

1 **Bosch-Serra<sup>a,\*</sup>, À.D., Yagüe<sup>ab</sup>, M.R., Teira-Esmatges<sup>a</sup>, M. R. 2014. Ammonia**  
2 **emissions from different fertilizing strategies in Mediterranean rainfed winter**  
3 **cereals. Atmospheric Environment 84:204-212**

4 ***DOI: 10.1016/j.atmosenv.2013.11.044.***

5  
6  
7  
8 <sup>a</sup>Department of Environment and Soil Sciences, University of Lleida, Avda Alcalde  
9 Rovira Roure 191, E-25198, Lleida, Spain.

10 <sup>b</sup>Department of Soil and Irrigation (EEAD-CSIC Associated Unit), Agrifood Research  
11 and Technology Centre Aragon (CITA), Avda. Montañana 930, E-50059, Zaragoza,  
12 Spain.

13 E-mails: angela.bosch@macs.udl.cat; mryague@aragon.es; rosa.teira@macs.udl.cat

14 \*Corresponding author contact information: Angela D. Bosch Serra

15 Tel: +34 973702899. Fax: +34 973792092. E-mail: angela.bosch@macs.udl.cat

16  
17  
18  
19 **Abbreviations:** DM: dry matter; M: mineral fertilizer; NH<sub>3</sub>: ammonia; NH<sub>4</sub><sup>+</sup>:  
20 ammonium; PS: slurry from fattening pigs; PS<sup>S</sup>: slurry from sows; S: sowing; T:  
21 tillering; TAN: total ammonium nitrogen; SWC: soil water content.

## ABSTRACT

1 Anthropogenic ammonia (NH<sub>3</sub>) emissions mainly result from agricultural activities  
2 where manure spreading plays a significant role. For a Mediterranean rainfed winter  
3 cereal system there is a lack of data regarding NH<sub>3</sub> emissions. The aim of this work is to  
4 provide field data on N losses due to NH<sub>3</sub> volatilization as a consequence of the  
5 introduction of slurries in fertilization strategies and also, to assess the influence of  
6 environmental conditions and slurry characteristics on emissions. The fertilizing  
7 strategies include the use of slurry from fattening pigs (PS), sows (PS<sup>S</sup>) and/or mineral  
8 fertilizer (M) as ammonium nitrate. Fertilizers were spread over the calcareous soil at  
9 sowing and/or at tillering at rates from 15 to 45 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> for M and from 48.8 to  
10 250.3 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> for slurries. The NH<sub>3</sub> emissions were quantified during three  
11 cropping seasons. Average losses from the total ammonium nitrogen applied ranged  
12 from 7 to 78% for M and 6 to 64% for slurries and they were not directly proportional  
13 to the amounts of applied ammonium. The best results on NH<sub>3</sub> volatilization reduction  
14 were registered when soil water content (SWC, 0-30 cm) was below 56% of its field  
15 capacity and also, when slurry dry matter (DM) was in the interval of 6.1-9.3% for PS  
16 or much lower (0.8%) for PS<sup>S</sup>. High slurry DM favoured crust formation and the lower  
17 rates promoted infiltration, both of which reduced NH<sub>3</sub> emissions. Nevertheless, at  
18 tillering, the lower DM content was the most effective in controlling emissions (<9 kg  
19 NH<sub>3</sub>-N ha<sup>-1</sup>) and equalled M fertilizer in cumulative NH<sub>3</sub> loss (p>0.05). A single slurry  
20 application at tillering did not negatively affect yield biomass. The combining of  
21 recommended timing of applications with slurry DM content and SWC should allow  
22 producers to minimize volatilization while maintaining financial benefits.  
23  
24

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

3

## 1 **1. Introduction**

2 Ammonia volatilization is a physical process influenced by the concentration of  
3 total ammonium nitrogen in the soil solution (TAN;  $\text{NH}_3\text{-N}$  plus  $\text{NH}_4^+\text{-N}$ ) and by the  
4 resistance of  $\text{NH}_3$  to movement from the soil matrix (Sommer et al., 2004). In  
5 agriculture, the consequence of such processes is the reduction of the fertilizer value of  
6 manures (Jarvis and Pain, 1990; Sørensen and Amato, 2002; Sommer et al., 2006) but  
7 also, once this volatilized  $\text{NH}_3$  deposits, it becomes a threat to the environment through  
8 acidification, eutrophication or direct toxic effects (Pearson and Stewart, 1993).  
9 According to the European Directive 2001/81/CE relating to air protection and  
10 thresholds on national emissions, it is necessary to establish the temporal and  
11 cumulative emissions of  $\text{NH}_3$  derived from fertilization practices. Furthermore, from  
12 liquid manure systems in Europe, differences exist between the models used for national  
13 agricultural  $\text{NH}_3$  emission inventories (Reidy et al., 2008) due to the influence of soil  
14 characteristics as well as to other factors such as weather or slurry composition  
15 (Sommer et al., 2003).

16 Different techniques have been employed to measure  $\text{NH}_3$  losses and all of them  
17 have limitations (Sintermann et al. 2011). The most used are semi-static chambers  
18 because they easily adapt to small plots, they permit monitoring multiple treatments in  
19 the same crop season, have a low cost, and require reagents and materials commonly  
20 available (Grant et al., 1996). However, absolute estimates of  $\text{NH}_3\text{-N}$  loss can be  
21 underestimated (Pozzi et al., 2012) because according to Søggaard et al. (2002) wind  
22 speed increases, by 4% per  $\text{m s}^{-1}$ , total  $\text{NH}_3$  volatilization.

23 For Mediterranean areas, information on ammonia emissions is scarce.  
24 However,  $\text{NH}_3$  volatilization is an important environmental issue as calcareous soils  
25 favour  $\text{NH}_3$  volatilization. Soil carbonate reacts with water to form bicarbonate ( $\text{HCO}_3^-$ )

1 and the hydroxyl radical ( $\text{OH}^\cdot$ ) reacts with  $\text{NH}_4^+\text{-N}$  to form  $\text{NH}_3$  gas and water: such  
2 processes may act over different periods depending on other soil characteristics,  
3 environmental conditions, and fertilizer management (Bouwmeester et al., 1985; Kissel  
4 and Cabrera, 2005).

5 For Mediterranean conditions, articles from Générumont and Cellier (1997),  
6 Morvan et al. (1997) and Sanz et al. (2010) dealing with  $\text{NH}_3$  volatilization from slurry  
7 applied on bare soil are available. They generally involve parameters such as slurry  
8 application times (March, June, September–October) or dry matter (DM) content  
9 (between 1.4 to 4.7%) which do not cover the current application times or the actual  
10 range of slurry composition in the Spanish regions being studied (Yagüe et al., 2012).  
11 The DM content of slurry is an important factor as it can greatly alter the amount of  
12  $\text{NH}_3$  volatilized (Misselbrook et al., 2000; Sommer et al., 2001; Thompson and  
13 Meisinger, 2002).

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

22 A few studies related to the evaluation of the use of pig slurries in winter cereals  
23 were found: Petersen (1996) and Sieling et al. (1998) studied N use efficiency, Sommer  
24 et al. (1997) and Meade et al. (2011) measured  $\text{NH}_3$  losses at tillering or from mid-  
25 tillering onwards but under North European soil and weather conditions.

