Laboratory assessment of ammonia volatilization from pig slurries applied on intact soil cores from till and no-till plots

Stefania C. Maris (Maris, SC)1, Angela D. Bosch-Serra (Bosch-Serra, AD)1, M. Rosa Teira-Esmatges (Teira-Esmatges, MR)1, Francesc Domingo-Olivé (Domingo-Olivé, F)2 and Elena González-Llinàs (González-Llinàs, E)2

1 University of Lleida, Dept. Environment and Soil Sciences. 25198 Lleida, Spain  2 IRTA, Mas Badia Agricultural Experimental Station. 17134 La Tallada d’Empordà, Girona, Spain

Abstract

**Aim of study:** Agricultural activities are the main source of volatilized ammonia (NH3). Maximum rates are reached within a few hours after slurry application. This study aimed to evaluate the influence of soil texture, tillage and slurry dry matter (DM) on NH3 volatilization.

**Area of study:** Mediterranean semiarid environments (NE Spain).

**Material and methods:** Ammonia volatilization from pig slurry directly applied on the soil surface was quantified in the laboratory, in soil samples from two experimental sites with different soil textures: silty loam and sandy loam. Field treatments consisted of two tillage management practices: till by disc-harrowing or no-till. At topdressing (cereal tillering), tillage treatments were combined with slurries of different DM contents applied onto the silty loam soil. Measurements were done for two cereal cropping seasons and during the period of maximum NH3 flux (12 h after slurry application). A photoacoustic analyzer was used.

**Main results:** Slurry spreading at sowing resulted in low volatilization (0.7-9% of NH4+-N applied) as it also did at topdressing (0.3-1.4% of NH4+-N applied). At sowing, ammonia volatilization from high DM slurry (>7.5%) was significantly enhanced by no-till in both soils. At topdressing, this result was also found in records on silty loam soil. No differences were found between tillage systems when slurry of low DM content was applied, whatever the soil texture and application moment. Although NH3 volatilization was probably affected by the laboratory conditions, the comparisons between treatments were still valuable.

**Research highlights:** Ammonia volatilization abatement can be improved (<1 kg NH3-N ha-1) if fertilization is done after crop establishment using low DM slurries (<3.5%).

**Additional keywords:** calcareous soils; fertilization; Mediterranean agricultural systems; NH3; no-till; soil texture; winter cereals.

**Abbreviations used:** DM (dry matter); HDM (high dry matter); LDM (low dry matter); NT (no-tillage); T (tillage); TAN (total ammonium-N).

**Authors’ contributions:** Field maintenance was done by ADBS and EGL; ADBS, FDO and MRTE contributed to the design of the experiment; SCM and EGL were in charge of soil sampling; SCM and MRTE contributed to measurements; SCM wrote the initial version of the manuscript and performed data analysis with ADBS; ADBS, MRTE and SCM improved the final manuscript according to the suggestions and comments of the reviewers. All authors read and approved the final version of the manuscript.

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**Correspondence** should be addressed to Angela D. Bosch-Serra: angela.bosch@udl.cat
Introduction

Agricultural activities are the main origin of ammonia (NH$_3$) volatilization (Metz et al., 2007). Mineral N fertilizers and the application of manures lead to approximately 60% of the volatilized NH$_3$ (Cameron et al., 2013). Ammonia emissions from nitrogen fertilizer application negatively impact both the quality of the environment and human health; therefore, there is a need to develop methods to reduce NH$_3$ volatilization, to reduce the wastage of fertilizer resources, and to improve nitrogen use efficiency (Lam et al., 2019).

Ammonia volatilization is influenced by several factors such as soil type and humidity, fertilizer characteristics and tillage systems (Sommer et al., 2003). Calcareous soils are prone to volatilization (Iqbal et al., 2013). Ammonia volatilization is also related to the dry matter (DM) content of the applied fertilizer as it can affect soil pore sealing and infiltration, causing ponding at the soil surface which, in turn, might increase NH$_3$ volatilisation (Sommer et al., 2003). Fine textured soils with relatively high clay content have smaller pores and when developed under the influence of similar vegetation and climatic conditions generally show higher cation exchange capacity, organic matter content and water holding capacity than coarse textured soils. Consequently, fine textured soils are less conducive to volatile loss of ammonia than sandy soils (Sommer et al., 2003). However, the higher tortuosity of fine textured soils can lead to a reduced rate of infiltration of surface-applied mineral fertilizer or pig slurry and its reaction products, which may result in significant NH$_3$ loss from the surface (Stevens et al., 1989).

