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Ammonia Volatilization from Pig Slurries in a Semiarid Agricultural Rainfed Area

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Abstract: Slurries are one of the main NH_3 emission sources. Nitrogen losses impact air quality, and they constrain the sustainability of farming activities. In a rainfed Mediterranean agricultural system, the aim was to quantify NH_3 emissions at a time when plants do not yet cover the soil surface and according to fertilization practices. One treatment was slurry from fattening pigs (PSF) applied before cereal sowing and incorporated into the soil; two treatments were PSF or from sows (PSS) applied at the cereal tillering stage (topdressing); and two more treatments received slurries twice, before sowing and as topdressing. Ammonia emissions were quantified with semi-static chambers during 145 h (before sowing) and 576 h (at cereal tillering) after slurry application. Before sowing, tillage after slurry application controlled NH_3-N emissions, but they accounted for 14% of the total NH_4-N applied. At tillering, average NH_3-N emissions also accounted for ca. 14% of total NH_4-N applied as PSF or PSS, respectively. Slurry dry matter from 84 kg m^{-3} (PSS) up to 127 kg m^{-3} (PSF), combined with low soil moisture content (below 30% of water holding capacity) at application time, helped in NH_3 emission control. Slurry applications before sowing did not enhance later NH_3-N emissions at topdressing.

Keywords: ammonia emission rate; fattening pig slurry; precursor of particulate matter; sow slurry

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1. Introduction

Agriculture is considered one of the dominant sources of atmospheric ammonia (NH_3), contributing to over 81% of its global emissions [1], and close to 94% in Europe [2]. Such emissions are very important in rainfed semiarid areas, where N losses from the soil can be mainly attributed to NH_4–N volatilization [3]. It also represents a cost for farmers because it reduces N use efficiency from fertilizers. There is also a related environmental impact [4], which includes climate change aspects since ammonia is a precursor of nitrous oxide, a potent greenhouse gas. In Europe, NH_3 emissions from agriculture are the precursor (50% of the total) of the particulate matter with a diameter of 2.5 µm or less (PM2.5) [5–7]. It is well known that PM2.5 has a great negative potential impact on human health [8] as it has been related to premature deaths. In Spain, annual NH_3 emissions fluctuated between 418 and 524 kt NH_3 in the period from 1990 to 2019. The increment was mainly related to the significant growth of the national cattle herd, mainly located in the northeastern part of the country [2]. Another important source comes from pig (*Sus scrofa domesticus*) slurries. Spain is the EU-27 country with the largest pig census [9]. The pig production areas give rise to large amounts of faeces and urine, usually mixed with some water during management to give a pig slurry with an ammonium nitrogen (AN) average content of 65% of total N (TN) in this material [10]. In Spain, slurries are mainly used on agricultural land (92%) as fertilizers [11]. In these areas, farmers apply slurries in autumn before sowing winter cereals, despite the lack of water, awaiting the later rains of the winter. Moreover, when using slurries from pigs as fertilizer, a second application can be made at the cereal tillering stage, during a period in which the cereal plant develops and progressively covers the surface. Under rainfed Mediterranean conditions in which there is the greatest probability of high rainfall during autumn, linked to low crop evapotranspiration, such rain may increase the risk of N losses by leaching. Although some N is needed for early cereal growth, higher N use efficiency is expected in winter cereals when the slurry application is divided between sowing (autumn) and cereal tillering development in spring [12].

Ammonia volatilization from the soil is associated with the chemical and physical properties of the material added, but also with the method and time of application, the soil properties, and the meteorological conditions [13]. The highest ammonia emission rate is produced immediately after slurry application, with approximately half of the losses occurring during the first few hours [14,15]. To avoid this, in most of the EU countries various strategies have been tried experimentally to reduce NH_3 volatilization [16,17]. Variations in air temperature, wind speed, solar radiation, slurry rate applied, and AN content can significantly affect NH_3 emissions [18–20]. In addition, relative humidity increases and small amounts of rainwater or irrigation (which increase slurry infiltration) reduce NH_3 volatilization [21,22]. High slurry dry matter (DM) content can enhance NH_3 emission when moist, but it favors crust formation when dried, which in turn increases the liquid phase resistance and reduces NH_3 volatilization rates [23]. Emissions can be reduced while the slurry dries because ion diffusion resistance increases [18]. We hypothesized that applications before sowing time might enhance NH_3 volatilization in subsequent (topdressing) slurry applications. The basis of this influence is of interest because it could improve our understanding of soil water and N dynamics in dryland Mediterranean conditions, and EU emission inventories [24]. This work will also contribute to providing data about NH_3 abatement for the sustainability of the agricultural system.

