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Abbreviations: DM: dry matter; M: mineral fertilizer; NH_3: ammonia; NH_4^+: ammonium; PS: slurry from fattening pigs; PS^S: slurry from sows; S: sowing; T: tillering; TAN: total ammonium nitrogen; SWC: soil water content.

ABSTRACT

Anthropogenic ammonia (NH_3) emissions mainly result from agricultural activities where manure spreading plays a significant role. For a Mediterranean rainfed winter cereal system there is a lack of data regarding NH_3 emissions. The aim of this work is to provide field data on N losses due to NH_3 volatilization as a consequence of the introduction of slurries in fertilization strategies and also, to assess the influence of environmental conditions and slurry characteristics on emissions. The fertilizing strategies include the use of slurry from fattening pigs (PS), sows (PS^S) and/or mineral fertilizer (M) as ammonium nitrate. Fertilizers were spread over the calcareous soil at sowing and/or at tillering at rates from 15 to 45 kg NH_4^+-N ha^{-1} for M and from 48.8 to 250.3 kg NH_4^+-N ha^{-1} for slurries. The NH_3 emissions were quantified during three cropping seasons. Average losses from the total ammonium nitrogen applied ranged from 7 to 78% for M and 6 to 64% for slurries and they were not directly proportional to the amounts of applied ammonium. The best results on NH_3 volatilization reduction were registered when soil water content (SWC, 0-30 cm) was below 56% of its field capacity and also, when slurry dry matter (DM) was in the interval of 6.1-9.3% for PS or much lower (0.8%) for PS^S. High slurry DM favoured crust formation and the lower rates promoted infiltration, both of which reduced NH_3 emissions. Nevertheless, at tillering, the lower DM content was the most effective in controlling emissions (<9 kg NH_3-N ha^{-1}) and equalled M fertilizer in cumulative NH_3 loss ($p>0.05$). A single slurry application at tillering did not negatively affect yield biomass. The combining of recommended timing of applications with slurry DM content and SWC should allow producers to minimize volatilization while maintaining financial benefits.

Keywords: best management practices, environmental impact, agricultural gas emissions, nitrogen, pig slurry, semiarid climate.

1. Introduction

Ammonia volatilization is a physical process influenced by the concentration of total ammonium nitrogen in the soil solution (TAN; NH_3-N plus NH_4^+-N) and by the resistance of NH_3 to movement from the soil matrix (Sommer et al., 2004). In agriculture, the consequence of such processes is the reduction of the fertilizer value of manures (Jarvis and Pain, 1990; Sørensen and Amato, 2002; Sommer et al., 2006) but also, once this volatilized NH_3 deposits, it becomes a threat to the environment through acidification, eutrophication or direct toxic effects (Pearson and Stewart, 1993). According to the European Directive 2001/81/CE relating to air protection and thresholds on national emissions, it is necessary to establish the temporal and cumulative emissions of NH_3 derived from fertilization practices. Furthermore, from liquid manure systems in Europe, differences exist between the models used for national agricultural NH_3 emission inventories (Reidy et al., 2008) due to the influence of soil characteristics as well as to other factors such as weather or slurry composition (Sommer et al., 2003).

Different techniques have been employed to measure NH_3 losses and all of them have limitations (Sintermann et al. 2011). The most used are semi-static chambers because they easily adapt to small plots, they permit monitoring multiple treatments in the same crop season, have a low cost, and require reagents and materials commonly available (Grant et al., 1996). However, absolute estimates of NH_3-N loss can be underestimated (Pozzi et al., 2012) because according to Søgaard et al. (2002) wind speed increases, by 4% per m s^{-1}, total NH_3 volatilization.

For Mediterranean areas, information on ammonia emissions is scarce. However, NH_3 volatilization is an important environmental issue as calcareous soils favour NH_3 volatilization. Soil carbonate reacts with water to form bicarbonate (HCO_3^-)

and the hydroxyl radical (OH^-) reacts with NH_4^+-N to form NH_3 gas and water: such processes may act over different periods depending on other soil characteristics, environmental conditions, and fertilizer management (Bouwmester et al., 1985; Kissel and Cabrera, 2005).

For Mediterranean conditions, articles from Génermont and Cellier (1997), Morvan et al. (1997) and Sanz et al. (2010) dealing with NH_3 volatilization from slurry applied on bare soil are available. They generally involve parameters such as slurry application times (March, June, September–October) or dry matter (DM) content (between 1.4 to 4.7%) which do not cover the current application times or the actual range of slurry composition in the Spanish regions being studied (Yagüe et al., 2012). The DM content of slurry is an important factor as it can greatly alter the amount of NH_3 volatilized (Misselbrook et al., 2000; Sommer et al., 2001; Thompson and Meisinger, 2002).

Moreover, the Ebro river basin contains a concentration of about 49% (11.3 million pigs) of the total pig Spanish herd (MARM, 2013). Slurry is usually spread by splash-plate on the fields as fertilizer, mainly on bare soil (before sowing) followed by harrowing or, less frequently, it may be applied on the winter cereal crop before tillering as a top dressing, although at this cereal stage the most popular practice is to apply mineral fertilizer (i.e. ammonium nitrate). Slurry application at tillering has recently started to be used in Spain as a strategy to reduce fertilizer costs or as an attempt to improve slurry management over the year by splitting the time of application.

A few studies related to the evaluation of the use of pig slurries in winter cereals were found: Petersen (1996) and Sieling et al. (1998) studied N use efficiency, Sommer et al. (1997) and Meade et al. (2011) measured NH_3 losses at tillering or from mid-tillering onwards but under North European soil and weather conditions.

