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Application of dairy manure amended with mineral fertilizer on stubble-covered soil: effects on ammonia emissions †

Arejacy Silva [1], David Fangueiro [2,]*

1 LEAF, Instituto Superior de Agronomia, Universidade de Lisboa; Instituto Federal de São Paulo; arejacy.silva@ifsp.edu.br
2 LEAF, Instituto Superior de Agronomia, Universidade de Lisboa; dfangueiro@isa.ulisboa.pt
* Correspondence: dfangueiro@isa.ulisboa.pt
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Abstract: The reduction in the manure application rates, through enrichment with mineral fertilizer has the potential to reduce costs, decrease environmental pollution and extend the manure benefits to greater acreage. A pot experiment was carried out to assess ammonia emissions from dairy manure amended with mineral fertilizers applied on wheat stubble. The treatments were: control (no fertilization), urea (U), calcium ammonium nitrate (AN), dairy manure (MAN), urea + dairy manure (UMAN), calcium ammonium nitrate + dairy manure (ANMAN). A dynamic chamber system was used to measure NH_3 emissions during seven days after soil application. UMAN and ANMAN treatments led to higher NH_3 emissions than each isolated component. This might be motivated mainly by the manure pH. Thus, the enrichment of dairy manure with U or AN for application on stubble-covered soil should not be recommended. Nevertheless, some manure pre-treatments as acidification or the use of other mineral fertilizers might improve such solution.

Keywords: ammonia; nitrogen; organic-mineral fertilizer; manure; no-tillage

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1. Introduction

Mineral fertilizers are the major source of nitrogen (N) to crops [1,2]. However, manure application contributes to the increase of soil organic matter and the addition of beneficial microbes, besides also delivering nutrients to plants [3]. The transport costs within and between farms and higher application rates needed relative to mineral fertilizers are some of the limitations associated with manure application [4].

The mixture of manure and mineral fertilizer might be an alternative to decrease manure application rates, enabling to cover more agricultural lands, improving application efficiency and also, reducing over-fertilization with phosphorus, as generally occurred when using manure [5]. The chances of water contamination through manure runoff following heavy precipitation or snow melting can be reduced by applying manure on soil covered with crop residues [6]. However, livestock manure is the main contributor to ammonia (NH_3) emissions. The ammonia emitted from livestock manure and mineral fertilizers constitute an important loss of reactive nitrogen and also represents a threat to human health. Furthermore, the NH_3-N carried to land or water may surpass the critical nitrogen load of the ecosystems causing eutrophication [7,8,9].

Despite the evident benefits of the joint application of manure and mineral fertilizer, it is necessary to evaluate all potential impact of this technique on the environment and crop production, as well. The present work aimed to assess the impact of urea and calcium ammonium nitrate amendment to manure, right before application to stubble-covered soil , on ammonia emissions.

2. Materials and Methods

The experiment was carried out for seven days in a greenhouse at Instituto Superior de Agronomia, Lisbon, Portugal (coordinates 38º 42′ 29.786′′ N; 9º 11′ 6.18′′ W). The average maximum and minimum temperatures in the greenhouse during the experimental period were 26.4 °C and 10.6 °C. The manure used came from the storage tank of a typical commercial dairy farm located in the Setubal region, Portugal.

The pots were filled with 2 kg of clay loam soil referenced as Vertic soil (texture characteristics: 16.8 % coarse sand, 33.7% fine sand, 20.9% silt and 28.6% clay), covered by wheat stubbles (300 g m^{-2}). The treatments, with 3 replicates, conducted in a completely randomized design, were: Unfertilized soil (Control); soil application of: Urea (U), Calcium ammonium nitrate (AN), Dairy manure (MAN), Urea + dairy Manure (UMAN), Calcium ammonium nitrate + dairy Manure (ANMAN). The manure, mineral fertilizers and their combinations were spread by hand on the stubbles, at a rate of 0.5 g of total-nitrogen (Total-N) per pot. For the organic-mineral combinations, the mixture was done right before the application and each component contributed 50% of total-N. Soil moisture was initially set up at 60% of soil water holding capacity, before fertilizers application, and then adjusted only on the fourth day by water addition. The urea (U) used in this experiment contained 46% of total-N and the calcium ammonium nitrate (AN) contained 27% of total-N plus 4% of CaO. The main soil and dairy cattle manure characteristics are shown in table 1.

Table 1. Main soil and manure characteristics (mean of 3 replicates).