This work aims to evaluate NH_3 volatilization using semi-open static chambers when pig slurries from different origins but with high dry matter contents are applied at different times and rates in a typical rainfed Mediterranean agricultural system.

2. Materials and Methods

2.1. Experimental Site and Design

The experiment was set up in a semiarid Mediterranean climatic area in the NE of Spain (Figure 1), with the coordinates 41°52′29′′ N, 1°09′13′′ E. The mean annual precipitation is 450 mm.

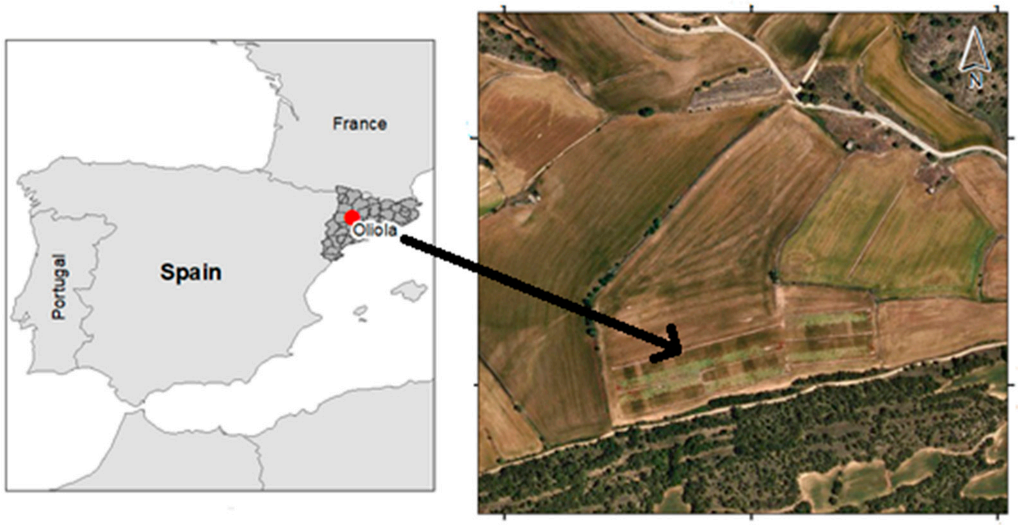

Figure 1. Experimental site location in Oliola (NE of Spain).

An automatic meteorological station located next to the experimental site provided daily climatic data. The soil was classified as a Typic Xerofluvent [25]. It is non-saline and calcareous. The main physicochemical characteristics of the upper layer (0–0.30 m) are shown in Table 1.

Table 1. Soil physicochemical characteristics of the upper layer (0–0.30 m).

Soil Property	Units	Value
Texture (Pipette method)		Silty loam
Sand	g kg^{-1}	131
Silt	g kg^{-1}	609
Clay	g kg^{-1}	260
pH (1:2.5; soil:distilled water)		8.2
Organic-C content (Walkley and Black method)	g kg^{-1}	11.7
Bulk density (Field cylinder method)	g cm^{-3}	1.65
Calcium carbonate equivalent (Bernard calcimeter method)	g kg^{-1}	300
Water field capacity (Pressure extraction, −33 kPa)	% (*w*/*w*)	17.2
Permanent wilting point (Pressure extraction, −1500 kPa)	% (*w*/*w*)	10.2

The experimental work was set up within a long-term fertilization experiment established fourteen years ago. Six N-treatments from two blocks (repetitions) were chosen for this study (Table 2). The distance between the two blocks was 100 m. The plot size was 137.5 m^2 (11 m wide and 12.5 m long) except for the control which was 87.5 m^2 (7 m wide and 12.5 m long). In the chosen experimental plots, barley (*Hordeum vulgare* L.) was sown in the last week of October and harvested in the fourth week of June.

