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Research article

A laboratory system to estimate ammonia volatilization

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Abstract – In addition to its environmental implications, ammonia volatilization is the principal source of variation of fertilizer efficiency. In a larger study estimating the effect of the dissolution step of fertilizer pellets on ammonia volatilization, we analyzed the sources of uncertainties in measuring low ammonia fluxes. The air humidity, and above all the air flow rate, are important contributors to the variation in fluxes. An exponential curve obtained from a set of 35 data points is proposed to normalize the ammonia emission rates according to the air flow rate ($R^2 = 0.52$). Modifications of the standard laboratory method are also proposed to improve the estimation of the low ammonia fluxes over a short timescale. However, the system was kept simple to manage, and reproducible to perform a statistical analysis of the results.

laboratory method / ammonia fluxes / uncertainties / pellet / synthetic fertilizer

1. INTRODUCTION

Ammonia volatilization (NH_3) is assumed to be a major contributor to variations in fertilizer efficiency [13, 15] and is recognized as an atmospheric pollutant mainly via its negative impacts on natural ecosystems [3, 5]. NH_3 volatilization may begin as soon as a fertilizer is applied if it contains ammonium (NH_4^+). The NH_3 fluxes just after application are very dependent on the environmental conditions (temperature, soil water content or soil pH), the type of fertilizer [8] and the rate of fertilizer application. The fluxes during the first hours are responsible for the greatest proportion of nitrogen loss into the atmosphere if favorable conditions are present. In some cases, high NH_3 fluxes are not observed immediately after fertilizer application when NH_4^+ is not directly available from the fertilizer. This delay can be due to the nature of the fertilizer (e.g. urea) which requires several days to hydrolyze, or to the physical form of the fertilizer such as pellets, which need to dissolve before volatilization. During the dissolution process itself, some NH_4^+ is released from the pellet and then may be lost by NH_3 volatilization, thus decreasing the N supply to crops. Currently, no studies have focused on the dissolution step of common fertilizers (other than slow or controlled release fertilizers) and its possible action on total NH_3 emission or N availability for crops. Air and soil humidity contents and soil surface temperature are the main factors able to influence the dissolution and, subsequently, the NH_4^+ release. As this process is rapid and influenced by many environmental factors, it is not easy to study it from field experiments. Laboratory experiments are useful because they allow one to separate these factors and to study their influence on NH_3 volatilization. Dynamic chambers are typically used for estimating ammonia volatilization under laboratory conditions [6, 19]. They are usually made of three parts: (1) a volatilization chamber where N fertilizer is applied to soil, (2) an acid trap for collecting emitted NH_3, and (3) a system to control air conditions (temperature, humidity and ammonia concentration) at the chamber inlet. However, the sources of uncertainty are numerous and could mask the effect of the studied factor, especially for low ammonia fluxes. The laboratory systems must provide good reproducibility, and several repetitions of a treatment are generally required.

We present in this article a simple-to-use system allowing an estimation of low fluxes over short timescales and, based on our experiments, we make an analysis of the possible sources of uncertainties in the NH_3 emission rates during the fertilizer dissolution step. A method is thus proposed for normalizing low NH_3 emission rates.

2. MATERIALS AND METHOD

2.1. Materials

2.1.1. Soil core sampling

In order to consider realistic volatilization conditions, we chose to use soil cores. They were sampled in the field after a