The quantification of NH_3 volatilization in semiarid areas has not been reported either in combined applications at sowing and at tillering, or when using different fertilization strategies which include slurry and/or mineral fertilizers. The use of available models for NH_3 emission estimation cannot be generalised, due to the importance of management practices (Smith et al., 2008; Sheppard and Bittman, 2013). A key point, when applying slurry as a fertilizer dressing, is NH_3 volatilization because slurries cannot be buried into the soil immediately after their application. Besides, if a previous application has been made it might increase NH_3 losses, as it is well known that the long-term application on soil of other liquid wastes affects soil water repellence and reduces infiltration capacity (Wallach et al., 2005; Vogeler, 2009).

The present work was set up in the framework of rainfed Mediterranean agricultural systems and it includes a wide range of applied NH_4^+-N during the winter cereal cropping season. The main objective was to provide basic field data on N losses due to NH_3 volatilization, but also to include the assessment of high yielding fertilizer strategies for the area, in which pig slurry must be taken into account. In this work, we focused on fertilizer dressing applications. The specific environmental objectives of this research were: i) at tillering, to assess the influence, on NH_3 volatilization from fertilizers, of pig slurry which has been previously applied at sowing; ii) at tillering, to compare NH_3 losses between pig slurries and mineral fertilization applied at different rates; and iii) to quantify, as a reference for slurry applied at tillering, other NH_3 losses from other fertilization strategies: minerals or slurries applied at sowing.

The evaluation of NH_3 volatilization from slurries will also increase the predictability of their nitrogen fertilizer value and will allow us to improve the recommendations on slurry use in fertilizer management plans.

2. Materials and methods

2.1. Description of the experimental site

This work was set up in the Ebro river basin (Spain, 41º 52’ 29”N, 1º 09’ 10”E; 443 masl) and was included in a broad experiment about N fertilization strategies. The soil of the site was classified as a Typic Xerofluvent (Soil Survey Staff, 1999), well drained, with a silty loam texture in the surface layer. The main top soil layer (0-0.30 m) has a low organic matter content (< 2%), is non saline (electrical conductivity, 1:5 w/v, is 0.18 dS m^{-1}), the pH is 8.2 (soil:water;1:2.5), the cation exchange capacity (CEC) is 11.1 $cmol^{+}$ kg^{-1} and the soil has a high carbonate content (close to 30%). Gravimetric soil water content at field capacity is 0.27 (w/w).

The climate is semiarid Mediterranean (Fig. 1), with high summer average temperatures (>20ºC), low annual precipitation (<450 mm yr^{-1}) and high average reference crop evapotranspiration (1013 mm yr^{-1}).

2.2. Experimental set up

The size of plots receiving pig slurry was 274 m^2 (11 m wide and 25 m long) and the size of the control plot and plots receiving mineral fertilization was 174 m^2 (7 m wide and 25 m long). Soil water content of the top layer (0-30 cm) was determined gravimetrically (Table 1) before each fertilizer application.

Fertilization strategies, as a combination of fertilizer type and application timing, were implemented in the 2002/03 crop season for agronomic evaluation and exactly maintained over the different cropping seasons. The crops sown were wheat (2002/03, 2005/06) or barley (2003/04, 2004/05, 2006/07).

Ammonia volatilization started to be evaluated in 2003/04 and was only done for selected fertilization strategies (Table 2). It was conducted during three cropping seasons after fertilizer dressing at tillering: 2003/04 (the first one), 2005/06 (the second one) and 2006/07 (the third one) during 288 h, 360 h, and 384 h, respectively. The measurements needed for quantification were stopped when a stable low volatilization rate was attained although, in 2006/07, measurements were maintained for almost 1400 h after application just to verify the minimum period required for accumulated stable NH_3 volatilization data. During the third crop season (2006/07), measurements of NH_3 volatilization from slurry applications at sowing (during a time interval of 390 h) were also implemented. Data were obtained daily at the greatest frequency. At sowing, the first sample was obtained during the next 6 h after slurry spreading because after the first sampling, slurry was buried but after doing so, NH_3 measurements were resumed immediately.

The chosen fertilizer strategies in 2005/06 and 2006/07 took previous results (including yields, Table 2) into account and were adapted to the objectives to be attained in each cropping season. Nevertheless, the overall goal was always to achieve a comprehensive recommended strategy: minimum NH_3 losses and high yields, which explains why, in each season, one or two new strategies (where NH_3 volatilization was not previously quantified) were also added.

The control plot was selected between plots which never received mineral N fertilizer nor pig slurry. The applied fertilizers were: fattening pig slurry (PS), sow slurry (PS^S), and mineral fertilizer (M; ammonium nitrate 33.5% of N). The fertilization doses were: 20, 40 and 60 t PS ha^{-1} (named 1PS, 2PS and 3PS, respectively) and 90 t PS^S ha^{-1} ($4PS^S$). The rate of 20 t ha^{-1} (1PS) is around the minimum dose that can be applied uniformly with the commonly available technology: a tank fitted with a splash-plate from which slurry is spread on the soil. Slurry rates were controlled on the field through the tractor speed (calibration was done previously on a bare field). Ammonium nitrate (NH_4NO_3) was applied at 15, 30 and 45 kg NH_4^+-N ha^{-1} (named 1M, 2M, and

3M respectively). Doses were applied at sowing (S-) or at tillering (T-), or at both crop timings (S-/T-). The NH_4^+-N and total-N applied on each occasion were determined through laboratory analysis of the slurry and the quantification of the effective applied dose (Table 2) by weighing the slurry tank before and after spreading on each plot.

2.2.1. Slurry sampling and selection

Slurry samples were always taken before application and they were kept refrigerated until their arrival at the laboratory. The quantified parameters were (Table 2): dry matter (gravimetrically), NH_4^+-N (modified Kjeldahl method), and total-N (Kjeldahl method). In the first crop season, at sowing and at tillering dressing fertilization, DM content of pig slurries from fattening pigs (6.1 to 8.5%) was an example of the actual trend of slurry volume reduction (DM increment) in some areas (Teira-Esmatges and Flotats, 2003). In the second and the third crop seasons, at tillering dressing fertilization, in order to generalize and reinforce the advantages of pig slurries applied at tillering based on NH_3 volatilization, slurries were previously chosen before being applied. The criterion for selection was to enlarge the scope of their DM content across the experiment. The DM was indirectly estimated by a densimeter. DM ranged from 4.4% to 10.6% for PS and from 0.8 to 4.1% for PS^S.

