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Comparison of techniques for ammonia emission mitigation during storage of livestock manure and assessment of their effect in the management chain

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Abstract

The reduction of ammonia (NH_3) emissions associated with manure management requires identification and implementation of effective techniques. The objective of this study was to measure potential ammonia emissions from animal manure and evaluate emission reductions for five mitigation techniques (straw, sawdust, clay, oil and sulphuric acid). Although numerous studies have evaluated individual mitigation techniques, the variability of their effect with different types of slurries has not been fully investigated. Furthermore, the assessment of ammonia emissions from the subsequent land application of stored manure (or slurry) using different techniques would indicate the practical consequences of the entire slurry management chain. The effects of mitigation techniques were evaluated using a model to simulate field application of slurry. Three techniques were compared: broadcast spreading, band spreading and closed-slot injection. Simulations utilised data from experiments conducted at a controlled temperature on six slurries of three different types: pig, cattle and digestate. Ammonia emissions from the raw slurries (*i.e.*, untreated slurry) were determined using the dynamic chamber technique and compared with those from the slurries treated using each of five mitigation techniques. A subsample of one 1 L of each slurry was transferred into 2 L plastic bottles. An airflow of 1 L min^{-1} across the headspace was established and then emissions were measured over a period of 24 h. The air outlet was connected to two serial acids traps filled with 1% boric acid. The quantity of NH_3 trapped was determined by titration. Acidification and oil addition were the most effective techniques, reducing ammonia emission from raw slurries by more than 95% and 80%, respectively. The mitigation effects of straw and sawdust were higher for cattle slurry and digestate than for pig slurry, while clay had an opposite effect. The overall assessment of ammonia emissions from storage and subsequent field application showed that acidification followed by closed-slot injection emitted at most 12% of the emissions from the reference system, while emissions from acidification followed by band spreading were between 14% and 22% of those from the reference system. The latter appears to be both more effective than broadcast spreading and technically more easily operated than a closed-slot injector.

Introduction

European agriculture is responsible of 94% of ammonia (NH_3) emissions in Europe (European Environment Agency, 2017), and approximately 75% of NH_3 emissions derive from livestock manure management (Webb *et al.*, 2005). NH_3 volatilisation during manure storage represents approximately 19% of nitrogen (N) excreted by animals housed in barns, and an additional 19% is lost during field application of the manure (Oenema *et al.*, 2007).

The most important factors influencing NH_3 emission from slurry are the concentration of total ammoniacal nitrogen (TAN) in the slurry, the emitting surface, pH of the slurry, the air velocity and the slurry temperature (Feilberg and Sommer, 2013). To reduce NH_3 emissions during manure/slurry storage and subsequent land application, mitigation techniques must be implemented that are able to reduce the effects of these parameters. Strategies examined by the scientific community for reducing NH_3 losses are numerous and the reported effectiveness of the strategies varies significantly (Ndegwa *et al.*, 2008; Hou *et al.*, 2015).

A possible solution for abating NH_3 emissions from slurry is the use of additives during slurry storage, such as urease inhibitors, adsorbents, acidifying additives, saponins, and digestive-biological additives (McCrory and Hobbs, 2001). Urease inhibitors have shown promise at the laboratory scale, but their use has not become widespread in practice (Ndegwa *et al.*, 2008). Digestive-biological additives have yielded contrasting results (Provolo *et al.*, 2016) as have adsorbents such as peat, saponins

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and specific additives (Ndegwa *et al.*, 2008). Zeolite and perlite as adsorbents have yielded less variable results (Hörnig *et al.*, 1999; Portejoie *et al.*, 2003). Acidification has a particular relevance as a mitigation technique in the whole-chain manure management system from housing to land application, given its high capacity to reduce not only NH_3 emissions, but also emissions of other greenhouse gases (GHG) (Kai *et al.,* 2008; Fangueiro *et al.*, 2015; Hou *et al.*, 2015; Misselbrook *et al.*, 2016; Regueiro *et al.*, 2016; Mohankumar Sajeev *et al.*, 2018). Addition of sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) to slurry can reduce NH_3 emissions (McCrory and Hobbs, 2001). Strong acids such as these provide better results than weaker acids (such as lactic, acetic or citric acid) because of the former's greater capacity for pH reduction (Regueiro *et al.*, 2016). As regards GHGs, methane (CH_4) emissions from slurry are significantly reduced by acidification (Petersen *et al.*, 2012, 2014), while reduction of nitrous oxide (N_2O) emissions from land-applied acidified slurry is variable (Petersen and Sommer, 2011; Mohankumar Sajeev *et al.*, 2018).

