Journal of Environmental Management 149 (2015) 46–56

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Review

Acidification of animal slurry– a review

David Fangueiro [a], [*], Maibritt Hjorth [b], Fabrizio Gioelli [c]

[a] UIQA/LEAF-Instituto Superior de Agronomia, Ulisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal
[b] Department of Engineering, Aarhus University, Hangøvej 2, 8200 Århus N, Denmark
[c] Dipartimento di Scienze Agrarie Forestali e Alimentari, Università degli Studi di Torino, Largo Paolo Braccini, 2, 10095 Grugliasco (To), Italy

ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form
26 September 2014
Accepted 3 October 2014
Available online

Keywords:
Manure management
Slurry composition
Gaseous emissions
Nutrient leaching
Slurry treatment
Organic fertilizer

ABSTRACT

Ammonia emissions are a major problem associated with animal slurry management, and solutions to overcome this problem are required worldwide by farmers and stakeholders. An obvious way to minimize ammonia emissions from slurry is to decrease slurry pH by addition of acids or other substances. This solution has been used commonly since 2010 in countries such as Denmark, and its efficiency with regard to the minimization of NH_3 emissions has been documented in many studies. Nevertheless, the impact of such treatment on other gaseous emissions during storage is not clear, since the studies performed so far have provided different scenarios. Similarly, the impact of the soil application of acidified slurry on plant production and diffuse pollution has been considered in several studies. Also, the impact of acidification upon combination with other slurry treatment technologies (e.g. mechanical separation, anaerobic digestion …) is important to consider. Here, a compilation and critical review of all these studies has been performed in order to fully understand the global impact of slurry acidification and assess the applicability of this treatment for slurry management.

1. Introduction

The increased demand for food worldwide has led to the intensification of livestock production over the last few decades. Some consequences of such intensification are: a) a geographic concentration of husbandry and dissociation of arable farms and husbandry specialized farms in some regions; b) an increase of animal manure production, namely slurry (liquid manure) in pig and cattle units and poultry litter. Therefore, farmers have to consider new strategies for manure management in order to minimize its environmental impact and increase its fertilizing value (Petersen et al., 2007).

Ammonia (NH_3) emission is a major problem when considering manure management due to its impact on the environment (McCrory and Hobbs, 2001; Erisman et al., 2008) and on humans and animal welfare (ECETOC, 1994; Colina et al., 2000; Ritz et al., 2004). Emissions of NH_3 from barns and slurry stores represent up to 80% of the total NH_3 emissions from agricultural activities (Anderson et al., 2003). Furthermore, during and after slurry application to soil, more than 50% of the applied N can be lost by NH_3 emissions with close to 50% of the total emission occurring during the first 24 h (Sommer and Hutchings, 2001; Sommer et al., 2003). These NH_3 emissions also correspond to a significant loss of NH_4^+ (Misselbrook et al., 2002; Huijsmans et al., 2007), that strongly reduces the fertilizer values of slurry (Sørensen and Amato, 2002).

In some European countries, animal production is controlled by the potential NH_3 release, and mitigation solutions are now compulsory. Several solutions, such as diet manipulation (Portejoie et al., 2004; Aarnink and Verstegen, 2007), covering of the storage tanks (Portejoie et al., 2003; Balsari et al., 2006), and slurry injection for slurry application to soil (Webb et al., 2010) have been proposed to minimize NH_3 emissions and their efficiency has been reviewed recently by Ndegwa et al. (2008). However, these techniques do not cover the whole slurry management chain (abating gaseous losses in one part of the chain – e.g. the storage pit – may increase the emission in other parts, e.g. land application) and the efficiency of such solutions varies depending on a wide range of factors such as the slurry and soil characteristics.

A simple way to avoid NH_3 emissions is to create conditions that minimize the concentration of NH_3 relative to NH_4^+, namely by lowering the slurry pH. This process, called slurry acidification, has been developed and tested over the last 30 years and is now running at the farm scale in a limited number of countries, such as Denmark. Farmers are motivated to adopt this treatment because of: the permission of authorities to expand farm production due to

---

[*] Corresponding author. Tel.: + 351 213 653 199; fax: + 351 213 653 180.
E-mail address: dfangueiro@isa.utl.pt (D. Fangueiro).

http://dx.doi.org/10.1016/j.jenvman.2014.10.001
0301-4797/

the guaranteed reduction in NH_3 emission, the lack of requirement for slurry injection or sub-plowing after surface application (Christensen and Sommer, 2013), and increased crop yield (Birkmose and Vestergaard, 2013). In other countries, by 2012, such farm-scale application of acidification was absent or very limited.

Many studies have been conducted to assess the efficiency of slurry acidification with regard to the reduction of NH_3 emissions. But lowering the pH will impact multiple chemical and microbial processes in the slurry, changing the composition of the acidified liquid manure. In consequence, slurry acidification might increase the emissions of other gases, such as nitrous oxide or methane, and, after soil application, the fertilizer value of the acidified slurry as well as the associated nitrogen, phosphorous or carbon dynamics might differ from patterns already known for non-acidified slurry (Wenzel and Petersen, 2009). Finally, contrasting results relative to non-acidified slurry might be expected following the application of other technologies, such as solid–liquid separation or anaerobic digestion, to acidified slurry. The literature on all these aspects is still limited and needs to be compiled. A clear overview of the existing knowledge of slurry acidification – highlighting the advantages and limitations – is needed, to improve the acidification process and stimulate the adoption of this mitigation technology.

The aim of the present review is to clearly describe the processes available for slurry acidification and to highlight the main differences along the slurry management chain between acidified and non-acidified slurry.

2. Technologies

2.1. Additives and target pH

The concept of reducing slurry pH to abate nitrogen losses to the air relies on the equilibrium between NH_4^+ dissolved in the slurry and NH_3 (Fig. 1-A). This reduction is achieved by slurry amendment with natural or chemical additives (Table 1).

Strong acids are the additives used most commonly (Eq. (1)): in particular, sulfuric acid is used by all the companies dealing with slurry acidification, but HCl and HNO_3 have been tested also. Some limitations to their use, such as their relatively high cost, corrosiveness, and hazards to animal and human health, are important issues that need to be improved (Rotz, 2004).

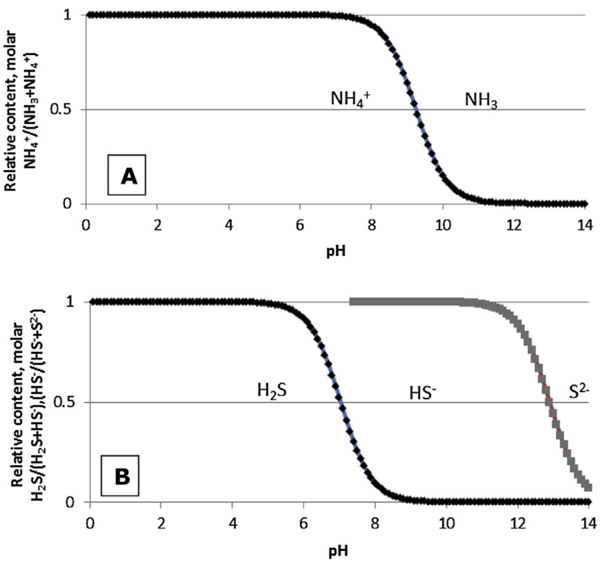

Fig. 1. Effect of slurry pH on its relative content of TAN (A) and sulfide (B).

Table 1
Additives used for slurry acidification and target pH.