Table 2. Slurry rates, total nitrogen, and ammonium nitrogen added by the different treatments. Other physicochemical values of pig slurry applied before sowing (October) and at cereal tillering (February) from fattening pigs (PSF) and sows are included.

Parameters	Sowing	Tillering	
	PSF	PSF	Sows
Slurry rate (Mg ha^{-1})	20 [1]	35 [2]	77 [3]
Total N added (kg N ha^{-1})	152 [1]	265 [2]	233 [3]
Ammonium-N added (kg N ha^{-1})	101 [1]	183 [2]	119 [3]
pH	8.5	8.6	8.5
Electrical conductivity	6.7	6.6	2.4
Dry matter (kg m^{-3})	127	101	84
Organic N (kg m^{-3})	2.6	2.4	1.5
Total N (kg m^{-3})	7.7	7.6	3.1
Ammonium-N (kg m^{-3})	5.1	5.3	1.6
Total organic-C (kg m^{-3})	49	39	24

[1] Rate applied at cereal sowing to treatments S20, S24, S28; [2] Rate applied at cereal tillering to treatments S04, S24; [3] Rate applied at cereal tillering to treatments S08, S28.

Treatments and the associated code numbers include the timing of slurry (S) application and N dose. The first number of the code indicates the treatment before sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. The second number of the code indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}. Thus, two of the N-treatments were based on the same amount of N applied at the cereal tillering stage (2 of Feekes scale [26]) (ca. 250 kg N ha^{-1}), but from different types of pig slurry: fattening pigs (35 Mg ha^{-1}) (code 4) or sows (77 Mg ha^{-1}) (code 8). They were combined (codes S24 and S28) or not (codes S04 and S08) with fattening pig slurry applied before sowing (20 Mg ha^{-1}). Slurry applied only before sowing (code S20, 20 Mg ha^{-1}) was the fifth treatment. Treatments were randomized against the block.

Pig slurry analyses from fattening pigs (PFS) showed higher values of DM, electrical conductivity, TN, and AN, than slurry from sows (PSS) (Table 2). Slurries PFS also had a higher ratio of organic-C over DM.

A control plot with no N-addition (code S00) but receiving P and K (40 and 56 kg ha^{-1}, respectively) was included. The slurry application was always carried out over the soil surface using a commercial splash plate spreader. Before sowing, the slurry was incorporated into the soil (9 h after application) by superficial disc harrowing (~15 cm depth). At early tillering, when less than 30% of the area was shaded by plants, slurries were left over the soil without incorporation.

2.2. Field Ammonia Emission Measurements

The measurements were first conducted when slurries applied over the surface were incorporated before sowing, and secondly when they were not incorporated, after application at the cereal tillering stage. The slurry application was conducted on 20 October before sowing and on 2 February 2016 at the early cereal tillering stage (as topdressing). Slurries completely covered the surface. Immediately after application, NH_3 emission measurements were started. Before sowing, they were maintained for 145 h; thus, they were set up before slurry incorporation and continued after harrowing. At topdressing, they were maintained for 576 h.

Semi-open static chambers adapted from [27–29], three for each plot (six per treatment), were used. Each semi-static chamber consisted of a plastic cylinder (0.2 m diameter and 0.2 m high) made of LD PET (Low-Density PolyEthylene Terephthalate) with a pair of removable low-density (20 kg m^{-3}) polyfoam sponges. The inner sponge disc (foam I) was placed 0.1 m high inside the cylinder, sustained by a cross of metal wire, and the upper sponge (foam II) was set at the top. The foam discs were previously soaked in an acid solution of 80 mL oxalic acid in acetone (3% w/v), well dried, and preserved in hermetically sealed plastic bags up until their placement in the field. Foam I trapped the NH_3 emitted from the soil surface. Foam II protected the interior trap from atmospheric ammonia. Immediately after the slurry was applied to each plot, the semi-static chambers were vertically introduced 25 mm deep into the soil following the sown line, avoiding soil surface disturbance. Foam discs were periodically changed. On rainy days, the semi-static chambers were closed with a transparent plastic bag. Thus, no data were obtained from these foams during the rainy period. Foam disc I was renewed at 9, 24, 32, 49, 56, 80, and 145 h after sowing slurry application. At cereal tillering, foam disc I was renewed at 7, 24, 31, 48, 55, 72, 79, and 103 h after topdressing slurry. Measurements were also carried out from 168 to 192 and from 360, 408, 480, 528, and 576 h later. Foam discs were individually stored in plastic bags and kept in the laboratory fridge for the NH_3 extraction and quantification.

