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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

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Mediterranean conditions

29 Abstract

30 Swine slurry (SS) is usually stored in open ponds in Mediterranean conditions before 31 being applied to crop fields. During this storage nitrogen (N) is lost to the atmosphere 32 mainly by ammonia volatilization diminishing the fertilizer value of the slurry and 33 causing environmental problems. Permeable covers made from plant materials are low-34 cost alternatives to reduce these losses. This work evaluates the effectiveness of four 35 composite permeable covers to conserve N during SS storage under semi-arid 36 Mediterranean conditions. The covers, supported by a raschel mesh floating over the 37 SS, were 3.5 and 7 cm thickness pine bark (PB3.5 and PB7), 8 cm thickness pruned 38 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 39 40 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 41 42 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 43 44 physical degradation. In general, the nutrient concentrations in SS and their ratios 45 changed during storage and the C/N ratio at the end of the experiment was affected by 46 the type of cover pointing to differential effects between covers. The pine bark and 47 cornstalk covers were more effective than pruned wood to conserve N in SS stored for 48 four months, a period that matches satisfactorily with the spring-summer months of 49 typical SS storage in semi-arid Mediterranean conditions.

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

52 Introduction

53

54 Pork meat accounts for around 36% of global meat consumption, with 941 million 55 heads of swine being farmed in 2008 (FAOSTAT 2010). Spain, with 26 million 56 animals, is the sixth largest producer worldwide (FAOSTAT 2010) and the northeast of 57 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 58 59 Spain (MAPA 2010) and at least the same number of open slurry storage facilities 60 (slurry ponds). Agricultural slurry is invariably stored in ponds on farms before being 61 spread to fields as fertilizer.

62 Animal farming is the principal source of ammonia release into the atmosphere, 63 contributing approximately 50% of total ammonia emissions (Portejoie et al. 2003). 64 Environmental factors, such as ambient temperature, wind velocity, and solar radiation, 65 affect the rate of ammonia loss from open storage facilities (Sommer 1997; Portejoie et 66 al. 2003). The semiarid Mediterranean climate provides favourable conditions for 67 ammonia volatilization (high solar radiation and temperatures and high winds) and 68 covered ponds could help to reduce this contamination. Besides environmental factors, 69 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 70 71 slurry solution described by the Hendersen-Hasselbach equation), pH and slurry 72 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 NH_4^+ -N m⁻³), 73 with 75% of N being in the NH_4^+ form, and for that reason it is more susceptible to NH_3 74 75 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).

82 Storage is a phase of manure management where cost-effective measures for 83 conservation of N in the slurry can be achieved (Misselbrook et al. 2005). Several 84 different strategies are available to mitigate ammonia emission during storage. The 85 addition of additives and manipulation of the diets (McCrory and Hobbs 2001; Portejoie 86 et al. 2002; Velthof et al. 2005) are potentially effective but expensive. The use of 87 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), 88 89 although their cost is also considerable. In contrast, permeable covers (perlite, oil, clay 90 balls, geotextile), including "bio-covers" (cornstalks, sawdust, wood-shavings, rice-91 hulls, ground-corncobs, grass-clippings), are less expensive but have the disadvantage 92 that they do not last for long periods and are less effective at reducing the emissions of 93 gases and odors. Composite covers, which attempt to combine the best aspects of 94 several materials, could improve buoyance and durability (degradation) and help to 95 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.

105 In the semiarid Mediterranean conditions of the study area, SS is applied to agricultural 106 fields mainly in two periods: February to March to fields where maize will be cropped, 107 and end of August to November to fields to be cropped to winter cereals. There are no 108 more opportunities for land SS applications, and SS accumulates in open storage 109 containers during the rest of the year. Particularly important is the period between April 110 and beginning of August when meteorological conditions are very favourable for 111 ammonia volatilization (Ni et al. 2000b; Balsari et al. 2006; Griffin et al. 2007). A study 112 of the efficacy and durability of composite bio-covers to conserve slurry N in the 113 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 10month storage evolution of the slurry characteristics in Mediterranean conditions.

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119 Materials and methods

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121 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.

130 Several types of low-cost materials were tested for buoyancy, resistance to permanent 131 contact with SS, availability and acquisition price, and three of them were selected for 132 the experiment: cherry and walnut pruned-wood fragments, dry cornstalk plants (the 133 part that is left in the field after harvest), and burnt pine bark. The Ebro valley is 134 characterized by high winds that can move the covers and reduce their effectiveness. 135 Therefore, the covers were located within a double polypropylene raschel mesh tied to 136 the containers with metallic pressure clamps. The pressure clamps were adjusted 137 manually when necessary to assure that the covers remained floating over the slurry at 138 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.