As a conservation tillage practice, no-tillage (NT) has been adopted worldwide as a way to control soil erosion or to increase soil organic carbon sequestration, which usually leads to a yield increase and, subsequently, to higher economic benefits for farmers. However, some reports have drawn attention to a volatilization increase with NT compared to conventional tillage (Mkhabela et al., 2008), through the improvement of soil urease activity and the greater presence of crop residues on the surface that prevent the infiltration of the N fertilizer (dissolved in water or as animal effluent) into soil (Mkhabela et al., 2008; Rochette et al., 2009).

These factors are of special relevance in European NH$_3$ volatilization. Europe produces 25% of the world’s pigs (Sus scrofa domesticus), and nowadays Spain is the biggest producer (MAGRAMA, 2017). In Spain pig slurries are mainly directly applied as fertilizers to cropped fields, in which no-tillage is implemented over 700·10$^3$ ha (MAGRAMA, 2017).

The first 20 hours after slurry application are the most crucial timespan in terms of NH$_3$-N losses. Thompson et al. (1990) and Bittman et al. (2005) found that 57-85% of total NH$_3$-N volatilization occurred in the first 24 hours after applying mineral fertilizer or surface applied manure. In a recent study Yagüe et al. (2019) found that the maximum NH$_3$ flux volatilization was always observed during the earliest period of measurements (3.5-5 hours) after slurry spreading.

Estimated NH$_3$ volatilization in Spanish soils has been found to range from 7% to 78% of the total ammonium N applied with mineral fertilizers or pig slurries (Bosch-Serra et al., 2014). Surface applications promoted by legislators at different administrative levels (EU, 2016; DOGC, 2019) can reduce these figures close to 1% of total N applied, mainly at cereal tillering applications (Yagüe et al., 2019). However, if all plant residues are left on the surface, and slurry infiltration is constrained, volatilization might rise.

Bosch-Serra et al. (2014) and Yagüe et al. (2019) are the only papers we could find that measured NH$_3$ volatilization in semiarid areas under different fertilization strategies (pig slurry and/or mineral fertilizers) applied at sowing and at tillering to winter cereals. In both studies, the NH$_3$ volatilization was measured by using dynamic chambers coupled with acid traps. Nevertheless, using acid traps is time-consuming (e.g. acid solution collection, separate laboratory analysis for NH$_3$ determination), with variable and, in general, low temporal resolution, especially when only small amounts of NH$_3$ are emitted. This second drawback leads to loss of information, especially during the first hours after fertilizer application when emission rates vary rapidly. In addition, to date, none of these studies performed in Mediterranean areas used the system made up of the dynamic chamber method and a photoacoustic analyser. Worldwide there are a few studies on the accuracy and reliability of the photoacoustic analyser with dynamic chambers for NH$_3$ emission assessment (Monaco et al., 2012).

We hypothesized that tillage (T) might abate volatilization when compared with NT. This abatement of NH$_3$ volatilization could be further improved when combining T with the use of slurries of low DM content, although the results could be affected by soil texture due to its influence on slurry infiltration. Hence, the objectives of this study were: i) to compare NH$_3$ volatilization under different tillage systems (no-tillage vs. disc-harrowing tillage) when pig slurry with high DM content (>7%) was applied at sowing over two different textured soils: silty loam and sandy loam; and ii) to evaluate the influence of the DM content of pig slurries applied at the cereal tillering stage (topdressing) on volatilization under different tillage systems (no-tillage vs. disc-harrowing tillage) in the silty loam soil and the sandy loam soil.

The results of this study might help decision makers to develop environmental and agronomic NH$_3$ abatement management practices (tillage systems, slurry rates and their application periods).
Material and methods

Site description and experimental design

The framework of this work was within long-term pig slurry fertilization experiments in which comparison of the tillage systems (NT and T) was implemented two years before the present study started.

The experimental sites (two) are located in the Ebro river basin (NE Spain) on calcareous soils (Table S1 [suppl.]). The soil of the first site (Oliola, 41°51′29″N, 1°05′10″E at 443 m a.s.l.) has a silty loam texture and it is classified as a Typic Xerochrept (Soil Survey Staff, 2014) (Table S1 [suppl.]). The soil of the second site (Torroella de Montgrí, 42°02′30″N, 3°07′35″E at 31 m a.s.l.) has a sandy loam texture and it is classified as a Xerofluvent (Soil Survey Staff, 2014). At both experimental sites, the climate is semiarid Mediterranean, with high summer average temperatures (>20°C), low annual precipitation (<650 mm yr⁻¹) and high average reference crop evapotranspiration (>1000 mm yr⁻¹).

In Oliola, two experiments were set up. In both experiments, the tillage systems (NT and T by disc-harrowing) was the main treatment. In the first experiment (randomized block design, three replicates), all plots received at sowing (without topdressing) pig slurry with a high DM content (~10%, HDM, Table S2 [suppl.]). In the second experiment, at the cereal tillering stage, two types of slurries (high, HDM, and low, LDM (<3.5%) dry matter content, Table S2 [suppl.]) were applied to NT and T plots (topdressing, unique application) following a split-block design with three replicates.

