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Slurry Acidification as a Solution to Minimize Ammonia Emissions from the Combined Application of Animal Manure and Synthetic Fertilizer in No-Tillage

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Abstract: The combined application of manure/slurry and synthetic fertilizer (SF) might be a solution to decrease transport and application costs involving those by-products as well as enable access to them in regions where availability is low. Moreover, their joint application can potentially reduce environmental pollution, enlarge the manure benefits to more areas, and enhance the SF efficiency. However, such a strategy might result in increased ammonia emissions when applied to crop residues. Two experiments were implemented to assess ammonia emissions from stubble-covered soil fertilized with manure amended with SF. In Experiment 1 (E1), urea (U) and calcium ammonium nitrate (AN) were applied combined with dairy manure (MAN). In Experiment 2 (E2), urea was combined with acidified pig slurry (APS) and applied just after sowing (T0) or eight days later (T8). The combinations U + MAN and AN + MAN increased the ammonia emissions, while APS decreased the emissions from U, in APS + U combination, by more than 75%. Therefore, manure combined with SF applied on stubble-covered soil should not be recommended. T8 reduced ammonia emissions from U. APS enhanced the efficiency of U, being then an interesting strategy to mitigate ammonia emissions when applied on stubble-covered soil, as in no-tillage.

Keywords: acidified slurry; organic-mineral fertilizer; manure; conservation agriculture; crop residues; stubble-covered soil; urea; in-season fertilization; slurry sidedressing

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1. Introduction

Most of the nitrogen (N) used in crop nutrition comes from mineral/synthetic fertilizers, of which urea is the major source [1–3]. On the other side, the use of manure as fertilizer contributes to the increase in soil organic matter and adds beneficial microbes, besides also delivering N and other elements to plants [4]. Nevertheless, the transport costs within and between farmlands and greater application rates required in relation to synthetic fertilizers (SF) are some of the limitations related, particularly with slurry fertilization [5].

Slurry acidification before field application became popular in some regions due to its potential to decrease ammonia (NH_3) emissions, even after surface application without soil incorporation or injection [6,7]. Thus, slurry acidification may be an attractive option, especially in no-tillage. Moreover, it can be hypothesized that the acidified slurry, due to its ability to reduce ammonia volatilization, might enhance urea efficiency when mixed before application to the soil.

The NH_3 volatilized from livestock manure and SF is a significant loss of reactive N and also represents a threat to human health by reacting with acidic compounds in the atmosphere, resulting in fine particles (PM 2.5) emissions [8,9]. Moreover, the NH_3-N drift may exceed the critical N load, negatively affecting ecosystems [9–11]. The nitrogen loss from fertilizer, by ammonia volatilization, may decrease the N fertilizer efficiency.

Therefore, farmers tend to go beyond the recommendation of crop fertilization as a way of compensating for the already expected N loss, resulting in higher costs and environmental risks [9].

The combined use of SF and manure might be an option to enrich the manure while decreasing manure application rates, making it possible to cover more agricultural lands, enabling access to manure/slurry where it is a scarce resource, to improve application operation efficiency and also, to decrease over-fertilization with phosphorus (P), as normally occurs when using manure [12]. In addition, it might be a solution to enhance SF efficiency.

Applying slurry during plant growth, as dressing fertilization, is a practice that can extend the window for slurry application. As the slurry is applied when plants can uptake nutrients, it might lead to greater nitrogen recovery by plants [13] and consequently to reduced nitrogen losses.

Conservation agriculture practices, such as no-tillage, have become increasingly adopted around the world because of their significant benefits in soil and water conservation. The risks of water contamination by manure runoff following strong precipitation or snow melting can be decreased by applying manure to soil protected by residues from previous crops [14]. In a conventional tillage system, the N loss through ammonia volatilization is usually tackled by the incorporation of organic or SF into the soil [6,15]. However, as the soil disturbance is undesirable under no-tillage, the fertilizer incorporation to soil is impracticable. The slurry injection to soil is recognized for its efficiency in reducing ammonia emissions, but some limitations such as small field plots, stony soils, and the significant investment required can hinder its adoption [16]. In general, practices that demand less-powered tractors and that spend less time are often preferred by farmers, even if it represents a risk of higher nitrogen loss. That is why the broadcast application of N sources, such as urea and animal slurry, is still a common practice [17]. Furthermore, the ammonia volatilization can be increased by the application of urea-based fertilizers on the crop residues as a result of the higher urease activity, so that more research is needed to provide innovative practices that might increase the efficiency of urea-containing fertilizers under no-tillage [18–20].

Notwithstanding the evident benefits of manure enrichment with SF, it is necessary to evaluate all potential impacts of this solution both on the environment and crop production. Equally important is to provide solutions by assessing strategies with the potential to increase the efficiency of the combined application of manure and SF to stubble-covered soil. The present work aimed to assess the ammonia emissions after application of (1) dairy manure amended with urea or calcium ammonium nitrate, (2) acidified pig slurry amended with urea at two different times (immediately after sowing or eight days later).