Additive	pH	Slurry	References
H_2SO_4	5.5	Pig	Jensen, 2002, Infarm A/S, 2014a, b
	–	Pig	Kai et al., 2008
	6.4	Pig	Biocover A/S, 2012; Nyord et al., 2013
	–	Pig	Nyord et al., 2013
	6.8	Pig	Nyord et al., 2013
	6.2	Pig	Sørensen and Eriksen, 2009, Nyord et al., 2013
	5.5	Pig	Infarm A/S, 2014a, 2014b
	6.0	Cattle	Sørensen and Eriksen, 2009
	6.4	Cattle	Biocover A/S, 2012
HCl	5.3	Pig	Panetta et al., 2005
HCl	4.5	Cattle	Eriksen et al., 2012, Petersen et al., 2012
HNO_3	5.8	Cattle	Husted et al., 1991
	6.7	Cattle	Vandre and Clemens, 1997
	6.0	Cattle	Stevens et al., 1992; Velthof and Oenema, 1993; Stevens et al., 1995
HNO_3	4.5	Cattle	Velthof and Oenema, 1993
Saccharose	5.8–6.5	Pig	Berg and Pazsiczki, 2006
Lactic acid	5.5–6.0	Pig	Berg et al., 2006; Berg and Pazsiczki, 2006
Superphosphate	–	Cattle	Safley et al., 1983; Husted et al., 1991
Superphosphate	5.5	Composted Pig slurry	Tran et al., 2011
Aluminum chloride		Pig and Poultry	Smith et al., 2001; Choi, 2004; Smith et al., 2004; Nahm, 2005
Aluminum sulfate		Pig, Poultry, Dairy	Kithome et al., 1999; Moore et al., 1999; Moore et al., 2000; Lefcourt and Meisinger, 2001; Shi et al., 2001; Sims and Luka-McCafferty, 2002; Armstrong et al., 2003, Nahm, 2005; Li et al., 2006
Calcium/magnesium carbonate	6.3–6.4	Poultry	Witter and Kirchmann, 1989; Nahm, 2005
Glucose	–	Cattle	Clemens et al., 2002
Elemental sulfur		Poultry	Mahimairaja et al., 1994

$$NH_3(g) + H^+(aq) \leftrightarrow NH_4^+(aq) \tag{1}$$

A base precipitating salt, such as aluminum chloride, can also be added to lower the pH (Eq. (2)). The added salt becomes a hydroxide after dissolution in water, the proton is liberated, and the reaction described in Eq. (1) can occur.

$$AlCl_3(s) + 3H_2O(l) \leftrightarrow Al(OH)_3(s) + 3HCl(aq) \tag{2}$$

Easily fermentable materials have also been tested for their ability to lower slurry pH. Such materials reduce the pH of the slurry as they stimulate endogenous anaerobic microorganisms to produce organic acids (McCrory and Hobbs, 2001; Berg and Pazsiczki, 2006). For example, added glucose can be converted, through microbial fermentation, into lactic acid (Eq. (3)) and reaction 1 then occurs.

$$C_6H_{12}O_6(aq) \rightarrow CH_3CHOHCOOH\ (aq) \tag{3}$$

The target pH ranges from 4.5 to 6.8 and the choice of a specific pH depends on several factors, such as the type of slurry, the acid/salt used, and the step of the slurry management chain at which the acidification is performed (Table 1). A pH of 5.5 is the selected target

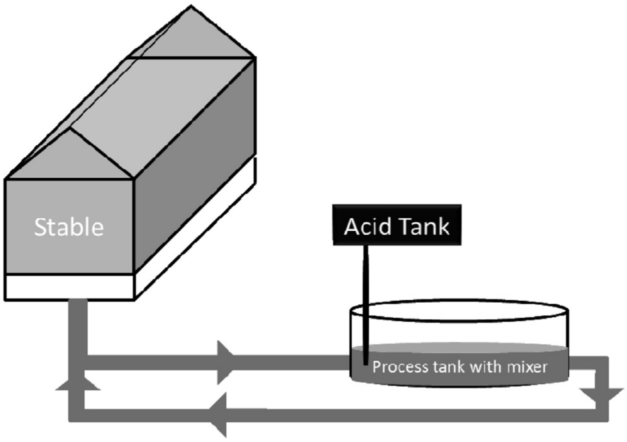

Fig. 2. In-house acidification.

for commercial in-house acidification systems (Infarm A/S, 2014a,b). We have therefore used this value for examples in this paper.

2.2. Acidification methodologies

The technologies available for acidification of animal slurry during the three major management steps are:

1 In-house acidification, considered a long-term acidification (Fig. 2) (Jensen, 2002; Kai et al., 2008; Wesnæs et al., 2009; Petersen et al., 2012; Infarm A/S, 2014a,b; Jørgen Hyldgaard Staldservice A/S, 2014). The additive (sulfuric acid) is applied on a daily or weekly basis to the slurry, in-house. The slurry is typically flushed from the slurry channels into a treatment tank; acid is added under stirring to reach a fixed pH level. Aeration is performed simultaneously to avoid foaming. Part of the slurry is returned to the slurry channels, and part is discarded in a storage tank.

2 Storage tank acidification, considered a short- or long-term acidification depending on its timing (Fig. 3) (Velthof and Oenema, 1993; Fangueiro et al., 2010, 2013; Petersen et al., 2012; Nyord et al., 2013; Harsø Maskiner A/S, 2014; Oerum Smeden, 2014). The additive is added to the storage tank or lagoon under heavy mixing. Foam is produced upon the addition, and its removal is the main constraint of this process. Acidification can be performed shortly before collection of the slurry for field application or several months before application (re-acidification may be necessary).

3 Acidification at field application, considered a short-term acidification (Fig. 4) (Biocover A/S, 2012; Birkmose and Vestergaard, 2013; Gyldenkaerne, 2013; Nyord et al., 2013; Kyndestoft Maskinfabrik Aps, 2014). The additive is applied to the slurry immediately before soil application, in a static mixer installed in the output of the slurry tanker.

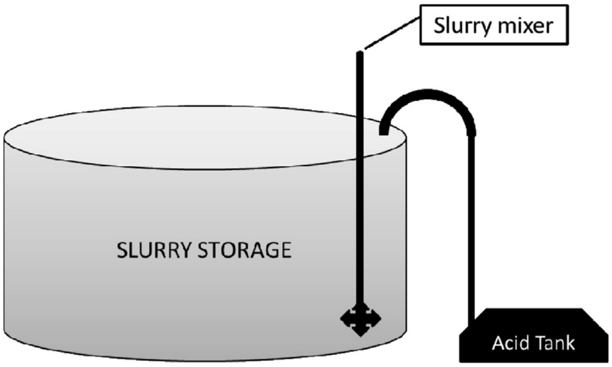

Fig. 3. Storage tank acidification.

Additional acidification techniques include self-acidification (Clemens et al., 2002) and the use of animal fodder additives (Li et al., 2006; Eriksen et al., 2010; Nørgaard et al., 2010) but, in the present paper, only the three previously mentioned technologies involving acid addition will be covered since they are the most widely used and studied.

Efficient and safe solutions for slurry acidification at the farm and field scale have been proposed by private companies, and slurry acidification has the potential to become a key solution for slurry management. Acidification became a full-scale commercial operation in Denmark in 2003. By 2012, approximately 10% of Danish slurry was acidified, with a continued increase expected for the coming years. By 2012 the minimum numbers of operating units in Denmark, for field application acidification, storage tank acidification, and in-house acidification were 100, 60, and 110, respectively (Birkmose and Vestergaard, 2013).

3. Slurry processes and slurry composition

Animal slurry is a chemically complex mixture of suspended particles and dissolved and volatile compounds that can be released into the gas phase. Multiple chemical, physical, and biological processes occur in slurry and many of these are influenced by pH changes (Christensen and Sommer, 2013; Jensen and Sommer, 2013). Therefore, changes in slurry characteristics after acidification are expected.

3.1. Chemical characteristics

3.1.1. Acid, base, and buffer

The speciation of acids and bases is controlled by their pKa values and is therefore pH dependent (Eq. (4)). In animal slurry, there are primarily six acid-base pairs: NH_4^+/NH_3, H_2CO_3/HCO_3^-, HCO_3^-/CO_3^{2-}, $RCOOH/RCOO^-$, $H_3PO_4/H_2PO_4^-$, $H_2PO_4^-/HPO_4^{2-}$, HPO_4^{2-}/PO_4^{3-}, H_2SO_4/HSO_4^-, HSO_4^-/SO_4^{2-}, H_2S/HS^-, and HS^-/S^{2-} (Christensen and Sommer, 2013).

At pH 7, the dominant species are NH_4^+, HCO_3^-, $RCOO^-$, $H_2PO_4^-$, SO_4^{2-}, and HS^-. The relative content of the acid (HA) of the compound A (base) can, for monoprotic acids, be calculated by assuming standard chemical conditions in manure:

$$\frac{[HA]}{[HA]+[A-]} = \frac{\frac{10^{-pH}}{10^{-pKa}}}{\frac{10^{-pH}}{10^{-pKa}+1}} \tag{4}$$

with [x] being the concentration of the compound x, and pKa being the pKa value for the acid/base pair. When lowering the slurry pH from 7.5 to 5.5, the relative acid content is strongly modified, with changes from 98.00% to 99.98 % for NH_4^+, from 9% to 91% for H_2CO_3, from 26% to 97% for H_2S, and from 0.2% to 15.0% for RCOOH (Eq. (4)), while, H_3PO_4 and H_2SO_4 remain residual.

All these transformations are due to fast reactions and should therefore be observed with both short- and long-term acidification technologies.

