7	5	5
12.5%	9	8	6	4	4	7	5	10	7	7
10%	15	12	9	7	7	11	8	15	11	11
7.5%	26	22	16	12	12	20	15	28	19	19
5%	59	50	36	27	28	46	33	62	44	43
1%	1 472	1 247	912	670	703	1 146	837	1 548	1 095	1 070

[a)] N50 = regular urea at 50 kg N ha^{-1}; N100 = regular urea at 100 kg N ha^{-1}; N100 + NBPT = N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea at 100 kg N ha^{-1}.

measurement of CO_2 emission within a 13 m × 14 m bare soil test plot in Germany.

Methodological considerations

The main advantages of the open chambers used in the present study are simple construction, low cost, easy handling in field experiments, allowing more replication, and free air circulation through the chamber, thereby minimizing the effect of chamber deployment on NH_3 exchange at the soil-atmosphere interface. This chamber can be used either in small experimental units, such as pots in greenhouse experiments, or in larger areas, such as the field plots in the present study. The concern regarding the variability observed in the present study for the open chamber would also be applicable to any type of chambers used to measure gaseous emissions from soil in field plot-based experiments. Our results showed the importance of using multiple chambers per plot to increase the precision of NH_3 emission measurements using open chambers. However, this strategy involves additional costs and time spent in field for the handling of the chambers. Taking into account that the error in laboratory analyses (part of E_m-type error) is usually negligible compared with the field sampling error (E_s-type error) (Cantarutti *et al.*, 2007), a viable method for reducing cost when using multiple chambers is the analysis of N concentration using a composite solution, obtained from traps (foams) of different chambers from a same field plot. It is also important to highlight that the conventional use of multiple plots per treatment (replicates) in field experiments intrinsically improves the precision of NH_3-N loss estimates, even when using a single chamber per plot.

The variability in the measurements of NH_3 volatilization using open chambers compared to other methods (*e.g.*, micrometeorological systems, closed dynamic chambers) and under contrasting types of soil and climate should be addressed in future research. This step is important to evaluate new techniques for enhancing the urea-N use efficiency in agricultural soils and for mitigating the environmental pollution caused by NH_3 volatilization.

CONCLUSIONS

Our study showed that using multiple open chambers per plot during the most critical period of NH_3 volatilization and associated errors is an effective way of reducing the uncertainty in the measurements of total NH_3-N losses in field experiments designed to evaluate the efficiency of urea-based fertilizers. Concentrating sampling efforts in the first two weeks after urea application, which is usually the most critical period of N losses and associated errors, is an efficient strategy to lessen uncertainty in the measurements of NH_3 volatilization. This strategy enhances the power of detection of NH_3-N loss abatement in field experiments, thus partially offsetting the uncertainty related to the small area of the chamber.

ACKNOWLEDGEMENTS

This study was supported by the International Atomic Energy Agency (IAEA), Vienna, Austria through a Coordinated Research Project (No. D15016), the "Carlos Chagas Filho" Foundation for Support of Research in the State of Rio de Janeiro (FAPERJ) of Brazil with grants awarded to BJRA, CPJ, RMB, and SU and postdoctoral scholarships to MRM and SS, the Brazilian National Council for Scientific and Technological Development (CNPq) for the Productivity Grant (PQ) awarded to BJRA, CPJ, RMB, and SU and scholarships to LFS, CAS, KEA, and RCS. We thank Altiberto M. Baêta, Carlos Brito Prestes, Eduardo Rodolfo Rodrigues da Silva, and Raysa Alves Vila Nova from Embrapa for their assistance with the field work and the laboratory analyses.

REFERENCES

Afshar R K, Lin R Y, Mohammed Y A, Chen C C. 2018. Agronomic effects of urease and nitrification inhibitors on ammonia volatilization and nitrogen utilization in a dryland farming system: Field and laboratory investigation. *J Clean Prod.* **172**: 4130–4139.

Alves A C, Oliveira P P, Herling V R, Trivelin P C, Luz P H, Alves T C, Rochetti R C, Barioni Jr W. 2011 New methods to quantify NH_3 volatilization from fertilized surface soil with urea. *Braz J Soil Sci.* **35**: 133–140.

Anderson J R. 1962. Urease activity, ammonia volatilization and related microbiological aspects in some South African soils. *In* Proceedings of the 36th Annual Congress of the South African Sugar Technologists Association, Durban. pp. 97–105.

Araújo E S, Marsola T, Miyazawa M, Soares L H B, Urquiaga S, Boddey R M, Alves B J R. 2009. Calibration of a semi-opened static chamber for the quantification of volatilized ammonia from soil. *Pesq Agropec Bras* (in Portuguese). **44**: 769–776.