1           The quantification of  $\text{NH}_3$  volatilization in semiarid areas has not been reported  
2 either in combined applications at sowing and at tillering, or when using different  
3 fertilization strategies which include slurry and/or mineral fertilizers. The use of  
4 available models for  $\text{NH}_3$  emission estimation cannot be generalised, due to the  
5 importance of management practices (Smith et al., 2008; Sheppard and Bittman, 2013).  
6 A key point, when applying slurry as a fertilizer dressing, is  $\text{NH}_3$  volatilization because  
7 slurries cannot be buried into the soil immediately after their application. Besides, if a  
8 previous application has been made it might increase  $\text{NH}_3$  losses, as it is well known  
9 that the long-term application on soil of other liquid wastes affects soil water repellence  
10 and reduces infiltration capacity (Wallach et al., 2005; Vogeler, 2009).

11           The present work was set up in the framework of rainfed Mediterranean  
12 agricultural systems and it includes a wide range of applied  $\text{NH}_4^+\text{-N}$  during the winter  
13 cereal cropping season. The main objective was to provide basic field data on N losses  
14 due to  $\text{NH}_3$  volatilization, but also to include the assessment of high yielding fertilizer  
15 strategies for the area, in which pig slurry must be taken into account. In this work, we  
16 focused on fertilizer dressing applications. The specific environmental objectives of this  
17 research were: i) at tillering, to assess the influence, on  $\text{NH}_3$  volatilization from  
18 fertilizers, of pig slurry which has been previously applied at sowing; ii) at tillering, to  
19 compare  $\text{NH}_3$  losses between pig slurries and mineral fertilization applied at different  
20 rates; and iii) to quantify, as a reference for slurry applied at tillering, other  $\text{NH}_3$  losses  
21 from other fertilization strategies: minerals or slurries applied at sowing.

22           The evaluation of  $\text{NH}_3$  volatilization from slurries will also increase the  
23 predictability of their nitrogen fertilizer value and will allow us to improve the  
24 recommendations on slurry use in fertilizer management plans.

25

## 1 **2. Materials and methods**

### 2 *2.1. Description of the experimental site*

3 This work was set up in the Ebro river basin (Spain, 41° 52' 29"N, 1° 09' 10"E;  
4 443 masl) and was included in a broad experiment about N fertilization strategies. The  
5 soil of the site was classified as a Typic Xerofluvent (Soil Survey Staff, 1999), well  
6 drained, with a silty loam texture in the surface layer. The main top soil layer (0-0.30 m)  
7 has a low organic matter content (< 2%), is non saline (electrical conductivity, 1:5 w/v,  
8 is 0.18 dS m<sup>-1</sup>), the pH is 8.2 (soil:water;1:2.5), the cation exchange capacity (CEC) is  
9 11.1 cmol<sup>+</sup> kg<sup>-1</sup> and the soil has a high carbonate content (close to 30%). Gravimetric  
10 soil water content at field capacity is 0.27 (w/w).

11 The climate is semiarid Mediterranean (Fig. 1), with high summer average  
12 temperatures (>20°C), low annual precipitation (<450 mm yr<sup>-1</sup>) and high average  
13 reference crop evapotranspiration (1013 mm yr<sup>-1</sup>).

### 14 *2.2. Experimental set up*

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

19 Fertilization strategies, as a combination of fertilizer type and application timing,  
20 were implemented in the 2002/03 crop season for agronomic evaluation and exactly  
21 maintained over the different cropping seasons. The crops sown were wheat (2002/03,  
22 2005/06) or barley (2003/04, 2004/05, 2006/07).

23 Ammonia volatilization started to be evaluated in 2003/04 and was only done for  
24 selected fertilization strategies (Table 2). It was conducted during three cropping  
25 seasons after fertilizer dressing at tillering: 2003/04 (the first one), 2005/06 (the second

1 one) and 2006/07 (the third one) during 288 h, 360 h, and 384 h, respectively. The  
2 measurements needed for quantification were stopped when a stable low volatilization  
3 rate was attained although, in 2006/07, measurements were maintained for almost 1400  
4 h after application just to verify the minimum period required for accumulated stable  
5 NH<sub>3</sub> volatilization data. During the third crop season (2006/07), measurements of NH<sub>3</sub>  
6 volatilization from slurry applications at sowing (during a time interval of 390 h) were  
7 also implemented. Data were obtained daily at the greatest frequency. At sowing, the  
8 first sample was obtained during the next 6 h after slurry spreading because after the  
9 first sampling, slurry was buried but after doing so, NH<sub>3</sub> measurements were resumed  
10 immediately.

11 The chosen fertilizer strategies in 2005/06 and 2006/07 took previous results  
12 (including yields, Table 2) into account and were adapted to the objectives to be  
13 attained in each cropping season. Nevertheless, the overall goal was always to achieve a  
14 comprehensive recommended strategy: minimum NH<sub>3</sub> losses and high yields, which  
15 explains why, in each season, one or two new strategies (where NH<sub>3</sub> volatilization was  
16 not previously quantified) were also added.

17 The control plot was selected between plots which never received mineral N  
18 fertilizer nor pig slurry. The applied fertilizers were: fattening pig slurry (PS), sow  
19 slurry (PS<sup>S</sup>), and mineral fertilizer (M; ammonium nitrate 33.5% of N). The fertilization  
20 doses were: 20, 40 and 60 t PS ha<sup>-1</sup> (named 1PS, 2PS and 3PS, respectively) and 90 t  
21 PS<sup>S</sup> ha<sup>-1</sup> (4PS<sup>S</sup>). The rate of 20 t ha<sup>-1</sup> (1PS) is around the minimum dose that can be  
22 applied uniformly with the commonly available technology: a tank fitted with a splash-  
23 plate from which slurry is spread on the soil. Slurry rates were controlled on the field  
24 through the tractor speed (calibration was done previously on a bare field). Ammonium  
25 nitrate (NH<sub>4</sub>NO<sub>3</sub>) was applied at 15, 30 and 45 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> (named 1M, 2M, and

1 3M respectively). Doses were applied at sowing (S-) or at tillering (T-), or at both crop  
2 timings (S-/T-). The  $\text{NH}_4^+$ -N and total-N applied on each occasion were determined  
3 through laboratory analysis of the slurry and the quantification of the effective applied  
4 dose (Table 2) by weighing the slurry tank before and after spreading on each plot.

#### 5 *2.2.1. Slurry sampling and selection*

6 Slurry samples were always taken before application and they were kept  
7 refrigerated until their arrival at the laboratory. The quantified parameters were (Table  
8 2): dry matter (gravimetrically),  $\text{NH}_4^+$ -N (modified Kjeldahl method), and total-N  
9 (Kjeldahl method). In the first crop season, at sowing and at tillering dressing  
10 fertilization, DM content of pig slurries from fattening pigs (6.1 to 8.5%) was an  
11 example of the actual trend of slurry volume reduction (DM increment) in some areas  
12 (Teira-Esmatges and Flotats, 2003). In the second and the third crop seasons, at tillering  
13 dressing fertilization, in order to generalize and reinforce the advantages of pig slurries  
14 applied at tillering based on  $\text{NH}_3$  volatilization, slurries were previously chosen before  
15 being applied. The criterion for selection was to enlarge the scope of their DM content  
16 across the experiment. The DM was indirectly estimated by a densimeter. DM ranged  
17 from 4.4% to 10.6% for PS and from 0.8 to 4.1% for PS<sup>S</sup>.

18 The variability in  $\text{NH}_4^+$ -N slurry content (Table 2), represented the normal  
19 variability that occurs in these agricultural systems (Yagüe et al., 2012).