Ammonium oxalate extraction was completed with water up to 500 mL. The pH of the dilution was adjusted with NaOH (40% w/v) and NH_3 was quantified using a selective electrode (Crison, micropH 2002; Alella, Barcelona, Spain). A total of 119 foams were analyzed before sowing and 540 at topdressing.

2.3. Slurry Sampling and Analyses

Fresh slurry samples were collected and analyzed for pH, electrical conductivity, DM (gravimetry, 105 °C), organic-C by calcination at 550 °C, total N by the Kjeldahl method [30], and ammonium nitrogen (NH_4^+-N) by distillation and titration according to methods 4500-NH_3B-C from [31]. Organic-N was calculated as the subtraction of total N and ammonium-N (Table 2). Soil water holding capacity (−33 kPa), permanent wilting point (−1500 kPa), and soil water availability were determined according to [32]. Soil was sampled (0–0.1 m) to measure soil moisture content.

2.4. Statistical Analysis

The values obtained in foam I from the control treatment were treated as natural soil emissions. They were not included in the statistical analysis.

The statistical package SAS version 9.4 [33] was used for statistical analysis. The REG procedure was used to establish the best data adjustment for NH_3 emissions in each treatment using the mean values of each sampling date. The General Linear Model procedure (GLM) was used for the analysis of final ammonia (NH_3-N) cumulative values after slurry application before sowing and at cereal tillering. Cumulative emissions as a percentage of the ammonium nitrogen applied were also analyzed. In each plot, the three measurements were used for this GLM analysis. Means were compared with the studentized range test of Tukey (α = 0.05).

3. Results

During the initial period of measurements before sowing, no rain events occurred; wind speed varied between 0.65 and 1.7 m s^{-1}; mean air temperature and humidity were 12 °C and 76%, respectively.

At the cereal tillering stage, from the slurry application up to the end of measurements, rain events contributed 23 mm (Figure 2). The heaviest rain was recorded on 27 February (25 mm) when measurements were stopped (576 h after slurry application). Wind speed ranged from 0.3 to 4.2 m s^{-1}. The air temperature did not exceed 12 °C. The relative humidity of the air varied from 47 to 97%. Soil moisture (0–0.1 m) was between 9 and 21% (w/w) within the soil water field capacity and the permanent wilting point.

