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5 **Effect of covers on swine slurry nitrogen conservation during storage in**
6 **Mediterranean conditions**

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25 Abbreviations: SS, swine slurry; GHG, greenhouse gas; TAN, Total ammoniacal

26 nitrogen, N, nitrogen, NH₄⁺, Ammonium

Effect of covers on swine slurry nitrogen conservation during storage in Mediterranean conditions

Abstract

Swine slurry (SS) is usually stored in open ponds in Mediterranean conditions before being applied to crop fields. During this storage nitrogen (N) is lost to the atmosphere mainly by ammonia volatilization diminishing the fertilizer value of the slurry and causing environmental problems. Permeable covers made from plant materials are low-cost alternatives to reduce these losses. This work evaluates the effectiveness of four composite permeable covers to conserve N during SS storage under semi-arid Mediterranean conditions. The covers, supported by a raschel mesh floating over the SS, were 3.5 and 7 cm thickness pine bark (PB3.5 and PB7), 8 cm thickness pruned wood (PW8), and 8 cm thickness cornstalk (CS8) and uncovered treatment (C). In the first four storage months, the pine bark and cornstalk covers conserved ammonium more effectively than the pruned wood and the control treatments (73 to 76% of the initial mass of SS ammonium conserved in the PB3.5, PB7 and CS8 treatments, against 51% and 39% in the PW8 and C treatments). In contrast, after ten months of SS storage all treatments behaved similarly (conservation of ammonium below 20%) due to cover's physical degradation. In general, the nutrient concentrations in SS and their ratios changed during storage and the C/N ratio at the end of the experiment was affected by the type of cover pointing to differential effects between covers. The pine bark and cornstalk covers were more effective than pruned wood to conserve N in SS stored for four months, a period that matches satisfactorily with the spring-summer months of typical SS storage in semi-arid Mediterranean conditions.

Key words: ammonium-N balance, composite-covers, Mediterranean climate, storage, swine slurry.

Introduction

Pork meat accounts for around 36% of global meat consumption, with 941 million heads of swine being farmed in 2008 (FAOSTAT 2010). Spain, with 26 million animals, is the sixth largest producer worldwide (FAOSTAT 2010) and the northeast of Spain (regions of Catalonia and Aragón) accounts for more than 44% of Spanish production. This area concentrates more than 11500 pig farms around 11.5 % of total in Spain (MAPA 2010) and at least the same number of open slurry storage facilities (slurry ponds). Agricultural slurry is invariably stored in ponds on farms before being spread to fields as fertilizer.

Animal farming is the principal source of ammonia release into the atmosphere, contributing approximately 50% of total ammonia emissions (Portejoie et al. 2003). Environmental factors, such as ambient temperature, wind velocity, and solar radiation, affect the rate of ammonia loss from open storage facilities (Sommer 1997; Portejoie et al. 2003). The semiarid Mediterranean climate provides favourable conditions for ammonia volatilization (high solar radiation and temperatures and high winds) and covered ponds could help to reduce this contamination. Besides environmental factors, the most important characteristics of the slurry affecting ammonia volatilization are the concentration of total ammoniacal nitrogen (TAN, the sum of NH_4^+ and free NH_3 in the slurry solution described by the Hendersen-Hasselbach equation), pH and slurry exposure area (Ni et al. 2000a; Webb et al. 2005). Swine slurry (SS) presents, on average, the highest NH_4^+ concentration amongst slurries (range 2 to 7 kg $\text{NH}_4^+\text{-N m}^{-3}$), with 75% of N being in the NH_4^+ form, and for that reason it is more susceptible to NH_3 losses than other slurries.

The loss of nitrogen (N) to the atmosphere from SS storage reduces the N content of the slurry and its value as fertilizer. Also, it may lead to adverse effects such as atmospheric deposition resulting in soil acidification or eutrophication of continental and coastal waters, and an increase in atmospheric greenhouse gases, especially nitrous oxide (N₂O) (Mosier et al. 1998; Amon et al. 2006; Petersen and Miller 2006; Sakamoto et al. 2006; Ndegwa et al. 2008).