Another approach for reducing NH_3 emissions from manure/slurry is to cover the storage facility by using a tent roof or floating cover on the slurry surface (Guarino *et al.*, 2006; Ndegwa *et al.*, 2008), even if the effects of storage covers on GHG emissions are not well defined (VanderZaag *et al.*, 2008). A cover can reduce NH_3 emission by decreasing the airflow across the slurry surface, but can increase emissions of GHG, especially N_2O (Hansen *et al.*, 2009; Rodhe *et al.*, 2015). Several typologies of covers have been investigated. Floating covers can be constructed of a variety of materials that provide very different performances, length of service and strength during homogenisation of the stored slurry (Guarino *et al.*, 2006; Ndegwa *et al.*, 2008).

The natural crust that forms on some slurries serves as a reliable and inexpensive cover, but the integrity of the crust is strictly dependent on the dry matter content of the slurry (Misselbrook *et al.*, 2005). Studies using straw, sawdust and wood chips as supplemental crust materials have observed a reduction of NH_3 emissions (Hörnig *et al.,* 1999; Guarino *et al.,* 2006). These materials tend to reduce or have no effect on CH_4 emissions, and increase N_2O emissions (Hansen *et al.*, 2009). Leca® (or expanded clay), has a significant effect on NH_3 emissions abatement (Balsari *et al.*, 2006; Guarino *et al.,* 2006; Misselbrook *et al.*, 2016), as do perlite and zeolite (Hörnig *et al.*, 1999; Portejoie *et al.*, 2003). Oil (Portejoie *et al.,* 2003; Guarino *et al.,* 2006) and plastic-synthetic film (Hörnig *et al.*, 1999; Portejoie *et al.*, 2003) used alone or as supplemental materials have greater potential among all the covers discussed, even considering that over time oil tends to mix with the crust and lose effectiveness (Hörnig *et al.*, 1999).

Regardless of the adopted strategy to reduce or eliminate NH_3 emissions from storages, the techniques exert their main effect only during one stage of the manure management chain. The subsequent process of utilising the stored manure/slurry on land must be done carefully to avoid losing the NH_3 emission reduction benefits gained during storage (Hou *et al.*, 2015). Land application techniques such as injection of slurry into closed or open slots allow slurry to be incorporated beneath the soil. These and other techniques such as band spreading using a trailing hose or trailing shoe are preferable to broadcast spreading because they reduce the exposed slurry surface and favour infiltration (Santonja *et al.*, 2017). The evaluation and comparison of land application techniques in terms of NH_3 emissions can be accomplished using models specifically developed for this purpose. Several models have been developed (Søgaard *et al.,* 2002; Thorman *et al.,* 2008; Loubet *et al.,* 2010; Langevin *et al.,* 2015; Hafner *et al.,* 2018), but among them, ALFAM model (Søgaard *et al.,* 2002) is the most used.

Although numerous studies have been conducted on techniques that mitigate NH_3 emission, the variability in the effectiveness of these techniques for different types of slurries has not been fully investigated. Furthermore, assessments have rarely considered the effectiveness of a given emission reduction technique throughout the entire manure management chain. The assessment of NH_3 emissions during storage and the subsequent land application process using different mitigation techniques would provide useful indications of the practical consequences of these techniques throughout the slurry management chain.

In this study, laboratory experiments were combined with mathematic simulation to compare five NH_3 emission mitigation techniques applied to six types of slurries. The objective of the study was to analyse the effectiveness of each mitigation technique in reducing NH_3 emissions, and to quantify the effectiveness as a function of the type and composition of slurry. Then, based on the experimental results, NH_3 emissions during land application of the slurries were simulated, comparing three application techniques. The overall assessment of the slurry management chain (from storage to land application) identified the most effective combination of techniques for reducing NH_3 emissions.

Materials and methods

Slurries used in the experiments

The effect of different NH_3 emission mitigation techniques was evaluated on six types of slurries (two pig slurries; two cattle slurries and two digestate) collected from commercial farms in the Italian region of Lombardy.

Pig slurry no. 1 was collected from a fattening pig farm in Pompiano (BS) where animals were housed on a slatted floor with a slurry storage pit located underneath. The sample from this farm came from the liquid fraction resulting from separation of the raw slurry using screw press equipment.

Pig slurry no. 2 came from a fattening pig farm located in Camisano (CR) where animals were housed on a slatted floor with a shallow slurry receiving pit underneath that was emptied periodically with a vacuum system. The sample was taken from the receiving pit without further treatment.

Cattle slurry no. 1 was collected from a dairy cow farm in Lodi Vecchio (LO) where animals were housed in cubicles. The sample was obtained from a storage tank that received slurry from different buildings.