2. Materials and Methods

This work describes two sequential experiments conducted to evaluate ammonia emission from the combined application of manure/slurry and synthetic fertilizer in no-tillage conditions. Initially, only experiment 1 (E1), in which dairy manure was amended with urea or calcium ammonium nitrate, was planned. However, due to surprising results, a new study was carried out, experiment 2 (E2), where a potential solution was assessed, under conditions more favorable to ammonia emissions, using pig slurry applied to sandy soil.

The lab-scale studies were implemented in a greenhouse at the School of Agriculture, University of Lisbon, Portugal (coordinates 38°42′29.786″ N; 9°11′6.18″ W). The daily average (maximum and minimum) ambient temperatures were respectively, 26.4 °C and 10.6 °C to the first, and 19 °C and 10.7 °C to the second experiment.

2.1. Experiment 1 (E1)

This experiment assessed the ammonia emissions from stubble-covered soils fertilized with dairy manure, SF, and the combination of both. In this first trial, the pots were filled with clay soil, and the dairy manure applied contained low ammoniacal-N, which were both conditions representative of the Portuguese systems producing cattle manure.

The manure was collected from the storage tank of a commercial dairy farm situated in the Setubal region, Portugal. First, 2 kg of dry clay loam soil (Vertic soil) with 50.5% sand, 20.9% silt, and 28.6% clay was used to fill each pot, and the soil surface was covered by wheat stubbles (300 g m^{-2}). Some characteristics of the soil and manure can be found in Table 1.

Table 1. Soil and dairy manure parameters (mean, *n* = 3).

Parameters	Soil	Dairy Manure
Total Nitrogen (g kg^{-1})	1.70	11.50 *
NH_4-Nitrogen (g kg^{-1})	0.01	3.86 *
P (g kg^{-1})	0.21 **	8.05 *
K (g kg^{-1})	0.40	37.17 *
OM (%)	3.50	65.70 *
pH (H_2O)	7.10	7.40
Dry Matter (%)	-	28.50

* Based on dry matter. ** Extractable P.

The experiment was performed, with six treatments, in a completely randomized design that was replicated three times: Control/Unfertilized soil (N0); soil application of Dairy manure (MAN), Urea (U), Calcium ammonium nitrate (AN), Urea + Dairy manure (UMAN), and Calcium ammonium nitrate + Dairy manure (ANMAN). The manure, synthetic fertilizers, and their mixture were applied by hand on the stubbles at a rate of 0.5 g of total nitrogen (Total-N) per pot (0.25 g N/kg dry soil). For the manure/synthetic fertilizer combinations, the mixture was performed right before the application, and each component contributed to 50% of total-N. At first, soil humidity was set up at 60% of soil water-holding capacity by watering with deionized water before fertilizers application and on the fourth day. The urea (U) contained 46% of total-N, and the calcium ammonium nitrate (AN) contained 27% of total-nitrogen plus 4% of calcium oxide.

2.2. Experiment 2 (E2)

In the second experiment, pig slurry and sandy soil were used, in order to increase the potential for ammonia emissions. We hypothesized that ammonia emissions could be decreased by the slurry acidification, even if the slurry is mixed with urea, and by the postponed fertilization. Thereby, acidified pig slurry, urea, and the combination of both were evaluated concerning ammonia emissions after application on stubble-covered soil. The application was performed at two different times concerning the seeding.

A Haplic arenosol (texture characteristics: 92.2% sand, 4.5% silt, and 3.3% clay) was used to fill the pots (2 kg pot^{-1}). The soil surface, in each pot, was covered by wheat stubbles (300 g m^{-2}). The treatments, three times replicated, in a factorial design, consisted of the following: Control/Unfertilized soil (N0); Urea (U) applied at T0 or T8, Acidified pig slurry (APS) applied at T0 or T8, Acidified pig slurry + Urea (APSU) applied at T0 or T8, being T0: application at sowing, and T8: application 8 days after sowing. Oat seeds were sown in a nursery 8 days before the experiment started for the T8 treatment. On day 0, for the T0, 12 oat seeds were sown, in two rows per pot, and then, the soil was covered by stubbles. On the same day, for the T8, 10 newly emerged oat plants aged 8 days were transplanted in two rows per pot in the soil, and the stubbles were carefully placed close to the plants. After that, the fertilizers were applied in bands by hand along the sides of the rows over the stubbles in order to provide, in each pot, 0.5 g of total nitrogen (total-N). For the APSU, the mixture was executed right before the application, and each component contributed to 50% of the total-N. The pig slurry, from the storage tank of a regular commercial pig farm, was acidified with concentrated sulfuric acid, targeting a pH value of 5.5. Soil humidity was maintained at around 70% of soil water-holding capacity throughout the experimental period. The urea fertilizer used contained 46% of total nitrogen. The main soil and pig slurry characteristics are summarized in Table 2.

Table 2. Soil and pig slurry parameters (mean, n = 3).

Parameters	Soil	Pig Slurry
Total Nitrogen (g kg^{-1})	0.66	86.12 *
NH_4-Nitrogen (g kg^{-1})	0.021	58.85 *
P (g kg^{-1})	0.011 **	9.81 *
K (g kg^{-1})	0.098	30.14 *
OM (%)	1.10	69.60 *
pH (H_2O)	6.72	8.08
Dry Matter (%)	-	2.09

* Based on dry matter. ** Extractable P.