145

146 *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 ET_0 , respectively). During the study period (February to December 2008), precipitation (435 mm) was 37% and reference ET_0 was 151 7% higher than the historical averages. The Ebro valley is an area characterized by 152 strong winds (Troen and Petersen 1989). During the study period, the daily average 153 wind speed was 2.25 m s⁻¹ and the maximum daily wind speed was 13.62 m s⁻¹ 154 (measured at 2 m above the soil surface).

155

156 Sampling and analytical procedures

157 The physicochemical characteristics of the swine slurry were characterized at the 158 beginning (12 February 2008) of the experiment in a composite sample of five random 159 samples. In addition, a composite sample for each of the 5 treatments consisting of 160 equal volumes of the SS slurry sampled in each of the three replications was used for 161 the characterization of the slurry at the end of the experiment (23 December 2008). 162 These samples were analyzed for pH (potentiometry in a 1:5 dilution), electrical 163 conductivity at 25 °C, dry matter (gravimetry at 105 °C), organic matter (calcination at 164 550 °C), organic-N (Kjeldahl method), ammonium-N (modified Kjeldahl method) and 165 phosphorus and potassium concentrations (wet acid digestion and Inductively Coupled 166 Plasma analysis) (Table 1).

167 The height of SS in each container was measured at the beginning of the experiment on 168 19 February, then monthly on 17 March, 21 April, 27 May, 27 June, 31 July, and 28 169 August, and finally at the end of the experiment on 23 December 2008. At the same 170 time, the SS in each container was sampled at three depths: 0.20, 0.40 and 0.60 m from 171 the bottom of the containers, using a sampler for layered strata sludge (Eijkelkamp 172 12.42 multisampler, diameter 40 mm). The sampling was performed from top to bottom 173 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 174

175 remaining sample was returned to the containers on the same day to minimize176 modifications of SS volumes.

177 The samples taken on 19 February, 27 June and 23 December were analyzed separately 178 for each depth. A composite sample consisting of an equal volume of the samples taken 179 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, 180 181 1991; Van Kessel et al., 1999) and density using a Proton nr 37711 densimeter were 182 determined in each sample or composite sample. These methods were selected because 183 they have enough precision for the objectives of the experiment and are easy to use in 184 the field.

185

186 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 $(1.81\pm0.09 \text{ kg NH}_4^+\text{-N m}^-\text{-3})$ did not differ significantly from the ammonium concentration measured in the 12 February slurry sample $(1.78 \text{ kg NH}_4^+\text{-N} \text{ m}^-\text{-3})$.

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) .

196
$$ANM(kgNH_4^+ - N) = ANC(kgNH_4^+ - N \cdot m^{-3}) \cdot H(m) \cdot S(m^2)$$
 (1)

197 The average ammonium losses in each container between any two sampling dates were 198 estimated as the difference in ammonium mass between the two dates, and was expressed 199 as ammonium loss rate (ALR, gNH_4^+ m⁻² day⁻¹) dividing by the area of the container 200 (S=1.2 m²) and the number of days elapsed between the two sampling dates (D_{ji} =date j – 201 date i) (Eq. 2).

202
$$\operatorname{ALR}(g \cdot \operatorname{NH}_{4}^{+} - \operatorname{N} \cdot \operatorname{m}^{-2} \cdot \operatorname{day}^{-1}) = \frac{\operatorname{ANM}(g \operatorname{NH}_{4}^{+} - \operatorname{N})_{\operatorname{date j}} - \operatorname{ANM}(g \operatorname{NH}_{4}^{+} - \operatorname{N})_{\operatorname{date i}}}{\operatorname{S}(\operatorname{m}^{2}) \cdot \operatorname{D}_{ji}(\operatorname{day})}$$
 (2)

203 The effect of the covers on the height of SS and its ammonium concentration and mass 204 at the different sampling dates was analysed as repeated measured data using the PROC 205 MIXED procedure in SAS (Little et al. 1998; Daudén et al. 2004; Yagüe and Quílez 206 2010). The first order autoregressive structure within treatments and a random effect 207 between treatments resulted as best among the covariance structures tested (compound 208 symmetric, unstructured and first order autoregressive + random effect) on the basis of 209 the Schwarz Bayesian criterion. There was no significant interaction between treatments 210 and sampling times for any of the three variables. The effects of the covers on the rate 211 of ammonium loss and the mass of ammonium conserved in the SS containers after 4 212 and 10 months storage were evaluated by analysis of variance using the GLM 213 procedure. Treatments were compared using the Tukey mean separation procedure (p≤ 214 0.05).