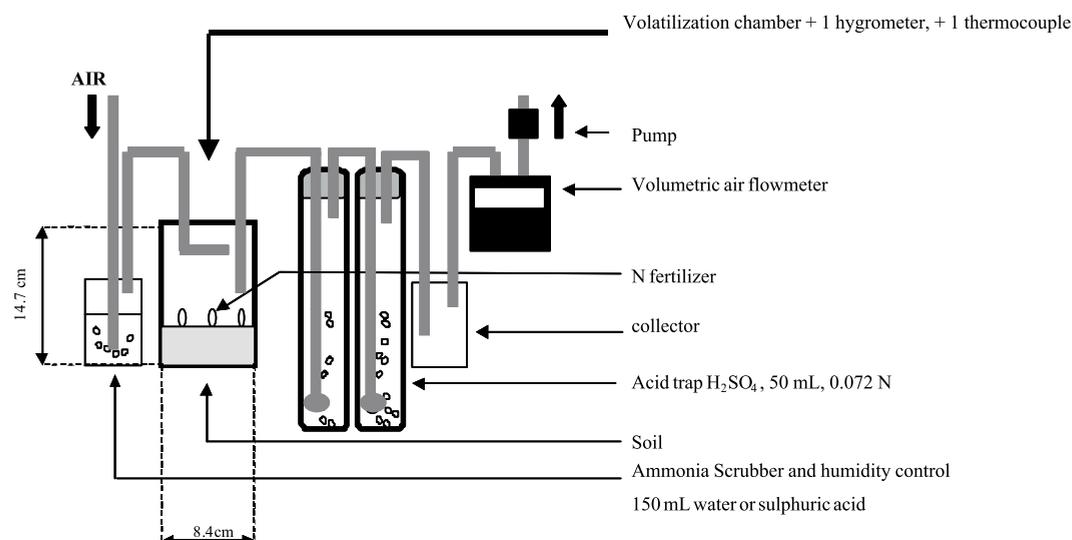* Corresponding author: Sophie.Genermont@grignon.inra.fr

Figure 1. Schema of the volatilization chamber.

Table I. Physical and chemical properties of soil.

	pH		CaCO$_3$	CEC	Clay	Silt	Sand
	H$_2$O	KCl	g·kg^{-1}	cmol·kg^{-1}		g·kg^{-1}	
Silty loam	8.2	7.5	47	22.5	31.0	54.3	14.7

rainfall by using a PVC cylinder driven into a silty clay soil (Tab. I) [10].

The soil cores were 50.2 cm^2 in cross-sectional area, and 8 cm in height. Three samples of approx. 50 g were collected at the same time between the cores to characterize the N mineral content. When wet soil cores were needed, the core samples were immediately inserted into the volatilization chamber in the controlled laboratory area. To study NH$_3$ volatilization over dry soil, the cores were air-dried (20 °C) for 7 days.

2.1.2. Volatilization chamber

Each soil core was placed in a glass, cylindrical chamber (55.4 cm^2 cross-section, 14.7 cm high). The air volume inside the chamber above the soil surface was 2.7×10^{-4} m^3 (Fig. 1). Air was drawn through the chamber using a polyethylene tube (3.2 mm i.d.). The inlet was positioned near the inner side of the cover of the volatilization chamber, whereas the outlet was 0.5 cm from the soil surface. Polyethylene material was chosen to limit ammonia adsorption [14]. In this system, the air circulation was provided by one pump (HX1, Piot et Tirouflet, France) per chamber, rendering each chamber independent. The flow rate was chosen to ensure a minimal exchange rate, but also to prevent an overly rapid drying of the soil surface. It corresponded to an air renewal rate of 11 air chamber volumes·min^{-1} with an average air flow rate of 0.177 m^3·h^{-1}. The air flow rate was monitored over each volatilization chamber by using one volumetric air flow meter per chamber (Gallus 2000, Schlumberger, France) with a 2% accuracy. The volatilization chamber was connected to an acid trap (see Sect. 2.1.4)

Table II. Strength of H$_2$SO$_4$ solution required to give definite air humidities at 25 °C, from [20].

[H$_2$SO$_4$] %	64.8	55.9	50.9	43.4	36.0	30.4	18.5
Relative humidity (%)	10	25	35	50	65	75	90

2.1.3. Incoming and outgoing air characteristics

The air humidity and NH$_3$ content of the incoming air were controlled by bubbling it through a scrubber containing 150 mL of either H$_2$SO$_4$ or water. The acid concentration of the scrubber should be chosen according to the temperature (because of small variations in acid density) and chosen air humidity. Table II presents different sulfuric acid concentrations and resulting air humidities obtained after bubbling. The acid concentration of the scrubber should be chosen according to the temperature and air humidity objectives [20]. To measure the outgoing air concentration in ammonia, the scrubber was designed to obtain an efficient trapping of NH$_3$ by the acid solution (H$_2$SO$_4$, 0.072N). The container was a 120-mL glass test tube, 280 mm high and 24 mm i.d. filled with 50 mL of acid solution. The plunging tube was made of glass (3.5 mm i.d.) and reached the bottom of the container. At the end, there was a bulb with 4–5 tiny holes to produce small bubbles in order to increase ammonia trapping in the solution.