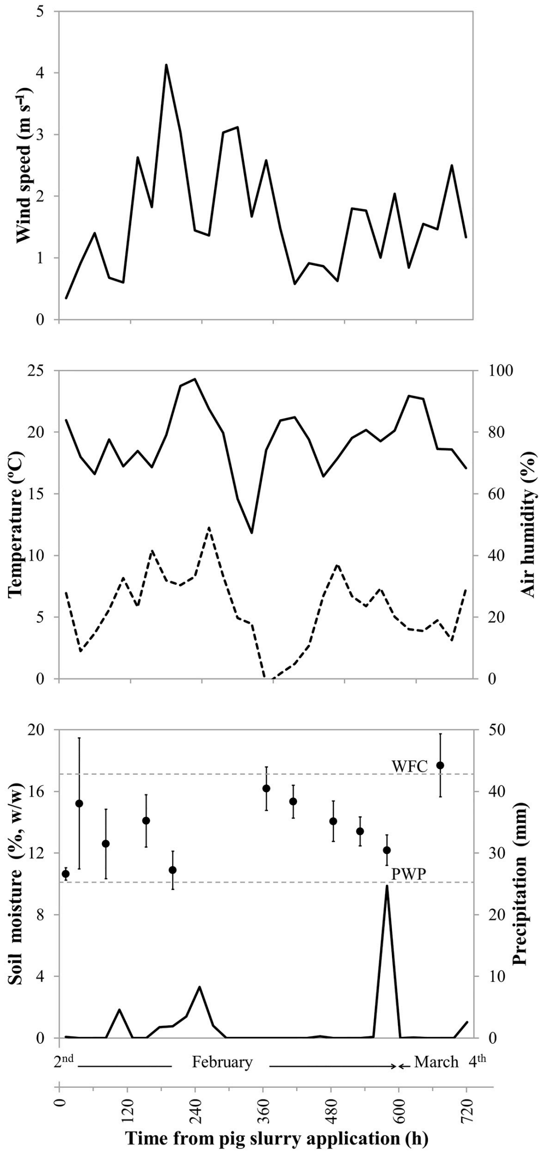

Figure 2. Mean meteorological conditions (temperature in dotted line) and soil moisture content from 0–0.1 m (black points) after pig slurry application on February 2, at the cereal tillering stage. Soil moisture is plotted with two references: permanent wilting point (PWP) and the water content at field capacity (WFC). The difference between WFC and PWP is the amount of soil water available to plants.

Logarithmic distributions were fitted for NH_3 emissions in each treatment (Table 3).

Table 3. Accumulated ammonia volatilization (y, NH_3-N kg ha^{-1}) over time (x, hour) according to the slurry treatment before sowing and/or at cereal tillering.

Application Time	Treatment Codes [1]	Equation	R^2
Sowing	S20	$y = 1.1875 \cdot \ln(x) + 8.1362$	0.94
Tillering	S04	$y = 6.8756 \cdot \ln(x) - 12.372$	0.97
	S08	$y = 2.3432 \cdot \ln(x) - 3.6139$	0.97
	S24	$y = 6.9631 \cdot \ln(x) - 11.721$	0.97
	S28	$y = 2.8267 \cdot \ln(x) - 5.1685$	0.98

[1] Code numbers are related to the timing of slurry (S) application and N dose. First number indicates the treatment before sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

Before sowing, the highest NH_3 flux rates (1.15 kg N ha^{-1} h^{-1}) were measured 9 h after PSF application, just before incorporation by tillage (disk harrower). From 24 h, NH_3 emissions in the fertilized soil were similar to the control treatment: 0.06 kg N ha^{-1} h^{-1} from S20 vs. 0.01 kg N ha^{-1} h^{-1} from S00. A maximum emission of 14% of AN (14 kg N ha^{-1}) was recorded (Figure 3a).