Parameters	Soil	Manure
Total Nitrogen (g kg^{-1})	1.70	11.5**
NH_4-Nitrogen (g kg^{-1})	0.01	3,86**
pH (H_2O)	7.1	7.40
Dry Matter* (%)	-	28.50

* % of raw manure. ** Based on dry matter .

2.1. Ammonia measurements

After the application of the fertilizers on the stubble, the ammonia emissions were collected from each pot topped with a PVC chamber (0.035 m^2 area), through a dynamic chamber system similar to the one described by [10] for 7 days. A constant airflow (3 L min^{-1}) was maintained inside the chambers, using a laboratory suction pump regulated by a needle valve, and an acid trap containing 200 mL of H_3PO_4 (0.05 M), connected to each chamber to collect the NH_3 emitted. The acid solution in each acid trap was replaced after 4, 8 and 12 h, in the first 24 h, twice a day in the 2nd and 3rd days and then every 24 h until day 7. At the end of each sampling period, the total ammoniacal N (TAN) content in the solution of each acid trap was analyzed by automated segmented-flow spectrophotometry [11]. Ammonia emission rates (E, mg N m^{-2} h^{-1}) for each sampling period were calculated according to Eq. (1).

$$E = \frac{TAN \times V}{S \times t}, \quad (1)$$

where, TAN is the total ammoniacal N concentration of the acid solution (in mg L^{-1}), V is the volume of acid solution (in L), S is the soil surface area (in m^2), and t is the time interval of the NH_3 trapping (in h). Total NH_3 emissions were also expressed as the sum of the amount of NH_3 emitted during each time interval and expressed as % of total nitrogen applied.

2.2. Statistical analysis

Statistical analysis of ammonia emissions, using ANOVA, were undertaken with Statistix 9. The least significant differences (LSD) were used to compare means with a probability level of 5%, and normalization of the data was not required.

3. Results

The cumulative ammonia emissions expressed in mg NH_3-N per pot and as % of Total-N applied are presented in Table 2. The highest cumulative amounts of volatilized ammonia ($p < 0.05$) were registered when manure was amended with both mineral fertilizers.

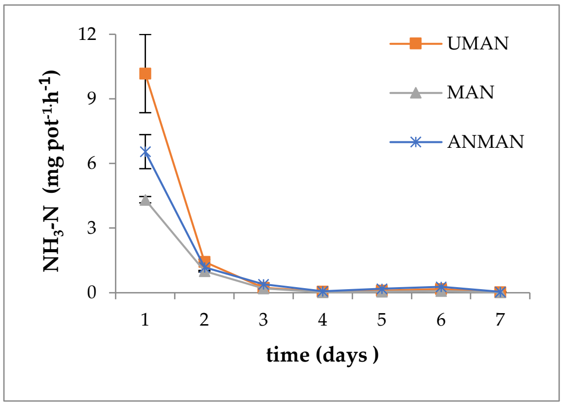
Table 2. Cumulative ammonia emission expressed as mg NH_3-N pot^{-1} and as a percentage of total nitrogen applied (removed the Control emission). For each parameter, in the same column, values followed by different letters are significantly different based on the LSD test (mean of 3 replicates).

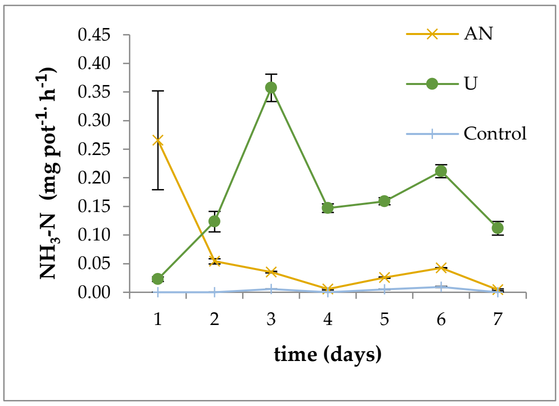
	Cumulative NH_3 emission mg NH_3-N pot^{-1}	% of Total-N applied
UMAN	117.5 ^{a}	23.4 ^{a}
ANMAN	96.8 ^{a}	19.3 ^{a}
MAN	62.7 ^{b}	12.5 ^{b}
U	25.7 ^{c}	5.0 ^{c}
AN	5.9 ^{cd}	1.1 ^{c}
Control	0.51 ^{d}	-

In MAN, 12.5% of total-N applied (~37% of TAN applied) was lost as ammonia. Although the relatively low total-N loss, this represents an amount significantly higher than those observed in mineral fertilizers (U and AN), but less than N lost from UMAN (23.4%) and ANMAN (19.3%).