Animal slurries have a strong buffer capacity that has to be considered when acidification is performed (Sommer and Husted, 1995). On the one hand, it will affect the amount of acid required and, on the other, the buffer capacity can be affected by such addition. Indeed, as can be seen in Fig. 5, calculated from data in Sommer and Husted (1995), the buffer capacity of slurry varies significantly

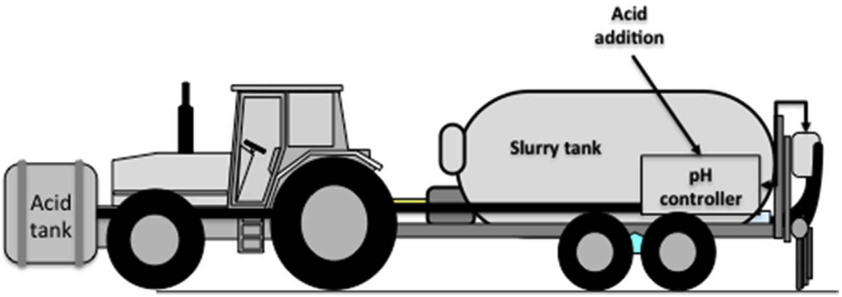

Fig. 4. Field application acidification.

with pH. It is of note that when acidification is performed by the addition of a strong acid, such as sulfuric acid, the amount of this buffer will increase, while the content of other buffer components, such as carbonate, will decline (see Section 3.1.3).

3.1.2. *Inorganic compounds*

The main inorganic components of animal slurry include Fe, Al, Zn, Cu, P, Mg, Ca, NH_3, and H_2CO_3 (Sommer and Husted, 1995). These can be found in solution, adsorbed onto particulate matter, or precipitated. Struvite ($MgPO_4NH_4$) and dicalcium phosphate ($CaHPO_4$) are the main precipitates in animal slurry (Gungor et al., 2007). But, precipitations are pH dependent, with most precipitates being dissolved at low pH values. For example, Ca is fully precipitated as $CaCO_3$ at high pH and as $CaHPO_4$ at medium pH, but is mostly dissolved as Ca^{2+} at low pH (Lindsay, 1979).

Previous studies (Fangueiro et al., 2009; Daumer et al., 2010; Roboredo et al., 2012) observed almost complete dissolution of slurry P when lowering the pH, and part of this has been attributed to dissolution of struvite (Christensen et al., 2009). The acidified slurry thus has higher concentrations of dissolved inorganic compounds – relative to untreated slurry – with positive impacts on its fertilizer value, namely phosphorus (Roboredo et al., 2012). The decrease of slurry pH is generally accompanied by an increase of its conductivity, due mainly to the dissolution of minerals (Hjorth et al., 2013). Because the chemical reactions are rapid, the dissolution of the inorganic minerals may occur for both the short- and long-term acidification technologies.

3.1.3. *Organic matter degradation*

The enzymatic and microbially controlled degradation of slurry organic matter under anaerobic conditions rely on hydrolysis, acidogenesis, acetogenesis, methanogenesis, and sulfate reduction. Recent studies (Hjorth et al., 2013) indicated that hydrolysis may be accelerated at lower pH, and changed from being enzymatically mediated to being chemically catalyzed. Sulfuric acid addition has also been indicated to decelerate all the other microbial pathways, acidogenesis (Hjorth et al., 2013), acetogenesis (Sørensen and Eriksen, 2009; Hjorth et al., 2013), and methanogenesis (Ottosen et al., 2009; Petersen et al., 2012). In some studies, sulfate reduction has been shown to be unaffected, whereas in others it decreased (Eriksen et al., 2012; Dai and Blanes-Vidal, 2013; Hjorth et al., 2013). Indeed, it is well known that enzymes are pH selective, since the active site charges and the steric structures can change with pH. Similarly, microorganisms are pH sensitive and, in some pH intervals, no alternative microbial community exists. Ottosen et al. (2009) observed a lower oxygen consumption rate of acidified slurry relative to untreated slurry, indicating changes in the biological pathways. Furthermore, as previously referred to, the concentrations of some inhibitory substances, including protonated acids, can vary with pH. These changes in the degradation pathways of acidified slurry have a direct effect on the slurry composition with a higher content of large, dissolved organic compounds and lower contents of non-dissolved and small, dissolved organic compounds. Microbial reactions are often slower than chemical reactions; thus, the changes in the pattern of organic matter degradation are likely to be relevant only for long-term, continuous in-house and storage tank acidification performed long before application, but not for short-term storage tank acidification or acidification at field application.

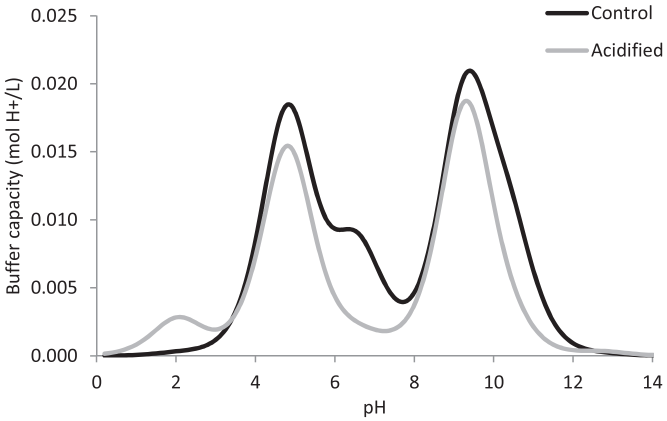

Fig. 5. Effect of pH on the buffer capacity of the slurry.

3.1.4. *Microbial/pathogens*

As evident from the impact of slurry acidification on the degradation patterns of the organic matter, the microbial community must also be influenced or, at least, changed in its activity levels by acidification (Ottosen et al., 2009). However, only a limited number of studies (Ottosen et al., 2009; Zhang et al., 2011) can be found in relation to the impact of slurry acidification on the composition and activity of the microbial community. Ottosen et al. (2009) reported that slurry acidification greatly reduced the microbial activity, while Zhang et al. (2011) observed, in some specific conditions, a weaker effect of acidification on species of pathogenic bacteria. Nevertheless, acidification is commonly used for disinfection of poultry litter. The effect of poultry litter acidification on the decrease of pathogen persistence is not consensual. Line and Bailey (2006) observed no significant effect of litter acidification on *Campylobacter* spp. populations and *Salmonella* spp. However, Rothrock et al. (2008) reported that litter acidification significantly affected the microbial community, reducing the presence of some groups and increasing others. Indeed, one result of acidification was a 3–4 order of magnitude increase in the concentration of fungal urease and uricase producers (Cook et al., 2008; Rothrock et al., 2008). There is a significant lack of knowledge regarding the impact of slurry acidification on the microbial community and pathogens that needs to be overcome since microbial activity rules many slurry processes and needs to be understood to allow improvements of the acidification process; for example, in regard to possible subsequent biogas production.

3.2. *Physical properties*

The physical properties of slurry, controlled by the chemical properties affected by pH, can disturb the soil application process. The color of acidified manure is less brown and more greyish (Infarm A/S, personal communication), likely due to the increased hydrolysis of organic matter. The particle surface charges have been observed to be less negative upon acidification (Zhu et al., 2012; Hjorth et al., 2013), which is reasonable as the majority of acid-bases have fewer charges after protonation, and in agreement with the generally low iso-electrical point of organic colloids (Moayadi et al., 2011). A recent study (Hjorth et al., 2013) showed that acidified slurry contains fewer particles <0.05 mm than untreated slurry, which can be explained by particle aggregation because of lower electrostatic repulsion between particles under the conditions of higher conductivity and less negative surface charge. This is supported by observations of lowered viscosity (Infarm A/S, personal communication; Hjorth et al., 2013). However, the data available on particle sizes in acidified slurry are still limited and do not reach similar conclusions. Similarly, the effect of slurry acidification on dry matter content is also not consensual, with some studies reporting an increase and others a decrease (Eriksen et al., 2008; Kai et al., 2008; Fangueiro et al., 2009, 2010; Eriksen et al., 2012; Moset et al., 2012a; Fangueiro et al., 2013; Hjorth et al., 2013).

4. Gaseous emissions

4.1. *Theoretical aspects*

The pH has a large influence on the gaseous emissions of acid-base compounds, since these emissions are related linearly to the content of the potentially released compounds. For a pH decrease from 7.5 to 5.5, the concentration of the gaseous acid-base compound decreases from 1.8% to 0.02% for NH_3 and increases from 9% to 91% for H_2CO_3, from 0.2% to 15% for RCOOH, and from 26% to 97% for H_2S (See Section 3.1.1 – Eq. (4)). It is of note that H_2CO_3 is not directly released but controls the CO_2 emissions. Thus, based only on this calculation, lowering the slurry pH from 7.5 to 5.5 would lead to a decrease of the NH_3 emission to only 1% of the normal emission. However, it would increase the emissions of H_2S (3 times greater), CO_2 (10 times greater), and volatile fatty acids (100 times greater). Nevertheless, the transfer through the slurry–air interface – which depends on the slurry viscosity, air velocity over the slurry surface, and temperature – has also to be considered, particularly when considering gaseous emissions during storage. An increase in the absolute gaseous emissions is to be expected, since acidified slurry generally has lower viscosity.