2.1.4. Instrumentation

Air and soil surface temperatures were measured with copper–constantan thermocouples. The relative humidity of incoming

air was measured by a hygrometer (HMP35A, Vaisala, France) in each volatilization chamber. All data were recorded every 5 s and averaged over 15-min intervals with dataloggers (21X, Campbell Scientific, UK). The ammonium content of the acid traps and soil cores was analyzed by the Berthelot method [2] and by the Griess-Illoway reaction cited by [11] for nitrate content of soil cores with a colorimeter analyzer (Technicon II, Technicon, USA).

2.1.5. Sample schedule and calculation of NH$_3$ emission

On the first day during pellet dissolution, samples of the acid trap solutions were taken every 2 hours during the first 14 hours, followed by a 6-hour pause, and then every 4 hours until the end of the second day. From days 3 to 10, samples were taken twice a day. In order to avoid lengthy interruption in the chambers when changing the solution of the bubblers, we only sampled 2 mL in each container during the first 24 hours and changed the solution when its volume was lower than 44 mL. The 2 mL were sampled using a 5-mL micropipette (Pipetman, Gilson, U.S.A.) with a thin polycarbonate vinyl tube (1 mm i.d., 220 mm long) that reached the middle of the acid trap. The whole micropipette and tube system was calibrated by making 9 replicates of 2 mL, sampling deionized water and weighing it. The average volume of the 9 replicates was used to calculate the $[NH_4^+\text{-}N]$ in the acid trap. The NH$_3$-N concentration in the outgoing air was calculated from the data of $[NH_4^+\text{-}N]$ concentration in the acid traps multiplied by the volume of acid and divided by the exposure time and the air volume. The ammonia content of the incoming air was measured and found negligible. Ammonia fluxes (% NH_4^+-N applied·day^{-1}) were calculated by multiplying the increase in ammonia concentration between incoming and outgoing air by the total air flow rate during the exposure time and dividing the result by the treatment area and NH_4^+-N application rate.

The relative measurement deviation of ammonia fluxes was estimated from the calculation of ammonia fluxes and estimated to be 7%.

2.2. Tests

To verify the value and the stability of the air humidity of the incoming air, a volatilization chamber without soil was included in each set of experiments. The tests were performed at 3 expected air relative humidities (R.H.): 40, 50 and 90%, at 8 °C. The sulfuric acid concentrations for the scrubber were therefore chosen to be 51.2% and 0% (pure water), respectively. Two sulfuric acid scrubbers were installed in series to obtain a 40% R.H. objective. The efficiency of the NH$_3$ traps was evaluated for each experiment by connecting a second trap in series and determining the amount of NH$_3$ recovered in the second trap relative to the first. The first trap was changed regularly to monitor the NH$_3$ volatilization as described above and the second one was maintained in place throughout the whole experiment and analyzed at the end. The connecting tube was identical to the polyethylene tube between the volatilization chamber and the first acid trap.

The efficiency of the system was determined by generating NH$_3$ volatilization from an ammonium chloride solution (20 mL, 1.9 g·L^{-1} equivalent to 150 kgN·ha^{-1}) over 3 days without

soil. NH$_3$ volatilization was induced by adding 3 mL of NaOH 9.96 M to the solution, thus increasing the pH to 8. The chamber height (55 mm) was adapted to obtain the same air volume, and consequently, air renewal rate, as if soil were present in the chamber. The NH$_3$ volatilization was stopped by adding 16 mL of H$_2$SO$_4$ solution (0.072 N), decreasing the pH to close to 1. The air circulation was stopped one hour after acid addition to flush any NH$_3$ from the chamber into the acid trap and tubes. The ammonium contents of the acid trap and any solution remaining in the chamber were also analyzed. This test was repeated with 11 volatilization chambers

2.3. Experiments

Experiments were conducted with the system previously described to measure the ammonia volatilization during dissolution of common fertilizer pellets and its relative proportion to total ammonia losses. The system was used to create various durations of dissolution with environmental conditions that favor greater or lesser water absorption by the pellet from the soil, the air, or both. These experiments were carried out in a dark controlled area to maintain constant air and soil temperatures.