2.3. Analytical Analysis

Manure and stubble were dried at 105 °C, to constant weight, to determine the dry matter, and the organic matter (OM) content was obtained by loss on ignition after calcination at 550 °C (4 h). The pH was determined directly using a pH meter (Orion 3 star). Total N was obtained by Kjeldahl acid digestion, while the ammonium N concentration was determined directly, by distillation and titration [21]. Potassium (K) content was quantified after hydrochloric acid (HCl) treatment of the ash through graphite furnace atomic absorption spectrophotometry (Unicam M Series), and P was determined using the ammonium vanadomolybdate method [22] by molecular absorption spectrophotometry (Hitachi 2000).

For the determination of the soil texture, by sedimentation, the pipette method was used [23]. Organic carbon (OC) was obtained by catalytic oxidation of the sample at 1100 °C followed by CO_2 detection by NDIR in a Primacs TOC Analyzer (Skalar Analytical B.V., Breda, NL, USA), and the organic matter (OM) value was achieved assuming OM contains 58% OC [24]. The pH, in a soil:water (1:2.5 w/v) suspension, was verified using a pH meter after stirring. The Kjeldahl method was used to obtain total N [21]. The determination of mineral N content was performed by extraction of 6 g of soil in 30 mL of KCl solution (2 M) [25] followed by ammonium quantification through molecular absorption spectrophotometry in a SanPlus (Skalar Analytical B.V., Breda, NL, USA) segmented flow analyzer, respectively, by the Berthelot method and with the Griess–Ilosvay reagent [26]. K and P content were obtained according to the Egner–Riehm method [27].

2.4. Ammonia Measurements

The NH_3 emissions were gathered from each pot covered by a PVC chamber (0.035 m^2 area) after the application of the fertilizers, for 7 days in E1 and 8 days in E2, through a dynamic chamber system, as decribed by [11] (Figure 1). A continuous airflow rate of 3 L min^{-1} produced from a suction pump regulated by a needle valve was kept inside the chambers. Each chamber was linked to an acid trap containing 200 mL of orthophosphoric acid (0.05 M) to collect the ammonia emitted. For E1, the acid solution in each trap was substituted after 4, 8, and 12 h in the first 24 h, twice a day on days 2 and 3 and then every 24 h until day 7. For E2, the acid solution in each trap was substituted after 4, 8, and 12 h in the first 24 h, twice a day on day 2, and then every 24 h until the eighth day. The total ammonia N content in the solution of each acid trap, at the end of each sampling period, was analyzed by automated segmented-flow spectrophotometry [28]. NH_3 emission rates (E, mg N m^{-2} h^{-1}) for each sampling period were calculated according to Equation (1).

$$E = \frac{TAN \times V}{S \times t} \tag{1}$$

where TAN = Total ammoniacal nitrogen concentration of the acid solution (mg L^{-1}), V = Volume of acid solution (L), S = Soil surface area (m^2), and t = Duration of sampling period (h). Total ammonia emissions were also presented as the sum of the amount of NH_3 emitted in each time interval and as percentage of total nitrogen and percentage of NH_4-N applied.

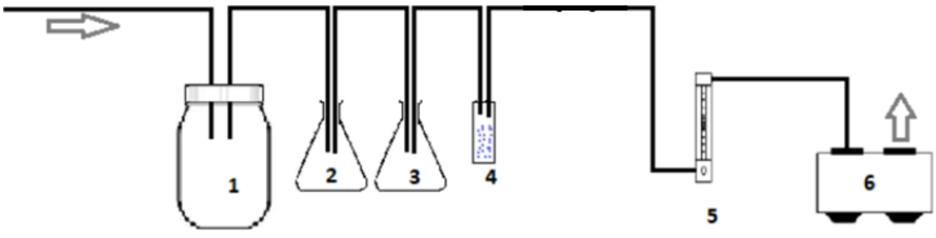


Figure 1. Schematic diagram of the version used to measure ammonia emissions: 1. The reactor; 2. Acid trap; 3. Water; 4. Desiccant; 5. Flowmeter; 6. Suction pump (adapted from [11]).

2.5. Statistical Analysis

The data collected were subjected to analysis of variance (one-way ANOVA in E1 and two-way ANOVA in E2). The least significant differences (LSD) test was used to compare means at $p < 0.05$ in E1. For the E2, the Tukey test was used to compare means, at $p < 0.05$, and log-transformations were performed to ensure the normality and homogeneity of the variances. The analyses were carried out using the software Statistix, version 9.

3. Results

3.1. Experiment 1

The cumulative NH_3 emissions expressed as mg NH_3-N per pot, as percentage of Total-N and NH_4-N applied, and also the differences between the observed and expected emissions, can be found in Table 3. The highest ammonia emissions ($p < 0.05$) were observed when manure was amended with both SF.