#### 20 *2.2.2. Quantification of $\text{NH}_3$ volatilization*

21 Ammonia volatilization was sampled using semi-static chambers based on Grant  
22 et al.'s (1996) description. On each plot, semi-static chambers were placed in triplicate.  
23 The chambers consisted of a LD PET (Low Density PolyEthylene Terephthalate)  
24 cylinder of 234 mm diameter and 150 mm height which was introduced 40 mm deep in  
25 the soil, taking care to cause minimal soil disturbance. On the top of the cylinder, a

1 synthetic mesh tissue was placed to support a 240 mm diameter foam disk covering all  
2 of the cylinder cross-section. The foam had been previously soaked with a fixed volume  
3 of acetone (30% v/v) containing oxalic acid (3% w/v) and allowed to evaporate and dry  
4 in a well-ventilated hood before it was placed on the mesh in the field. Another mesh on  
5 top of the foam was used to prevent the foam from moving. Each foam disk was  
6 renewed daily during the experiment from immediately after fertilizer application and at  
7 different intervals later on. In case of rain, chambers were covered as soon as possible  
8 by big plastic bags to avoid the wetting of samples and they were uncovered once the  
9 rain was over. Upon renewal, each sponge was placed in a zip lock freezer bag to  
10 transport it to the laboratory. Each sponge was soaked with distilled water (four times  
11 with 500 mL) and the extract collected and made up to 2 L. The extract was quantified  
12 by means of an ammonia selective electrode (Crison, micropH 2002) after the addition  
13 of NaOH (40% w/v) to the ammonium oxalate sample for pH adjustment, and  
14 calculated using the daily calibration curve of the electrode. Ammonia concentration  
15 can be expressed as an emission flux and represented over time. The cumulative NH<sub>3</sub>  
16 volatilization during the sampling period can be calculated by integrating the area under  
17 the fluxes' curve.

### 18 *2.2.3. Other agricultural practices*

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

### 23 *2.3. Statistical analysis*

24 The effect of the fertilizer application on NH<sub>3</sub> losses was evaluated by analysis  
25 of variance (one-way), and separation of means was done by the Duncan multiple range

1 test ( $\alpha=0.05$ ). The control (ammonia threshold value) was not included as a treatment in  
2 the statistical analysis because the goal was to compare  $\text{NH}_3$  losses between fertilization  
3 strategies (including the optimum and overfertilized ones). The statistical analysis was  
4 made using the SAS statistical package (SAS Institute, 1999-2001).

5

### 6 **3. Results and discussion**

7 In all crop seasons, during a minimum period of six days following slurry  
8 spreading, weather was dry, although foggy mornings were not uncommon (Table 1). In  
9 the first crop season, 5.4 mm of rain fell at the tillering period (216 h after slurry  
10 application). No rainfall occurred in the second season. In the third crop season, 10.3  
11 mm of rain fell at the sowing period (312 h after slurry application) and 6.3 mm at the  
12 tillering period (144 h after fertilizer spreading). These rainfall events were not  
13 considered relevant in affecting cumulative  $\text{NH}_3$  emission measurements.

#### 14 *3.1. Effect of slurry at sowing on $\text{NH}_3$ volatilization at dressing. First crop season*

15 At tillering (Table 3),  $\text{NH}_3$  volatilization from pig slurry (T-1PS, T-3PS) was not  
16 significantly affected by the pig slurry applied at sowing (S-2PS). Nevertheless, a slight  
17 tendency to increase  $\text{NH}_3$  volatilization (by 2-3 kg  $\text{NH}_3\text{-N ha}^{-1}$ ) when slurry had  
18 previously been applied as fertilizer at sowing (three months earlier) can be observed.  
19 Ammonia volatilization was quite low: 5-18 kg  $\text{NH}_3\text{-N ha}^{-1}$ . The highest value  
20 corresponded to the highest PS dose (T-3PS, 60 t  $\text{ha}^{-1}$ ), which is much greater than the  
21 recommended N dose for winter cereals. However, in long-term applications, in high N  
22 demanding crops, it could be of interest to go deeper into these potential interactions  
23 which could be related, as mentioned in the introduction, to the development of  
24 hydrophobic soil properties linked to the characteristics of applied liquid wastes.

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

3           In classical strategies, where slurry at sowing is complemented by an N mineral  
4 dressing (T-2M; 60 kg N ha<sup>-1</sup> as NH<sub>4</sub>NO<sub>3</sub>), NH<sub>3</sub> volatilization (around 5 kg NH<sub>3</sub>-N ha<sup>-1</sup>)  
5 was not affected by the rate of the slurry previously applied at sowing (Table 3).

### 6 *3.2. Effect of dressing fertilization on NH<sub>3</sub> volatilization. Three cropping seasons*

7           In the first crop season, at tillering (Fig. 3A), whatever the fertilization at sowing  
8 was, no significant differences between mineral (T-2M, 4.8 kg NH<sub>3</sub>-N ha<sup>-1</sup> volatilized)  
9 and the lowest rate of pig slurry applied (T-1PS, 6.6 NH<sub>3</sub>-N kg ha<sup>-1</sup> volatilized) could be  
10 observed though, in this case, the applied amount of NH<sub>4</sub><sup>+</sup>-N as PS was double the  
11 mineral dose (Table 2). This fact means that relative losses associated with the mineral  
12 fertilizer (T-2M) were significantly higher (16.1% of TAN applied) than from the  
13 lowest slurry rate (T-1PS, 9.1% TAN applied). Thus, T-1PS was more efficient in  
14 reducing volatilization, although the pattern of losses with time actually followed the T-  
15 2M curve closely (Fig. 3A). Soil moisture was at 56% of its field capacity and foggy  
16 days (Table 1) favoured the solubility process for the mineral fertilizer granules.

17           Although not significant (p>0.05), when slurry rate was tripled (T-3PS), the  
18 percentage of losses, compared with T-1PS, only decreased slightly, from 9.1 to 6.9%  
19 of TAN applied (Fig. 3A). The general low cumulative NH<sub>3</sub>-N losses (from 6.6 to 16.7  
20 kg NH<sub>3</sub>-N ha<sup>-1</sup>, T-1PS vs. T-3PS) were associated with low air temperatures below 5°C  
21 during sampling (Fig. 2). These results agree with those of Sommer and Hutchings  
22 (2001) on the expected NH<sub>3</sub> volatilization for surface-applied manure when combining  
23 two variables: air temperature and slurry DM content.

24           According to the cumulative NH<sub>3</sub> volatilization for this first cropping season, PS  
25 can be recommended as a dressing fertilizer instead of the NH<sub>4</sub>NO<sub>3</sub> which is widely

1 used in the area. The T-1PS strategy also results in an acceptable N efficiency (24.3 kg  
2 grain kg N applied<sup>-1</sup>). Nevertheless, from the agronomic point of view, the lowest yield  
3 achieved (2911 kg ha<sup>-1</sup>) with this strategy (119.7 kg N ha<sup>-1</sup> at tillering, without N  
4 fertilization at sowing), in comparison with other more productive ones (Table 2),  
5 required further evaluation in consecutive crop seasons (including accuracy in N dose  
6 versus crop demand or the addition of N residual effects) before recommending its  
7 potential adoption as a fertilization strategy at field level.