Cattle slurry no. 2 was obtained from a dairy cow farm in Caravaggio (BG) and was collected from a pit that received manure scraped from the solid floor of the passageways in buildings where the animals were housed.

Digestate no. 1 was obtained from a cooperative biogas plant (1 MWe) in Martinengo (BG). The feedstock was comprised of 35% pig slurry, 50% cattle slurry, 5% poultry and cattle manure, and 10% other biomass (maize and sorghum silage, corn flour). Samples were obtained from the liquid fraction of the digestate following mechanical separation (screw press).

Digestate no. 2 was obtained from a farm biogas installation (250 kWe) in Lodi Vecchio (LO). The feedstock was comprised of 90% cattle slurry and 10% corn silage. Samples were taken from raw digested slurry (digestate).

Each slurry was analysed before an experiment to determine the content of total Kjeldahl nitrogen (TKN), TAN, total solids (TS), volatile solids (VS), and pH using standard methods (APHA/AWWA/WEF, 2012).

Experimental conditions

Ammonia emissions from the various slurries and treatments were determined using the dynamic chamber method according to the methodology used for laboratory scale studies by other researchers (Dinuccio *et al.*, 2008; Petersen *et al.*, 2012).

A subsample of one 1 L of each slurry was transferred into 2 L plastic bottles (Petersen *et al.*, 2012). An airflow of 1 L min^{-1} across the headspace was established and then emissions were measured over a period of 24 h. The air outlet was connected to two serial acids traps filled with 1% boric acid. The bottles were placed in a controlled temperature container set at 20°C to avoid effect of temperature variation during an experiment. The lids of the bottles were connected to two Teflon® tubes (6 mm inner diameter). One tube (the air inlet) was open to draw in ambient air. The second tube (the air outlet) was connected to the first of two Drechsel bottles containing 200 mL of 1% boric acid solution to capture the NH_3 contained in the air discharged from the sample bottle. The second Drechsel bottle was connected to a gas measuring indicator and an analog flow meter to regulate and monitor the flow of air obtained from the chamber system. The air was drawn through the piping system at a continuous flow rate of 1 L min^{-1} by a pump (EVO30 series, Ead) connected to the analogue flow regulator. An additional acid trap was used as reference to measure the NH_3 concentration of the ambient air. Before each experiment, the flows were calibrated using a digital flow meter (PFM710S-C4-A, SMC). At the end of each experiment, the contents of the Drechsel bottles were titrated with 0.1N sulphuric acid to determine the amount of NH_3 trapped.

The NH_3 emissions were calculated according to Eq. (1):

$$E = \frac{(M_{out} - M_{in})}{T \cdot V} \tag{1}$$

where E is the emission (mg day^{-1} L^{-1}), M_{out} is the mass (mg) of NH_3 captured in the Drechsel bottles (acid traps), M_{in} is the mass (mg) of NH_3 in the reference acid trap, and T is the duration of the sampling period (day) and V the volume of the slurry in the bottle (L). To compare the results with other previously reported research, the emissions were referenced also to the initial TAN and TKN content.

Ammonia emissions from each treatment-slurry combination were measured for 24 h in duplicate using raw (untreated) slurry as reference and the following mitigation techniques:

- *Straw*: a layer approximately 1 cm thick of barley straw was carefully placed on the surface of slurry in both bottles;
- *Sawdust*: a sawdust layer approximately 1 cm thick was placed on the surface of slurry in both bottles;
- *Clay*: an amount of commercial clay granules was scattered on the slurry surface to achieve complete coverage in both bottles;
- *Oil*: oil was gently poured onto the slurry surface to create a layer 3 mm thick in both bottles;
- *Acidification*: sulphuric acid (98% purity) was added to the slurry in both bottles and gently mixed; acid was added until the pH of the mixture was less than 5.5.

Each technique was applied soon after filling the bottles with raw slurry and just before the start of the experiments.

Statistical analysis

To evaluate the effect of the mitigation techniques on each slurry, the Kruskal-Wallis test was performed using the software R (version 3.5.0, https://www.r-project.org/). The alpha parameter was set as 0.05, and the Fisher's least significant difference was used as the criterion for the post-hoc test.