215 Relationships between variables, when necessary, were established by regression 216 analysis ($p \le 0.05$). Statistical analysis were performed with the statistical package SAS 217 (SAS Institute 1999-2001).

- 218
- 219 Results
- 220 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.

229
$$NH_4 - N$$
 (kg m⁻³, Quantofix) = $-0.08 + 0.99 \cdot NH_4 - N$ (kg m⁻³, Laboratory), R² = 0.99
230 (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.

238

239 Changes in SS heigh, 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) (Table3).

The ammonium mass in the SS stored in the containers decreased with time faster than the SS heigh. 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).

256 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 257 258 (Fig. 2). A significant interaction between treatment and time period was observed. 259 Ammonium loss in the uncovered treatment was maximum in May, reaching almost 12 g NH4⁺-N m⁻² day⁻¹, and decreased afterwards due to decreased SS ammonium 260 261 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 NH_4^+ -N m⁻² day⁻¹ in the period 262 263 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 NH4⁺-N m⁻² day⁻¹ for PB7 and PB3.5 264 265 respectively; Fig. 2), whereas losses in cornstalk treatments were low during the first three months (≤ 3 g NH₄⁺-N m⁻² day⁻¹), increased to 9.0 g NH₄⁺-N m⁻² day⁻¹ in July and 266 reached the peak of 15.2 g NH_4^+ -N m⁻² day⁻¹ in August (Fig. 2). 267

268

269 Variations in SS ammonium concentrations and densities at different layers

270 Density of SS decreased with time from 1010 ± 0.65 g L⁻¹ on 19 February to 1007 ± 1.16 g 271 L⁻¹ on 27 June and to 1005 ± 1.64 g L⁻¹ on 23 December. No significant differences in density were detected between layers or between cover treatments in any of the threesampling dates.

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

276

277 Discussion

278 The containers used in this study for SS storage had a limited depth (1 m) and volume 279 of SS (1200 L), which may lead to differences in gas generation, diffusion and emission 280 processes compared with larger on-farm storage facilities. In addition, the experiment 281 was performed under static conditions-no slurry was added after the start of the 282 experiment—, whereas the SS is periodically poured into the storage facilities under 283 real farm conditions. Despite these constraints, it was assumed that the behaviour of the 284 stored SS under the tested covers will resemble the behaviour of the top 1 m SS in a 285 farm pond, the layer most affected by the environmental conditions (Muck et al. 1984; 286 Olesen and Sommer 1993).

287 To evaluate the effects of the covers on N conservation in SS, the changes in 288 concentration and mass of ammonium were analyzed and changes in the amount of 289 organic N were not analyzed. The transformation from organic N to ammonium N in 290 open slurry storage has not been commonly considered in studies quantifying ammonia 291 losses from slurry storages (Hutchings et al. 1996; Rotz et al. 2006). Following Dahlin 292 et al. (2005) aerobic storage conditions lead to a stabilization of N in organically bound 293 forms, under the assumption that the organic N entering storage was that excreted in 294 faces, and no loss or transformation would occur prior to storage. Based on Patni and 295 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 initiallypresent 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 4–7 kg NH_4^+ -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.

304

305 Ammonium losses during storage

306 Average ammonia losses from the uncovered treatment in the period 19 February to 28 August was 6.7 g NH_4^+ -N m⁻² day⁻¹ (8.1 g NH_3 m⁻² day⁻¹). Most of these losses are 307 308 hypothetically due to ammonia volatilization, as N losses due to emission of N oxides is 309 likely to be very low (Berg et al. 2006; Loyon et al. 2007)). Under the precedent 310 hypothesis, the rate of ammonia emission was higher than that measured in other 311 studies, despite its low initial ammonium concentration. Balsari et al. (2006) reported ammonia losses of 0.98–2.68 g NH₃ m⁻² day⁻¹ and the UK Environmental Agency 312 (2008) 3.84 g NH₃ m⁻² day⁻¹, both from uncovered farm ponds. In the case of stirred 313 314 slurry, where convective transport of ammonium to the surface layers is active. Sommer et al. (1993) reported volatilization losses of 3-5 g NH₃-N m⁻² day⁻¹. Smith et al. (2007) 315 316 found higher ammonia losses from dairy slurry in small-scale tanks, similar to those 317 used in this experiment, than from farm ponds. These authors concluded that ammonia 318 losses measured in small-scale tanks are not representative of real slurry storages. 319 although they were satisfactory for comparative studies.