Storage is a phase of manure management where cost-effective measures for conservation of N in the slurry can be achieved (Misselbrook et al. 2005). Several different strategies are available to mitigate ammonia emission during storage. The addition of additives and manipulation of the diets (McCrory and Hobbs 2001; Portejoie et al. 2002; Velthof et al. 2005) are potentially effective but expensive. The use of impermeable covers (floating film) has been shown to reduce ammonia emissions between 55% and 100% (Sommer 1993; Hörning et al. 1999; Portejoie et al. 2003), although their cost is also considerable. In contrast, permeable covers (perlite, oil, clay balls, geotextile), including “bio-covers” (cornstalks, sawdust, wood-shavings, rice-hulls, ground-corncoobs, grass-clippings), are less expensive but have the disadvantage that they do not last for long periods and are less effective at reducing the emissions of gases and odors. Composite covers, which attempt to combine the best aspects of several materials, could improve buoyance and durability (degradation) and help to conserve N in the slurry (VanderZaag et al. 2008).

Numerous studies have evaluated the effectiveness of permeable covers for mitigating ammonia losses. However, most studies have evaluated the covers only for short periods of time, and only a few (Barrington and Garcia Moreno 1995; Filson et al. 1996; Bundy 1997; Clanton et al. 2001; Bicudo et al. 2002, and 2004; Berg et al. 2006; Hudson et al. 2001, 2006a, and 2006b) have included periods longer than two months.

Furthermore, the majority of these studies were performed under laboratory conditions or in the field in the cooler months, and only Bicudo (2004) evaluated different geotextile covers in the field for the period April-October with more favourable conditions for ammonia volatilization, during two consecutive years.

In the semiarid Mediterranean conditions of the study area, SS is applied to agricultural fields mainly in two periods: February to March to fields where maize will be cropped, and end of August to November to fields to be cropped to winter cereals. There are no more opportunities for land SS applications, and SS accumulates in open storage containers during the rest of the year. Particularly important is the period between April and beginning of August when meteorological conditions are very favourable for ammonia volatilization (Ni et al. 2000b; Balsari et al. 2006; Griffin et al. 2007). A study of the efficacy and durability of composite bio-covers to conserve slurry N in the spring-summer period in semiarid Mediterranean conditions is notably lacking.

The objectives of this work were (i) to assess the effectiveness and durability of different composite covers (bio-covers embodied in a mesh) to conserve slurry N during the spring-summer storage period and (ii) to study the effects of these covers on the 10-month storage evolution of the slurry characteristics in Mediterranean conditions.

Materials and methods

Experimental design

The field study was conducted over the period 19 February to 23 December 2008 at the Agrifood Research and Technology Centre of Aragon's experimental farm (Zaragoza, Spain). Fifteen containers (height=1 m, surface area=1.2 m², volume=1200 L) were used as small-scale slurry storage. The containers were filled with SS in the farm

(1050–1068 L), transported to the experimental field and buried in the ground on 12 February 2008 to simulate the conditions of the ponds typically used in the pig farms. The containers remained hermetically closed until 19 February 2008, when covers were installed and the experiment was initiated.

Several types of low-cost materials were tested for buoyancy, resistance to permanent contact with SS, availability and acquisition price, and three of them were selected for the experiment: cherry and walnut pruned-wood fragments, dry cornstalk plants (the part that is left in the field after harvest), and burnt pine bark. The Ebro valley is characterized by high winds that can move the covers and reduce their effectiveness. Therefore, the covers were located within a double polypropylene raschel mesh tied to the containers with metallic pressure clamps. The pressure clamps were adjusted manually when necessary to assure that the covers remained floating over the slurry at all times.

Pruned wood was added at 13.3 kg per m² to form an 8-cm layer (PW8), cornstalks at 5.7 kg per m² to form an 8-cm layer (CS8) and pine bark at 8.3 and 16.6 kg per m² to form 3.5- (PB3.5) and 7-cm (PB7) layers, respectively. A control treatment (C) with no cover was included as reference. The containers were buried in a band perpendicular to the predominant wind direction, and the five treatments (PW8, CS8, PB3.5, PB7, and C) were set up in the field in a randomized block design with three replications.