3. RESULTS

3.1. Air humidity control

During the test of relative humidity control, the average relative humidity in the controlled room where the dynamic chambers were placed was 85% (Tab. III). Without soil, when air was bubbled in water, the average incoming R.H. was measured at 91%, corresponding to a 6% increase in the controlled room R.H. When the air was bubbled in a sulfuric acid solution, depending on the number of scrubbers, the average incoming air was 58% or 40%, corresponding to a 27 or 45% decrease in controlled room R.H. The 90% and 40% R.H. objectives were met, but not the 50% objective. It is certain that the 50% objective (measured R.H of 58%) was not met because the plunging tube was too short, leading to a decrease in exchange conditions between the air and acid.

In the presence of an evaporating soil, the R.H. inside the chamber increased by 5% and 15% for the humid soils under high and low R.H. of incoming air, respectively. The R.H. increased by 2% and 17% for a dry soil under high and low R.H. conditions.

3.2. Yield of the acid trap system for measuring ammonia air concentration

At the end of the experiment, the second trap was removed to measure NH$_4^+$ content and check whether the first traps had collected all the ammonia emitted during the whole experiment. The efficiency of the first acid trap was very satisfactory (98%, Tab. IV). In one experiment, significant quantities of ammoniacal N were found in the second trap, representing up to 16% of the total quantity collected by the first traps of each volatilization chamber. This difference was attributed to a fault in the air-tightness of the tubes, leading to air contamination of the second acid trap.

Table III. Measured average humidity content in the volatilization chamber depending on water soil content and relative humidity (R.H.) of the incoming air at 8 °C.

	Nature of the bubbling solution		
	water	sulfuric acid 51.2%	
R.H. of the controlled area	85%		85%
R.H. of incoming air objectives	90%	50% (1 scrubber)	40% (2 scrubbers)
R.H. of incoming air of the volatilization chamber	91%	58%	40%
R.H. inside the volatilization chamber depending on $\psi^{\dagger}$			
ψ(m) −12.45	96%		
−4.57		73%	
−32.71	93%		
−42.93			57%

†: hydric potential of the soil core inside the volatilization chamber.

Table IV. Efficiency of the first acid trap, calculating the % of recovery in the second acid trap, which was maintained throughout the experiment.

Air flow rate $(m^3 \cdot h^{-1})$	Sampling period (hour)	NH_3 concentration in the air $(\mu g \cdot m^{-3})$	Air temperature (°C)	Air relative humidity (%)	Number of measurements	Efficiency of the first trap (%)
0.048–0.234	2–24	0–280	8	70–100	27	98 Min: 84 Max: 99.98

3.3. Variation in ammonia volatilization with air flow rate

Figure 2a shows the measured ammonia volatilization flux from the different experiments as a function of the air flow rate. These data were obtained from a set of 6 experiments at 8 °C under various hydric potentials (−42.9 to −4.6 m) and air humidity conditions (air relative humidity <70% or >90%) with 3 replicates per treatment. The ammonia fluxes ranged from 0.018 to 0.175% NH_4^+-N ·day^{-1}. The data exhibited a clear increasing trend, which can be described by an exponential. The best fit was obtained with an exponential function with a correlation coefficient of 0.52. In Figure 2b, the same data are represented in normalized form.

3.4. Efficiency of the experimental system

The efficiency of the system ranges from 80 to 107% of the total NH_4^+-N applied for an air flow rate ranging from 0.069 m$^3 \cdot$h^{-1} to 0.222 m$^3 \cdot$h^{-1} (Fig. 3). On average, the total loss of ammonia was measured to be 7.3% of the total NH_4^+-N applied, but in one chamber NH_3 volatilization represented 12.0% of the total NH_4^+-N applied because of an additional amount of NaOH. The average yield of the volatilization chamber system was 98% with a standard deviation of 5% (Tab. V).

4. DISCUSSION

Air humidity must be controlled in such experiments as it can influence ammonia volatilization through different processes, both directly and indirectly. It has a direct effect not only on pellet degradation and ammonium release [1], but also on the soil drying which enhances volatilization when it is slow [7]. The existence of a critical relative humidity demonstrates that wide variations in ammonia volatilization can result from low variations in relative humidity. Moreover, it is essential that no dew is deposited on the chamber or tube walls since it would be a strong sink for ammonia, which could induce a large underestimation of volatilization. Finally, it has an indirect effect through soil or effluent evaporation, thus promoting soil evaporation and nitrogen rising to the surface, or surface crusting.