4.2. *Real measurements*

Ammonia, methane, and carbon dioxide are emitted during all three steps of the slurry management process: in the barn, during storage, and after soil application. It has been shown that denitrification and nitrous oxide emissions from slurry stores are very limited and can be discounted (Sommer, 1997; Sommer et al., 2000; Dinuccio et al., 2008). On the other hand, CH_4 emissions at field scale are significantly lower than during storage and can be neglected (Chadwick et al., 2011). Similarly, H_2S is mainly emitted during slurry storage, as it has been demonstrated to be only released in the initial few minutes following land application (Feilberg et al., 2014). Therefore, we will consider that nitrous oxide is mainly emitted after soil application whereas H_2S and CH_4 are emitted exclusively during storage and in-house. An overview of the effects of slurry acidification on gaseous emissions is presented in Table 2.

4.2.1. *Nitrogen emissions*

The main goal of slurry acidification is to minimize NH_3 emissions, which should be reduced due to the higher NH_4^+/NH_3 ratio (Fig. 1-A). For the long-term acidifications (in-house and early storage tank acidification), the organic matter degradation may be decelerated (Section 3.1.3), lowering the production of total ammonium nitrogen (TAN) from proteins. However, a change in the TAN production from urea has not yet been observed.

The lowest pH values tested range from 4.0 (Stevens et al., 1989) to 4.5 (Hartung and Phillips, 1994). At these values, less than 1% of the ammonium nitrogen was emitted to the air, compared to non-acidified slurry. Kai et al. (2008) concluded that, when trying to minimize the N losses, slurry acidification is equivalent to or more

Table 2
Overall effect of slurry acidification on gaseous emissions.

Gas	Effect of acidification on emissions			References
NH_3	↘	In-house	✓ 37% with nitric acid ✓ 50–70 % with sulfuric acid	Monteny and Erisman, 1998; Kai et al., 2008; Infarm A/S, 2014a, 2014b
		Storage	✓ 50–88 % with sulfuric acid ✓ 60–98% with aluminum sulfate ✓ 27–71% with other acids	Lefcourt and Meisinger, 2001; Shi et al., 2001; Berg et al., 2006; Kai et al., 2008
		Field	✓ 40–80% with pig slurry (different acids) ✓ 15–80% with cattle slurry (different acids)	Stevens et al., 1989; Frost et al., 1990; Bussink and Bruins, 1992; Stevens et al., 1992; Pain et al., 1994; Frost, 1994; Kai et al., 2008; Biocover A/S, 2012; Nyord et al., 2013
N_2O	↗	Field	✓ >100% with nitric acid ✓ 23% with sulfuric acid	Velthof and Oenema, 1993; Fangueiro et al., 2010
CO_2	→ (initial burst)	Storage		Fangueiro et al., 2010; Dai and Blanes-Vidal, 2013; Fangueiro et al., 2013
H_2S	→ / ↘ (initial burst)	Storage		Eriksen et al., 2012; Dai and Blanes-Vidal, 2013
CH_4	↘	Storage	✓ 90% with lactic acid ✓ 40–65% with hydrochloric acid ✓ 17–75% with nitric acid	Berg et al., 2006; Berg and Pazsiczki, 2006; Petersen et al., 2012

efficient than other solutions such as covering the slurry store with leca® pebbles, straw, natural surface crust, or a PVC cover.

As previously referred to, the efficiency of acidification with regard to reducing NH_3 emissions depends on parameters such as the additive, target pH, slurry type, and step in the slurry management chain (Ndegwa et al., 2008). Several studies have confirmed that NH_3 emissions are directly related to the final pH of the slurry, following the addition of the amendment (Stevens et al., 1989; Vandre and Clemens, 1997; Berg, 2003; Petersen et al., 2012; Dai and Blanes-Vidal, 2013). The efficiency of the additives used to decrease NH_3 emissions during storage varies significantly. The most efficient are strong acids such as H_2SO_4 or HCl (Ndegwa et al., 2008). Berg et al. (2006) reported that lactic acid reduced NH_3 emissions by 65–88%, with pH values between 5.7 and 4.2, whereas nitric acid reduced NH_3 emissions by only 29–71% for the same pH values. Other acidifying agents, such as alum, have been used, mainly with poultry manure, and gave decreases in NH_3 emissions similar to those obtained with strong acids. The addition of aluminum sulfate to cattle slurry gave decreases in NH_3 emissions of 60% at pH 5 (Lefcourt and Meisinger, 2001) and 98% at pH 4.2 (Shi et al., 2001).

With field application acidification, decreases of NH_3 emissions in the range of 40–80% with pig slurry (Stevens et al., 1989; Biocover A/S, 2012; Nyord et al., 2013) and 15–80% with cattle slurry (Stevens et al., 1989; Frost et al., 1990; Bussink and Bruins, 1992; Stevens et al., 1992; Frost, 1994; Pain et al., 1994) can be achieved.

Only a limited number of studies have considered the impact of slurry acidification on N_2O emissions following soil application. Velthof and Oenema (1993) concluded that acidification of slurry with HNO_3 led to higher N_2O emissions, but they attributed this to the addition of NO_3^- via the acid rather than to the pH change. They also compared two target pH values and stressed the importance of the acidification time: when acidification was performed immediately before soil application, slurry pH (6 or 4.5) had no effect on N_2O emissions, but when acidified one week prior to soil application, higher N_2O emissions were observed from slurry acidified to pH 6 rather than pH 4.5. Fangueiro et al. (2010) followed the N_2O emissions from a sandy soil amended with acidified or non-acidified pig slurry, or with the liquid and solid fractions obtained after separation of the acidified and raw slurry. Over the first 47 days of incubation, lower N_2O emissions were observed from the acidified slurry and the liquid and solid fractions. But later, higher emissions were observed from acidified raw slurry – whereas emissions from the acidified liquid and solid fractions remained lower than from the non-acidified liquid and solid fractions, respectively. The authors also reported that the start of the N_2O emissions was delayed for the acidified slurry: as will be seen later (Section 5.1), acidification can delay nitrification and consequently denitrification, the main source of N_2O.

4.2.2. Carbon emissions

Carbon dioxide is a well-known greenhouse gas, but in some studies of slurry management CO_2 emissions are not considered because they belong to the natural carbon cycle. However, when considering slurry acidification, one has to ensure that such treatment does not induce an increase in CO_2 emissions, although this could be expected due to the higher H_2CO_3/HCO_3^- ratio. For long-term acidifications (Section 2.2), the organic matter degradation may be decelerated (Section 3.1.3), lowering the production of carbonate. In contrast, the acidification also causes dissolution of minerals, increasing the content of dissolved carbonate (Section 3.1.2).

The emission of CO_2 occurs mainly during the acidification process (Dai and Blanes-Vidal, 2013; Fangueiro et al., 2013), when emission rates can be 2–10 times higher than during the subsequent storage. However, Fangueiro et al. (2013) observed lower CO_2 emissions from acidified than from non-acidified slurry over the whole storage period. Dai and Blanes-Vidal (2013) did not find significant differences over 40 days. It is noteworthy that a larger and faster decay of CO_2 emissions is observed in acidified relative to non-acidified slurry during the first days of storage.

Following soil application, lower CO_2 emissions were observed in soil amended with acidified pig or cattle slurry relative to non-acidified slurries (Fangueiro et al., 2010, 2013). Acidification may change the dry matter content (Section 3.1.3); these authors showed that this effect is more significant in slurries of low dry matter content. Such decreased CO_2 emissions can reflect lower microbial activity in the soil, with a negative impact on nutrients cycling. Nevertheless, the lower the CO_2 emissions, the higher the amount of carbon stored in the soil.

Slurry acidification acts on methanogenesis; therefore, CH_4 emissions should be lowered by long-term acidification treatments, but not by short-term acidification (Section 3.1.3). The reason may be an increased amount of protonated acids, which act as an inhibitor (Ottosen et al., 2009). Only a few studies have looked at the impact of acidification on methane emissions during slurry storage. Berg et al. (2006) reported that slurry acidification decreased CH_4 emissions during storage but also that such decreases did not depend on the target pH below pH 5. The effect on CH_4 emissions depends strongly on the acid used. Published studies targeting different pHs reported decreases >90% with lactic acid against 67–87% with H_2SO_4, 40–65% with HCl, and 17–75% with nitric acid (Berg et al., 2006; Berg and Pazsiczki, 2006; Petersen et al., 2012).