The variability in NH_4^+-N slurry content (Table 2), represented the normal variability that occurs in these agricultural systems (Yagüe et al., 2012).

2.2.2. Quantification of NH_3 volatilization

Ammonia volatilization was sampled using semi-static chambers based on Grant et al.'s (1996) description. On each plot, semi-static chambers were placed in triplicate. The chambers consisted of a LD PET (Low Density PolyEthylene Terephthalate) cylinder of 234 mm diameter and 150 mm height which was introduced 40 mm deep in the soil, taking care to cause minimal soil disturbance. On the top of the cylinder, a synthetic mesh tissue was placed to support a 240 mm diameter foam disk covering all of the cylinder cross-section. The foam had been previously soaked with a fixed volume of acetone (30% v/v) containing oxalic acid (3% w/v) and allowed to evaporate and dry in a well-ventilated hood before it was placed on the mesh in the field. Another mesh on top of the foam was used to prevent the foam from moving. Each foam disk was renewed daily during the experiment from immediately after fertilizer application and at different intervals later on. In case of rain, chambers were covered as soon as possible by big plastic bags to avoid the wetting of samples and they were uncovered once the rain was over. Upon renewal, each sponge was placed in a zip lock freezer bag to transport it to the laboratory. Each sponge was soaked with distilled water (four times with 500 mL) and the extract collected and made up to 2 L. The extract was quantified by means of an ammonia selective electrode (Crison, micropH 2002) after the addition of NaOH (40% w/v) to the ammonium oxalate sample for pH adjustment, and calculated using the daily calibration curve of the electrode. Ammonia concentration can be expressed as an emission flux and represented over time. The cumulative NH_3 volatilization during the sampling period can be calculated by integrating the area under the fluxes' curve.

2.2.3. Other agricultural practices

In June each year, after harvesting, straw was removed from the field. Slurry was spread in autumn (October or November) before sowing by means of a splash-plate and buried by disc harrowing within the 24h following application according to legislation. At tillering (February or March) fertilizer was not buried.

2.3. Statistical analysis

The effect of the fertilizer application on NH_3 losses was evaluated by analysis of variance (one-way), and separation of means was done by the Duncan multiple range test (α=0.05). The control (ammonia threshold value) was not included as a treatment in the statistical analysis because the goal was to compare NH_3 losses between fertilization strategies (including the optimum and overfertilized ones). The statistical analysis was made using the SAS statistical package (SAS Institute, 1999-2001).

3. Results and discussion

In all crop seasons, during a minimum period of six days following slurry spreading, weather was dry, although foggy mornings were not uncommon (Table 1). In the first crop season, 5.4 mm of rain fell at the tillering period (216 h after slurry application). No rainfall occurred in the second season. In the third crop season, 10.3 mm of rain fell at the sowing period (312 h after slurry application) and 6.3 mm at the tillering period (144 h after fertilizer spreading). These rainfall events were not considered relevant in affecting cumulative NH_3 emission measurements.

3.1. Effect of slurry at sowing on NH_3 volatilization at dressing. First crop season

At tillering (Table 3), NH_3 volatilization from pig slurry (T-1PS, T-3PS) was not significantly affected by the pig slurry applied at sowing (S-2PS). Nevertheless, a slight tendency to increase NH_3 volatilization (by 2-3 kg NH_3-N ha^{-1}) when slurry had previously been applied as fertilizer at sowing (three months earlier) can be observed. Ammonia volatilization was quite low: 5-18 kg NH_3-N ha^{-1}. The highest value corresponded to the highest PS dose (T-3PS, 60 t ha^{-1}), which is much greater than the recommended N dose for winter cereals. However, in long-term applications, in high N demanding crops, it could be of interest to go deeper into these potential interactions which could be related, as mentioned in the introduction, to the development of hydrophobic soil properties linked to the characteristics of applied liquid wastes.

When yields and N efficiencies are accounted for (Table 2), slurry fertilization at sowing is not necessary when PS is distributed in a single application at tillering.

In classical strategies, where slurry at sowing is complemented by an N mineral dressing (T-2M; 60 kg N ha^{-1} as NH_4NO_3), NH_3 volatilization (around 5 kg NH_3-N ha^{-1}) was not affected by the rate of the slurry previously applied at sowing (Table 3).

3.2. Effect of dressing fertilization on NH_3 volatilization. Three cropping seasons

In the first crop season, at tillering (Fig. 3A), whatever the fertilization at sowing was, no significant differences between mineral (T-2M, 4.8 kg NH_3-N ha^{-1} volatilized) and the lowest rate of pig slurry applied (T-1PS, 6.6 NH_3-N kg ha^{-1} volatilized) could be observed though, in this case, the applied amount of NH_4^+-N as PS was double the mineral dose (Table 2). This fact means that relative losses associated with the mineral fertilizer (T-2M) were significantly higher (16.1% of TAN applied) than from the lowest slurry rate (T-1PS, 9.1% TAN applied). Thus, T-1PS was more efficient in reducing volatilization, although the pattern of losses with time actually followed the T-2M curve closely (Fig. 3A). Soil moisture was at 56% of its field capacity and foggy days (Table 1) favoured the solubility process for the mineral fertilizer granules.

Although not significant ($p>0.05$), when slurry rate was tripled (T-3PS), the percentage of losses, compared with T-1PS, only decreased slightly, from 9.1 to 6.9% of TAN applied (Fig. 3A). The general low cumulative NH_3-N losses (from 6.6 to 16.7 kg NH_3-N ha^{-1}, T-1PS vs. T-3PS) were associated with low air temperatures below 5ºC during sampling (Fig. 2). These results agree with those of Sommer and Hutchings (2001) on the expected NH_3 volatilization for surface-applied manure when combining two variables: air temperature and slurry DM content.