8         During the second and third crop seasons, if mineral fertilization (T-2M, 30 kg  
9 NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> applied) is taken as a reference, NH<sub>3</sub> volatilization accounted, respectively,  
10 for 39.0 and 19.7% of TAN applied (equivalent to 11.7 and 5.9 kg NH<sub>3</sub>-N ha<sup>-1</sup>).  
11 Differences can be attributed to soil and weather conditions (Table 1, Fig. 2). In the  
12 second season, soil water content (SWC, 0-30 cm) was at 61% of its field capacity  
13 which favoured granule solubilization and subsequent NH<sub>3</sub> volatilization. By contrast,  
14 in the third season, soil water content was lower (45% of field capacity) and  
15 temperatures higher (Fig. 2), both limiting solubilization. Nevertheless, in this  
16 environment where NH<sub>4</sub>NO<sub>3</sub> is commonly used as a dressing (T-2M or T-3M), even  
17 when soil is quite wet (61% of its field capacity), range of NH<sub>3</sub>-N losses (20-39% of  
18 total applied N, Fig. 3B) are in agreement with ones described in literature for similar  
19 soil (pH>7, low CEC) and dry climate characteristics (Meisinger and Randall 1991;  
20 FAO, 2001). Also, they are much lower than those described for some other N mineral  
21 fertilization practices. As an example, for surface-applied urea, Pacholski et al. (2006)  
22 found, in a calcareous soil in China, that cumulative losses could be up to 48% of total  
23 applied N and Rochette et al. (2009) recorded losses equivalent to 64% of total N.

24         When comparing volatilization from PS (T-1PS), values from the second season  
25 (63.8% of TAN applied, 54.5 kg NH<sub>3</sub>-N ha<sup>-1</sup>, Fig. 3B) were roughly double the

1 accumulated  $\text{NH}_3\text{-N}$  losses recorded in the third season (41.5% of TAN applied, 20.3 kg  
2  $\text{NH}_3\text{-N ha}^{-1}$ , Fig. 3C), and they were also much higher than those recorded for the first  
3 season (9.1% of TAN applied, 6.6 kg  $\text{NH}_3\text{-N ha}^{-1}$ ).

4         These results can be explained because in the third season, PS with a high DM  
5 content (~10%) and average temperatures higher than 12°C favoured a crust surface  
6 formation which in turn increased the liquid phase resistance (Sommer et al., 1991)  
7 inducing lower  $\text{NH}_3$  volatilization rates, in agreement with Thompson and Meisinger's  
8 (2002) observations. In contrast, the most liquid slurry (T-4  $\text{PS}^{\text{S}}$ , 0.8% DM) infiltrated  
9 rapidly. As a consequence, in both cases, volatilization was minimized (Fig. 3C) to  
10 41.5-34.6% of TAN applied in the case of PS (T-1PS-T-3PS, respectively) and to 7.2%  
11 of TAN applied in the case of  $\text{PS}^{\text{S}}$  (8.5 kg  $\text{NH}_3\text{-N ha}^{-1}$ ). The concept of cutting down  
12  $\text{NH}_3$  volatilization by means of facilitating infiltration of slurry (low DM content) into  
13 soil (i.e. decanted slurry, mechanically assisted infiltration) is supported by Brandral et  
14 al. (2009). As slurry infiltrates, it reduces the pool of TAN at the soil surface; the  
15 concentration of  $\text{NH}_3$  is reduced and, therefore, subsequent volatilization is also lower  
16 (Thompson et al., 1990). In our case, an easier infiltration explains that T-4 $\text{PS}^{\text{S}}$  strategy  
17 attained similar  $\text{NH}_3$  losses (Fig. 3C) and yields (Table 2) compared with mineral  
18 fertilizer strategies (S-1M/T2M or T-3M) in the third season.

19         Surprisingly, the high  $\text{NH}_3$  volatilization in the second crop season for slurries  
20 moved away from the expected results according to SWC, air temperatures and their  
21 similar DM content (independently of the origin: PS or  $\text{PS}^{\text{S}}$ ). When comparing these  
22 results with the raw data of Misselbrook et al. (2005), referring specifically to DM  
23 slurry content and  $\text{NH}_3$  volatilization, it should be noted that they observed maximum  
24 losses at 4.5% DM content. These losses, for the specific site, doubled (% TAN applied)  
25 the ones registered at lower DM (<3.9%), or tripled when compared with higher DM

1 values (>5.6%). These observations indicate that there is a critical DM content at which  
2 pig slurry is not either liquid enough to easily infiltrate, or thick enough to favour crust  
3 formation. The situation described coincides with that of the second season, whatever  
4 was the slurry's origin (4.1- 4.4% DM), and the effect was more evident at the lowest  
5 rate (T-1PS) where losses attained 64% of TAN applied.

6 In all cases, accumulated  $\text{NH}_3$  losses stabilized within the first 250 h following  
7 slurry application (Fig. 3), and it was not found that  $\text{NH}_3$  volatilization was prolonged  
8 over time as DM increased, in agreement with Sommer et al. (2006) and Ni et al.  
9 (2012).

### 10 *3.3. Effect of other fertilization strategies on $\text{NH}_3$ volatilization: pig slurry at sowing* 11 *and mineral fertilization. Third crop season*

12 In the third crop season, the weather conditions on the days of slurry spreading  
13 at sowing and at tillering were similar, although soil water content was at 33% and 45%  
14 of its field capacity, respectively (Table 1). At sowing (S-1PS and S-3PS), although  
15 slurry was buried 6 h after application, accumulated losses of between 23.0 and 42.1 kg  
16  $\text{NH}_3\text{-N kg ha}^{-1}$  (Table 4) were in the range of values found at tillering for T-1PS and T-  
17 3PS (Fig. 3C; 20.3 and 37.9 kg  $\text{NH}_3\text{-N kg ha}^{-1}$ ).

18 Increasing rates from S-1PS to S-3PS reduced the volatilization ratio (from 39.5  
19 to 16.9% of TAN applied) but because of the higher amount of applied ammonium,  
20 total  $\text{NH}_3$  losses increased significantly (Table 4). With these figures in mind (Fig. 3A,  
21 B, and C) and using T-1PS as a reference (ammonium values, Table 2), the idea is  
22 reinforced that fertilization at sowing can be avoided as yields were not reduced by  
23 doing so (Table 2), and that it can well be substituted by a single application at tillering.  
24 Other authors also report a higher efficiency of N applied at tillering rather than at  
25 sowing when using mineral fertilizer in rainfed conditions (López-Bellido et al., 2006).

1           The assessment of mineral fertilization, in terms of NH<sub>3</sub> volatilization, was done  
2 in two strategies in the third season: S-1M plus T-2M and T-3M (Table 2). The mineral  
3 fractioned strategy (S-1M/T-2M), showed that low application rates at sowing (S-1M,  
4 15 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> as NH<sub>4</sub>NO<sub>3</sub>) volatilized 62.6% of the applied TAN (Table 4) and at  
5 tillering dressing (T-2M, 15 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> as NH<sub>4</sub>NO<sub>3</sub>) volatilized 19.7% of the  
6 applied TAN (strategy S-1M/T-2M; 15.3 kg NH<sub>3</sub>-N ha<sup>-1</sup>), more than treatment T-3M  
7 (9.1 kg NH<sub>3</sub>-N ha<sup>-1</sup>, 20.2% of TAN). Furthermore, fractionation of N (as NH<sub>4</sub>NO<sub>3</sub>) is  
8 not always associated with an increment in the yield trend (Table 2).