4.2.3. Hydrogen sulfide

Hydrogen sulfide emissions were unaffected by acidification in some studies, but in others showed a decrease (Eriksen et al., 2012; Dai and Blanes-Vidal, 2013; Hjorth et al., 2013). An increase of H_2S emissions has been observed immediately after acidification (Dai and Blanes-Vidal, 2013); this can happen because existing sulfide is protonated (Fig. 1-B) and also due to the initiation of mixing (Dai and Blanes-Vidal, 2013). When acidification is performed with H_2SO_4, an increase of H_2S may occur since the activity of sulfate-reducing bacteria can be stimulated by the addition of inorganic sulfur (Dai and Blanes-Vidal, 2013). Nevertheless, such bacteria are also sensitive to pH; consequently, acidification to low pH may limit their activity and hence H_2S emissions (Eriksen et al., 2008). Furthermore, H_2S emissions can be avoided by oxygenation of acidified slurry (Jensen, 2002). Additionally, the lower rate of organic matter degradation – including protein (Section 3.1.3) – may decrease the production of sulfate and thus sulfide.

5. Following land application

5.1. Plant nutrient availability and crop production

A delay of ammonium N nitrification was observed in soils amended with acidified slurries, relative to non-acidified ones (Fangueiro et al., 2010, 2013). This delay lasted for about 20 days, for both pig and cattle slurry. Furthermore, for more than 60 days, the NH_4^+ concentration in soil amended with acidified slurry or the liquid fraction of slurry remained significantly higher than in soil amended with the raw materials. The reasons for this are not clear and might involve a combination of nitrification delay, reduction/inhibition of nitrogen immobilization, and stimulation of organic N mineralization (Fangueiro et al., 2009). The effect of slurry acidification on the mineral fertilizer equivalent (MFE) has been estimated in several studies, but the results varied significantly (Fig. 6). Sørensen and Eriksen (2009) observed no significant effects of

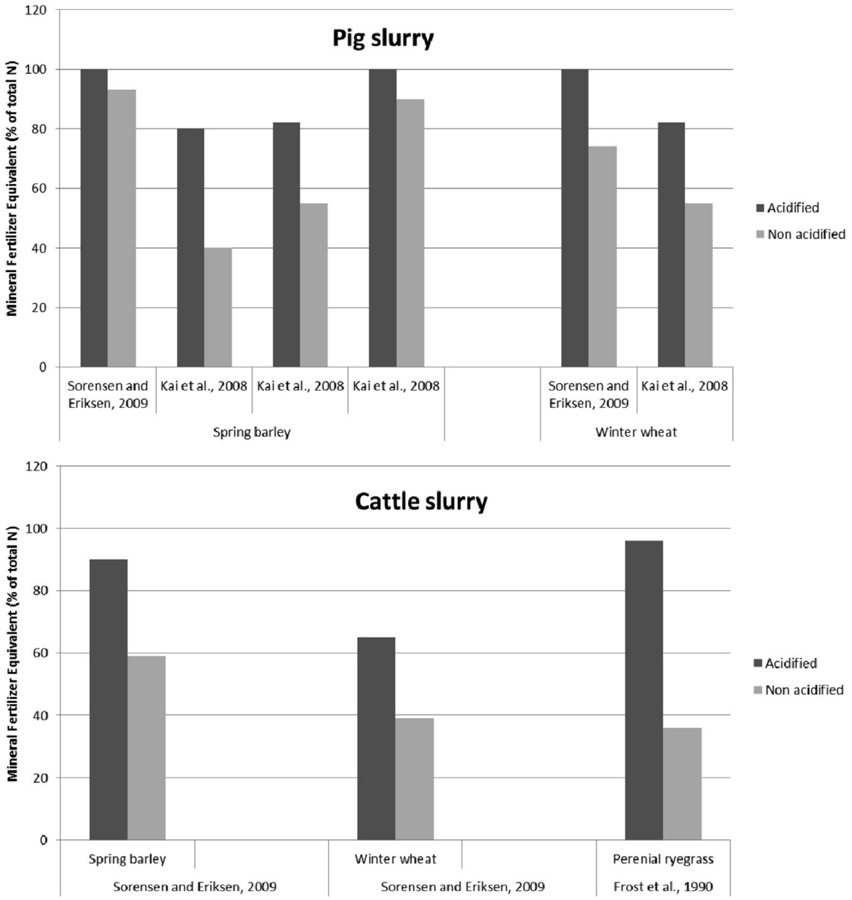

Fig. 6. Effect of slurry acidification on Mineral Fertilizer equivalent.

slurry acidification on the MFE when slurry was incorporated before sowing a barley crop. However, the same authors reported an increase of the MFE in a range of 39–63% for cattle slurry and 74–100% with pig slurry, when acidified slurry was band applied. Kai et al. (2008) reported a 43% increase of the MFE with application of acidified slurry, relative to raw slurry, in a three-year experiment with a winter wheat and spring barley rotation. These authors also reported that N fertilization is easier to manage with acidified slurry, since its NH_4^+ content is more constant relative to non-acidified slurry due to minimal NH_3 losses. This point is essential to increasing the farmer's confidence in using slurry as a substitute for mineral fertilizer.

Roboredo et al. (2012) followed the dynamics of P in soil amended with acidified or non-acidified pig slurry, and observed a significant effect of acidification on the P availability in soil as well as its evolution with time. Slurry acidification increased the most labile fraction of P and no P immobilization was observed in soil amended with acidified slurry. Slurry acidification can indeed induce the dissolution of some inorganic phosphates, leading to higher inorganic P concentrations in the most labile fraction (Section 3.1.2). Petersen et al. (2013) also reported an increase of P availability in soils amended with acidified slurry, relative to non-acidified slurry.

The content of easily accessible organic matter may increase (Section 3.1.3) in soil amended with acidified slurry. This will impact directly on soil microbial activity and indirectly on crop production and nutrient removal, since the dynamics of most nutrients are positively correlated with carbon availability.

The increased availability of nutrients in soils amended with acidified slurry led to significant increases in yields of winter wheat (Kai et al., 2008; Birkmose and Vestergaard, 2013), spring Barley (Kai et al., 2008), and maize (Petersen et al., 2013). When applied to permanent grasslands, acidified slurry also increased herbage yields (Frost et al., 1990; Pain et al., 1994) but, according to Pain et al. (1994), this effect was observed only at the first cut following autumn application whereas in the remaining cuts no differences were observed. Nevertheless, more field trials are still needed to accurately assess this effect.

5.2. *Leaching and runoff*

The speciation of the acid/bases has a significant influence on the chemical system of slurry, namely its ionic strength, particle surface charges, interactions between particles and dissolved compounds, and microbial cell membrane transfer. Therefore, even after soil application, effects of slurry acidification on nutrients leaching can be anticipated. However, only few data from studies performed in controlled conditions are available and field-scale data are still missing. Macedo et al. (2013), in a pot experiment, compared the effects of acidified and non-acidified cattle slurry application to soil and reported no significant differences between the two treatments on nitrate – except during the first 10–15 days, when the NO_3^- concentration in the soil solution resulting from the acidified slurry treatment was 10–20 times lower. This is in agreement with the inhibition/delay of nitrification observed in soils amended with acidified slurry. Semitela et al. (2013) observed, in a sandy soil, higher potential nitrate leaching over the first 30 days following application of non-acidified slurry, relative to acidified slurry, but the opposite was observed after day 30. However, the same authors did not report significant differences between acidified and non-acidified slurry in a sandy loam soil. Fangueiro et al. (2014), in a soil column experiment, did not observe significant differences in the leachate pH, but lower nitrate leaching and higher leaching of salts were observed in soils amended with acidified slurry relative to non-acidified slurry. Macedo et al. (2013) also reported that acidification strongly increased the P concentration in the soil solution, particularly during the first 20 days after slurry application.

It is to be noted that the impact of slurry acidification on nutrients and pathogens run-off has not been considered yet. Although, the risk of surface water contamination by run off is significant since acidified slurry may not be incorporated after application in soils.

6. Potential combination of acidification with other treatment technologies

6.1. Slurry aeration

Slurry aeration is applied upon acidification to minimize foaming, though it is typically applied to stored slurry to induce nitrification-denitrification and to reduce its odor potential by creating an aerobic environment. Part of the rationale of the odor reduction derives from a rapid, aerobic biological degradation of the volatile fatty acids (VFA) contained in slurry – resulting in a reduction of hydrogen sulfide emissions. Nevertheless, the decrease of the VFA concentration in slurry causes an increase of pH, thus contributing to increased ammonia losses (Zhang and Zhu, 2005). Therefore, aeration and acidification may be seen as antagonistic treatments.

Sørensen and Eriksen (2009) showed an insignificant effect of the aeration of slurry acidified to pH 5.5 with sulfuric acid (3.24 g S kg^{-1} pig slurry) on slurry total N, ammonium N, total S and organic N concentration, when compared to non-acidified slurry. The same authors also observed no influence of acidification on the content of VFA. In contrast, Cooper and Cornforth (1978) and Zhang and Zhu (2005) performed studies under different temperatures, redox levels, and treatment times, and observed a significant increase of the decomposition of VFA due to aeration of pig slurry.