Meteorological conditions

The climate of the area is semiarid (Fig. 1) with high temperatures, low precipitation and high evapotranspiration (1982-2008 annual averages of 15.0 °C, 337 mm and 1090 mm FAO Penman-Monteith reference ET₀, respectively). During the study period (February to December 2008), precipitation (435 mm) was 37% and reference ET₀ was

7% higher than the historical averages. The Ebro valley is an area characterized by strong winds (Troen and Petersen 1989). During the study period, the daily average wind speed was 2.25 m s^{-1} and the maximum daily wind speed was 13.62 m s^{-1} (measured at 2 m above the soil surface).

Sampling and analytical procedures

The physicochemical characteristics of the swine slurry were characterized at the beginning (12 February 2008) of the experiment in a composite sample of five random samples. In addition, a composite sample for each of the 5 treatments consisting of equal volumes of the SS slurry sampled in each of the three replications was used for the characterization of the slurry at the end of the experiment (23 December 2008). These samples were analyzed for pH (potentiometry in a 1:5 dilution), electrical conductivity at $25 \text{ }^{\circ}\text{C}$, dry matter (gravimetry at $105 \text{ }^{\circ}\text{C}$), organic matter (calcination at $550 \text{ }^{\circ}\text{C}$), organic-N (Kjeldahl method), ammonium-N (modified Kjeldahl method) and phosphorus and potassium concentrations (wet acid digestion and Inductively Coupled Plasma analysis) (Table 1).

The height of SS in each container was measured at the beginning of the experiment on 19 February, then monthly on 17 March, 21 April, 27 May, 27 June, 31 July, and 28 August, and finally at the end of the experiment on 23 December 2008. At the same time, the SS in each container was sampled at three depths: 0.20, 0.40 and 0.60 m from the bottom of the containers, using a sampler for layered strata sludge (Eijkelkamp 12.42 multisampler, diameter 40 mm). The sampling was performed from top to bottom very slowly to avoid mixing between layers and modification of the slurry's characteristics. A 150-mL sample of SS was used for analytical determinations and the

remaining sample was returned to the containers on the same day to minimize modifications of SS volumes.

The samples taken on 19 February, 27 June and 23 December were analyzed separately for each depth. A composite sample consisting of an equal volume of the samples taken at each depth in each container was prepared for the rest of the sampling dates. Ammonium concentration using a Quantofix[®] volume-meter (Piccini and Bortone, 1991; Van Kessel et al., 1999) and density using a Proton nr 37711 densimeter were determined in each sample or composite sample. These methods were selected because they have enough precision for the objectives of the experiment and are easy to use in the field.

Data Analysis

The ammonium concentrations measured in the 19 February samples were taken as the initial ammonium concentration in each container as the average ammonium concentration ($1.81 \pm 0.09 \text{ kg NH}_4^+ \text{-N m}^{-3}$) did not differ significantly from the ammonium concentration measured in the 12 February slurry sample ($1.78 \text{ kg NH}_4^+ \text{-N m}^{-3}$).

The mass of ammonium in each container was calculated for each sampling date using Eq. 1, where ANM and ANC denote the mass and concentration of ammonium-N in the containers respectively, H is the height of the slurry in the container and S is the surface of the container (1.2 m^2).

$$\text{ANM}(\text{kgNH}_4^+ - \text{N}) = \text{ANC}(\text{kgNH}_4^+ - \text{N} \cdot \text{m}^{-3}) \cdot \text{H}(\text{m}) \cdot \text{S}(\text{m}^2) \quad (1)$$

The average ammonium losses in each container between any two sampling dates were estimated as the difference in ammonium mass between the two dates, and was expressed as ammonium loss rate (ALR, $\text{gNH}_4^+ \text{ m}^{-2} \text{ day}^{-1}$) dividing by the area of the container

($S=1.2 \text{ m}^2$) and the number of days elapsed between the two sampling dates ($D_{ji} = \text{date } j - \text{date } i$) (Eq. 2).

$$ALR (\text{g} \cdot \text{NH}_4^+ - \text{N} \cdot \text{m}^{-2} \cdot \text{day}^{-1}) = \frac{ANM (\text{g} \text{ NH}_4^+ - \text{N})_{\text{date } j} - ANM (\text{g} \text{ NH}_4^+ - \text{N})_{\text{date } i}}{S (\text{m}^2) \cdot D_{ji} (\text{day})} \quad (2)$$

The effect of the covers on the height of SS and its ammonium concentration and mass at the different sampling dates was analysed as repeated measured data using the PROC MIXED procedure in SAS (Little et al. 1998; Daudén et al. 2004; Yagüe and Quílez 2010). The first order autoregressive structure within treatments and a random effect between treatments resulted as best among the covariance structures tested (compound symmetric, unstructured and first order autoregressive + random effect) on the basis of the Schwarz Bayesian criterion. There was no significant interaction between treatments and sampling times for any of the three variables. The effects of the covers on the rate of ammonium loss and the mass of ammonium conserved in the SS containers after 4 and 10 months storage were evaluated by analysis of variance using the GLM procedure. Treatments were compared using the Tukey mean separation procedure ($p \leq 0.05$).