Assessment of the slurry management chain

To assess the effect of each mitigation technique used during slurry storage on the entire management chain, the distribution techniques for applying the slurry to land had to be considered. To do so, the NH_3 emissions from slurry during field application with different approaches (broadcast spreading, band spreading and closed-slot injection) were simulated. The procedure to realise the simulation involved the following steps:

- *Selection* of *Ef* for raw slurry (*i.e.*, untreated slurry) during the entire storage period. The values selected referred to slurry storage in open tanks, *i.e.*, 9% for cattle slurry, 15% for pig slurry and 28% for digestate (Feilberg and Sommer, 2013).
- *Calculation* of emission reductions resulting from different coverings and acid addition when compared to emissions from raw slurry, using the results of the experiments.
- *Estimation* of *Ef* for the land application of slurry. This emission factor referred to the initial content of TAN applied on the field and was estimated for the three techniques evaluated using the ALFAM model (Søgaard *et al.*, 2002). To calculate NH_3 losses during field application, the values for parameters in the model were set as follows. For TS and TAN, the values of chemical analyses made in the experimental part of this study were used. Soil moisture was set to *wet*, air temperature was set at 18°C (average temperature during the land application period), and wind speed was set at 2 m s^{-1}. The slurry type was set to *pig* or *cattle* according to the type, and digestate was considered as *cattle slurry*. The application rate, expressed in metric tons per ha (t ha^{-1}), was calculated for each slurry type on the basis of its TKN content and assuming an application of 340 kg TKN ha^{-1}. The model was used considering that the slurry is not incorporated and setting the *wind tunnel* as measuring technique.
- For acidified slurries, not included as option in the ALFAM model, an average reduction in NH_3 losses was considered. A 60% reduction of losses compared to raw slurry was assumed (Kai *et al.,* 2008; Fangueiro *et al.,* 2015).
- Storage of raw slurries without mitigation techniques followed by field application using a broadcast spreader was considered as the reference management chain for each slurry. Total NH_3 losses for the reference management chain were obtained by adding the emissions during storage to the emissions from broadcast spreading, calculated relative to the residual TAN after storage.
- The total NH_3 emissions from each management chain were compared to those from the reference chain and the proportions of NH_3 emissions attributable to storage and field application were calculated.

Results and discussion

Comparison of mitigation techniques

The initial characteristics of the slurries as collected are reported in Table 1.

The results shown in Table 2 highlight a statistically significant difference ($P<0.05$) for all the mitigation techniques for each of the six slurries examined, with the exception of slurry Cattle no. 1 for which the effects were less obvious. The interactions raw-straw, straw-sawdust, clay-oil, sawdust-H_2SO_4 were not statistically significant. For Cattle no. 1 the NH_3 emissions were affected by the high TS content (8.7%) that might have masked the effect of the mitigation techniques more strongly than for the other slurries. Although high TS content reduces NH_3 emissions and makes formation of a natural crust easier (Misselbrook *et al*., 2005), there was not enough time for crust formation in this study. Nevertheless, the effects of floating covers on NH_3 emission were more pronounced for slurries with relatively low TS content and the differences were diminished for slurries with high TS content, especially with sawdust for which the performance was comparable to that of acid. Cattle no. 1 and Cattle no. 2 emitted less NH_3 than Pig and Digestate samples because of the higher TS content of the cattle slurries, lower TAN and acidic pH (but near neutral). On the contrary Digestate no. 1 and Digestate no. 2 had higher NH_3 emissions than the other slurries (except Pig no. 2) because of their higher TAN content and alkaline pH, which was similar to that for Pig no. 1 and Pig no. 2. As reported in Table 3 and Figure 1, for almost all slurries H_2SO_4 addition resulted in largest reduction of NH_3 emissions (>89%, mean 95%), followed by oil (>75% emission reduction, mean 87%). The single exception to these results was for sample Cattle no. 1 because the effect of sawdust (95% emission reduction) was stronger on Cattle no. 1 than on other slurries, probably due to the sawdust's combination with the fibres already present in the slurry. These reductions are in agreement with those reported in other studies, and slightly better in

Table 1. Chemical characteristics of the slurries used in the experiments.

Slurry	pH	TKN (g L^{-1})	TAN (g L^{-1})	TAN/TKN	TS (%)	VS/TS (%)
Pig no. 1	7.9	2.95	2.55	86	1.3	46
Pig no. 2	7.7	5.13	3.60	70	5.0	59
Cattle no. 1	6.7	3.34	1.64	49	8.7	82
Cattle no. 2	7.2	2.43	0.99	41	7.0	84
Digestate no. 1	8.2	6.01	4.13	69	3.6	63
Digestate no. 2	8.0	4.11	2.44	59	6.9	74

TKN, total Kjeldahl nitrogen; TAN, total ammoniacal nitrogen; TS, total solids; VS, volatile solids.

Table 2. Ammonia losses (as total ammoniacal nitrogen) of six slurries (mean and standard deviation). Post-hoc test ($P<0.05$) on mitigation techniques are related to each slurry sample.