Table 3. Cumulative NH_3 emission (mg NH_3-N pot^{-1}) as a percentage of total-N and NH_4-N applied (excluded control emissions). The expected NH_3-N emissions considering the contribution of 50% from each one of the components of the mixture (U + MAN or AN + MAN) and the percentage of observed emission increase compared to expected. Values followed by different letters, in the same column, are significantly different based on the LSD test (mean, $n = 3$).

Treatments	Cumulative NH_3 Emission mg NH_3-N pot^{-1}	% of Total-N Applied	% of NH_4-N Applied
UMAN	117.5 ^{a}	23.4 ^{a}	-
ANMAN	96.8 ^{a}	19.3 ^{a}	46.00
MAN	62.7 ^{b}	12.5 ^{b}	36.50
U	25.7 ^{c}	5.0 ^{c}	-
AN	5.9 ^{cd}	1.1 ^{c}	2.14
Control-N0	0.51 ^{d}	-	-
Expected Emission (U + MAN)	12.85 + 31.35 = 44.20	-	-
% of Increase UMAN: U + MAN	165.8	-	-
Expected Emission (AN + MAN)	2.95 + 31.35 = 34.30	-	-
% of Increase ANMAN: AN + MAN	182.2	-	-

Notes: U: Urea; AN: Calcium ammonium nitrate; MAN: Dairy manure; ANMAN: AN + MAN; UMAN: U + MAN; expected emissions were calculated by summing 50% of the cumulative emissions of each material.

MAN treatment lost 12.5% of total-N applied (36.5% of applied TAN) by ammonia volatilization, which was an amount significantly greater than those observed in SF (U and AN) but lower than N lost from UMAN (23.4%) and ANMAN (19.3%). Initially, the expected emissions from UMAN and ANMAN were the sum of the contribution of every single fertilizer (50% of NH_3 emission from MAN plus 50% of NH_3 emission from SF). However, the observed NH_3-N emissions from UMAN and ANMAN were much higher than the expected emission. As a synergistic effect, UMAN emitted 165.8% more than the expected emissions from the relative contribution of U and MAN, and ANMAN also emitted 182.2% more than the relative contribution of AN and MAN.

The daily ammonia emission rates from all fertilizers peaked on the first day, which was followed by a reduction to negligible levels after the fourth day, except for U, which only reached the peak on the third day. Yet on the seventh day, U emitted more NH_3, albeit in a small quantity, than the other fertilizers. The first and second highest peaks were reported in UMAN and ANMAN, respectively (Figure 2). In Figure 3a,b, the dynamics of NH_3-N daily emissions, expressed as the percentage of NH_3-N daily emission rates in relation to the total emissions (100%), are presented. UMAN, ANMAN, and MAN had most of their emissions (≈80%), in the two first days. Diversely, the ammonia emissions from AN, U, and control were much less intense, namely U that only reached half of its total NH_3-N emission on the fourth day.

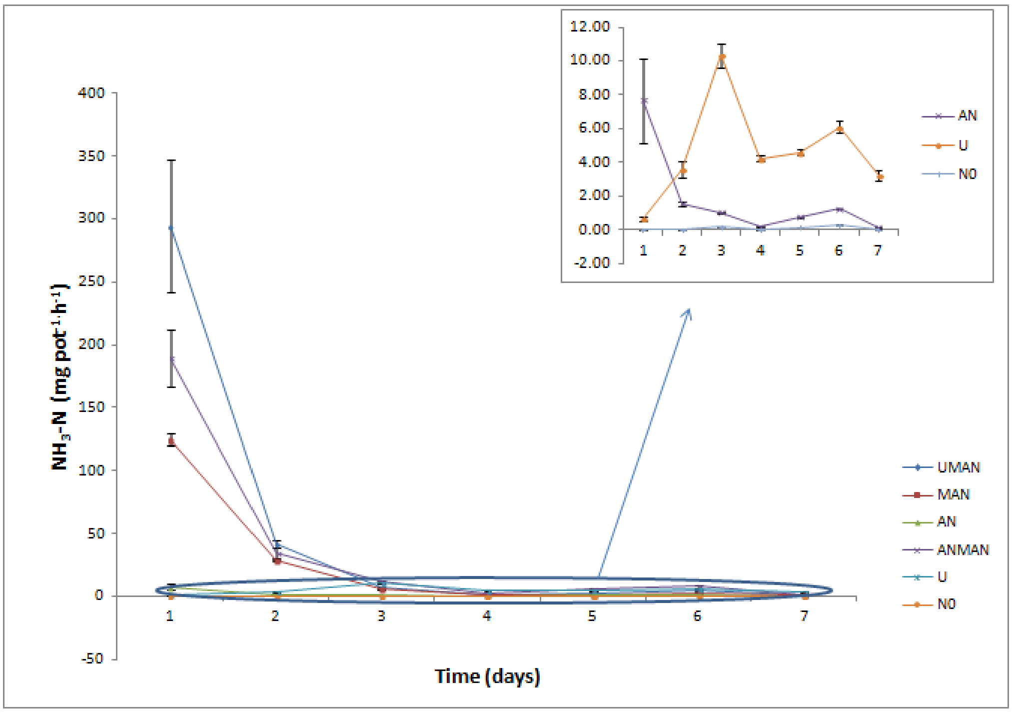
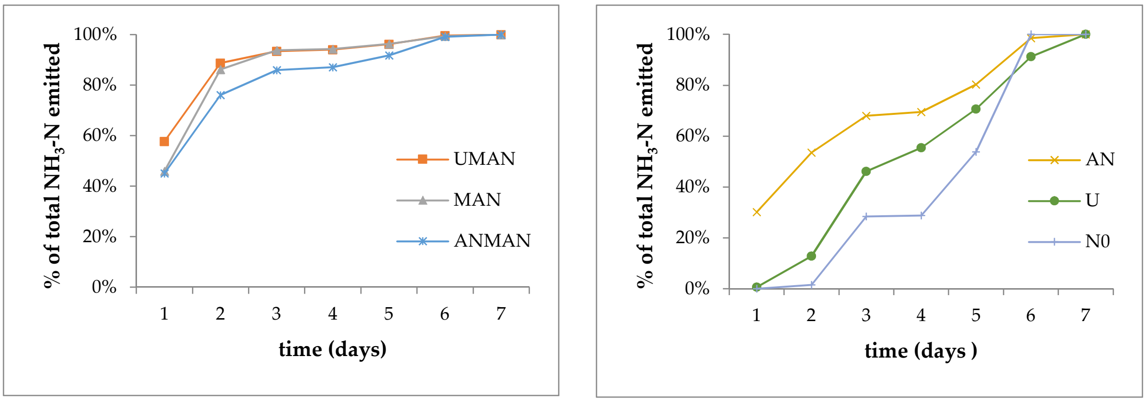