Relationships between variables, when necessary, were established by regression analysis ($p \leq 0.05$). Statistical analysis were performed with the statistical package SAS (SAS Institute 1999-2001).

Results

Laboratory and field ammonium concentrations

The physicochemical characteristics of the SS used in the experiment (initial sample) and the characteristics of the slurry after storage for 10 months in the five treatments are shown in Table 1.

The SS ammonium concentrations determined in the field by Quantofix[®] method and in the laboratory (modified Kjeldahl) were significantly related ($p < 0.001$), but field concentrations were lower than lab concentrations, as shown by the linear regression (Eq. 3) with an slope that did not differ from unity but with an intercept significantly different from zero.

$$NH_4 - N \text{ (kg m}^{-3}, \text{Quantofix)} = -0.08 + 0.99 \cdot NH_4 - N \text{ (kg m}^{-3}, \text{Laboratory)}, \quad R^2 = 0.99$$

(3)

Even though Quantofix[®] is a reliable method for determining ammonium-N concentration (Piccini and Bortone 1991; Van Kessel et al. 1999; Van Kessel and Reeves 2000; Monge et al. 2001; and Irañeta and Abaigar 2002), it gave a biased estimation of ammonium concentrations. Thus, the mass of ammonium in the SS stored in the containers was slightly underestimated. However, we did not transform Quantofix[®] values into laboratory values as we were interested in the comparison between treatments and the hypothesis tests are not affected.

Changes in SS heigth, ammonium concentration and mass during storage

Ammonium concentrations progressively decreased in all treatments along the February to December study period (Table 2). After four storage months, (27 June), ammonium concentrations in the PB3.5, PB7 and CS8 treatments were higher than those in the uncovered (Control) and PW8 treatments.

The heigth of the SS in the containers also decreased along the experiment, with the largest decrease being observed during the summer months due to the high evaporative demand (Table 3). After ten storage months, the uncovered treatment showed the highest SS height decrease (55% of the initial depth), whereas in the other four

treatments the SS height decreased varied between 27% (PB7) and 41% (CS8) (Table 3).

The ammonium mass in the SS stored in the containers decreased with time faster than the SS height. After four storage months (27 June), ammonium N conservation were lowest in the uncovered treatment (39%), followed by PW8 (51%) and CS8, PB3.5 and PB7 (73–76%). After ten storage months (23 December) ammonium conserved ranged between 0 % and 19%, indicating an important decrease in the SS fertilization value and a relevant atmospheric pollution during storage (Table 4).

The rate of ammonium loss was highest in the period between May and August due to high temperatures and evapotranspiration rates typical of this Mediterranean region (Fig. 2). A significant interaction between treatment and time period was observed. Ammonium loss in the uncovered treatment was maximum in May, reaching almost 12 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$, and decreased afterwards due to decreased SS ammonium concentrations. The PW8 treatment did not differ from the uncovered treatment at any time, with ammonium losses ranging from 3.0 to 9.6 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$ in the period 19 February to 31 August. Ammonium losses rate in the two pine bark (PB) treatments reached the maximum in July (10.2 and 15.4 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$ for PB7 and PB3.5 respectively; Fig. 2), whereas losses in cornstalk treatments were low during the first three months (<3 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$), increased to 9.0 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$ in July and reached the peak of 15.2 g $\text{NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$ in August (Fig. 2).

Variations in SS ammonium concentrations and densities at different layers

Density of SS decreased with time from $1010 \pm 0.65 \text{ g L}^{-1}$ on 19 February to $1007 \pm 1.16 \text{ g L}^{-1}$ on 27 June and to $1005 \pm 1.64 \text{ g L}^{-1}$ on 23 December. No significant differences in

density were detected between layers or between cover treatments in any of the three sampling dates.