Several techniques can be used to control air humidity. It can be done by using regulated systems either by bubbling a stream of air through a controlled temperature bath or tubing, or by controlling the ratio of dry and saturated air. The solution that we tested – bubbling air through acid solution with different concentrations – is much simpler from a technical point of view. Moreover, it generated a fairly constant humidity and is well reproducible [20]. However, it must be calibrated, as equilibrium is not reached between the air and the solution. Another advantage is that it also absorbs ammonia very efficiently, which generates ammonia-free air in a very simple way. Our results showed that it is important to measure air humidity at the inlet of the chamber to understand more clearly any differences between experiments. Indeed, with both wet and dry soils, the increase in relative humidity could be larger than 15%.

Figure 3 shows how important it is to control or at least to know the air renewal rate in the chamber. Over a small difference in flow rates (2%, i.e. the accuracy of the volumetric air flow meter) the flux was multiplied by 1.03 according to Figure 2.
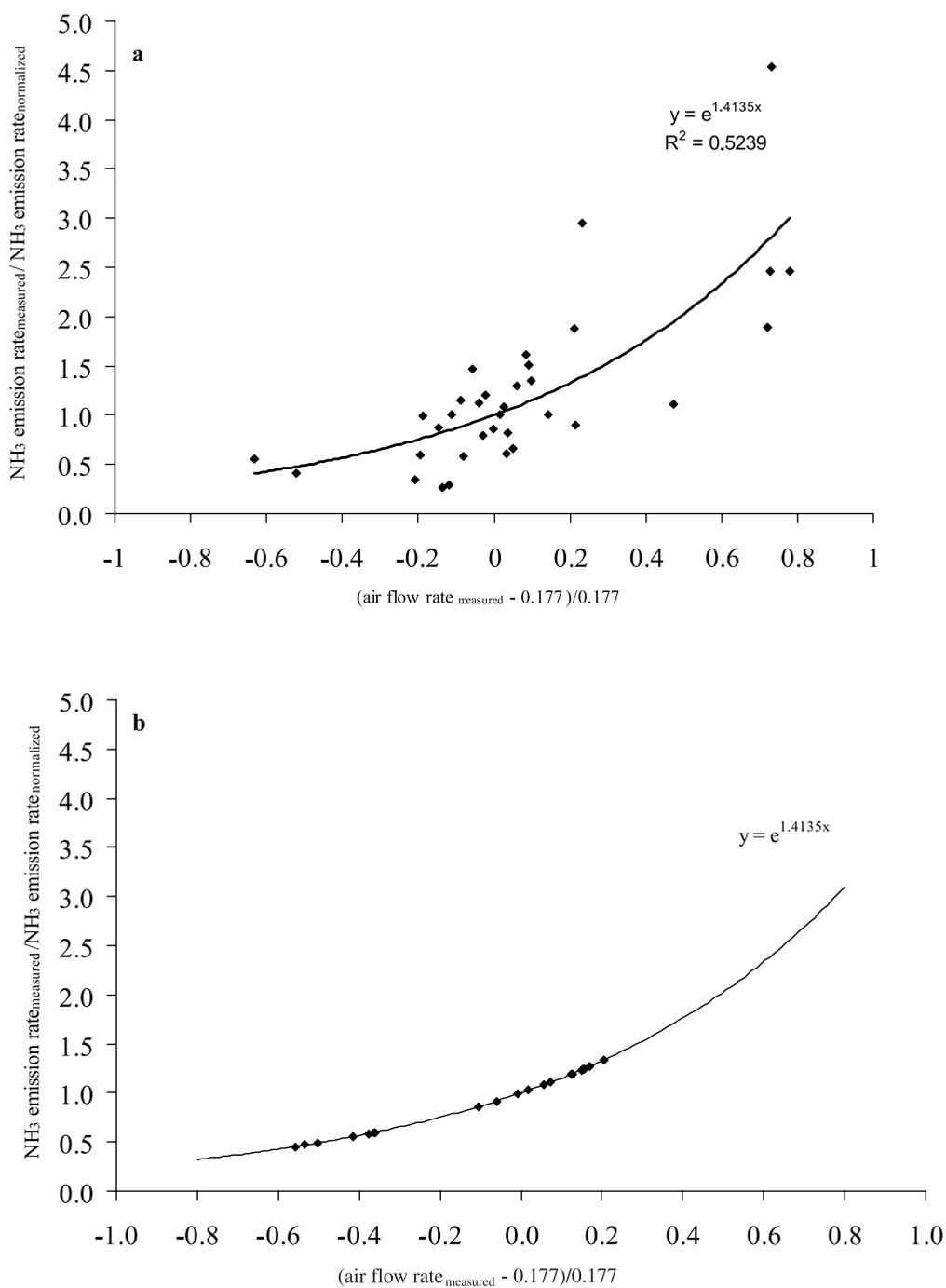
Figure 2. Effect of the air flow rate on NH$_3$ emission (a) and after normalization (b).