	Mitigation techniques - TAN lost (mg*L^{-1})											
Slurry	None (raw)		Straw		Sawdust		Clay		Oil		H_2SO_4	
	Mean	σ	Mean	σ	Mean	σ	Mean	σ	Mean	σ	Mean	σ
Cattle no. 1	16.66	0.40^{a}	7.18	0.35^{ab}	0.81	0.05^{d}	3.96	0.35^{bc}	3.40	0.35^{c}	0.77	0.10^{d}
Cattle no. 2	23.07	2.22^{a}	7.53	0.75^{b}	5.04	0.40^{e}	13.09	0.10^{c}	5.85	0.45^{d}	2.56	0.15^{f}
Digestate no. 1	87.82	4.01^{a}	46.20	2.47^{b}	38.22	0.79^{e}	40.67	1.09^{c}	2.93	0.42^{d}	1.89	0.10^{f}
Digestate no. 2	92.96	1.98^{a}	52.85	1.29^{b}	40.01	0.94^{e}	35.21	1.48^{c}	3.92	0.40^{d}	2.10	0.10^{f}
Pig no. 1	41.41	1.44^{a}	34.86	1.58^{b}	37.45	1.29^{e}	29.12	2.57^{c}	2.24	0.20^{d}	4.24	0.64^{f}
Pig no. 2	100.39	6.13^{a}	68.11	2.28^{b}	86.38	0.69^{e}	49.21	0.59^{c}	17.05	0.15^{d}	2.52	0.30^{f}

TAN, total ammoniacal nitrogen. $^{a-f}$Different letters mean significant differences on each row.

Table 3. Reductions of total ammoniacal nitrogen losses using various mitigation techniques compared to losses from raw (untreated) slurries.

Mitigation techniques	Slurries						
	Mean	Cattle no. 1	Cattle no. 2	Digestate no. 1	Digestate no. 2	Pig no. 1	Pig no. 2
	Reduction of TAN losses (% of raw losses)						
Straw	44	57	67	47	43	16	32
Sawdust	52	95	78	56	57	10	14
Clay	53	76	43	54	62	30	51
Oil	87	80	75	97	96	95	83
H_2SO_4	95	95	89	98	98	90	97

TAN, total ammoniacal nitrogen.

some cases. As regards acidification, Regueiro *et al.* (2016) acidified cattle and pig slurry to pH 5.5 using sulphuric acid and aluminium sulphate. The H_2SO_4 reduced emissions from pig slurry by 75% and emissions from dairy cow slurry by 81%; likewise, the aluminium sulphate reduced emissions by 69% from pig slurry and by 87% from dairy slurry. Misselbrook *et al*. (2016) added sulphuric acid to cattle slurry and achieved a 75% reduction of NH_3 emissions during two months of storage. Petersen *et al.* (2014) reported an emission reduction of 84% from pig slurry acidified to pH 5.5 and a reduction of 49% from pig slurry acidified to pH 6.5. The emission reduction from pig slurry (<93%) achieved using oil in this study is aligned with results of Portejoie *et al*. (2003). Guarino *et al*. (2006) covered slurry with 3 mm of oil and achieved emission reductions of 79.5% for pig slurry and 68.5% for cattle slurry. In contrast, Hornig *et al*. (1999) achieved only a 50% reduction of emissions from pig slurry covered with 3 mm of oil. Straw almost halved (mean 44%) NH_3 emission compared to emissions from raw slurry, while sawdust (mean 52%) and clay (mean 53%) provided slightly better abatements. For Pig no. 1 and Pig no. 2, the effects of the straw and sawdust were lower (10-32%) compared to the effect on Cattle slurries (57-95%) and Digestates (43-56%); nevertheless, the effects were statistically significant (Table 2). These coverings (straw and sawdust) exhibited poor performance on the pig slurries probably due to the low level of TS and the low ratio VS/TS of these slurries; both parameters promoted precipitation of solids rather than crust formation. This lower capacity to reduce emissions was also reported by Guarino *et al.* (2006), even though their research showed slightly better performance on pig slurry (34.2%) and cattle slurry (58.6%), as did the study of Hörnig *et al.* (1999) on pig slurry (30%). The cover with straw reduces NH_3 emissions but might increase N_2O emission, with a greater impact if it is kept dry rather than wet (Hansen *et al.*, 2009).