Ammonium concentrations were not significantly different between the different layers under each cover on the three sampling dates (Table 5).

Discussion

The containers used in this study for SS storage had a limited depth (1 m) and volume of SS (1200 L), which may lead to differences in gas generation, diffusion and emission processes compared with larger on-farm storage facilities. In addition, the experiment was performed under static conditions—no slurry was added after the start of the experiment—, whereas the SS is periodically poured into the storage facilities under real farm conditions. Despite these constraints, it was assumed that the behaviour of the stored SS under the tested covers will resemble the behaviour of the top 1 m SS in a farm pond, the layer most affected by the environmental conditions (Muck et al. 1984; Olesen and Sommer 1993).

To evaluate the effects of the covers on N conservation in SS, the changes in concentration and mass of ammonium were analyzed and changes in the amount of organic N were not analyzed. The transformation from organic N to ammonium N in open slurry storage has not been commonly considered in studies quantifying ammonia losses from slurry storages (Hutchings et al. 1996; Rotz et al. 2006). Following Dahlin et al. (2005) aerobic storage conditions lead to a stabilization of N in organically bound forms, under the assumption that the organic N entering storage was that excreted in faces, and no loss or transformation would occur prior to storage. Based on Patni and Jui (1991) results, the mass of ammonium-N produced by organic N mineralization was

estimated as negligible ($< 12\%$) in comparison to the amount of ammonium initially present in SS.

The initial ammonium concentration in the SS tested was low for a fattening pig farm (Table 1), since the usual range in the study area is about $4\text{--}7 \text{ kg NH}_4^+\text{-N m}^{-3}$ (Orús 1996; Monge et al. 2001) and phosphorus and potassium concentrations were also low. The N/K₂O ratio in SS (1:0.67) is in the range found in fattening farms of northern Spain (Irañeta and Abaigar 2002; Orús 1996), suggesting that SS is diluted due to inefficient water management.

Ammonium losses during storage

Average ammonia losses from the uncovered treatment in the period 19 February to 28 August was $6.7 \text{ g NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$ ($8.1 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$). Most of these losses are hypothetically due to ammonia volatilization, as N losses due to emission of N oxides is likely to be very low (Berg et al. 2006; Loyon et al. 2007)). Under the precedent hypothesis, the rate of ammonia emission was higher than that measured in other studies, despite its low initial ammonium concentration. Balsari et al. (2006) reported ammonia losses of $0.98\text{--}2.68 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$ and the UK Environmental Agency (2008) $3.84 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$, both from uncovered farm ponds. In the case of stirred slurry, where convective transport of ammonium to the surface layers is active, Sommer et al. (1993) reported volatilization losses of $3\text{--}5 \text{ g NH}_3\text{-N m}^{-2} \text{ day}^{-1}$. Smith et al. (2007) found higher ammonia losses from dairy slurry in small-scale tanks, similar to those used in this experiment, than from farm ponds. These authors concluded that ammonia losses measured in small-scale tanks are not representative of real slurry storages, although they were satisfactory for comparative studies.

320 The degradation of the covers with time, due to its contact with the slurry, affected their
321 buoyancy (qualitative visual detection) and diminished their efficacy (Fig. 2). The
322 degradation of each cover is visualized from the rate of ammonium losses at each date.
323 Thus, both PB covers lost effectiveness (Fig. 2) between 27 June and 31 July (4 to 5
324 months), and CS8 between 31 July and 28 August (5 and 6 months). In the case of the
325 PW8 cover, a physical degradation was observed from the beginning of the experiment.
326 The durability of the composite bio-covers agrees with that obtained under other
327 climatic conditions. Hudson et al. (2006a) found that a straw cover started to deteriorate
328 physically after only a few weeks, and proposed a five-month life span for this type of
329 cover. Similarly, Clanton et al. (2001) and Burns (2007) found that some permeable
330 covers, such as those made with blown straw or cornstalks, lasted for two to six months
331 depending on weather and SS thickness (the thicker the slurry, the longer the floating of
332 the straw).
333 Hudson et al. (2006a, 2006b) and Burns (2007) observed that covers form a physical
334 barrier to ammonia diffusion, and they may adsorb the ammonia volatilized from the
335 slurry surface, which also reduces volatilization (Portejoie et al. 2003). The amount of
336 N retained in the covers was not evaluated in our experiment.
337 Ammonium losses under the different covers were compared over a four-month period
338 because the storage ponds in the region are required to have a minimum storage volume
339 equivalent to the SS produced in four months. Furthermore, the initial low SS
340 ammonium concentration did not allow comparisons over longer timescales as the
341 ammonium concentration dropped below $1 \text{ kg NH}_4\text{-N m}^{-3}$ in some containers after the
342 first four months. This is also a consequence of the experimental static conditions, with
343 no further SS being added during the experimental period. The average ammonium
344 losses in the period 19 February to 27 June (4 months) was 60% lower for PB3.5, PB7