#### 9 *3.4. Selection of fertilization strategies*

10           The fertilization strategies to be recommended are selected through combining  
11 environmental criteria: minimizing NH<sub>3</sub> volatilization (<20 kg NH<sub>3</sub>-N ha<sup>-1</sup> which is  
12 below 12% of N applied) with agronomic criteria: maximum yields (4000-5000 kg ha<sup>-1</sup>)  
13 for the agricultural system, N efficiency (>30 kg grain kg N applied<sup>-1</sup>), amount of N to  
14 fulfil legislation (European Union, 1991) in nitrate vulnerable zones (<170 kg N ha<sup>-1</sup>).

15           Within these criteria, the application of PS<sup>S</sup> (low DM content) can successfully  
16 replace NH<sub>4</sub>NO<sub>3</sub> at tillering, particularly when SWC is under half of its field capacity  
17 (losses below 9 kg NH<sub>3</sub>-N ha<sup>-1</sup>). Slurry from fattening pigs (~1PS) can be used too,  
18 unless its DM content is around 4.1-4.4%. Nevertheless, if DM goes up, in this case  
19 (~1PS) and referring to the highest attained yields (4450 kg ha<sup>-1</sup>), total NH<sub>3</sub> losses  
20 increase significantly (up to 20 kg NH<sub>3</sub>-N ha<sup>-1</sup>) as they can easily double the records for  
21 PS<sup>S</sup>.

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

25

#### 1 **4. Conclusions**

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

7 Nevertheless, NH<sub>3</sub> volatilization from applied slurries is strongly affected by  
8 DM content in the studied range (from 0.8 to 10.6%). The highest amount of NH<sub>3</sub>  
9 volatilization (up to 64% of TAN applied) is linked to slurry DM of around 4.1-4.4%.  
10 The lowest NH<sub>3</sub> volatilization is associated with low DM (0.8%) slurry. The infiltration  
11 in a non-wet soil (SWC < 56% of field capacity) is enhanced by the more liquid slurries  
12 which results in accumulated NH<sub>3</sub> losses (<9 kg NH<sub>3</sub>-N ha<sup>-1</sup>) equivalent to the lowest  
13 values obtained when applying NH<sub>4</sub>NO<sub>3</sub>, without affecting dry matter yields (~3.6 Mg  
14 ha<sup>-1</sup>). The most solid slurries (DM~6.1-9.3%) are another option as they favour crust  
15 formation which complicates NH<sub>3</sub> transport from the soil surface to the atmosphere. As  
16 rates increase, relative losses diminish (up to 17% TAN), although total accumulated  
17 NH<sub>3</sub> losses significantly increase with applied rates.

18 Further research is needed on the quantification of NH<sub>3</sub> emissions related to  
19 slurry DM and the interaction with soil conditions, as a way to improve the management  
20 of slurry application and the development of field practices which can lead to a  
21 reduction of NH<sub>3</sub> losses. Soil and slurry characteristics, as well as management  
22 practices, should be included in algorithms for NH<sub>3</sub> emissions in order to obtain feasible  
23 NH<sub>3</sub> emission estimates.

24

25

1 **Acknowledgements**

2 The authors thank J. M. Pijuan for field assistance and J. Vendrell, E. Sola, M. Batlle  
3 and S. Lucha for field and laboratory assistance. The support from the Department of  
4 Agriculture, Livestock, Fisheries, Food and Natural Environment (Generalitat de  
5 Catalunya, Catalonia, Spain) is fully acknowledged. This study was financed by the  
6 National Institute for Agricultural and Food Scientific Research and Technology of  
7 Spain-INIA (projects: REN01-1590, RTA04-114, RTA2010-126) and by FEDER  
8 (European Fund for Regional Development) and FEADER (European Agricultural Fund  
9 for Rural Development) funds.

10

11 **References**

12 Bouwmester, R.J.B., Vlek, P.L.G., Stumpe, J.M., 1985. Effect of environmental factors  
13 on ammonium volatilization from urea-fertilizer soil. Soil Science Society of  
14 America Journal 49, 376-381.

15 Brandral, R., Bittman, S., Kwalenko, G., Buckley, K., Chantigny, M.H., Hunt, D.E.,  
16 Bounaix, F., Friensen, A., 2009. Enhancing soil infiltration reduces gaseous  
17 emissions and improves N uptake from applied dairy slurry. Journal of  
18 Environmental Quality 38, 1372-1382.

19 European Union, 1991. Council directive 91/676/EEC of 12 December concerning the  
20 protection of waters against pollution caused by nitrates from agricultural sources.  
21 Official Journal of European Communities L375. Brussels, Belgium.

22 FAO, 2001. Global estimates of gaseous emissions of NH<sub>3</sub>, NO and N<sub>2</sub>O from  
23 agricultural land. Available at:  
24 <http://www.fao.org/documents/en/empty.jsp?cx=018170620143701104933%3Aqq>

1 82jsfba7w&cof=FORID%3A11&q=NH3%2C+NO++N2O+&search\_radio=fao&x  
2 =13&y=7 (verified 11.10.13).

3 Générumont, S., Cellier, P., 1997. A mechanistic model for estimating ammonia  
4 volatilization from slurry applied to bare soil. *Agricultural and Forest Meteorology*  
5 88, 145-167.

6 Grant, C.A., Jia, S., Brown, K.R., Bailey, L.D., 1996. Volatile losses of NH<sub>3</sub> from  
7 surface applied urea and urea ammonium nitrate with and without the urease  
8 inhibitors NBP or ammonium thiosulphate. *Canadian Journal of Soil Science* 76,  
9 417-419.

10 Jarvis, S.C., Pain, B.F., 1990. Ammonia volatilization from agricultural land.  
11 *International Fertiliser Society Proceedings* 298, 1-35.

12 Kissel, D.E., Cabrera, M.L., 2005. Ammonia, in: Hillel, D. (Ed.), *Encyclopedia of Soils*  
13 *in the Environment*. Taylor and Francis, New York, pp. 56-64.

14 López-Bellido, L., López-Bellido, R.J., López-Bellido, A.J., 2006. Fertilizer nitrogen  
15 efficiency in durum wheat under rainfed Mediterranean conditions: effect of split  
16 applications. *Agronomy Journal* 88, 55-62.

17 MARM, 2013. Anuario de estadística. Available at:  
18 <http://www.magrama.gob.es/es/estadistica/temas/default.aspx> (verified  
19 11.10.13).

20 Meade, G., Pierce, K., O'Doherty, J.V., Mueller, C., Lanigan, G., Mc Cabe, T., 2011.  
21 Ammonia and nitrous oxide emissions following land application of high and low  
22 nitrogen pig manures to winter wheat at three growth stages. *Agriculture*  
23 *Ecosystems and Environment* 140, 208-217.

24 Meisinger, J.J., Randall G.W., 1991. Estimating nitrogen budgets for soil crop systems.  
25 Chapter 5, in: Follett, R.F., Keeney, D.R., Cruse, R.M. (Eds.), *Managing nitrogen*

1 for groundwater quality and farm profitability. Soil Science Society of America,  
2 Inc. Madison, Wisconsin, pp. 85-124.

3 Misselbrook, M.H., Van der Weeden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J.,  
4 Smith, K.A., Phillips, V.R., Demmers, T.G.M., 2000. Ammonia emission factors  
5 from UK agriculture. *Atmospheric Environment* 34, 870-880.

6 Misselbrook, T.H., Nicholson, F.A., Chambers, B.J., 2005. Predicting ammonia losses  
7 following the application of livestock manure to land. *Bioresource Technology* 96,  
8 159-168.