Figure 2. NH_3–N daily emission rates (mg pot^{-1} h^{-1}). Error bars represent the standard error values (mean, *n* = 3). U: Urea; AN: Calcium ammonium nitrate; MAN: Dairy manure; ANMAN: AN + MAN; UMAN: U + MAN; N0: Control.



(**a**) (**b**)

Figure 3. NH_3-N emission dynamics (percentage of the total NH_3-N emitted by day). (**a**) Emissions dynamics from UMAN, MAN, and ANMAN. (**b**) Emissions dynamics from AN, U, N0. U: Urea; AN: Calcium ammonium nitrate; MAN: Dairy manure; ANMAN: AN + MAN; UMAN: U + MAN; N0: Control.

3.2. Experiment 2

The analysis of variance demonstrated a significant effect from the fertilizer type, application time and interaction between fertilizer type and application time. The cumulative NH_3 emissions expressed as mg NH_3-N per pot, as percentage of Total-N and NH_4-N applied, and also the differences between the observed and expected emissions from APSU at T0 and T8 as well as the two-way ANOVA results are displayed in Table 4.

Table 4. Cumulative NH_3 emissions (mg NH_3-N pot^{-1}) as a percentage of total-N and NH_4-N applied (excluding control emission), two-way ANOVA, the expected NH_3-N emissions considering the contribution of 50% from each one of the components of the mixture (APS + U at T0 and T8), and the percentage of emission reduction observed compared to expected. Values followed by different letters, in the same column, are significantly different based on the Tukey test (mean, *n* = 3).

Treatments	**Cumulative NH_3 Emission mg NH_3-N pot^{-1}**	**% of Total-N Applied**	**% of NH_4-N Applied**
U T0	62.06 ^{a}	12.29 ^{a}	-
U T8	26.96 ^{b}	5.27 ^{b}	-
APSU T0	6.44 ^{c}	1.16 ^{c}	-
APSU T8	6.79 ^{c}	1.23 ^{c}	-
APS T0	1.76 ^{d}	0.23 ^{d}	0.33
APS T8	1.60 ^{d}	0.20 ^{d}	0.28
Control-N0	0.63 ^{e}	-	-
Two-way ANOVA			
Fertilizer Type (FT)	***		
Application Time (AT)	*		
FT*AT	**		
Expected emission (T0: APS + U)	0.88 + 31.03 = 31.91		
% of reduction APSU: APS + U	79.8		
Expected emission (T8: APS + U)	0.80 + 13.48 = 14.28		
% of reduction APSU: APS + U	52.5		

Notes: *** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$. Treatments: U: Urea; APS: Acidified pig slurry; APSU: U + APS; N0: Control; T0: Fertilizer applied right after sowing; T8: Fertilizer applied 8 days after sowing. Expected emissions were calculated by summing 50% of the cumulative emissions of each material.

The highest cumulative ammonia emissions were reported in urea treatment ($p < 0.001$) with values four to 10 times higher than in APSU. The time of application influenced significantly ammonia emissions from U. The urea application at T8 reduced the NH_3-N emissions and consequently the nitrogen losses by half relative to T0. While the mixture of non-acidified manure and SF led to an increase in ammonia emissions (Experiment 1, Table 3), the combined application of U and APS led to a decrease in NH_3 emissions compared to urea treatment, regardless of the application time (Table 4, Figure 4). The observed emission from APSU was much lower than the expected emission (sum of 50% of APS emission and 50% of the U emission), 79.8% and 52.5%, respectively at T0 and T8. APS, as expected, led to the lowest ammonia emissions from fertilized soil, resulting in negligible nitrogen losses (≈0.2%) of the total-nitrogen applied), independently of the application time (Table 4, Figure 4).