According to the cumulative NH_3 volatilization for this first cropping season, PS can be recommended as a dressing fertilizer instead of the NH_4NO_3 which is widely used in the area. The T-1PS strategy also results in an acceptable N efficiency (24.3 kg grain kg N applied^{-1}). Nevertheless, from the agronomic point of view, the lowest yield achieved (2911 kg ha^{-1}) with this strategy (119.7 kg N ha^{-1} at tillering, without N fertilization at sowing), in comparison with other more productive ones (Table 2), required further evaluation in consecutive crop seasons (including accuracy in N dose versus crop demand or the addition of N residual effects) before recommending its potential adoption as a fertilization strategy at field level.

During the second and third crop seasons, if mineral fertilization (T-2M, 30 kg NH_4^+-N ha^{-1} applied) is taken as a reference, NH_3 volatilization accounted, respectively, for 39.0 and 19.7% of TAN applied (equivalent to 11.7 and 5.9 kg NH_3-N ha^{-1}). Differences can be attributed to soil and weather conditions (Table 1, Fig. 2). In the second season, soil water content (SWC, 0-30 cm) was at 61% of its field capacity which favoured granule solubilization and subsequent NH_3 volatilization. By contrast, in the third season, soil water content was lower (45% of field capacity) and temperatures higher (Fig. 2), both limiting solubilization. Nevertheless, in this environment where NH_4NO_3 is commonly used as a dressing (T-2M or T-3M), even when soil is quite wet (61% of its field capacity), range of NH_3-N losses (20-39% of total applied N, Fig. 3B) are in agreement with ones described in literature for similar soil (pH>7, low CEC) and dry climate characteristics (Meisinger and Randall 1991; FAO, 2001). Also, they are much lower than those described for some other N mineral fertilization practices. As an example, for surface–applied urea, Pacholski et al. (2006) found, in a calcareous soil in China, that cumulative losses could be up to 48% of total applied N and Rochette et al. (2009) recorded losses equivalent to 64% of total N.

When comparing volatilization from PS (T-1PS), values from the second season (63.8% of TAN applied, 54.5 kg NH_3-N ha^{-1}, Fig. 3B) were roughly double the accumulated NH_3-N losses recorded in the third season (41.5% of TAN applied, 20.3 kg NH_3-N ha^{-1}, Fig. 3C), and they were also much higher than those recorded for the first season (9.1% of TAN applied, 6.6 kg NH_3-N ha^{-1}).

These results can be explained because in the third season, PS with a high DM content (~10%) and average temperatures higher than 12ºC favoured a crust surface formation which in turn increased the liquid phase resistance (Sommer et al., 1991) inducing lower NH_3 volatilization rates, in agreement with Thompson and Meisinger's (2002) observations. In contrast, the most liquid slurry (T-4 PS^S, 0.8% DM) infiltrated rapidly. As a consequence, in both cases, volatilization was minimized (Fig. 3C) to 41.5-34.6% of TAN applied in the case of PS (T-1PS-T-3PS, respectively) and to 7.2% of TAN applied in the case of PS^S (8.5 kg NH_3-N ha^{-1}). The concept of cutting down NH_3 volatilization by means of facilitating infiltration of slurry (low DM content) into soil (i.e. decanted slurry, mechanically assisted infiltration) is supported by Brandral et al. (2009). As slurry infiltrates, it reduces the pool of TAN at the soil surface; the concentration of NH_3 is reduced and, therefore, subsequent volatilization is also lower (Thompson et al., 1990). In our case, an easier infiltration explains that T-4PS^S strategy attained similar NH_3 losses (Fig. 3C) and yields (Table 2) compared with mineral fertilizer strategies (S-1M/T2M or T-3M) in the third season.

Surprisingly, the high NH_3 volatilization in the second crop season for slurries moved away from the expected results according to SWC, air temperatures and their similar DM content (independently of the origin: PS or PS^S). When comparing these results with the raw data of Misselbrook et al. (2005), referring specifically to DM slurry content and NH_3 volatilization, it should be noted that they observed maximum losses at 4.5% DM content. These losses, for the specific site, doubled (% TAN applied) the ones registered at lower DM (<3.9%), or tripled when compared with higher DM values (>5.6%). These observations indicate that there is a critical DM content at which pig slurry is not either liquid enough to easily infiltrate, or thick enough to favour crust formation. The situation described coincides with that of the second season, whatever was the slurry's origin (4.1- 4.4% DM), and the effect was more evident at the lowest rate (T-1PS) where losses attained 64% of TAN applied.

In all cases, accumulated NH_3 losses stabilized within the first 250 h following slurry application (Fig. 3), and it was not found that NH_3 volatilization was prolonged over time as DM increased, in agreement with Sommer et al. (2006) and Ni et al. (2012).

3.3. Effect of other fertilization strategies on NH_3 volatilization: pig slurry at sowing and mineral fertilization. Third crop season

In the third crop season, the weather conditions on the days of slurry spreading at sowing and at tillering were similar, although soil water content was at 33% and 45% of its field capacity, respectively (Table 1). At sowing (S-1PS and S-3PS), although slurry was buried 6 h after application, accumulated losses of between 23.0 and 42.1 kg NH_3-N kg ha^{-1} (Table 4) were in the range of values found at tillering for T-1PS and T-3PS (Fig. 3C; 20.3 and 37.9 kg NH_3-N kg ha^{-1}).