6.2. Composting

Nitrogen volatilization during composting is highly influenced by the temperature and pH of the compost (Tran et al., 2011). Despite increased implementation of manure composting, few data on the effect of acidification on gaseous losses and the N content in the final product are available in the literature. Mahimairaja et al. (1994) found that the addition of elemental sulfur to poultry manure (which reduced the pH to 6.1–6.6) prior to composting reduced the emission of NH_3 (compared to non-acidified poultry manure) by 43%–70% depending on the bulking agent. However, no increase in the $NH_4^+ - N$ or $NO_3^- - N$ concentration was observed in composted acidified slurry, suggesting that elemental sulfur addition inhibited the decomposition of uric acid or promoted N immobilization. Gu et al. (2011) assessed the effect of 0.25%–0.50% sulfur (dry weight) and 0.25%–0.50% sulfur in combination with *Thiobacillus thioparus* on the composting of cattle manure. The pH decreased to 6.0–6.3 and a significantly-higher ammonium concentration (with respect to untreated cattle manure) was observed in the amended composting materials. Nevertheless, the 0.5% treatments represented an excess of sulfur, as reflected in the temperature and germination indexes. Addition of $CaCl_2$ or alum to poultry litter or superphosphate $Ca(H_2PO_4)_2$ to solid pig manure also decreased NH_3 emissions during composting, by 10–74% relative to the controls (Kithome et al., 1999; Tran et al., 2011).

6.3. Solid–liquid separation

The liquid fraction from wastewater centrifugation has been observed to increase in volume from 55% to 75% upon lowering the pH from 6.8 to 1.5 (Chen et al., 2001). Similarly, liquid fractions obtained after slurry separation by screw pressing, decanter centrifugation, and flocculation + dewatering increased in volume from 82% to 91%, from 79% to 88%, and from 45% to 56%, respectively, after long-term in-house acidification from pH 7.0 to 5.3 (Cocolo et al., 2013). Lower dewatering resistance has also been observed after acidification of sewage sludge, which can be explained partly by a lower absolute zeta potential (Zhu et al., 2012) (see also Section 3.2). In contrast, a short-term acidification from pH 8.5 to pH 6.0 did not influence the volume of the liquid fraction obtained by centrifugation (Fangueiro et al., 2009). The increased volume of the liquid fraction after in-house slurry acidification seemed to be due to an operationally-simplified settling of the particles and drainage of the liquid fraction (Cocolo et al., 2013); the long-term acidified slurry showed fewer small particles, decreased liquid viscosity, and increased filtration velocity. The short-term acidification may not provide sufficient time for the particle size changes to occur and thus no variation in the liquid fraction volume was observed. The dry matter content in the liquid fraction from acidified slurry has been shown to be greater than in the control slurry (Fangueiro et al., 2009; Cocolo et al., 2013). This can be explained by a more-rapid separation, causing flushing of nutrients to the filtrate or providing less time for settling of small particles upon centrifugation. In addition, an increase of ash, volatile solids, and protein was also observed in the liquid fraction from acidified slurry (Chen et al., 2001; Cocolo et al., 2013). However, no effect was reported in relation to dissolved components such as VFA, K, and sulfide. The acidification caused dissolution of minerals (see Section 3.1.2); thus, the concentrations of P, Mg, Ca, and dissolved divalent, non-precipitating ions such as Cu or Zn increased in the liquid fraction (Fangueiro et al., 2009; Cocolo et al., 2013).

6.4. Anaerobic digestion

Biogas production from H_2SO_4-acidified animal slurry and its liquid fraction has been observed to be below that of the non-acidified slurry and liquid fraction, respectively (Moset et al., 2012a; Sutaryo et al., 2013). This lower biogas production seems to be due to sulfate inhibition (Colleran et al., 1995, 1998; Moset et al., 2012a) or to toxic conditions for some microorganisms, induced by the high levels of sulfide produced by the sulfate-reducing bacteria. In contrast, biogas production from the solid fraction of acidified slurry is typically not lower than from the non-acidified solid fraction (Sutaryo et al., 2013; Sommer et al., 2014) – probably because the contents of the dissolved VFA and sulfate in the acidified solid fraction are low (Sutaryo et al., 2012). Co-digestion of acidified slurry with non-acidified slurry has been proved to increase biogas production by up to 20%, in a mixture with 10–20% acidified slurry (Moset et al., 2012a, 2012b). The organic degradation during storage of the slurry, before feeding it into the biogas reactor, caused an increased content of easily-degradable organic components (Section 3.1.3); this is a likely reason for the increased biogas production. Hence, co-digestion with acidified slurry must balance the beneficial increased content of easily-degradable organic components and the detrimental increased sulfate content. The application of other additives

(Section 2.1) for the acidification rather than H_2SO_4 should not cause sulfate inhibition, but it may cause other toxicity or microbial competition problems.

7. Conclusions

Acidification of animal slurry has proved to be an efficient solution to minimize NH_3 emissions in-house, during storage, and after soil application, as well as to increase the fertilizer value of slurry, without negative impacts on other gaseous emissions. Furthermore, acidification impacts positively on other slurry treatments such as solid–liquid separation or composting; upon the use of a non-sulfur containing additive, it may also impact positively on biogas production. Nevertheless, acidification of slurry might induce higher losses by leaching, due to solubilization of mineral elements.

Today, the main limiting factor of this technology is the handling of concentrated acid that has to be performed by specialized workers and, in consequence, increases the cost. Alternatives to concentrated acids already exist but more research is still needed to improve both their technical and economic aspects. Moreover, the lack of specific equipment for the acidification of solid manures and the separated solid fraction narrows the possible fields of application of the treatment.

More information is needed to have clear evidence that this technology does not induce any pollution swapping. Since slurry acidification is running successfully in Denmark, it is realistic that the technology can be applied in many other countries. However, such dissemination of acidification depends mainly on the country's legislation that will be altered only with a solid scientific basis. The present review highlights the lack of information relative to the long-term impact of acidified slurry application to soil as well as the need for more research on slurry acidification.

Acknowledgments

The research leading to these results has received funding from the Portuguese Fundação para a Ciência e a Tecnologia (FCT) through the projects “Animal slurry management: sustainable practices at field scale” (PTDC/AGR-PRO/119428/2010) and (ProjectPEst-OE/AGR/UI0528/2011), and from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007–2013/under REA grant agreement n° [289887]. The authors were also supported by the Danish Council for Strategic Research (DSF) under the research program “Strategic Research in Sustainable Energy and Environment”, through the project (Ref. 09-067246) “Clean and environmentally friendly animal waste technologies for fertilizer and energy production (Cleanwaste)”. David Fangueiro has received a grant from the FCT (SFRH/BPD/84229/2012). This document reflects only the author's view and the Union is not liable for any use that may be made of the information contained therein.

References

Aarnink, A.J.A., Verstegen, M.W.A., 2007. Nutrition, key factor to reduce environmental load from pig production. Livest. Sci. 109, 194–203.

Anderson, N., Strader, R., Davidson, C., 2003. Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. Environ. Int. 29, 277–286.

Armstrong, K.A., Burns, R.T., Walker, F.R., Wilhelm, L.R., Raman, D.R., 2003. Ammonia concentrations in poultry broiler production units treated with liquid alum. In: Air Pollution from Agricultural Operations III, Proceedings of the 12–15 October 2003 Conference (Research Triangle Park, North Carolina USA), pp. 116–122.

Balsari, P., Dinuccio, E., Gioelli, F., 2006. A low cost solution for ammonia emission abatement from slurry storage. Int. Congr. Ser. 1293, 323–326.

Berg, W., 2003. Reducing ammonia emissions by combining covering and acidifying liquid manure. In: 3rd International Conference on Air Pollution from Agricultural Operations. Raleigh NC., USA, 12–15 October 2003.

Berg, W., Pazsiczki, I., 2006. Mitigation of manure emission during manure storage. Int. Congr. Ser. 1293, 213–216.

Berg, W., Türk, M., Hellebrand, H.J., 2006. Effects of Acidifying Liquid Cattle Manure with Nitric or Lactic Acid on Gaseous Emissions. Workshop on Agricultural Air Quality. Washington D.C USA, (June 2006), pp. 492–498.

Biocover A/S, 2012. Vera Statement. http://www.veracert.eu/-/media/DS/Files/Downloads/Artikler/VERA/VERA_erklaering_2012_okt_enkeltside.pdf (accessed 07.05.14.).