The daily ammonia emissions rates from UT0 and UT8 peaked 4 days after application, keeping the trend observed in the previous experiment. APSU T0 and APSU T8 emissions reached their plateau from day 2 to day 4. APS at both application times kept its daily emission rates at very low levels, close to N0 (Figure 4).

Despite APSU emitting significantly less ammonia than U at both application times, the release of NH_3 from APSU was more intense in the first 4 days followed by a decrease in emissions rate, while urea released more than 80% of the total NH_3 after day 3 (Figure 5a,b). On the fourth day, despite marking the beginning of the decline in emission intensity, APSU T0 and APSU T8 emitted at least 25% more NH_3-N than any other treatment. The dynamics of APS emissions (T0 and T8) behaved similarly to those of N0.

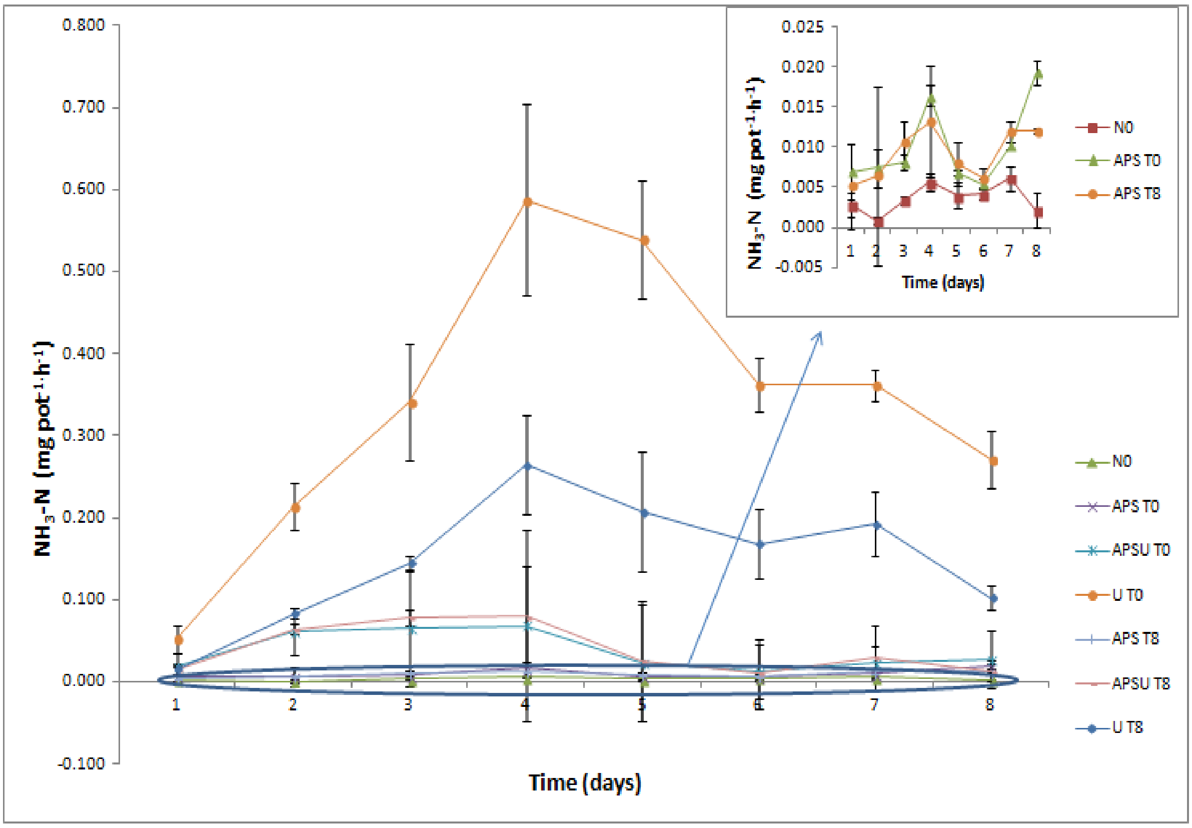
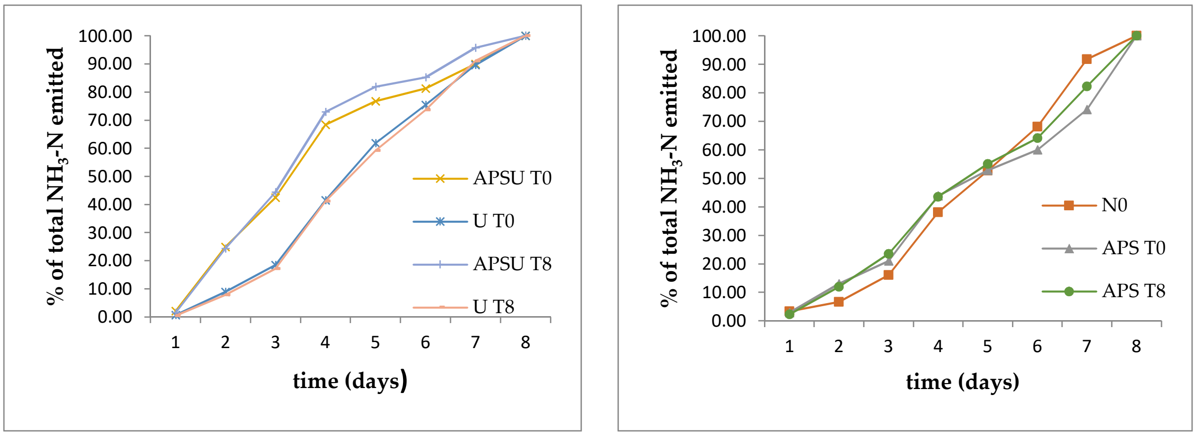