Barton L, Wolf B, Rowlings D, Scheer C, Kiese R, Grace P, Stefanova K, Butterbach-Bahl K. 2015. Sampling frequency affects estimates of annual nitrous oxide fluxes. *Sci Rep.* **5**: 15912.

Black A S, Sherlock R R, Cameron K C, Smith N P, Goh K M. 1985. Comparison of three field methods for measuring ammonia volatilization from urea granules broadcast on to pasture. *J Soil Sci.* **36**: 271–280.

Black A S, Sherlock R R, Smith N P. 1987. Effect of timing of simulated rainfall on ammonia volatilization from urea, applied to soil of varying moisture content. *Eur J Soil Sci.* **38**: 679–687.

Blake G R, Hartge K H. 1986. Bulk density. *In* Klute A (ed.) Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. 2nd Edn. American Society of Agronomy and Soil Science Society of America, Madison. pp. 363–367.

Cantarutti R B, Barros N F, Martinez H E P, Novais R F. 2007. Fertilidade do Solo (Soil Fertility) (in Portuguese). Brazilian Society of Soil Science, Viçosa.

Cantú R R, Aita C, Doneda A, Giacomini D A, Dessbesell A, Arenhardt M, De Bastiani G G, Pujol S B, Rochette P, Chantigny M H, Giacomini S J. 2017. Alternatives to regular urea for abating N losses in lettuce production under sub-tropical climate. *Biol Fertil Soils.* **53**: 589–599.

Chadwick D R, Cardenas L M, Misselbrook T H, Smith K A, Rees R M, Watson C J, McGeough K L, Williams J R, Cloy J M, Thorman R E, Dhanoa M S. 2014. Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments. *Eur J Soil Sci.* **65**: 295–307.

Ellis P D. 2010. The Essential Guide to Effect Sizes: Statistical Power, Meta-Analysis, and the Interpretation of Research Results. Cambridge University Press, Cambridge.

Ernst J W, Massey H F. 1960. The effects of several factors on volatilization of ammonia formed from urea in the soil. *Soil Sci Soc Am J.* **24**: 87–90.

Eurostat (Statistics Explained). 2018. Air pollution statistics—Emission inventories. Available online at https://ec.europa.eu/eurostat/statistics-explained/index.php/Air_pollution_statistics_-_emission_inventories (verified on February 14, 2019).

Ferguson R B, Kissel D E, Koelliker J K, Basel W. 1984. Ammonia volatilization from surface-applied urea: Effect of hydrogen ion buffering capacity. *Soil Sci Soc Am J.* **48**: 578–582.

Food and Agriculture Organization of the United Nations (FAO). 2015. World Reference Base for Soil Resources 2014 (Update 2015): International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. FAO, Rome.

Gioacchini P, Nastri A, Marzadori C, Giovannini C, Antisari L V, Gessa C. 2002. Influence of urease and nitrification inhibitors on N losses from soils fertilized with urea. *Biol Fertil Soils*. **36**: 129–135.

Gomez K A, Gomez A A. 1984. Statistical Procedures for Agricultural Research. 2nd Edn. John Wiley & Sons, New York.

Hargrove W L, Kissel D E. 1979. Ammonia volatilization from surface applications of urea in the field and laboratory. *Soil Sci Soc Am J*. **43**: 359–363.

Heffer P, Prud'homme M. 2016. Fertilizer Outlook 2016–2020. *In* International Fertilizer Association (ed.) 84th IFA Annual Conference, Moscow. pp. 1–5.

Herbst M, Prolingheuer N, Graf A, Huisman J A, Weihermu¨ller L, Vanderborght J. 2009. Characterization and understanding of bare soil respiration spatial variability at plot scale. *Vadose Zone J*. **8**: 762–771.

Jewitt T N. 1942. Loss of ammonia from ammonium sulfate applied to alkaline soils. *Soil Sci*. **54**: 401–409.

Klein C D, Novoa R S A, Ogle S, Smith K A, Rochette P, Wirth T C, McConkey B G, Mosier A, Rypdal K, Walsh M, Williams S A. 2007. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Institute for Global Environmental Strategies, Hayama.

Liu Y, Li Y F, Harris P, Cardenas L M, Dunn R M, Sint H, Murray P J, Lee M R, Wu L H. 2018. Modelling field scale spatial variation in water run-off, soil moisture, N_2O emissions and herbage biomass of a grazed pasture using the SPACSYS model. *Geoderma*. **315**: 49–58.

Lockyer D R. 1984. A system for the measurement in the field of losses of ammonia through volatilisation. *J Sci Food Agric*. **35**: 837–848.