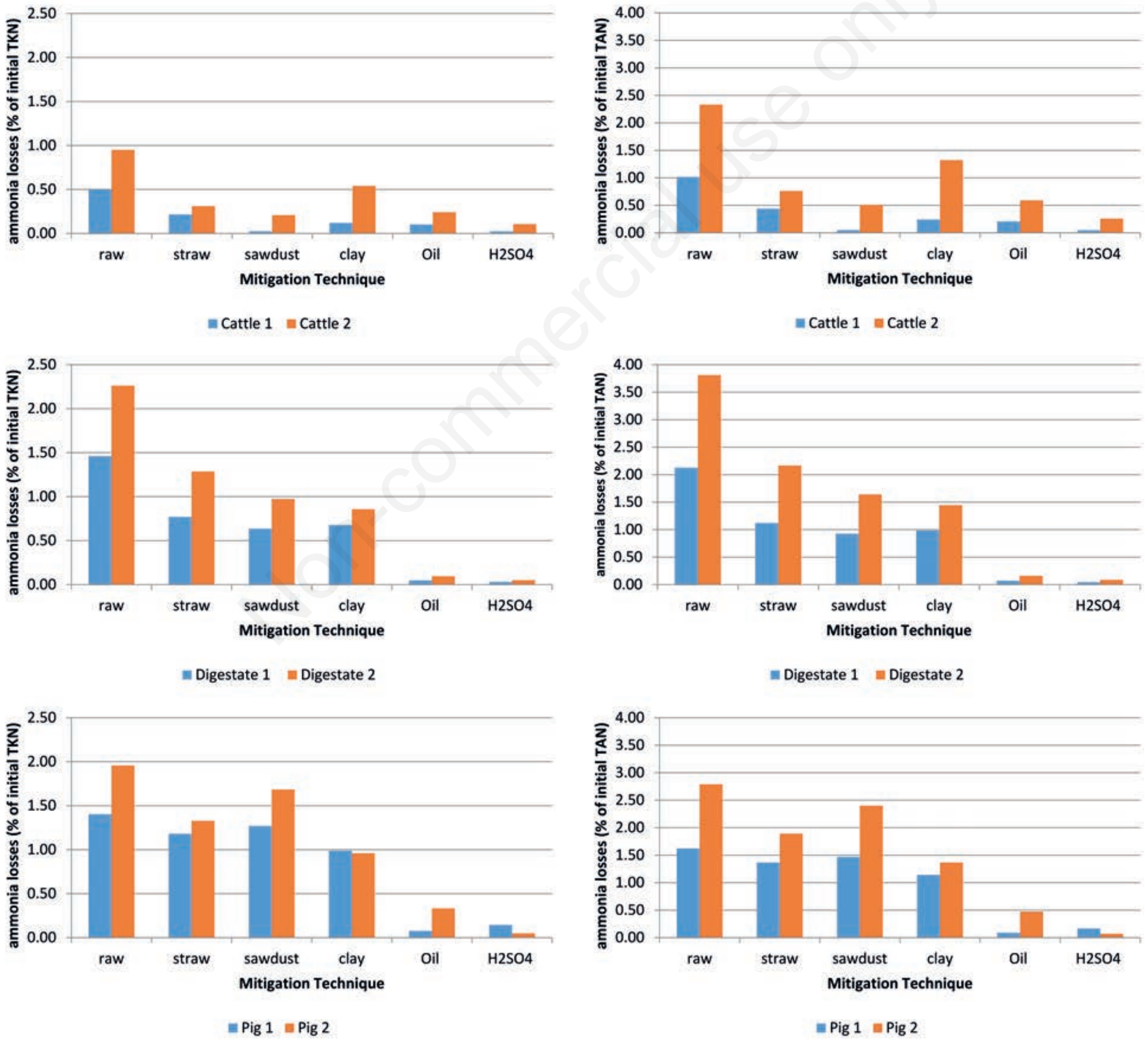

Figure 1. Losses of ammonia compared to the initial total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) content, after 1 day.

The emission reduction effectiveness of clay was greater for Cattle no. 1 (76%) than for Cattle no. 2 (43%) and for other samples (30-62%) (Figure 1). The average NH_3 emission reduction achieved using clay was 53% considering all slurries. Contrasting results from the use of clay have been reported by others. Balsari *et al.* (2006) achieved NH_3 emission reductions from pig slurry of 73% and 87%, in winter and summer respectively, and Misselbrook *et al.* (2016) achieved an emission reduction of 77% on pig slurry. Guarino *et al.* (2006) reported a very low emission reduction effect of clay both on pig slurry (16.8%) and cattle slurry (1.9%).

Assessment of the slurry management chain from storage to field application

As described in the previous section, floating covers and acidification facilitated a significant reduction of NH_3 losses from stored slurries. However, high residual TAN in slurry after storage could result in higher emissions during land application, especially if a broadcast spreader was used (Figure 2). This observation was true for all mitigation techniques except acidification, which achieved better reductions of NH_3 emissions during both storage and the subsequent land application of the stored slurries.