The degradation of the covers with time, due to its contact with the slurry, affected their buoyancy (qualitative visual detection) and diminished their efficacy (Fig. 2). The degradation of each cover is visualized from the rate of ammonium losses at each date. Thus, both PB covers lost effectiveness (Fig. 2) between 27 June and 31 July (4 to 5 months), and CS8 between 31 July and 28 August (5 and 6 months). In the case of the PW8 cover, a physical degradation was observed from the beginning of the experiment.

The durability of the composite bio-covers agrees with that obtained under other climatic conditions. Hudson et al. (2006a) found that a straw cover started to deteriorate physically after only a few weeks, and proposed a five-month life span for this type of cover. Similarly, Clanton et al. (2001) and Burns (2007) found that some permeable covers, such as those made with blown straw or cornstalks, lasted for two to six months depending on weather and SS thickness (the thicker the slurry, the longer the floating of the straw).

Hudson et al. (2006a, 2006b) and Burns (2007) observed that covers form a physical barrier to ammonia diffusion, and they may adsorb the ammonia volatilized from the slurry surface, which also reduces volatilization (Portejoie et al. 2003). The amount of 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 ammonium concentration dropped below 1 kg NH₄-N m⁻³ in some containers after the 341 342 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).

348

349 Ammonium concentration and density at different SS depths

It is reasonable to assume that SS consists of discrete layers with different ammoniageneration 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).

361

362 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).

368 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).

375 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 376 377 that carbon losses were proportional to ammonium losses in the two PB treatments. 378 However, the C/N ratio in the other three treatments decreased by half ($C/N_{Control} = 7.3$, $C/N_{PW8} = 8.5$ and $C/N_{CS8} = 7.0$), indicating that carbon losses were approximately twice 379 380 the ammonium losses. Treatments PB3.5 and PB7 were more effective at reducing both 381 ammonium and carbon losses (presumably as CO₂ and CH₄; Patni and Jui 1987; Amon 382 et al. 2008). It is therefore important to evaluate ammonia, nitrous oxide, methane and 383 CO₂ emissions simultaneously, as abatement activities aimed at reducing the emission 384 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 K₂O 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 NH₄⁺ 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.

399

400 Conclusions

401 The results of this study indicate that the swine slurry stored in open containers in 402 Mediterranean semiarid conditions reduces significantly its fertilizer value during 403 storage and emits important amounts of N to the atmosphere. The composite covers 404 pine bark and cornstalk tested in this work were relatively effective for conserving N in 405 the stored swine slurry for about four months, between 73 to 76% of initial ammonium 406 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 407 408 a period longer than 6 months. The length of the storage period and the cover material 409 affect the slurry N and K concentrations and the ratio N/K and this effect should be 410 taken into account when using the slurry as a fertilizer.

411

412 **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 420 increase the useful life and will promote crust formation, and biologically active 421 materials that will retain nitrogen and carbon. In addition, GHG emissions should be 422 determined to assess the differential behaviour of cover materials in reducing the 423 emissions of different GH gases.

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580 Figures y Tables

- 581 **Figure 1.** Monthly precipitation (P), mean air temperature (T) and reference ET (ET₀,
- 582 FAO-Penman Monteith) for the 2008 experimental year and the 1982-2008 historical
- 583 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



590

591 **Table 1.** Swine slurry physicochemical characteristics determined in the laboratory at

592 the beginning (initial slurry, 19 February 2008) and end of the experiment (23

593 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	8 23 December 2008					
	Initial Slurry	Control	PB3.5	PB7	PW8	CS8	
рН	8.4	8.70	8.35	8.33	8.38	8.43	
Electrical Condutivity, 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_2O_5 , kg Mg ⁻¹	1.63	0.14	0.04	0.06	0.11	0.09	
K_2O , 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	

^{595 §} Measured in a 1:5 swine slurry:deionized water ratio

Table 2. Monthly and period (February to December) average swine slurry ammonium concentrations (kg NH_4^+ -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

601 the 0.05 probability level

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

Table 3. Average swine slurry heigths (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.

	10 E.L a	17Max	21 4	27. 4	27 1	21 J1	29 4	12D	Decrease
	19 Feb."	1/Mar.	21Apr.	271 v1ay	27 J un.	JIJUI.	20Aug.	25000	%
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	

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

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

610	Table 4. Average swine slurry ammonium mass (kg NH_4^+ -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.

	NH4 ⁺ n	nass (kg NI	H4 ⁺ -N)	NH4 ⁺ conserved (%)		
	19 Feb. ^a	27 Jun.	23 Dec.	Feb-June	Feb-Dec	
Control	I 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 0.17AE		73	9	
Treat ^b	NS	S	S	-	-	

617

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

619 the 0.05 probability level

620 ^bS: 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)

		19 February		27	7 June	23 December		
Treat	Depth m	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 NH4 ⁺ -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