Increasing rates from S-1PS to S-3PS reduced the volatilization ratio (from 39.5 to 16.9% of TAN applied) but because of the higher amount of applied ammonium, total NH_3 losses increased significantly (Table 4). With these figures in mind (Fig. 3A, B, and C) and using T-1PS as a reference (ammonium values, Table 2), the idea is reinforced that fertilization at sowing can be avoided as yields were not reduced by doing so (Table 2), and that it can well be substituted by a single application at tillering. Other authors also report a higher efficiency of N applied at tillering rather than at sowing when using mineral fertilizer in rainfed conditions (López-Bellido et al., 2006).

The assessment of mineral fertilization, in terms of NH_3 volatilization, was done in two strategies in the third season: S-1M plus T-2M and T-3M (Table 2). The mineral fractioned strategy (S-1M/T-2M), showed that low application rates at sowing (S-1M, 15 kg NH_4^+-N ha^{-1} as NH_4NO_3) volatilized 62.6% of the applied TAN (Table 4) and at tillering dressing (T-2M, 15 kg NH_4^+-N ha^{-1} as NH_4NO_3) volatilized 19.7% of the applied TAN (strategy S-1M/T-2M; 15.3 kg NH_3-N ha^{-1}), more than treatment T-3M (9.1 kg NH_3-N ha^{-1}, 20.2% of TAN). Furthermore, fractionation of N (as NH_4NO_3) is not always associated with an increment in the yield trend (Table 2).

3.4. Selection of fertilization strategies

The fertilization strategies to be recommended are selected through combining environmental criteria: minimizing NH_3 volatilization (<20 kg NH_3-N ha^{-1} which is below 12% of N applied) with agronomic criteria: maximum yields (4000-5000 kg ha^{-1}) for the agricultural system, N efficiency (>30 kg grain kg N $applied^{-1}$), amount of N to fulfil legislation (European Union, 1991) in nitrate vulnerable zones (<170 kg N ha^{-1}).

Within these criteria, the application of PS^S (low DM content) can successfully replace NH_4NO_3 at tillering, particularly when SWC is under half of its field capacity (losses below 9 kg NH_3-N ha^{-1}). Slurry from fattening pigs (~1PS) can be used too, unless its DM content is around 4.1-4.4%. Nevertheless, if DM goes up, in this case (~1PS) and referring to the highest attained yields (4450 kg ha^{-1}), total NH_3 losses increase significantly (up to 20 kg NH_3-N ha^{-1}) as they can easily double the records for PS^S.

Regarding the most favourable time for application (in order to better comply with the established agronomic criteria), fertilization at sowing with pig slurry did not bring any additional advantage in the evaluated parameters.

4. Conclusions

As a fertilization strategy, in this rainfed agricultural system, dressing at tillering with slurries is an environmentally (NH_3 loss control) and agronomically advantageous option, which can even allow the farmer to omit fertilization at sowing time. Furthermore, if slurry applications are split, NH_3 losses at dressing are not significantly affected by PS applied at sowing (3 months before).

Nevertheless, NH_3 volatilization from applied slurries is strongly affected by DM content in the studied range (from 0.8 to 10.6%). The highest amount of NH_3 volatilization (up to 64% of TAN applied) is linked to slurry DM of around 4.1-4.4%. The lowest NH_3 volatilization is associated with low DM (0.8%) slurry. The infiltration in a non-wet soil (SWC< 56% of field capacity) is enhanced by the more liquid slurries which results in accumulated NH_3 losses (<9 kg NH_3-N ha^{-1}) equivalent to the lowest values obtained when applying NH_4NO_3, without affecting dry matter yields (~3.6 Mg ha^{-1}). The most solid slurries (DM~6.1-9.3%) are another option as they favour crust formation which complicates NH_3 transport from the soil surface to the atmosphere. As rates increase, relative losses diminish (up to 17% TAN), although total accumulated NH_3 losses significantly increase with applied rates.

Further research is needed on the quantification of NH_3 emissions related to slurry DM and the interaction with soil conditions, as a way to improve the management of slurry application and the development of field practices which can lead to a reduction of NH_3 losses. Soil and slurry characteristics, as well as management practices, should be included in algorithms for NH_3 emissions in order to obtain feasible NH_3 emission estimates.

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Legends to Figures

Figure 1. Monthly rainfall, reference crop evapotranspiration (ET_0, FAO Penman-Monteith equation) and mean air temperature averages from an automatic meteorological station located in the experimental field (period 2000-2010).

Figure 2. Evolution of the mean air temperature during the 500 h following pig slurry spreading for each crop season and timing (at sowing or at cereal tillering).

Figure 3. Cumulative ammonia volatilization (kg NH_3-N ha^{-1}) after field fertilizer application (slurry or mineral fertilizer) and ammonia losses as percentage of the total ammonium nitrogen applied (TAN) at winter cereal tillering (T), during the first (A), second (B), and third (C) cropping seasons. Theoretical applied doses were: T-2M (30 kg NH_4-N ha^{-1} as ammonium nitrate), T-3M (45 kg NH_4-N ha^{-1} as ammonium nitrate), T-1PS (20 t ha^{-1}, slurry from fattening pigs), T-2PS (40 t ha^{-1}, slurry from fattening pigs), T-4PS^S (90 t ha^{-1}, slurry from sows). The application rates in terms of NH_4^+-N and total-N are described in Table 2. For each cropping season and within columns, means followed by the same letter are not significantly different according to Duncan's Multiple Range Test (α=0.05)

Table 1. Average main weather and soil conditions, on the day of slurry application, in each crop season.

Crop season	**First (mm.dd.yr)**	**Second (mm.dd.yr)**	**Third (mm.dd.yr)**	
Parameter[a]	**(02.12.04)**	**(02.23.06)**	**(11.04.06)**	**(02.12.07)**
Tmean (ºC)	3.1	2.0	10.2	12.0
Tmin (ºC)	-3.4	-3.5	4.2	4.7
Tmax (ºC)	12.4	7.8	16.4	16.5
Rainfall (foggy day, mm)	0.2	0.2	0.0	0.2
SWC[b] **(%, w/w)**	15.2	16.6	9.0	12.2

[a] Tmean: mean air temperature; Tmin: minimum air temperature; Tmax: maximum air temperature.
[b]SWC: soil water content (w/w) in the first 30 cm depth. At field capacity equals 27.1% (w/w).