In Torroella de Montgrí, two experiments were set up. In both experiments, the same two tillage systems (NT and T) were established (randomized block design, three replicates). In the first experiment, pig slurry was applied before cereal winter sowing (Table S2 [suppl.]); in the second experiment LMD slurry was applied at the cereal tillering stage (Table S2 [suppl.]).

The experiments and treatments defined for each site and year are summarised in Table 1. Under field conditions, disc-harrowing between 0.20 and 0.25 m was used to incorporate the stubble before sowing (October or November) and later on to bury the slurry. Tillage was performed not later than 12h following slurry application. At tillering (February or March) the fertilizer was not buried. Barley (Hordeum vulgare L.) was sown under rainfed conditions. Every cropping season, straw was removed from the fields according to farmers’ practice.

Ammonia volatilization: gas sampling and analysis

The volatilization study was done in the laboratory during two cropping seasons (2011-2012 and 2012-2013) in the silty loam soil, and during one crop season (2011-2012) in the sandy loam soil. The day before slurry application in the field, undisturbed soil cores were taken, using PVC tubes, which were 15 cm long and 7 cm in diameter, from two replicates (blocks). Each pig slurry applied on the field was analyzed for its main physical and chemical characteristics (Table S2 [suppl.]). A representative aliquot of the slurries was brought to the laboratory and stored at 4°C until the following day, when each type of slurry was applied to each soil at the same dose as it had been applied in the field (Table 1) and NH₃ volatilization monitoring started in the laboratory. The plant residue coverage in the undisturbed soil of NT cores was estimated to be close to 65% on the silty loam soil and to 55% on the sandy loam soil. Residues were maintained on the surface of the NT soil cores. No residues were left on the T soil surface.

Each soil core was placed in a chamber system coupled to a photoacoustic analyzer, in order to monitor NH₃ volatilization (Monaco et al., 2012). The chamber system for NH₃ volatilization consisted of a sealed glass jar (1.5 L) in which the undisturbed soil cores were placed. Each glass jar was equipped with a two-way key that allowed direct connection between soil cores and the photoacoustic analyzer (Innova 1412 Photoacoustic Multigas Monitor) via a Teflon® tube. The temperature in the laboratory followed the open-air fluctuations. Air samples from inside

| Framework | Slurry applied before sowing | Slurry applied at topdressing |
|-----------|-------------------------------|------------------------------|
| Soil texture | SIL | SIL | SL | SIL | SIL | SIL | SIL | SL |
| Date | Oct-11 | Oct-12 | Nov-11 | Feb-12 | Feb-12 | Feb-13 | Feb-13 | March-12 |
| Slurry type | HDM | HDM | HDM | HDM | LDM | HDM | LDM | LDM |
| Dose (kg N ha⁻¹) | 185 | 130 | 245 | 113 | 123 | 99 | 80 | 158 |
| Tillage system | T/NT | T/NT | T/NT | T/NT | T/NT | T/NT | T/NT | T/NT |

Table 1. Annual doses of pig slurry applied to the experimental sites with different textures: silty loam (SIL, site 1) and sandy loam (SL, site 2). The monitored treatments during two cropping seasons (2011-2012, 2012-2013) were defined according to the studied variables: moment of slurry application and tillage system (NT: no-tillage; T: tillage by disc-harrowing).
the glass jar were taken immediately after pig slurry was directly applied on the soil surface (simulating a trail hose field application). The air stream NH$_3$ concentration was measured semi-continuously during 12 h after application. The detection limit of the photoacoustic analyzer was 0.2 ppm of NH$_3$. The obtained data were converted to the actual NH$_3$–N volatilization surface rate by calculating the air flux rate using the time elapsed between measurements and the sampled air volume. The cumulative NH$_3$–N volatilization throughout the study period was calculated by integrating the volatilization curves over time.

In the laboratory, the minimum and maximum temperatures recorded during the 12 h after slurry application (sowing time) on the silty loam soil were 15.5 and 19 ºC in 2011, while in 2012 they were 12 and 17ºC. In 2013, at topdressing, the recorded temperatures for the same period of time were 8 and 12ºC. When measuring volatilization in soil samples from the sandy loam soil, the recorded minimum and maximum temperatures were 18.5 and 21ºC at sowing time (2011), while at topdressing (2012) they were 11.5 and 17ºC. Laboratory conditions (i.e. absence of direct solar radiation, wind) may have reduced volatilization, nevertheless the comparisons between treatments are still valuable.