and CS8 than for the Control and PW8, indicating that the former three covers were more effective to conserve N than Control, on the basis of the minimum four-month storage period required by the current legislation in this region (Table 4).

Ammonium concentration and density at different SS depths

It is reasonable to assume that SS consists of discrete layers with different ammonia-generation rates. Ammonia is generated in each slurry layer and diffuses to the top surface where it is constantly released into the atmosphere (Portejoie et al. 2003). Three basic processes are therefore involved in ammonia emission from SS ponds: generation, diffusion and surface emission (Zhang and Day 1996; Ni et al. 2000b).

The ammonium concentrations in this study were found to be the same on 27 June and 23 December in the three layers sampled in each treatment, (the top layer maintained a systematically lower concentration, although not statistically significant) thus implying rapid ammonia diffusion (Table 5). All covers acted as physical barriers that stopped or reduced air movement over the slurry's surface, increasing the surface's resistance to ammonia volatilization and reducing mass transfer (Portejoie et al. 2003).

Effect of covers on slurry characteristics after ten months' storage

Suspended solids and organic matter move downwards during settling, resulting in a compacted layer with higher solids and organic contents at the bottom of the containers (Portejoie et al. 2003). Thus, phosphorus decreased by between 91% and 97%, organic-N decreased by between 69% and 85% and organic matter decreased by between 84% and 87% in SS, due to sedimentation with the solid phase (Table 1).

At the end of the experiment, the pH in the four covered treatments ranged between 8.3 and 8.4, similar to the initial slurry pH (8.4), while the pH in the Control was 8.7, higher

than in the other treatments. A hypothesis test could not be set, as only a composite sample of the three replications was analyzed at the end of the experiment. The increase of pH observed in the Control could indicate that, in addition to reduced mass transfer, the covers also could reduce ammonia emissions by preventing an increase of the slurry's pH during storage (Ni et al. 2000b).

The C/N ratio of the slurry was 14.3 at the beginning of the experiment and did not change significantly in treatments PB3.5 and PB7 after 10 months storage, indicating that carbon losses were proportional to ammonium losses in the two PB treatments. However, the C/N ratio in the other three treatments decreased by half ($C/N_{\text{Control}} = 7.3$, $C/N_{\text{PW8}} = 8.5$ and $C/N_{\text{CS8}} = 7.0$), indicating that carbon losses were approximately twice the ammonium losses. Treatments PB3.5 and PB7 were more effective at reducing both ammonium and carbon losses (presumably as CO_2 and CH_4 ; Patni and Jui 1987; Amon et al. 2008). It is therefore important to evaluate ammonia, nitrous oxide, methane and CO_2 emissions simultaneously, as abatement activities aimed at reducing the emission of one of these gases may have an effect on the emissions of the others.

Potassium concentrations of the SS increased during storage by between 1.7 and 3 times the initial concentration (Table 1). This increase was associated with evaporation of water, as the initial to final K_2O concentration ratio was strongly linked to the ratio of final and initial slurry volumes.

The variation of P and K concentrations with respect to ammonium concentration in SS during storage has to be taken into account when using SS as a fertilizer. Some farmers measure the NH_4^+ content of slurry in order to adjust the application rate to the crops' N needs (N criteria). If the slurry is stored for a long period of time and is not mixed before being pumped for field applications, the crops could be over-fertilized in K and under-fertilized in P. However, if the slurry is stirred excessive amounts of both K and P

could be applied to the crops. This N/P/K imbalance between SS and crop requirements could restrict the use of SS in some crops. In addition, because transportation costs are based on SS volume, the economical viability of using SS as a total or partial substitute for mineral fertilizers comes into question.