Figure 4. NH_3–N daily emission rates (mg pot^{-1} h^{-1}). Error bars represent the standard error values (mean, $n = 3$). U: Urea; APS: Acidified pig slurry; APSU: U + APS; N0: Control; T0: Fertilizer applied right after sowing; T8: Fertilizer applied 8 days after sowing.



(**a**) (**b**)

Figure 5. NH_3-N emission dynamics (percentage of the total NH_3-N emitted by day). (**a**) Emissions dynamics from APSU T0, APSU T8, U T0, U T8. (**b**) Emissions dynamics from APS T0, APS T8, N0. U: Urea; APS: Acidified pig slurry; APSU: U + APS; N0: Control; T0: Fertilizer applied right after sowing; T8: Fertilizer applied 8 days after sowing.

4. Discussion

Notably, the combined application of MAN and U or MAN and AN led to a greater amount of NH_3-N emitted than the sum of emissions from each of the components separately (Table 3). UMAN emitted 4.47 and 1.87 times more NH_3-N than U and MAN, respectively. ANMAN emitted 16.4 and 1.54 times more than AN and MAN, respectively.

Ammonia emissions from manure, because of its alkaline pH and TAN content, normally exceed those from synthetic fertilizers [29], although ammonia emissions from manure fertilization, according to [18], are not as well comprehended as the emissions from the slurry. Therefore, the low cumulative NH_3-N emission from MAN and low percentage of total-N lost as ammonia might be justified by its low NH_4-N content and the propensity to form surface crust because of its low water content [10,30].

The highest amount of ammonia emitted from manure amended with SF is possibly justified primarily by the manure pH, which favored the dominance of NH_3 over NH_4 as described by [8,31–33]. In addition, as presented in Table 3, the observed NH_3-N emissions from UMAN and ANMAN were much greater than expected, respectively 165.8% and 182.2% higher. Additionally, we can hypothesize that the highest and more intense emissions from UMAN (Figures 2 and 3a,b) are likely determined primarily by the contact between U and urease enzyme present in manure, in a medium wetter than the soil, favoring the conversion from U to NH_3 and subsequent high-intensity emission stimulated by the alkaline medium. The manure pH appears to be the trigger to the increase in ANMAN's ammonia emissions as well. Thereby, when mixed, the manure potentiated the emissions from U and AN.

The observed low NH_3 volatilization from calcium ammonium nitrate, which contains 50% of the N in nitric form, is in accordance with data from [11,34]. The N loss from urea, in E1, was below expectations, even being in the range of values reported by [34,35]. In addition, an initial lag phase was detected in the NH_3-N daily emission rates from U in both experiments (Figures 2 and 4), influencing its dynamics (Figures 3b and 5a), which was mostly due to the time needed to convert urea into ammonia through the urease enzyme [18,35,36].

As discussed above, the high manure pH is likely the main cause for the surprising increase in the ammonia emissions from the applied mixture of raw dairy manure and mineral/synthetic fertilizers, especially the urea, on the soil covered with crop residues. Nevertheless, this assumption was evaluated in a subsequent experiment (E2) wherein urea was added to an acidified slurry (pH 5.5) and applied on stubble. In this case, the NH_3 emissions from urea in a low pH medium (acidified slurry) were assessed in more challenging conditions, which should potentially lead to higher NH_3 emissions, namely sandy soil (low cation exchange capacity) and pig slurry (low dry matter and high N-NH_4 content). Moreover, oat plants were included in this new experiment to allow assessing the influence of the application time on the amount of ammonia emitted, hoping to broaden the range of understanding over the ammonia emissions from organic-mineral fertilizer applied to stubble-covered soils.

The urea, in E2, was the fertilizer that emitted the greatest amount of ammonia ($p < 0.001$), which was significantly more than APSU, APS, and N0 (Table 4). The soil surface application of urea, without soil incorporation, commonly represents a substantial amount of nitrogen lost as ammonia emission, especially when the soil is covered by crop residues [8,19,37]. Although there was an obvious reduction of emissions from the fourth day (Figure 5a), it is noticeable that the eight-day trial was not enough to assess the total amount of NH_3-N emitted from urea applied on stubble-covered soil; therefore, the total cumulative ammonia emissions from U should be greater than the values reported here (Table 4, Figure 4). This point does not limit the value of our results or conclusions, but on the contrary, it reinforces the ability of APS to reduce ammonia emissions as well as its capability to enhance urea efficiency.