Considering the reference system (raw slurry and broadcast spreading), the cumulative NH_3 losses referenced to the initial TAN content were: 57.3% for Cattle no. 1, 46.4% for Cattle no. 2, 47% for Digestate no. 1, 59.4% for Digestate no. 2, 28.5% for Pig no. 1, and 35.4% for Pig no. 2. Pig slurries have lower emissions during land application than Cattle slurry and Digestate due to the lower TS content of Pig slurry and consequently quicker infiltration into the soil, reducing the exposure time of the liquid on soil surface (Søgaard *et al.*, 2002). As regards the effect of broadcast spreading on application emissions after storage with different mitigation techniques (Figure 2A), for Cattle slurry there was a reduction of 56.8% (acid) and an increase of 8.7% (sawdust) compared to the effect on raw slurry. For Digestate, there was a reduction of 45.3% (acid) and an increase of 40% (oil). Likewise, for Pig slurry there was a reduction of 53.4% (acid) and an increase of 20.7% (oil). The mitigation techniques that achieved the greatest reduction of NH_3 emission besides acidification (*i.e.*, sawdust for Cattle samples and oil for Digestate and Pig samples) lost most of their effectiveness due to emissions at field application. However, even though NH_3 emissions during application with a broadcast spreader increased for slurries after covered storage, the overall emissions were lower than those from raw slurry (although the benefit is very small for some techniques). As regards Cattle slurry, overall emissions represented between 91% (sawdust) and 96% (straw) of all losses in the management chain when the slurries were land applied with a broadcast spreader. For Digestate the comparable values were between 58% (oil) and 89% (straw), and for Pig slurry they were between 58% (oil) and 96% (sawdust). On the contrary the effect of acidification on the manure management chain was always relevant (38% overall emission for Cattle slurry; 27% for Pig slurry and 23% for Digestate). These results are in line with those reported by Hou *et al.* (2015), which in comparison to reference conditions (no storage mitigation and broadcast spreading) showed an overall reduction of NH_3 emissions by floating covers during storage despite an increase in emissions from the subsequent land application. Nevertheless, acidification was the most effective mitigation technique, especially if combined with soil incorporation of slurry following storage. The two techniques for field application, band spreading (Figure 2B) and closed-slot injection (Figure 2C) compared to the reference technique of broadcast spreading, did not affect the performance ratio among mitigation techniques during storage, but reduced NH_3 field emissions. According to Søgaard *et al.* (2002), these techniques respectively emit just 58% and 27% of the NH_3 emitted by the broadcast spreader. Considering the entire slurry management chain, emissions by the band spreader (Figure 2B) were lower than those from the reference system by approximately 35% (raw) and 88% (sulphuric acid) for Cattle slurry, by 22% (raw) and 86% (sulphuric acid) for Digestate, and by 25% (raw) and 83% (sulphuric acid) for Pig slurry. The emission reduction performance of acidification coupled with band spreading was similar to that found by Kai *et al.* (2008) who reported an emission rate of 71% less than a reference system considering storage and field application.

Overall NH_3 emissions of closed-slot injection (Figure 2C) were lower than those from the reference system by approximately 61% (raw) and 89% (sulphuric acid) for Cattle slurry, 39% (raw) and 93% (sulphuric acid) for Digestate, and 42% (raw) and 92% (sulphuric acid) for Pig slurry.

Conclusions

All mitigation techniques assessed in this study can achieve a significant reduction in NH_3 emissions from slurry storage for the three types of slurry examined; however, the type of slurry and its chemical composition affect the mitigation effect. Pig slurry and Digestate tend to have higher NH_3 emission potential than Cattle slurry. Among the techniques evaluated, acidification provides the best abatement of NH_3 emission during slurry storage with an average reduction of 95%, followed by covering slurry with oil (87%). Other floating covers using solid materials (straw, sawdust and clay) are less effective (NH_3 emissions reductions of 44%-53%) than acidification and oil, except in the case of sawdust used to cover Cattle slurry.

NH_3 emission factors for storage cannot be considered independently from the slurry characteristics, even for slurries of the same type. Reductions of NH_3 emissions may vary by 30% for the same type of slurry and mitigation technique, and by more than 50% among slurries. Therefore, to accurately assess NH_3 emissions from slurry, specific EFs have to be used. Further studies are required to improve knowledge of factors that influence NH_3 emissions in practical conditions when the use rigid or flexible covers are not feasible. Considering the entire slurry management chain, acidification seems to be the most effective NH_3 emission reduction technique as its effect continues during field application following storage. Unfortunately, the pH of acidified slurry may rise during storage and necessitate further addition of acid. Other mitigation techniques that are more limited than acidification in reducing NH_3 emissions during storage tend to lose overall effectiveness if the stored slurry is subsequently land-applied using a broadcast spreader. Therefore, for effective overall reduction of NH_3 emissions, such mitigation techniques during storage should be combined with a technique that controls emissions during land application, such as band spreading or closed-slot injection. Considering the cumulative NH_3 emissions throughout the slurry management chain from storage to subsequent field application, acidification combined with closed-slot injection can achieve remarkable emission reductions (emissions at least 88% lower than those from a reference system). Acidification followed by band spreading also can achieve good emission control, producing NH_3 emissions that are 78-86% lower than those from a reference system. The latter appears to be both more effective than broadcast spreading and technically more easily operated than closed-slot injection.