Conclusions

The results of this study indicate that the swine slurry stored in open containers in Mediterranean semiarid conditions reduces significantly its fertilizer value during storage and emits important amounts of N to the atmosphere. The composite covers pine bark and cornstalk tested in this work were relatively effective for conserving N in the stored swine slurry for about four months, between 73 to 76% of initial ammonium N was conserved, a time period that will be sufficient for the spring-summer months, when the SS is usually stored in ponds. However, no one of the covers was effective for a period longer than 6 months. The length of the storage period and the cover material affect the slurry N and K concentrations and the ratio N/K and this effect should be taken into account when using the slurry as a fertilizer.

Perspectives and future research needs

In Mediterranean conditions, such as those found in the middle Ebro Valley (Spain), a substantial reduction in ammonium losses from swine slurry storage ponds should be achieved to comply with emission targets established in the UNECE Gothenburg Treaty (UNECE 1999) and to conserve the fertilizer value of the SS. The results of this study show that the use of certain composite covers is a good abatement strategy towards achieving emissions reduction. Future research in this area should therefore be aimed at testing and selection of new materials (foam, oil, or other low cost materials) that will

increase the useful life and will promote crust formation, and biologically active materials that will retain nitrogen and carbon. In addition, GHG emissions should be determined to assess the differential behaviour of cover materials in reducing the emissions of different GH gases.

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Figures v Tables

Figure 1. Monthly precipitation (P), mean air temperature (T) and reference ET (ET₀, FAO-Penman Monteith) for the 2008 experimental year and the 1982-2008 historical period

Figure 2. Ammonium mass (kg NH₄-N) measured at each sampling date and rate of ammonium loss (g NH₄-N m⁻² day⁻¹) in between two consecutive sampling dates in the control (C), pine bark thickness 3.5 cm (PB3.5), pine bark thickness 7 cm (PB7), prune wood (PW8), and cornstalk (CS8) treatments. Vertical segments represent one standard deviation of the three replicates

Table 1. Swine slurry physicochemical characteristics determined in the laboratory at the beginning (initial slurry, 19 February 2008) and end of the experiment (23 December 2008) in the control (C), pine bark with 3.5 cm (PB3.5) and 7 cm (PB7) thickness, and prune wood (PW8), and cornstalk (CS8) with 8 cm thickness treatments

Parameters	19 February 2008	23 December 2008				
	Initial Slurry	Control	PB3.5	PB7	PW8	CS8
pH	8.4	8.70	8.35	8.33	8.38	8.43
Electrical Conductivity, dS m ⁻¹	1.98§	14.30	10.99	11.34	11.03	12.06
Dry matter, kg DM Mg ⁻¹	30.36	15.17	10.19	8.74	10.53	10.94
Organic matter, kg OM Mg ⁻¹	20.16	3.23	2.99	2.54	2.56	2.29
Organic N, kg N Mg ⁻¹	0.71	0.22	0.11	0.12	0.15	0.16
Ammonium N, kg N Mg ⁻¹	1.82	0.10	0.41	0.63	0.32	0.31
Total N, kg N Mg ⁻¹	2.54	0.32	0.53	0.79	0.47	0.47
P ₂ O ₅ , kg Mg ⁻¹	1.63	0.14	0.04	0.06	0.11	0.09
K ₂ O, kg Mg ⁻¹	1.71	4.98	3.21	2.84	3.46	3.42
C/N	14.1	7.3	13.4	10.5	8.5	7.0

§ Measured in a 1:5 swine slurry:deionized water ratio

Table 2. Monthly and period (February to December) average swine slurry ammonium concentrations ($\text{kg NH}_4^+ \text{-N m}^{-3}$) measured in the control (C), pine bark thickness 3.5 cm (PB3.5), pine bark thickness 7 cm (PB7), prune wood (PW8), and cornstalk (CS8) treatments determined by Quantofix® method.