A meaningful decrease in the cumulative NH_3 emissions was observed when urea was mixed with the acidified slurry. The acidification of the pig slurry provided a low pH medium that acted on the balance of the TAN, favoring the predominance of NH_4^+ over NH_3 and limiting ammonia emissions, even when mixed with urea. Consequently, the acidified pig slurry amendment reduced the susceptibility of urea to nitrogen losses by ammonia volatilization. Despite sulfuric acid already being used at a farm scale, promising additives should emerge from several studies [38,39], helping to make slurry acidification more viable by decreasing the risk associated with the handling of hazardous products as well as the cost involved.

The ammonia emissions observed in E2 were affected by the application time (T0, T8), fertilizer type (U, APS, APSU), and by the interaction of these two factors (Table 4).

Regarding the application time, the maximum amount of emitted ammonia ($p < 0.05$) occurred when U was applied right after the sowing (T0), which was probably because in T8, the plants were already able to uptake nutrients from the soil, namely nitrogen [29]. Therefore, some portion of ammonia might have been taken from the soil before it had the chance to be volatilized. This might be an indication that the application of the urea and ammoniacal sources of nitrogen (organic and synthetic) after plants' emergence can reduce ammonia emission, having the potential to increase the nitrogen use efficiency. Synchronizing N fertilization with plant nutrient demands may improve nitrogen availability for crops while decreasing the amount of N lost through gas emissions and leaching [13,20,29]. In addition, the post-seeding fertilizer application, besides delivering nutrients to the plants in a more opportune time to their needs, can also alleviate pressure on the farm's schedule such as the distribution of tasks, especially on the use of machinery [13]. Notwithstanding that the ammonia volatilized from fertilizers applied to soil can be absorbed in small quantities by plant leaves [40], it is unlikely to have occurred due to the unrepresentative leaf area of the oat plants in the first 8–16 days after sowing. The application time did not significantly affect the ammonia emissions from APSU and APS, which was likely because the lower levels of ammonia emissions from those treatments made it difficult to spot this trend. Despite the plant analysis being outside of the scope of this experiment, it is important to report the absence of any apparent damage in the oat plants caused by the band application of acidified pig slurry, urea, or the joining of these two fertilizers after plant emergence. On a field scale, the application of post-emergence slurry is usually carried out by side dressing or injection, avoiding the slurry spreading, which can damage the leaves [13].

The NH_3-N emissions from APSU at both application times were much more intense than the emissions from the other treatments (Figure 5a,b), mainly until the 4th day, which was possibly because of the action of the urease, present in the pig slurry, on the urea. The urease enzyme, present in post-harvest residues, as well as in the soil microorganisms and animal fecal matter, enhance the urea hydrolysis to carbonic acid and ammonia [8]. However, from the fourth day, the emission intensity was reduced possibly because of the low pH of the acidified pig slurry, which influenced the TAN balance, favoring ammonium production over ammonia.

APS decreased nitrogen loss from urea by reducing NH_3 emissions. Therefore, the joint application of urea and acidified pig slurry on stubble-covered soil enhanced urea efficiency.

5. Conclusions

Making slurry application viable in no-tillage/conservation agriculture systems is a decisive challenge. This study helps to better comprehend the behavior of the nitrogen from manure and manure amended with SF as well as the consequences of the application on stubble-covered soil of a mixture of urea and acidified slurry applied regarding ammonia emissions. In addition, it presents some solutions that can encourage the sustainable use of manure in stubble-covered surfaces, as in no-tillage. The combined application of MAN and U or AN on wheat stubble stimulated ammonia emissions regarding the isolated application of MAN or SF. Thus, the mixture of MAN and U or AN for application on stubble-covered soil should be avoided.

The results evidenced the feasibility of the joint application of urea and acidified pig slurry regarding ammonia emission. The acidified pig slurry was effective in reducing NH_3-N emissions when applied both alone or combined with urea, and it enhanced efficiency for the urea, reducing significantly the cumulative ammonia emission from that SF applied on crop residues. Moreover, the costs that involve slurry transport and application might drop by the combined application of slurry and mineral/synthetic fertilizer, since lower amounts of enriched slurry would be applied. In addition, the farmer can trim costs by reducing the need for commercial fertilizers and using slurry produced nearby as well.

The ammonia emissions from urea applied eight days after oat sowing were lower than urea fertilization on the sowing day. Thus, the efficiency of fertilizers prone to higher ammonia emissions, such as urea, can be improved by the post-emergence application of plants. Nevertheless, studies involving NH_3 emission from U applied on soil covered by stubble should last more than eight days.

Acidified pig slurry enhanced the efficiency of urea when in a combined application, being then an interesting strategy to decrease costs, promote the use of slurry as fertilizer, and mitigate ammonia emissions. Further studies over the joint application of acidified slurry and urea, that provide information on crop yield and greenhouse gas emissions, are required to reinforce this strategy as a solution for farm-scale adoption as well as contribute to new regulations that support slurry application in no-tillage and other conservation agriculture models.

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