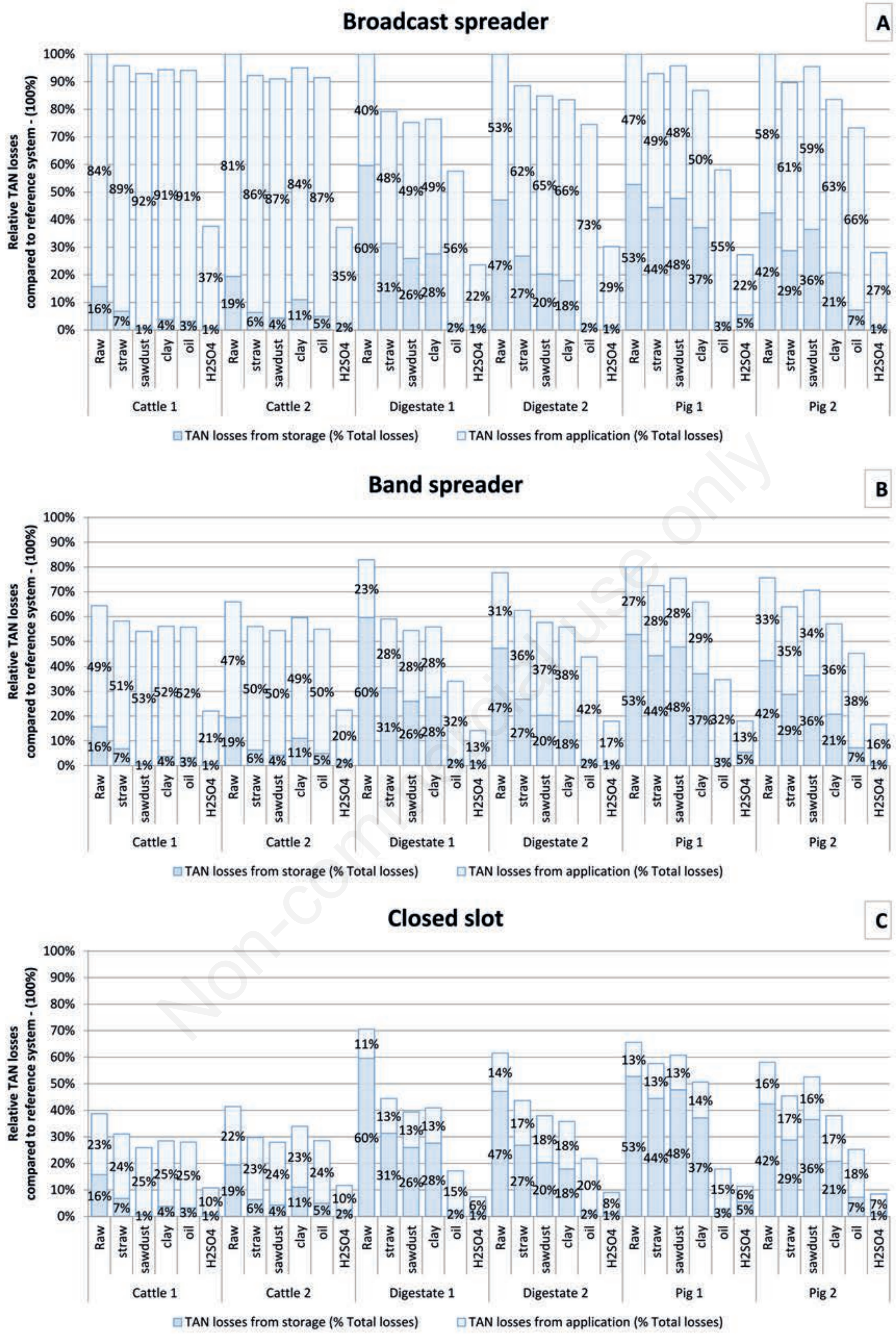

Figure 2. Cumulative losses of total ammoniacal nitrogen (TAN) from the slurry management chain (storage and field application) compared to those from the reference system (storage of raw slurry without mitigation and subsequent broadcast spreading): A) effect of mitigation techniques and their effect on field application using broadcast spreading; B) effects of mitigation techniques coupled with band spreading; C) effects of mitigation techniques coupled with closed-slot injection.

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