Table 2. Goals of the different ammonia volatilization measurements[a]. Specific characteristics of fertilization strategies were: type of fertilizer (slurry/mineral), application rate and timing (sowing/cereal tillering). Data of winter cereal yield biomass and N efficiency is also provided.

Season/ Main aim of the assessment	Timing[b] of measurement-Fertilization[c]	Sampling start (mm.dd.yr)	Fertilization at sowing (S-) Rate[c]	DM[d] (%)	NH_4^+-N ----- (kg ha^{-1}) -----	Total-N	Fertilization at tillering (T-) Rate[c]	DM[d] (%)	NH_4^+-N ----- (kg ha^{-1}) -----	Total-N	Biomass grain yield (kg ha^{-1})	Efficiency[e] (kg grain kg N $applied^{-1}$)
First crop season												
Influence of	T-1PS	02.12.04	2PS	8.2	109.9	164.8	1PS	8.5	72.2	119.7	2981	10.5 (16.4)
slurry sowing	T-1PS	02.12.04					1PS	8.5	72.2	119.7	2911	24.3 (40.3)
fertilization	T-3PS	02.12.04	2PS	8.2	107.8	160.7	3PS	6.1	242.2	365.2	4376	8.3 (12.5)
on NH_3 losses	T-3PS	02.12.04					3PS	6.1	242.2	365.2	4996	13.7 (20.6)
at tillering	T-2M	02.12.04	1PS	8.0	55.6	85.8	2M	-	30	60	4452	30.5 (52.0)
sidedressing	T-2M	02.12.04	2PS	8.0	123.8	186.3	2M	-	30	60	4876	19.8 (31.7)
Second crop season												
Influence of	T-1PS	02.23.06					1PS	4.4	85.4	182.0	2599	14.3 (30.4)
tillering	T-3PS	02.23.06					3PS	4.4	226.0	485.5	2394	4.9 (10.6)
sidedressing	T-4PS^{S}	02.23.06					4PS^{S}	4.1	190.7	325.5	2437	7.5 (12.8)
fertilization	T-2M	02.23.06	1M	-	15	30	2M	-	30	60	2846	31.6 (63.2)
on NH_3 losses	T-3M	02.23.06					3M	-	45	90	2100	23.3 (46.7)
Third crop season												
Influence of	S-1PS	11.04.06	1PS	7.8	58.2	95.2					2861	30.1 (49.2)
sowing or	S-2PS	11.04.06	2PS	9.3	177.2	248.7	4PS^{S}	0.8	116.8	135.3	3024	7.9 (10.3)
tillering	S-3PS	11.04.06	3PS	7.8	250.3	422.4					2754	6.5 (11.0)
sidedressing	T-1PS	02.12.07					1PS	10.6	48.8	149.1	4450	29.8 (91.2)
fertilization on	T-3PS	02.12.07					3PS	10.6	109.7	334.9	3095	9.2 (28.2)
NH_3 losses	T-4PS^{S}	02.12.07					4PS^{S}	0.8	116.8	135.3	3666	27.1 (31.4)
	T-3M	02.12.07					3M	-	45	90	3620	40.2 (80.4)

	S-1M/T-2M	11.04.06/ 02.12.07	1M	-	15	30	2M	-	30	60	3398	37.8 (75.5)

[a] Grey background colour indicates when and where measurements of NH_3 losses were done. Initial measure date coincides with fertilizer application (at sowing or/and at tillering).

[b] S-: Measurements of NH_3 volatilization at sowing; T-: Measurements of NH_3 volatilization at tillering, S-/T-: Measurements of NH_3 volatilization at sowing and at tillering.

[c] PS: Pig slurry from fattening pigs; PS^S: Pig slurry from sows; M: mineral fertilizer as ammonium nitrate (33.5% N). Numbers behind indicate the multiple of the rate from a minimum (approximate) dose of 20-22 t ha^{-1} for slurries and 30 kg N ha^{-1} for mineral treatments.

[d] DM: slurry dry matter content expressed as a percentage.

[e] Efficiency of nitrogen, expressed as a quotient of the grain yield biomass with regard to the total N applied. Numbers in brackets indicate the efficiency in terms of ammonium applied.

Table 3. Total ammonia volatilization and as a percentage of the total ammonium nitrogen applied (± standard deviation), in different fertilizer applications at tillering (with *vs*. without slurry fertilization at sowing), measured during the first crop season.

Aim of the assessment	**Timing of measurement[a] - Fertilization (rate and type)[b]**	**Fertilization at sowing**		**Fertilization at tillering**		**Ammonia volatilization at tillering**	
		Rate[b]	**NH_4^+-N[c] (kg ha^{-1})**	**Rate[b]**	**NH_4^+-N[c] (kg ha^{-1})**	**NH_3-N (kg ha^{-1})¶**	**% of TAN[d] applied**
Influence of slurry applied at sowing on NH_3 losses at tillering sidedressing	T-1PS	2PS	110 (165)	1PS	72 (120)	7.4±1.3	10.3±1.8
	T-1PS	-	-	1PS	72 (120)	5.3±1.0	7.2±1.4
	Significance					**NS**	**NS**
	T-3PS	2PS	108 (161)	3PS	242 (365)	18.3±5.1	7.6±2.1
	T-3PS	-	-	3PS	242 (365)	15.1±4.1	6.2±1.7
	Significance					**NS**	**NS**
	T-2M	1PS	56 (86)	2M	30 (60)	4.5±1.5	15.2±5.0
	T-2M	2PS	124 (186)	2M	30 (60)	5.1±3.5	17.1±11.6
	Significance					**NS**	**NS**

NS: Non significant ($p>0.05$).
[a] T-: Fertilization applied at cereal tillering, when measurements of NH_3 volatilization were done.
[b] PS: Pig slurry from fattening pigs; M: mineral fertilizer as ammonium nitrate (33.5% N). Numbers behind indicate the multiple of the rate from a minimum (approximate) dose of 20-22 t ha^{-1} for slurries and 30 kg N ha^{-1} for mineral treatments.
[c] Values in parenthesis are total N applied.
[d] TAN: total ammonium nitrogen.