Birkmose, T., Vestergaard, A., 2013. Acidification of slurry in barns, stores and during application: review of Danish research, trials and experience. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Bussink, D.W., Bruins, M.A., 1992. Reduction in ammonia volatilization using different slurry application techniques on grassland. Meststoffen 1, 31–36 (in Dutch).

Chadwick, D., Sommer, S., Thorman, R., Fangueiro, D., Cardenas, L., Amon, B., Misselbrook, T., 2011. Manure management: implications for greenhouse gas emissions. Anim. Feed Sci. Technol. 166–167, 514–531.

Chen, Y., Yang, H., Gu, G., 2001. Effect of acid surfactant treatment on activated sludge dewatering and settling. Water Res. 35, 2615–2620.

Choi, I.H., 2004. A Study on Reducing the Environmental Pollutants from Animal Feces and Urine. Taegu University, Gyong San, South Korea (Ph.D. thesis).

Christensen, M.L., Sommer, S.G., 2013. Manure characterization and inorganic chemistry. In: Sommer, S.G., Christensen, M.L., Schmidt, T., Jensen, L.S. (Eds.), Animal Manure Recycling: Treatment and Management. John Wiley & Sons, Ltd, Chichester, UK.

Christensen, M.L., Hjorth, M., Keiding, K., 2009. Characterization of pig slurry with reference to flocculation and separation. Water Res. 43, 773–783.

Clemens, J., Bergmann, S., Vandre, R., 2002. Reduced ammonia emissions from slurry after self-acidification with organic supplements. Environ. Technol. 23, 429–435.

Cocolo, G., Hjorth, M., Curnis, S., Provolo, G., 2013. Manure acidification affecting solid-liquid separation efficiency. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Colina, J., Lewis, A., Miller, P.S., 2000. A Review of the Ammonia Issue and Pork Production. Nebraska Swine Reports. Paper 108. http://digitalcommons.unl.edu/coopext_swine/108.

Colleran, E., Finnegan, S., Lens, P., 1995. Anaerobic treatment of sulphate containing waste streams. Ant. Van Leeuwenhoek 67, 29–46.

Colleran, E., Pender, S., Phipott, U., O-Flaherty, V., Leahy, B., 1998. Full-scale and laboratory-scale anaerobic treatment of citric acid production wastewater. Biodegradation 9, 233–245.

Cook, K.L., Rothrock, M.J., Warren, J.G., Sistani, K.R., Moore Jr., P.A., 2008. Effect of alum treatment on the concentration of total and ureolytic microorganisms in poultry litter. J. Environ. Qual. 37, 2360–2367.

Cooper, P., Cornforth, I.S., 1978. Volatile fatty acids in stored animal slurry. J. Sci. Food Agric. 29, 19–27.

Dai, X.R., Blanes-Vidal, V., 2013. Emissions of ammonia, carbon dioxide, and hydrogen sulfide from swine wastewater during and after acidification treatment: effect of pH, mixing and aeration. J. Environ. Manag. 115, 147–154.

Daumer, M.L., Picard, S., Saint-Cast, P., Dabert, P., 2010. Technical and economical assessment of formic acid to recycle phosphorus from pig slurry by a combined acidification-precipitation process. J. Hazard Mat. 180, 316–365.

Dinuccio, E., Berg, W., Balsari, P., 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmos. Environ. 42, 2448–2459.

ECETOC, 1994. In: Stringer, D.A. (Ed.), Technical Report n° 62, Ammonia Emissions to Air in Western Europe. Brussels, Belgium, (193 pp).

Eriksen, J., Sorensen, P., Eisgaard, L., 2008. The fate of sulfate in acidified pig slurry during storage and following application to cropped soil. J. Environ. Qual. 37 (1), 280–286.

Eriksen, J., Adamsen, A.P.S., Norgaard, J.V., Poulsen, H.D., Jensen, B.B., Petersen, S.O., 2010. Emissions of sulfur-containing odorants, ammonia, and methane from pig slurry: effects of dietary methionine and benzoic acid. J. Environ. Qual. 39, 1097–1107.

Eriksen, J., Andersen, A.J., Poulsen, H.V., Adamsen, A.P.S., Petersen, S.O., 2012. Sulfur turnover and emissions during storage of cattle slurry: effects of acidification and sulfur addition. J. Environ. Qual. 41 (5), 1633–1641.

Erisman, J.W., Bleeker, A., Hensen, A., Vermeulen, A., 2008. Agricultural air quality in Europe and the future perspectives. Atmos. Environ. 42, 3209–3217.

Fangueiro, D., Ribeiro, H., Vasconcelos, E., Coutinho, J., Cabral, F., 2009. Treatment by acidification followed by solid-liquid separation affects slurry and slurry fractions composition and their potential of N mineralization. Bioresour. Technol. 100 (20), 4914–4917.

Fangueiro, D., Ribeiro, H., Coutinho, J., Cardenas, L., Trindade, H., Cunha-Queda, C., Vasconcelos, E., Cabral, F., 2010. Nitrogen mineralization and CO_2 and N_2O emissions in a sandy soil amended with original or acidified pig slurries or with the relative fractions. Biol. Fert. Soil 46 (4), 383–391.

Fangueiro, D., Surgy, S., Coutinho, J., Vasconcelos, E., 2013. Impact of cattle slurry acidification on carbon and nitrogen dynamics during storage and after soil incorporation. J. Plant Nutr. Soil Sci. 176, 540–550.

Fangueiro, D., Surgy, S., Napier, V., Menaia, J., Vasconcelos, E., Coutinho, J., 2014. Impact of slurry management strategies on potential leaching of nutrients and pathogens in a sandy soil amended with cattle slurry. J. Environ. Manag. 146, 198–205.

Feilberg, A., Liu, D., Nyord, T., 2014. Temporal variation in odorant composition following land application of manure. Chem. Eng. Trans. 40, 55–60.

Frost, J.P., 1994. Effect of spreading method, application rate and dilution on ammonia volatilization from cattle slurry. Grass Forage Sci. 49, 391–400.

Frost, J.P., Stevens, R.J., Laughlin, R.J., 1990. Effect of separation and acidification on ammonia volatilization and on the efficiency of slurry nitrogen for herbage production. J. Agric. Sci. 115, 49–56.

Gu, W., Zhang, F., Xu, P., Tang, S., Xie, K., Huang, X., Huang, Q., 2011. Effects of sulphur and *Thiobacillus thioparus* on cow manure aerobic composting. Bioresour. Technol. 102, 6529–6535.

Gungor, K., Jurgensen, A., Karthikeyan, K.G., 2007. Determination of phosphorus speciation in dairy manure using XRD and XANES Spectroscopy. J. Environ. Qual. 36 (6), 1856–1863.

Gyldenkaerne, S., 2013. Estimation of the Green House Gas (GHG) Emission from the Manure Application System SyreN+. Report. Aarhus University, p. 11.

Harsø Maskiner A/S, 2014. http://harso.dk/tankforsuring-.html (accessed 07.05.14.).

Hartung, J., Phillips, V.R., 1994. Control of gaseous emissions from livestock buildings and manure stores. J. Agric. Eng. Res. 57, 173e189.

Hjorth, M., Cocolo, G., Jonassen, K., Sommer, S.G., 2013. Acidifications effect on transformations in and composition of animal slurry. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Huijsmans, J.F.M., Hol, J.M.G., Vermeulen, G.D., 2007. Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. Atmos. Environ. 37, 3669–3680.

Husted, S., Jensen, L.S., Jorgensen, S.S., 1991. Reducing ammonia loss from cattle slurry by the used of acidifying additives: the role of the buffer system. J. Sci. Food Agric. 57, 335–349.

Infarm A/S, 2014a. http://mst.dk/virksomhed-myndighed/landbrug/husdyrgodkendelser/den-bedste-tilgaengelige-teknik-(bat)-og-miljoeteknologi/teknologilisten/ (accessed 07.05.14.).

Infarm A/S, 2014b. http://infarm.dk (accessed 20.09.14.).

Jensen, A.O., 2002. Changing the environment in swine buildings using sulfuric acid. Trans. ASAE 45 (1), 223–227.

Jensen, L.S., Sommer, S.G., 2013. Manure organic matter – characteristics and microbial transformation. In: Sommer, S.G., Christensen, M.L., Schmidt, T., Jensen, L.S. (Eds.), Animal Manure Recycling: Treatment and Management. John Wiley & Sons, Ltd, Chichester, UK.

Jørgen Hyldgaard Staldservice A/S, 2014. http://www.jhstaldservic.dk/landbrug/tag/forsuring-teknologi-listen (accessed 07.05.14.).

Kai, P., Pedersen, P., Jensen, J.E., Hansen, M.N., Sommer, S.G., 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. Eur. J. Agron. 28, 148–154.

Kithome, M., Paul, J.W., Bomke, A.A., 1999. Reducing nitrogen losses during simulated composting of poultry manure using adsorbents or chemical amendments. J. Environ. Qual. 28, 194–201.