9 Morvan T., Leterme, P., Arsen, G., Mary, B., 1997. Nitrogen transformations after the  
10 spreading of pig slurry on bare soil and ryegrass using <sup>15</sup>N-labelled ammonium.  
11 *European Journal of Agronomy* 7, 181-188.

12 Ni, K., Pacholki, A., Gericke, D., Kage, H., 2012. Analysis of ammonia losses after  
13 application of biogas slurries by an empirical model. *Journal of Plant Nutrition and*  
14 *Soil Science* 175, 253-264.

15 Pacholski, A., Cai, R., Nieder, R., Richter, J., Fan, X., Zhu, Z., Roelcke, M., 2006.  
16 Calibration of a simple method for determining ammonia volatilization in field-  
17 comparative measurements in Henan Province in China. *Nutrient Cycling in*  
18 *Agroecosystems* 74, 259-273.

19 Pearson, J., Stewart, G.R., 1993. The deposition of atmospheric ammonia and its effect  
20 on plants, *Tansley Review* 56. *New Phytologist* 125, 283-205.

21 Petersen, J., 1996. Fertilization of spring barley by combination of pig slurry and  
22 mineral nitrogen fertilizer. *Journal of Agricultural Science* 127, 151-159.

23 Pozzi, C., Halvorson, A.D., Follett, R.F., Rodrigues, B.j., Poliodoro, J.C., Urquiaga, S.,  
24 2012. Nitrogen source effects on ammonia volatilization as measured with semi-  
25 static chambers. *Agronomy Journal* 104, 1595-1603.

1 Reidy, B., Dämmgen, U., Döhler, H., Eurich-Menden, B., Van-Evert, F.K., Hutchings,  
2 N.J., Luesink, H.H., Menzi, H., Misselbrook, T.H., Monteny, G.J., Webb, J., 2008.  
3 Comparison of models used for national agricultural ammonia emissions  
4 inventories in Europe: liquid manure systems. *Atmospheric Environment* 42,  
5 3452-3464.

6 Rochette, P., Angers, D.A., Chantigny, M.H., MacDonald, J.D., Gasser, M.O.,  
7 Bertrand, N., 2009. Reducing ammonia volatilization in a no till soil by  
8 incorporating urea and pig slurry in shallow bands. *Nutrient Cycling in*  
9 *Agroecosystems* 84, 71-80.

10 Sanz, A., Misselbrook, T., Sanz, M.J., Vallejo, A., 2010. Use of an inverse dispersion  
11 technique for estimating ammonia emission from surface-applied slurry.  
12 *Atmospheric Environment* 44, 999-1002.

13 SAS Institute, 1999-2001. SAS/TAT. Software V 8.2. SAS Institute Inc, Cary.

14 Sieling, K., Schröder, H., Hanus, H., 1998. Yield, N uptake, and apparent N-use  
15 efficiency of winter wheat and winter barley grown in different cropping systems.  
16 *Journal of Agricultural Science* 131, 375-387.

17 Sintermann, J., Neftel, A., Ammann, C., Häni, C., Hensen, A., Loubet, B., Flechard,  
18 C.R., 2011. Are ammonia emissions from field-applied slurry substantially over-  
19 estimated in European emission inventories?. *Biogeosciences Discussions* 8,  
20 10069-10118.

21 Sheppard, S.C., Bittman, S., 2013. Estimated net application of ammoniacal and  
22 organic N from manure, and potential for mitigating losses of ammonia in Canada.  
23 *Agriculture Ecosystems and Environment* 171, 90-102.

1 Smith, E., Gordon, R., Bourque, C., Campbell, A., 2008. Management strategies to  
2 simultaneously reduce ammonia, nitrous oxide and odour emissions from surface-  
3 applied swine manure. *Canadian Journal of Soil Science* 88, 571-584.

4 Soil Survey Staff., 1999. *Soil taxonomy, a basic system of soil classification for making*  
5 *and interpreting soil surveys*, 2<sup>nd</sup> ed. United States Department of Agriculture.  
6 Natural Resources Conservation service. Agriculture Handbook n° 436. US  
7 Government Printing, Washington.

8 Sommer, S.G., Friis, E., Bach, E., Schjorring, J.K., 1997. Ammonia volatilization from  
9 pig slurry applied with trail hoses or broadcast to winter wheat: effects of crop  
10 developmental stage, microclimate, and leaf ammonia absorption. *Journal of*  
11 *Environmental Quality* 26, 1153-1160.

12 Sommer, S.G., Générmont, S., Cellier, P., Hutching, N.J., Olesen, J.E., Morvan, T.,  
13 2003. Processes controlling ammonia emission from livestock slurry in the field.  
14 *European Journal of Agronomy* 19, 465-486.

15 Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure  
16 and its reduction (invited paper). *European Journal of Agronomy* 15, 1-15.

17 Sommer, S.G., Jensen, L.S., Clausen, S.B., Sogaard, H.T., 2006. Ammonia  
18 volatilization from surface-applied livestock slurry as affected by slurry  
19 composition and slurry infiltration depth. *Journal of Agricultural Science* 144,  
20 229-235.

21 Sommer, S.G., Olesen J.E., Christensen, B.T., 1991. Effects of temperature, wind  
22 speed and air humidity on ammonia volatilization from surface applied cattle  
23 slurry. *Journal of Agricultural Science* 117, 91-100.

24 Sommer, S.G., Schjoerring, J.K., Denmead, O.T., 2004. Ammonia emission from  
25 mineral fertilizers and fertilized crops. *Advances in Agronomy* 82, 557-621.

1 Søgaard, H.T., Sommer, S.G., Hutchings, N.J., Huijsmans, J.F.M., Bussink, D.W.,  
2 Nicholson, F. 2002. Ammonia volatilization from field-applied animal slurry - the  
3 ALFAM model. *Atmospheric Environment* 36, 3309-3319.

4 Sørensen, P., Amato, M., 2002. Remineralisation and residual effects of N after  
5 application of pig slurry to soil. *European Journal of Agronomy* 16, 81-95.

6 Teira-Esmatges, M.R., Flotats, X., 2003. A method for livestock waste management  
7 planning in NE Spain. *Waste Management* 23, 917-932.

8 Thompson, R.B., Pain, B.F., Lockeyer, D.R., 1990. Ammonia volatilization from cattle  
9 slurry following surface application to grassland. I. Influence of mechanical  
10 separation, changes in chemical composition during volatilization and the presence  
11 of the grass swards. *Plant and Soil* 125, 109-127.

12 Thompson, R.B., Meisinger, J.J., 2002. Factors affecting ammonia volatilization from  
13 land-applied cattle slurry in the mid-atlantic region. *Journal of Environmental*  
14 *Quality* 31, 1329-1338.

15 Vogeler, I., 2009. Effect of long-term wastewater application on physical soil  
16 properties. *Water Air and Soil Pollution* 196, 385-392.

17 Wallach, R., Ben-Arie, O., Graber, E.R., 2005. Soil water repellency induced by long-  
18 term irrigation with treated sewage effluent. *Journal of Environmental Quality* 34,  
19 1910-1920.

20 Yagüe, M.R., Bosch-Serra, A.D., Boixadera, J. 2012. Measurement and estimation of  
21 the fertiliser value of pig slurry by physicochemical models: usefulness and  
22 constraints. *Biosystems Engineering* 111, 206-216.