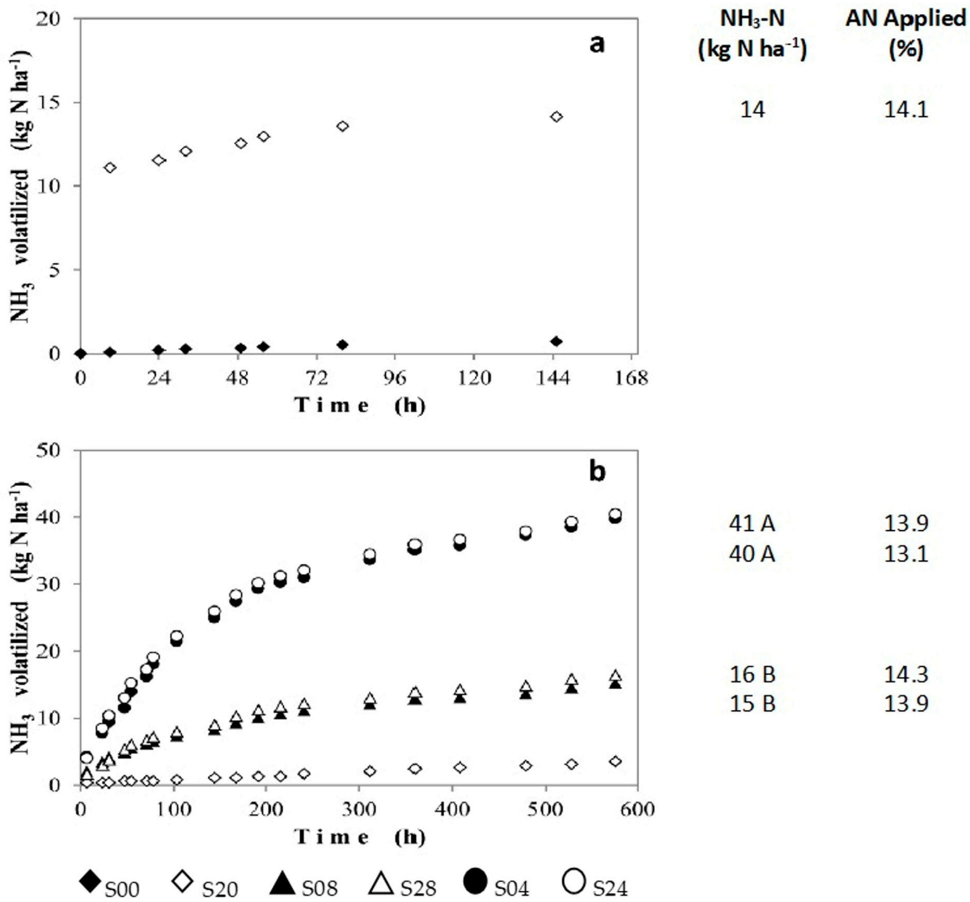

Figure 3. Ammonia (NH_3-N) cumulative average values after slurry application before sowing (**a**) and at cereal tillering (**b**). Cumulative emissions as a percentage of the ammonium nitrogen applied (AN) are also included. At tillering, maximum accumulative NH_3-N emissions, followed by the same capital letter, are not statistically different according to the Tukey test ($\alpha = 0.05$). The code treatment number is related to the timing of the slurry (S) application and the N dose. The first number indicates treatment before sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. The second number indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

At tillering, the highest NH_3 emission rates for all treatments were recorded during the first 7 h after slurry application, decreasing by half after 48 h and gradually matching the control from 192 h onwards. During the 72 h after slurry application, 50% of AN was lost to the atmosphere. This means that NH_3 losses were confined to one week. The maximum NH_3 emission rate was below 0.7 kg N ha^{-1} h^{-1} for PSF and 0.3 kg N ha^{-1} h^{-1} for PSS, accounting for a total maximum emission of 41 and 16 kg N ha^{-1}, respectively. These figures mean an emission equivalent of c. 14% of the AN was applied (Figure 3b), similar to that recorded before sowing time. For control treatments (S00 and S20), a threshold loss of 2.5 kg NH_3-N ha^{-1} was recorded.

Statistical differences were found in the total amount of NH_3 volatilized according to treatments (Table 4 and Figure 3b).

Table 4. Analysis of variance of total ammonia emitted, after slurry application at cereal tillering.

Source	df	Sum of Squares	Mean Square	F Ratio	*p*
Between treatments	3	2135.832	711.944	26.11	<0.0001
Between blocks	1	0.016	0.016	0.00	0.98
Between samples within treatments	8	605.739	75.717	2.78	0.06
Within samples (residual)	11	299.927	27.266		
Total	23	3041.514			

Also, at tillering, when accounting for the total emitted NH_3 on treatments that had received slurry previously before sowing (S24, S28), this figure was not significantly higher (Table 3) than for the ones that had not previously received slurry (S04, S08) (Figure 3b).

4. Discussion

Soil moisture conditions as percentages were similar at both application times, 11.3 and 10.6% before sowing and at tillering stages, respectively (Figure 2).

Before sowing, tillage after slurry application was a successful measure for the prompt control of NH_3 emissions (Figure 3a). In fact, abatement figures were more successful than the ones from a similar soil management (slurry and crop residues incorporation into the soil immediately after slurry application) recorded by [34]. It was probably because they reported values of soil water content above field capacity during the whole experiment [34], while our soil just reached a maximum average of 16% soil moisture at the soil surface layer, below its field capacity. Lack of soil moisture constrained volatilization as water sustains the reaction of NH_3 emission [35,36]. Furthermore, low soil water content enhances the infiltration of slurry liquid and hence the mass transport of NH_4^+ into the soil [36]. As the soil dries, potential losses are reduced [37].

At tillering, a slight positive emission trend was observed (Figure 3b), when slurries had been previously applied before sowing, although it was not significant.