	19Feb.^a	17Mar.	21Apr.	27May	27Jun.	31Jul.	28Aug.	23Dec.
Control	1.73A	1.53B	1.53A	1.07B	0.78B	0.50C	0.30B	0.00C
PB3.5	1.63A	1.65AB	1.63A	1.53A	1.38A	0.83B	0.63AB	0.28AB
PB7	1.67A	1.60AB	1.62A	1.43A	1.34A	1.03AB	0.77A	0.43A
PW8	1.87A	1.63ABC	1.92A	1.30AB	1.04B	0.83B	0.50AB	0.18BC
CS8	1.81A	1.72A	1.92A	1.57A	1.41A	1.17A	0.63AB	0.27AB
Treat^b	NS	S	NS	S	S	S	S	S

^a Within each column, values followed by the same letter do not differ significantly at the 0.05 probability level

^b S: Significant and NS: No significant at the 0.05 probability level

Table 3. Average swine slurry heights (cm) measured in the control (C), pine bark thickness 3.5 cm (PB3.5), pine bark thickness 7 cm (PB7), prune wood (PW8), and cornstalk (CS8) treatments. Last column presents the percent decrease in swine slurry depths on 23 December 2008 relative to the initial values on 19 February 2008.

	19 Feb. ^a	17Mar.	21Apr.	27May	27Jun.	31Jul.	28Aug.	23Dec.	Decrease %
Control	87.5A	83.8B	81.3A	78.8 B	73.0B	57.7B	44.7C	39.3B	55
PB3.5	89.0A	85.8AB	83.8A	84.7AB	81.0A	71.3A	62.5AB	60.0A	33
PB7	88.5A	86.5A	84.0A	86.8A	83.7A	75.2A	68.5A	64.6A	27
PW8	87.7A	85.3AB	81.3A	83.8AB	78.7AB	68.7A	60.3AB	58.1A	34
CS8	87.8A	86.2A	83.0A	81.8AB	78.3AB	68.3A	58.0B	51.6AB	41
Treat^b	NS	S	NS	S	S	S	S	S	

^a Within each column, values followed by the same letter do not differ significantly at the 0.05 probability level

^b S: Significant and NS: No significant at the 0.05 probability level

610 **Table 4.** Average swine slurry ammonium mass (kg NH₄⁺-N) measured in 19 February
611 (initial date), 27 June (4 months' storage), and 23 December (10 months' storage) in the
612 control (C), pine bark thickness 3.5 cm (PB3.5), pine bark thickness 7 cm (PB7), prune
613 wood (PW8), and cornstalk (CS8) treatments. Mass of ammonium conserved (in % of
614 the initial mass) in each treatment during the February to June and February to
615 December periods, Ammonium concentrations were determined by Quantofix®
616 method.

	NH ₄ ⁺ mass (kg NH ₄ ⁺ -N)			NH ₄ ⁺ conserved (%)	
	19 Feb. ^a	27 Jun.	23 Dec.	Feb-June	Feb-Dec
Control	1.72	0.67B	0.00B	39	0
PB3.5	1.76	1.34A	0.20AB	76	11
PB7	1.79	1.35A	0.34A	75	19
PW8	1.96	0.99B	0.13AB	51	7
CS8	1.81	1.32A	0.17AB	73	9
Treat^b	NS	S	S	-	-

617

618 ^a Within each column, values followed by the same letter do not differ significantly at
619 the 0.05 probability level

620 ^b S: Significant and NS: No significant at the 0.05 probability level

621 **Table 5.** Average swine slurry densities and ammonium concentrations (by
622 Quantofix®) measured at three depths from the bottom of the containers in the control
623 (C), and pine bark thickness 7 cm (PB7) treatments in 19 February (initial date), 27 June
624 (4 months' storage) and 23 December (10 months' storage)

Treat	Depth m	19 February		27 June		23 December	
		Density g L ⁻¹	kg NH ₄ ⁺ -N m ⁻³	Density g L ⁻¹	kg NH ₄ ⁺ -N m ⁻³	Density g L ⁻¹	kg NH ₄ ⁺ -N m ⁻³
Control	0.20	1011	1.68	1006	0.77	1005	0.00
Control	0.40	1010	1.73	1007	0.77	-	-
Control	0.60	1010	1.72	1006	0.77	-	-
PB7	0.20	1011	1.67	1007	1.42	1006	0.47
PB7	0.40	1010	1.68	1007	1.37	1003	0.40
PB7	0.60	1010	1.72	1006	1.25	-	-

625