23  
24

1 **Legends to Figures**

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

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

7 **Figure 3.** Cumulative ammonia volatilization ( $\text{kg NH}_3\text{-N ha}^{-1}$ ) after field fertilizer  
8 application (slurry or mineral fertilizer) and ammonia losses as percentage of the total  
9 ammonium nitrogen applied (TAN) at winter cereal tillering (T), during the first (A),  
10 second (B), and third (C) cropping seasons. Theoretical applied doses were: T-2M (30  
11  $\text{kg NH}_4\text{-N ha}^{-1}$  as ammonium nitrate), T-3M (45  $\text{kg NH}_4\text{-N ha}^{-1}$  as ammonium nitrate),  
12 T-1PS (20  $\text{t ha}^{-1}$ , slurry from fattening pigs), T-2PS (40  $\text{t ha}^{-1}$ , slurry from fattening  
13 pigs), T-4PS<sup>S</sup> (90  $\text{t ha}^{-1}$ , slurry from sows). The application rates in terms of  $\text{NH}_4^+\text{-N}$   
14 and total-N are described in Table 2. For each cropping season and within columns,  
15 means followed by the same letter are not significantly different according to Duncan's  
16 Multiple Range Test ( $\alpha=0.05$ )

17

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

3

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

4 <sup>a</sup> Tmean: mean air temperature; Tmin: minimum air temperature; Tmax: maximum air temperature.

5 <sup>b</sup>SWC: soil water content (w/w) in the first 30 cm depth. At field capacity equals 27.1% (w/w).

- 1 **Table 2.** Goals of the different ammonia volatilization measurements<sup>a</sup>. Specific characteristics of fertilization strategies were: type of fertilizer
- 2 (slurry/mineral), application rate and timing (sowing/cereal tillering). Data of winter cereal yield biomass and N efficiency is also provided.
- 3

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

1 <sup>a</sup> Grey background colour indicates when and where measurements of NH<sub>3</sub> losses were done. Initial measure date coincides with fertilizer application (at sowing or/and at  
2 tillering).

3 <sup>b</sup> S-: Measurements of NH<sub>3</sub> volatilization at sowing; T-: Measurements of NH<sub>3</sub> volatilization at tillering, S-/T-: Measurements of NH<sub>3</sub> volatilization at sowing and at tillering.

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

6 <sup>d</sup> DM: slurry dry matter content expressed as a percentage.

7 <sup>e</sup> 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  
8 ammonium applied.

9

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

Aim of the assessment	Timing of measurement <sup>a</sup> - Fertilization (rate and type) <sup>b</sup>	Fertilization at sowing		Fertilization at tillering		Ammonia volatilization at tillering	
		Rate <sup>b</sup>	NH <sub>4</sub> <sup>+</sup> -N <sup>c</sup> (kg ha <sup>-1</sup> )	Rate <sup>b</sup>	NH <sub>4</sub> <sup>+</sup> -N <sup>c</sup> (kg ha <sup>-1</sup> )	NH <sub>3</sub> -N (kg ha <sup>-1</sup> ) <sup>f</sup>	% of TAN <sup>d</sup> applied
<i>Influence of slurry applied at sowing on NH<sub>3</sub> losses at tillering</i>	T-1PS	2PS	110 (165)	1PS	72 (120)	7.4 $\pm$ 1.3	10.3 $\pm$ 1.8
	T-1PS	-	-	1PS	72 (120)	5.3 $\pm$ 1.0	7.2 $\pm$ 1.4
	<b>Significance</b>					<b>NS</b>	<b>NS</b>
<i>sidedressing</i>	T-3PS	2PS	108 (161)	3PS	242 (365)	18.3 $\pm$ 5.1	7.6 $\pm$ 2.1
	T-3PS	-	-	3PS	242 (365)	15.1 $\pm$ 4.1	6.2 $\pm$ 1.7
	<b>Significance</b>					<b>NS</b>	<b>NS</b>
<i>sidedressing</i>	T-2M	1PS	56 (86)	2M	30 (60)	4.5 $\pm$ 1.5	15.2 $\pm$ 5.0
	T-2M	2PS	124 (186)	2M	30 (60)	5.1 $\pm$ 3.5	17.1 $\pm$ 11.6
	<b>Significance</b>					<b>NS</b>	<b>NS</b>

4 NS: Non significant (p>0.05).

5 <sup>a</sup> T-: Fertilization applied at cereal tillering, when measurements of NH<sub>3</sub> volatilization were done.

6 <sup>b</sup> 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)  
 7 dose of 20-22 t ha<sup>-1</sup> for slurries and 30 kg N ha<sup>-1</sup> for mineral treatments.

8 <sup>c</sup> Values in parenthesis are total N applied.

9 <sup>d</sup> TAN: total ammonium nitrogen.

10

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

Aim of the assessment	Fertilization at sowing (S-)		Ammonia volatilization at sowing	
	Rate <sup>a</sup>	NH <sub>4</sub> <sup>+</sup> -N <sup>b</sup> (kg ha <sup>-1</sup> )	NH <sub>3</sub> -N (kg ha <sup>-1</sup> )	% of TAN <sup>c</sup> applied
<i>Influence of sowing fertilization on NH<sub>3</sub> losses</i>	S-1PS	58 (95)	23.0 $\pm$ 3.9 BC	39.5 $\pm$ 6.7 B
	S-2PS	177 (249)	28.5 $\pm$ 1.5 AB	16.1 $\pm$ 0.8 C
	S-3PS	250 (422)	42.1 $\pm$ 5.3 A	16.9 $\pm$ 2.1 C
	S-1M	15 (30)	9.4 $\pm$ 0.8 C	62.6 $\pm$ 5.2 A
	<b>Significance</b>		*** <sup>†</sup>	***

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

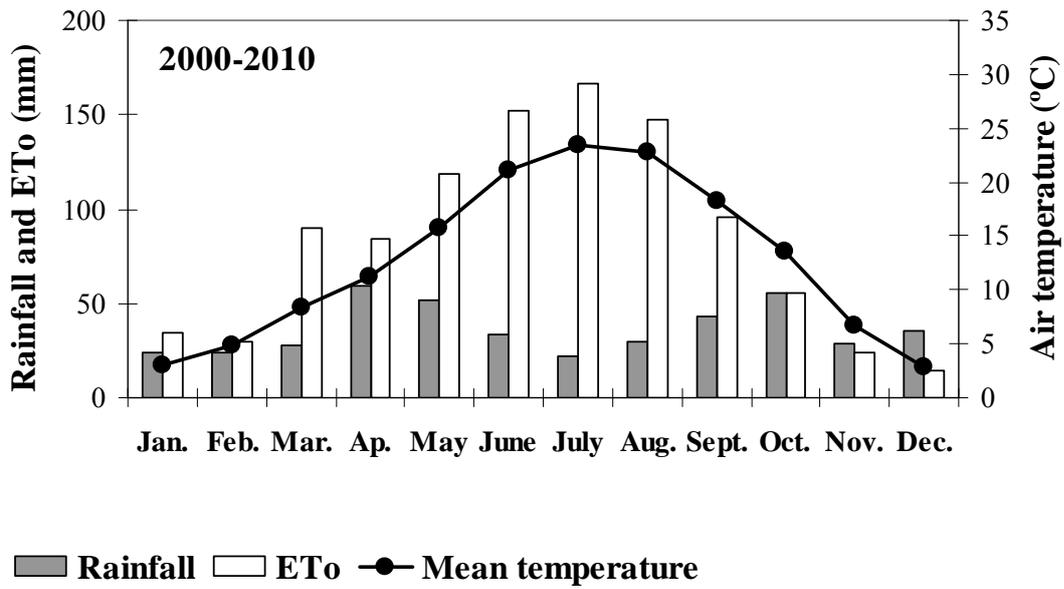
7 <sup>a</sup> PS: Pig slurry from fattening pigs; M: mineral fertilizer as ammonium nitrate (33.5% N). Numbers behind indicate the  
8 multiple of the rate from a minimum (approximate) dose of 20-22 t ha<sup>-1</sup> for slurries and 30 kg N ha<sup>-1</sup> for mineral treatments.