The daily ammonia emission rates showed that the highest peak was reported in UMAN followed by ANMAN. Daily rates from all fertilizers peaked on the first day and then decrease to negligible levels after the 4th day, except U that only reached the peak on the 3rd day (Figures 1a, 1b), and at the end of the 7th day, albeit in a small amount, urea still emitted more ammonia than the other treatments. All the treatments recorded another slight peak after the complementary irrigation performed on the 4th day.

The dynamics of emissions, presented as the percentage of NH_3-N daily emission rates related to the total NH_3-N emissions (100%), are shown in Figures 2a and 2b. More than 80% of total NH_3-N emissions from UMAN and ANMAN occurred in the two first days, while MAN reached that mark only on the 3rd day. Diversely, the ammonia emissions from AN, U and Control were much less intense, highlighting urea that only reaches half of its total NH_3-N emission on the 4th day.





(a) (b)

Figure 1: NH_3-N daily emission rates (mg pot^{-1} h^{-1}). Error bars represent the standard error values (mean of 3 replicates). (a) EmisScheme 2. NH_3-N emission dynamics (percentage of the total NH_3-N emitted). (a) NH_3-N emissions dynamics from UMAN, MAN, ANMAN. (b) NH_3-N emissions dynamics from AN, U, Control.

4. Discussion

It is noteworthy that the joint application of manure and urea or manure and calcium ammonium nitrate led to higher NH_3-N emission than the sum of emissions from each of the component separately (Table 2). UMAN emitted 1.87 and 4.47 times more NH_3-N than MAN and U, respectively. ANMAN emitted 1.54 and 16.4 times more than MAN and AN, respectively.

The NH_3-N losses from manure were expected to be higher than from mineral fertilizers [12] although, according to [13], losses of ammonia from solid manure applied to the soil are not well understood as the emissions from slurry application. Thus, the cumulative ammonia emission, as well as, the N lost relative to the applied total-N, from MAN is probably justified by its low NH_4-N content and the susceptibility to the formation of surface crust due to its high dry matter level [7,14].

The highest NH_3-N emission from manure amended with mineral fertilizers might be explained by the manure pH, which favoured the dominance of ammonia over ammonium as described by [15,16]. In addition, we can hypothesize that the highest and more intense ammonia emissions (Figures 1a, 1b, 2a, 2b) from UMAN might be determined firstly by the contact of the urea with the urease from manure in a medium wetter than the soil, favouring the conversion from urea to ammoniacal nitrogen, and thereafter the NH_3 volatilisation stimulated by the alkaline pH. The low ammonia emission from calcium ammonium nitrate, which contains 50% of the nitrogen in nitric form, is in agreement with data reported in other studies [8,17]. The N loss from U was below expectations, even if in agreement with the values described by [18]. Thereby, NH_3-N emission from U was probably kept at a low level because, after dissolution, the fertilizer was protected from airflow and solar radiation by the stubbles, as already observed by [19] after application of pig slurry on stubble, these authors attributed the reduction of ammonia emission to the protection provided by the stubble layer. Also, an initial lag phase was observed in the NH_3-N daily emission rates from U (Figure 1b), influencing its dynamics (Figure 2b), probably because of the time needed to convert urea into ammonia, through the urease enzyme [20,21]. Thus, assessment of ammonia emissions from urea applied to stubble-covered soil should last for more than the 7 days' time period usually considered in studies dealing with ammonia emissions from manure.

5. Conclusions

The application of dairy manure mixed with urea or calcium ammonium nitrate on stubble-covered soil stimulates ammonia emissions relative to the isolated application of manure or mineral fertilizer. Thus, the enrichment of dairy manure with U or AN for application on stubble-covered soil should not be recommended. Furthermore, assessments of ammonia emission from urea on crop residues should be done for more than 7 days.

This work contributes to better understand the losses of ammonia from manure and manure amended with mineral nitrogen fertilizers applied on the stubble. More studies regarding raw manure/mineral fertilizer combinations and management strategies, as acidification, that may reduce ammonia emissions from organic-mineral fertilizers are required to allow efficient use of this fertilizing strategy in no-tillage agriculture.

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