Table 4. Total ammonia emissions and as a percentage of the total ammonium nitrogen applied (± standard deviation) in different fertilizer applications at sowing, measured during the third crop season.

Aim of the assessment	**Fertilization at sowing (S-)**		**Ammonia volatilization at sowing**	
	Rate[a]	**NH_4^+-N**[b] **(kg ha^{-1})**	**NH_3-N (kg ha^{-1})**	**% of TAN**[c] **applied**
Influence of	S-1PS	58 (95)	23.0±3.9 BC	39.5±6.7 B
sowing	S-2PS	177 (249)	28.5±1.5 AB	16.1±0.8 C
fertilization	S-3PS	250 (422)	42.1±5.3 A	16.9±2.1 C
on NH_3	S-1M	15 (30)	9.4±0.8 C	62.6±5.2 A
losses	**Significance**		***¶	***

*** Significant ($p<0.001$). Within columns, means followed by the same letter are not significantly different according to Duncan Multiple Range Test (α=0.001).

[a] PS: Pig slurry from fattening pigs; M: mineral fertilizer as ammonium nitrate (33.5% N). Numbers behind indicate the multiple of the rate from a minimum (approximate) dose of 20-22 t ha^{-1} for slurries and 30 kg N ha^{-1} for mineral treatments.

[b] Values in parenthesis are total N applied.

[c] TAN: total ammonium nitrogen.

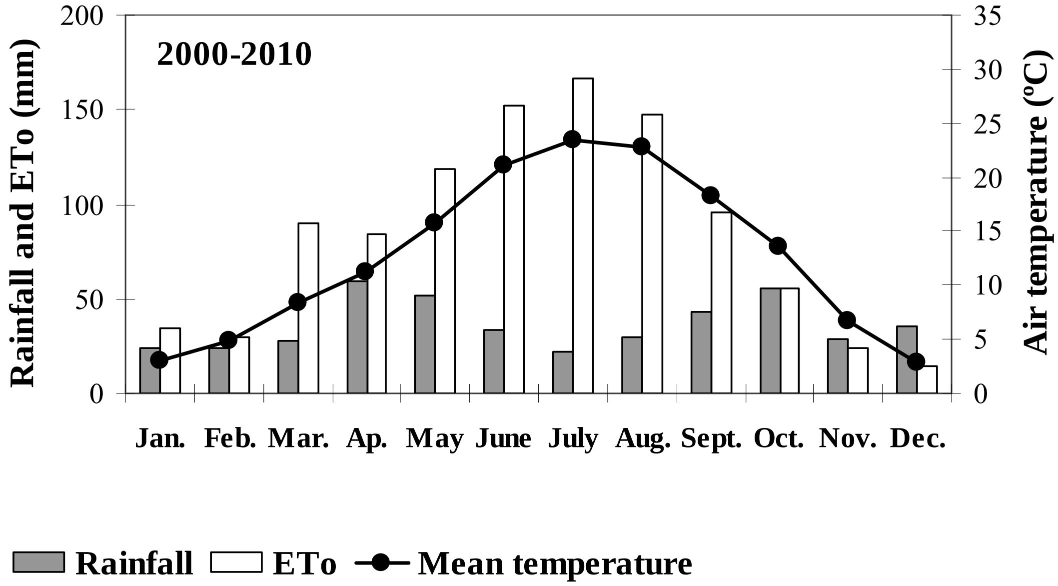
2000-2010
Rainfall and ETo (mm)
Air temperature (ºC)
200
150
100
50
0
35
30
25
20
15
10
5
0
Jan.
Feb.
Mar.
Ap.
May
June
July
Aug.
Sept.
Oct.
Nov.
Dec.
Rainfall
ETo
Mean temperature

Fig. 1.

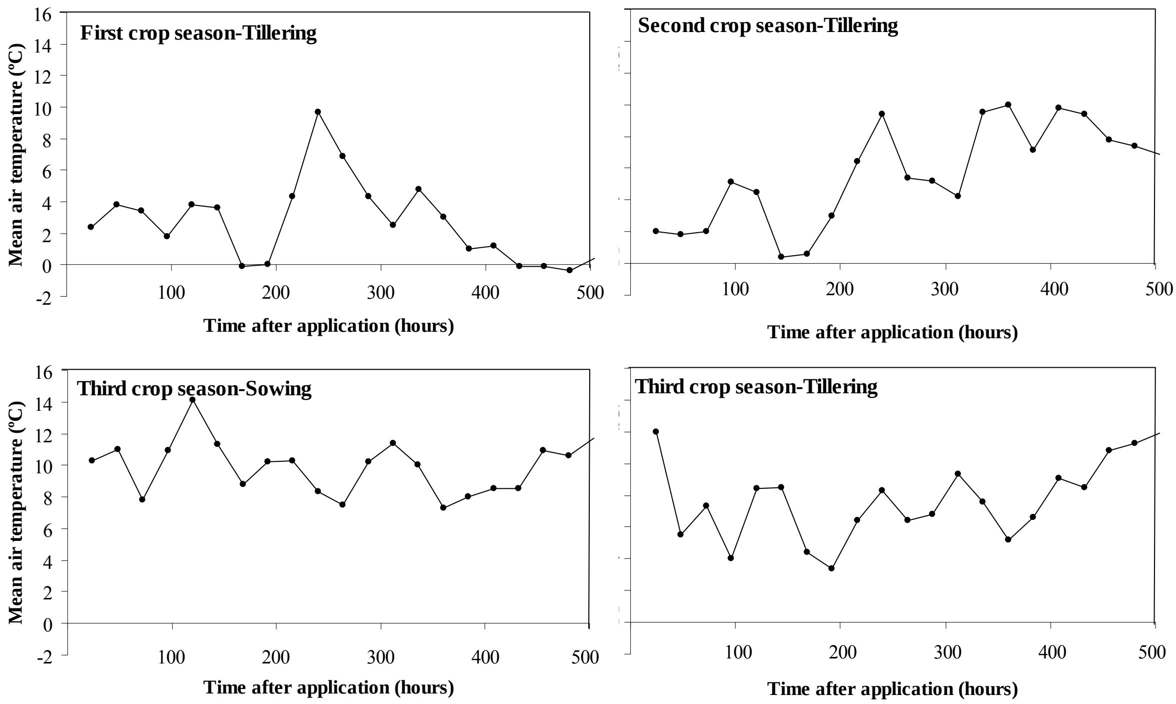
First crop season-Tillering
Second crop season-Tillering
Third crop season-Sowing
Third crop season-Tillering
Mean air temperature (ºC)
Time after application (hours)
16
14
12
10
8
6
4
2
0
-2
100
200
300
400
500