9 <sup>b</sup> Values in parenthesis are total N applied.

10 <sup>c</sup> TAN: total ammonium nitrogen.

11

1



**Fig. 1.**

2

1

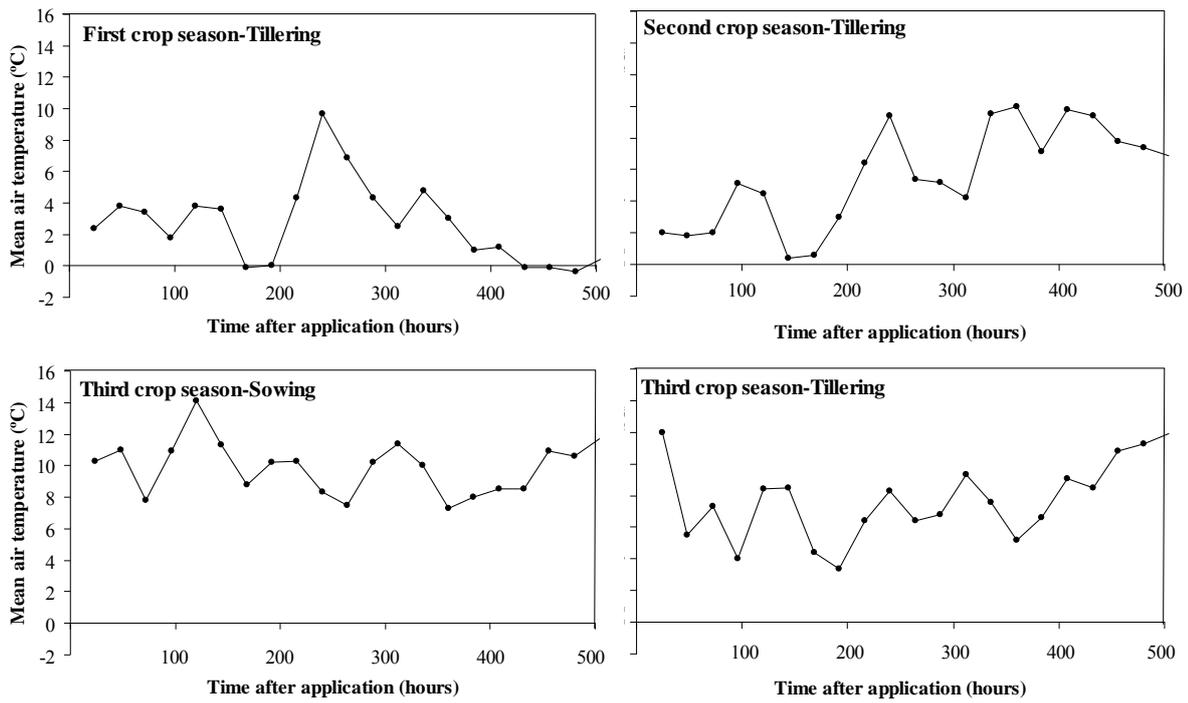


Fig. 2.

2

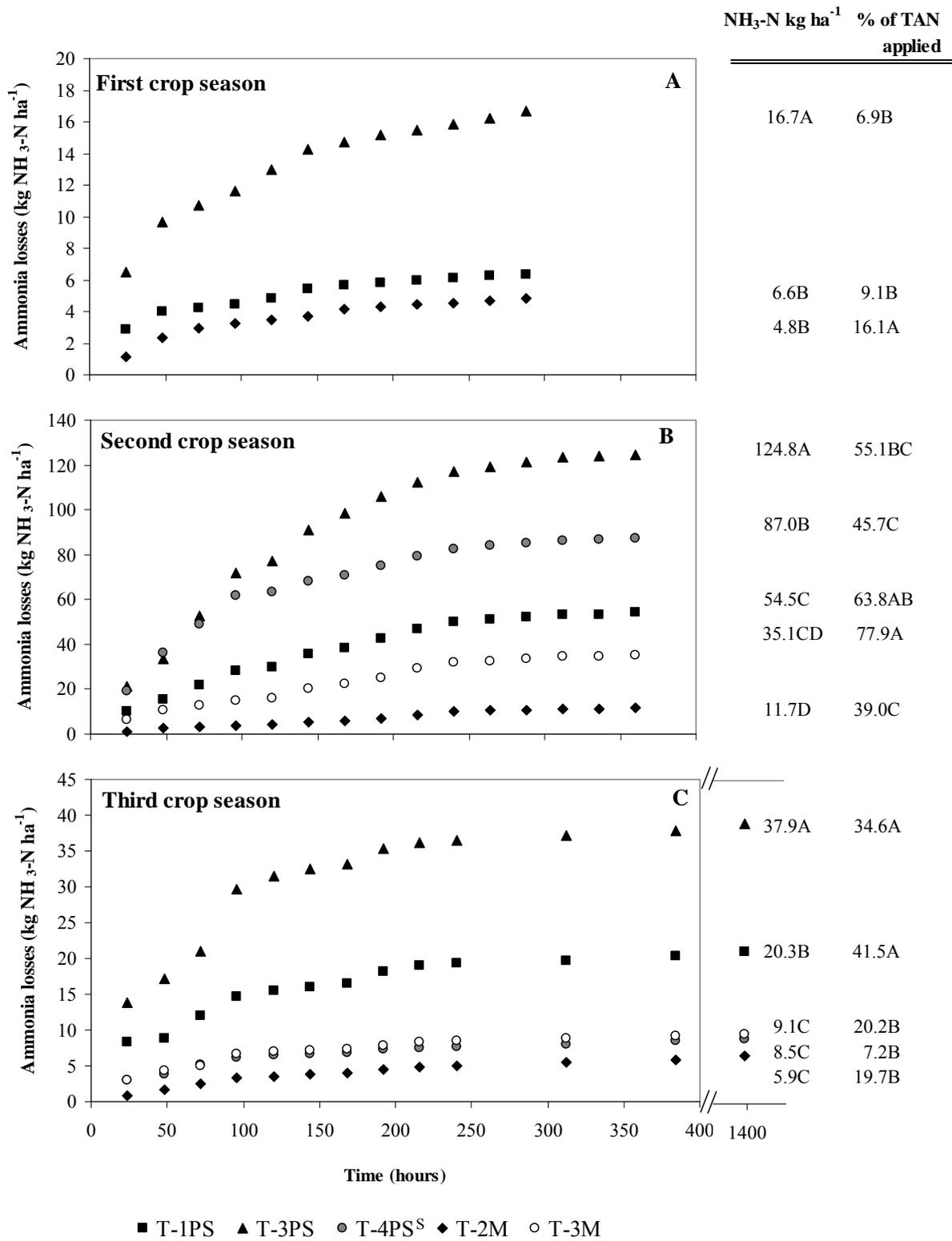


Fig. 3.