**Data analysis**

The effect of the tillage systems was evaluated by analysis of variance. Separation of means was done by the Duncan multiple range test ($\alpha = 0.05$). In the silty loam soil at cereal tillering, the effect of tillage systems combined with slurries of different DM content on cumulative NH$_3$ volatilization was analyzed according to the field split-block design in order to observe potential interactions between both variables. In the analysis, the interactions between replicates and tillage or between replicates and slurry DM were used as an error term. The statistical package JMP version 12 (SAS Institute), was used.

**Results and discussion**

Before barley sowing, the cumulative NH$_3$ volatilization for the 12 h period after slurry spreading followed a similar pattern for both soil textures, and it was significantly affected by the tillage system (Table 2). The highest NH$_3$ volatilization corresponded to the NT system (Table 2) where the recorded volatilization ranged from 1.74 in the sandy loam soil up to 7.14 kg NH$_3$-N ha$^{-1}$ in the silty loam soil which equaled 0.7% and 5.5% of the total N applied, respectively. In the silty loam soil, NH$_3$ volatilization was approx. 55%-104% higher from NT than from T. At cereal tillering stage (2012) in the sandy loam soil, when low DM slurry (3.2%) was surface applied (Table S2 [suppl.]), NH$_3$ volatilization average was also higher from NT than from T, but the difference was not significant (Table 2). In the silty loam soil, an interaction was found in 2012 between tillage system and slurry DM (Table 3) which indicated that NT only boosted NH$_3$ volatilization if HDM slurry was applied. In 2013, no interaction was found in the statistical analysis between

Table 2. Effect of tillage systems (T: tillage by disc-harrowing, NT: no-tillage) on cumulative NH$_3$ average volatilization during the 12 h ($\pm$ standard deviation) following surface application of pig slurry. Slurry with high dry matter content (>7%) was applied in different cereal cropping seasons before sowing (Oct-Nov) and over two soils (from two sites) with different texture: silty loam (SIL) and sandy loam (SL). Volatilization was also quantified when low dry matter slurry (3.2%) was surface applied at topdressing (March) in a SL soil.

| Period (mm-yy) | Site/ Texture | Tillage system | Slurry application | Cumulative NH$_3$ volatilization |
|---------------|----------------|----------------|--------------------|---------------------------------|
|               |                |                | Dose (t ha$^{-1}$) | Total N (kg ha$^{-1}$) | NH$_3$-N (kg ha$^{-1}$) | Anova data$^{[a]}$ | NH$_3$-N$^{[b]}$ (kg ha$^{-1}$) |
| Oct-11        | Site 1/ SIL    | T              | 25                 | 185                  | 111                        | 1/ 6844357.4/         | 2.52±0.02 b                        |
|               |                | NT             | 25                 | 185                  | 111                        | 0.009                  | 5.14±0.34 a                        |
| Oct-12        | Site 1/ SIL    | T              | 22                 | 130                  | 80                         | 1/ 6431592.1/         | 4.60±0.27 b                        |
|               |                | NT             | 22                 | 130                  | 80                         | 0.01                   | 7.14±0.23 a                        |
| Nov-11        | Site 2/ SL     | T              | 46                 | 245                  | 166                        | 1/ 60940.6/           | 1.49±0.07 b                        |
|               |                | NT             | 46                 | 245                  | 166                        | 0.043                  | 1.74±0.01 a                        |
| March-12      | Site 2/ SL     | T              | 34                 | 158                  | 127                        | 1/ 27146.9/           | 0.91±0.07                          |
|               |                | NT             | 34                 | 158                  | 127                        | 0.43                   | 1.08±0.23                          |

$^{[a]}$ Anova analysis; df: degrees of freedom; MS: mean square (data units were g ha$^{-1}$); $p$: significance. $^{[b]}$ Average values with different letters are significantly different according to the Duncan multiple range test for a $\alpha= 0.05$ probability level.
tillage and slurry DM. Also, no differences between treatments were found (Table S3 [suppl.]). However, the amounts of ammonia detected in both cases were low (<1.4 kg NH₃-N ha⁻¹).

The importance of soil surface roughness in volatilization reduction was demonstrated by Bacon et al. (1988). In the studied T plots, large pores enhanced slurry infiltration. As slurry infiltrates, it reduces the pool of total ammonium-N (TAN) at the soil surface, NH₃ concentration is also reduced and therefore, subsequent volatilization decreases (Thompson et al., 1990), and NH₃-N is protected from volatilization by adsorption onto soil colloids (Sadeghpour et al., 2015). As a result, NT showed higher volatilization potential, in agreement with the abatement measures, whatever the tillage system, can be an effective strategy to reduce NH₃-N volatilization in rainfed Mediterranean semiarid environments. The success of abatement measures, whatever the tillage system, will be more evident with slurries of low DM content.

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