Mariano E, Trivelin P C O, Vieira M X, Leite J M, Otto R, Franco H C J. 2012. Ammonia losses estimated by an open collector from urea applied to sugarcane straw. *Rev Bras Ciênc Solo*. **36**: 411–419.

Marshall V G, Debell D S. 1980. Comparison of four methods of measuring volatilization losses of nitrogen following urea fertilization of forest soils. *Can J Soil Sci*. **60**: 549–563.

Martins M R, Jantalia C P, Polidoro J C, Batista J N, Alves B J R, Boddey R M, Urquiaga S. 2015. Nitrous oxide and ammonia emissions from N fertilization of maize crop under no-till in a Cerrado soil. *Soil Till Res*. **151**: 75–81.

Martins M R, Sant'Anna S A C, Zaman M, Santos R C, Monteiro R C, Alves B J R, Jantalia C P, Boddey R M, Urquiaga S. 2017. Strategies for the use of urease and nitrification inhibitors with urea: Impact on N_2O and NH_3 emissions, fertilizer-^{15}N recovery and maize yield in a tropical soil. *Agr Ecosyst Environ*. **247**: 54–62.

Misselbrook T H, Nicholson F A, Chambers B J, Johnson R A. 2005. Measuring ammonia emissions from land applied manure: An intercomparison of commonly used samplers and techniques. *Environ Pollut* **135**: 389–397.

Mogollón J M, Lassaletta L, Beusen A H W, van Grinsven H J M, Westhoek H, Bouwman A F. 2018. Assessing future reactive nitrogen inputs into global croplands based on the shared socioeconomic pathways. *Environ Res Lett*. **13**: 044008.

Nômmik H. 1973. The effect of pellet size on the ammonia loss from urea applied to forest soil. *Plant Soil*. **39**: 309–318.

Pringle M J, Lark R M. 2006. Spatial analysis of model error, illustrated by soil carbon dioxide emissions. *Vadose Zone J*. **5**: 168–183.

R Development Core Team. 2017. R: A language and environment for statistical computing. R foundation for statistical computing, Vienna. Available online at http://www.r-project.org (verified on February 14, 2019).

Rawluk C D L, Grant C A, Racz G J. 2001. Ammonia volatilization from soils fertilized with urea and varying rates of urease inhibitor NBPT. *Can J Soil Sci*. **81**: 239–246.

Rochette P, MacDonald J D, Angers D A, Chantigny M H, Gasser M O, Bertrand N. 2009. Banding of urea increased ammonia volatilization in a dry acidic soil. *J Environ Qual*. **38**: 1383–1390.

Saggar S, Andrew R M, Tate K R, Hedley C B, Rodda N J, Townsend J A. 2004. Modelling nitrous oxide emissions from dairy-grazed pastures. *Nutr Cycl Agroecosys*. **68**: 243–255.

Sanz-Cobeña A, Misselbrook T H, Arce A, Mingot J I, Diez J A, Vallejo A. 2008. An inhibitor of urease activity effectively reduces ammonia emissions from soil treated with urea under Mediterranean conditions. *Agr Ecosyst Environ*. **126**: 243–249.

Singh J, Kunhikrishnan A, Bolan N S, Saggar S. 2013. Impact of urease inhibitor on ammonia and nitrous oxide emissions from temperate pasture soil cores receiving urea fertilizer and cattle urine. *Sci Total Environ*. **465**: 56–63.

Soares J R, Cantarella H, Menegale M L d C. 2012. Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors. *Soil Biol Biochem*. **52**: 82–89.

Sokoloff V P. 1938. Effect of neutral salts of sodium and calcium on carbon and nitrogen in soils. *J Agric Res*. **57**: 201–216.

United States Geological Survey (USGS). 2018. Nitrogen statistics and information. Available online at https://minerals.usgs.gov/minerals/pubs/commodity/nitrogen (verified on February 14, 2019).

Volk G M. 1959. Volatile loss of ammonia following surface application of urea to turf or bare soils. *Agron J*. **51**: 746–749.

Wang Z H, Liu X J, Ju X T, Zhang F S, Malhi S S. 2004. Ammonia volatilization loss from surface-broadcast urea: Comparison of vented- and closed-chamber methods and loss in winter wheat–summer maize rotation in North China plain. *Commun Soil Sci Plant Anal*. **35**: 2917–2939.

Weisstein E. 2019. Circular Segment. Available online at http://mathworld.wolfram.com/CircularSegment.html (verified on February 14, 2019).

Zhao Y L, Goldberg S D, Xu J C, Harrison R D. 2018. Spatial and seasonal variation in soil respiration along a slope in a rubber plantation and a natural forest in Xishuangbanna, southwest China. *J Mount Sci*. **15**: 695–707.