Under field conditions, temperature, wind speed, and rainfall influence NH_3 emissions after cattle and pig manure surface application [17,37,38]. In our experiment, at cereal tillering, changes in NH_3 emission fluxes over time were also affected by the mentioned weather parameters. It is well known that as temperature increases, the equilibrium gas-phase NH_3 concentration increases [39]. However, rain events followed by dry days could reduce the amount of NH_3-N emitted because of crust formation. Clay presence also favors crust development after rainfall events [40]. As stated, NH_3 does not volatilize from dry soils because of a lack of reactions [35]. Re-wetting (Figure 2) by a light rainfall (4.6 mm on the fifth day after application) did not enhance emissions, in accordance with other studies [38], which found reduced NH_3 emissions after rain simulations. Another reason might be that the main losses had already occurred (Figure 3b). The reduction of the superficial (0–0.1 m) soil water content below 10% of soil holding capacity (Figure 2) was followed by a general decrease in flux NH_3 emission and consequently in NH_3 accumulated losses (Figure 3b).

Despite the similar TN dose applied with both slurries at tillering, higher accumulated NH_3 emissions from PSF can be associated with the higher amounts of AN applied to the soil (Table 2), as absolute emissions are positively correlated with the log10 of manure AN concentration [15]. Nevertheless, our records were in the low range of emissions described by those authors, even though we were recording the molecular NH_3 diffusion and the incidence of turbulent mixing transfer with height is limited. As mentioned above, the weather conditions (common for the Mediterranean climate) limited the NH_3 emissions.

In topdressing application, without incorporation into the soil, emissions were higher as DM increased from 84 up to 101 kg m^{-3} (Table 2, Figure 3b). It is known that slurries with a low DM content are generally associated with lower ammonia emissions due to better infiltration into the soil, thereby reducing the contact area between the slurry and the air [19,41,42] as it has also been reported in other Mediterranean experiments [14]. However, in the present experiment slurry DM was high. Thus, its influence on NH_3 emissions might be explained because, at the highest slurry DM, the superficial crust could have reached liquid phase resistance later than in the lowest DM context. Crust presence is important, as it has been reported that a 50% decrease in NH_3 emissions occurred when it was formed in slurry tanks [21]. Other authors associated treatments with crust formation over the soil with low NH_3 emission rates [23]. In our case, as the slurries were applied in early February, the drying-phase period was prolonged until 192 h due to meteorological conditions (Figure 2).

Despite the similar TN applied at the tillering stage, differences were observed in the AN dose (Table 2). Several authors observed that, during the first 24 h after application, the volatilization rate was the highest [43]. Furthermore, it is well documented that most NH_3-N emissions in agricultural soils occur within a few days after fertilizer application [17,41]. The present study agrees with such findings, as the main NH_3-N emissions occurred during the first 72 h after application.

The slurry rates evaluated in this study confirm the impact of slurry applications covering the soil surface. At tillering, an average ca. 14% of the AN was lost (Figure 3b), even when temperatures, low soil moisture, and crust formation limited the NH_3 emission to the atmosphere (Figure 3). Considering the upcoming changes in temperature due to climate change, an increase in temperatures is expected, promoting an increase in the NH_3 volatilization [44] if water availability is not constrained. In countries such as Spain with a high livestock head number [9], possible future increases in NH_3 emissions are also a matter of human health concern.

According to recent research, the significant role of NH_3 in the formation of PM2.5 is relatively low compared to that of other precursors such as SO_2 and NOx [45]. The evaluation of different slurry types and application times under Mediterranean conditions provides data to contribute to the creation of evidence-based regulations for PM2.5 precursors. This is an important point as PM2.5 affects the shortwave radiation reaching the ground; thus, it influences meteorology and atmospheric chemistry [46]. In fact, some studies [47] point to the interactions between ammonia and temperature as the driving factors for PM2.5 concentrations. However, this point deserves future research in rural areas with high livestock pressure. In the context of the described climate conditions in semiarid environments, slurry DM and soil moisture content at fertilization time should be considered in the control of NH_3 emissions.

5. Conclusions

Before sowing, slurry incorporated by tillage into the soil controlled NH_3 emissions. At tillering, when slurries were not incorporated, 50% of NH_3-N emission from AN applied was reached 72 h after application. Losses were equivalent to 8.7 to 15.2 kg N ha^{-1} for PSS and PSF, respectively. The NH_3-N emissions at tillage were not enhanced by slurry applications at sowing. Our results also provide data to contribute to the creation of evidence-based regulations for PM2.5 and N_2O precursors, such as NH_3, from agricultural rainfed Mediterranean areas.

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