Table V. The modified system efficiency (% recovery).

Average efficiency	Standard deviation	Coefficient of variation	Median
98.21	5.39	5.49	96.52

It shows clearly the influence of the air flow and convective exchange conditions on the volatilization flux. Consequently, it is necessary to either control the air flow rate in such systems or at least to measure it. Such normalization could be used to take into account the differences between air flow rates, but also between sampling times to take into account the differing evolution
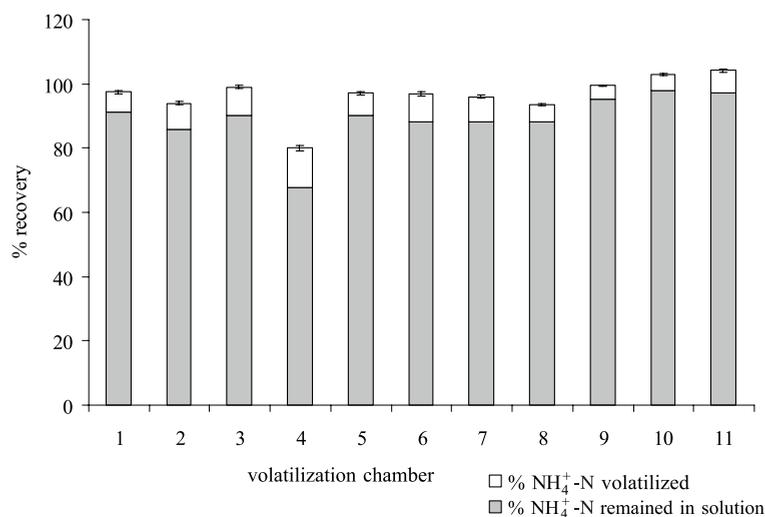
Figure 3. Efficiency of the 11 volatilization chamber system. Vertical bars represent the measurement deviation (7%).

of the ammoniacal pool in soil replicates. The normalized emission rate could be used to recalculate the ammonia fluxes over the same timescale to take into account probable differing evolutions of the NH_4^+-N pool in the soil between chambers. It would also be necessary to perform such a normalization to compare results from different experiments with different air renewal rates. According to the literature, laboratory experiments have been conducted with air renewal rates between 12 [12] and 20 volumes·min^{-1} [9]. Referring to our correction curve, emission rates should be divided, respectively, by 1.12 and 3.20 to be compared with our own results with a mean air renewal rate of 11.

In our experiment, an exponential relation between the air flow rate and NH_3 emission rate was found. Other relations, for example, linear [4, 6], could be found. Chao and Kroontje [4] proposed a linear correction curve, but it was established using only 2 air flow rates when at least three rates are preferable to check the linearity of the curve. Other authors have found nonlinear relations between the air flow rate and gas emission rate: a quadratic regression [17], an exponential relation [16], or a curvilinear relation [18]. Our correction curve was obtained using numerous experimental data. Despite the low value of R^2, it corresponds to a realistic correction of all the factors influencing the air renewal (variation of soil height, pumping, etc.) in laboratory methods using dynamic volatilization chambers, and could be used with confidence. The normalization proposed here is a way to reduce variability inside treatments and between them and then to perform a discriminant statistical test.

5. CONCLUSION

The method described here proposes several improvements over existing methods. It simplifies the control of incoming air. It is also less labor-intensive to follow ammonia emission rates over a short timespan. Using intact soil cores and better air stirring inside the chamber help to reflect a more realistic influence

of the soil. The correction curve can be used for comparisons between laboratory experiments carried out under different conditions.

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