Fig. 2.

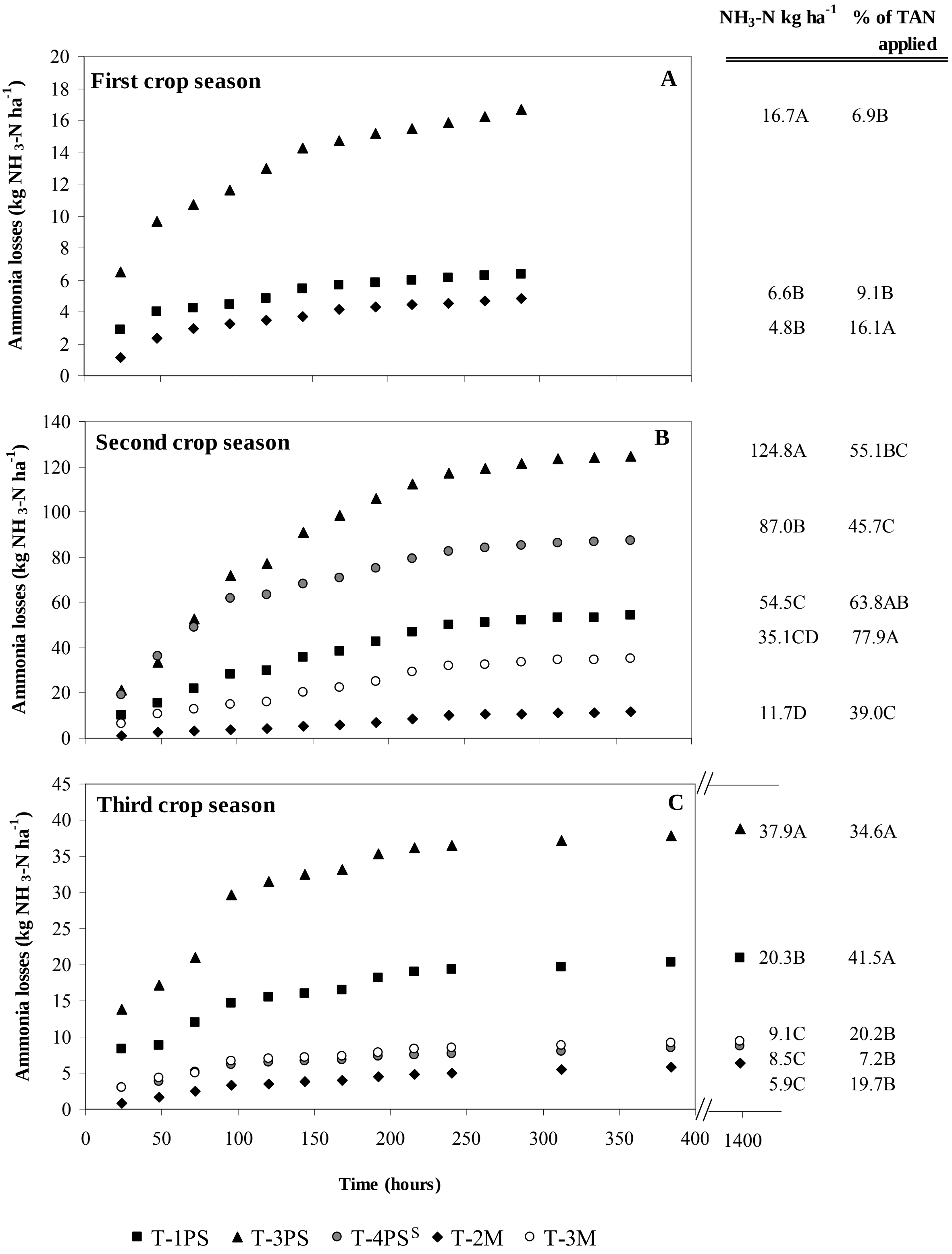
NH3-N kg ha-1
% of TAN applied
First crop season
A
16.7A 6.9B
6.6B 9.1B
4.8B 16.1A
Second crop season
B
124.8A 55.1BC
87.0B 45.7C
54.5C 63.8AB
35.1CD 77.9A
11.7D 39.0C
Third crop season
C
37.9A 34.6A
20.3B 41.5A
9.1C 20.2B
8.5C 7.2B
5.9C 19.7B
Ammonia losses (kg NH 3-N ha-1)
Time (hours)
T-1PS T-3PS T-4PSS T-2M T-3M

Fig. 3.