Kyndestoft Maskinfabrik Aps, 2014. http://mst.dk/media/mst/8059874/melt_indstilling_kyndestoft_till_g_fuldg_dskning_endelig140318.pdf (accessed 07.05.14.).

Lefcourt, A.M., Meisinger, J.J., 2001. Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. J. Dairy Sci. 84, 1814–1821.

Li, H., Xin, H., Burns, R.T., Liang, Y., 2006. Reduction of Ammonia Emission from Stored Poultry Manure Using Additives: Zeolite, Al+clear, Ferix-3 and PLT” Agricultural and Biosystems Engineering Conference Papers, Posters and Presentations 2006 ASABE Annual International Meeting, Portland, Oregon.

Lindsay, W.L., 1979. Chemical Equilibria in Soils. Wiley-Interscience, USA.

Line, J.E., Bailey, J.S., 2006. Effect of on-farm litter acidification treatments on *Campylobacter* and *Salmonella* populations in commercial broiler houses in northeast Georgia. Poult. Sci. 85, 1529–1534.

Macedo, S., Vasconcelos, E., Semitela, S., Coutinho, J., Fangueiro, D., 2013. Effects of soil application techniques and cattle slurry pre-treatment on NH_3 emissions and soil solution composition – a pot experiment. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Mahimairaja, S., Bolan, N.S., Hedley, M.J., MacGregor, A.N., 1994. Losses and transformation of nitrogen during composting of poultry manure with different amendments: an incubation experiment. Bioresour. Technol. 47, 265–273.

McCrory, D.F., Hobbs, P.J., 2001. Additives to reduce ammonia and odor emissions from livestock wastes: a review. J. Environ. Qual. 30, 345–355.

Misselbrook, T.H., Smith, K.A., Johnson, R.A., Pain, B.F., 2002. Slurry application techniques to reduce ammonia emissions: results of some UK field-scale experiments. Biosyst. Eng. 81 (3), 313–321.

Moayadi, H., Asadi, A., Huat, B.B.K., Kazemian, S., 2011. Zeta potential of organic soil in presence of calcium chloride, cement and polyvinyl alcohol. Int. J. Electrochem. Sci. 6, 4493–4503.

Monteny, G.J., Erisman, J.W., 1998. Ammonia emission from dairy cow buildings: a review of measurement techniques, influencing factors and possibilities for reduction. Neth. J. Agric. Sci. 46, 225–247.

Moore, P.A., Daniel, T.C., Edwards, D.R., 1999. Reducing phosphorus runoff and improving poultry production with alum. Poult. Sci. 78, 692–698.

Moore, P.A., Daniel, T.C., Edwards, D.R., 2000. Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminum sulfate. J. Environ. Qual. 29 (1), 37–49.

Moset, V., Cambra-López, M., Møller, H.B., 2012a. The inhibiting effect of sulfate on thermophilic anaerobic digestion of cattle and pig waste slurry. Trans. ASABE 55, 2309–2317.

Moset, V., Cerisuelo, A., Sutaryo, S., Møller, H.B., 2012b. Process performance of anaerobic co-digestion of raw and acidified pig slurry. Water Res. 46, 5019–5027.

Nahm, K.H., 2005. Environmental effects of chemical additives used in poultry litter and swine manure. Crit. Rev. Env. Sci. Tech. 35, 487–513.

Ndegwa, P.M., Hristov, A.N., Arogo, J., Sheffield, R.E., 2008. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. Biosyst. Eng. 100, 453–469.

Nørgaard, J.V., Fernández, J.A., Sørensen, K.U., Wamberg, S., Poulsen, H.D., Kristensen, N.B., 2010. Urine acidification and mineral metabolism in growing pigs fed diets supplemented with dietary methionine and benzoic acid. Livest. Sci. 134, 116–118.

Nyord, T., Liu, D., Eriksen, J., Adamsen, A.P.S., 2013. Effect of acidification and soil injection of animal slurry on ammonia and odour emission. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Oerum Smeden, 2014. http://www.oerum-smeden.dk/default.efact?pid=7577 (accessed 07.05.14.).

Ottosen, L.D.M., Poulsen, H.V., Nielsen, D.A., Finster, K., Nielsen, L.P., Revsbech, N.P., 2009. Observations on microbial activity in acidified pig slurry. Biosyst. Eng. 102 (3), 291–297.

Pain, B.F., Misselbrook, T.H., Rees, Y.J., 1994. Effects of nitrification inhibitor and acid addition to cattle slurry on nitrogen losses and herbage. Grass Forage Sci. 49, 209–215.

Panetta, D.M., Powers, W.J., Lorimor, J.C., 2005. Management strategy impacts on ammonia volatilization from swine manure. J. Environ. Qual. 34, 1119–1130.

Petersen, S.O., Sommer, S.G., Béline, F., Burton, C., Dach, J., Dourmad, J.Y., Leip, A., Misselbrook, T., Nicholson, F., Poulsen, H.D., Provolo, G., Sørensen, P., Vinneras, B., Weiske, A., Bernal, M.-P., Bohm, R., Juhász, C., Mihelic, R., Martinez, J., 2007. Recycling of livestock wastes and other residues—a whole farm perspective. Livest. Prod. Sci. 112, 180–191.

Petersen, S.O., Andersen, A.J., Eriksen, J., 2012. Effects of cattle slurry acidification on ammonia and methane evolution during storage. J. Environ. Qual. 41, 88–94.

Petersen, J., Lemming, C., Rubæk, G.H., 2013. Side-band injection of acidified cattle slurry as starter P-fertilization for maize seedlings. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Portejoie, S., Martinez, J., Guiziou, F., Coste, C.M., 2003. Effect of covering pig slurry stores on the ammonia emission processes. Bioresour. Technol. 87, 199–207.

Portejoie, S., Dourmad, J.Y., Martinez, J., Lebreton, Y., 2004. Effect of lowering dietary crude protein on nitrogen excretion, manure composition and ammonia emission from fattening pigs. Livest. Prod. Sci. 91, 45–55.

Ritz, C.W., Fairchild, B.D., Lack, M.P., 2004. Implications of ammonia production and emissions from commercial poultry facilities: a review. J. Appl. Poult. Res. 13, 684–692.

Roboredo, M., Fangueiro, D., Lage, S., Coutiho, J., 2012. Phosphorus dynamics in soils amended with acidified pig slurry and derived solid fraction. Geoderma 189–190, 328–333.

Rothrock Jr., M.J., Cook, K.L., Warren, J.G., Sistani, K.R., 2008. The effect of alum addition on poultry litter microbial communities. Poult. Sci. 87, 1493–1503.

Rotz, C.A., 2004. Management to reduce nitrogen losses in animal production. J. Anim. Sci. (Suppl) 82, 119–137.

Safley, L.M., Nelson, D.W., Westerman, P.W., 1983. Conserving manurial nitrogen. Trans. ASAE 30, 1166–1170.

Semitela, S., Martins, F., Coutinho, J., Cabral, F., Fangueiro, D., 2013. Ammonia emissions and potential nitrate leaching in soil amended with cattle slurry: effect of slurry pre-treatment by acidification and/or soil application method. In: Proceedings from the 15th RAMIRAN Conference, Versailles, France.

Shi, Y., Parker, D.B., Cole, N.A., Auvermann, B.W., Mehlhorn, J.E., 2001. Surface amendments to minimize ammonia emissions from beef cattle feedlots. Trans. ASAE 44, 677–682.

Sims, J.T., Luka-McCafferty, N.J., 2002. On-farm evaluation of aluminum sulfate (alum) as a poultry litter amendment: effect on litter properties. J. Environ. Qual. 31, 2066–2073.

Smith, D.R., Moore Jr., P.A., Griffis, C.L., Daniel, T.C., Edwards, D.R., Boothe, D.L., 2001. Effects of alum and aluminum chloride on phosphorus runoff from swine manure. J. Environ. Qual. 30, 992–998.

Smith, D.R., Moore, P.A., Haggard Jr., B.E., Maxwell, C.V., Daniel, T.C., vanDevander, K., Davis, M.E., 2004. Effect of aluminum chloride and dietary phytase on relative ammonia losses from swine manure. J. Anim. Sci. 82, 605–611.

Sommer, S.G., 1997. Ammonia volatilization from farm tanks containing anaerobically digested animal slurry. Atmos. Environ. 31, 863–868.

Sommer, S.G., Husted, S., 1995. A simple model of pH in slurry. J. Agric. Sci 124, 447–453.

Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure and its reduction—invited paper. Eur. J. Agric. 15, 1–15.

Sommer, S.G., Petersen, S.O., Søgaard, H.T., 2000. Emission of greenhouse gases from stored cattle slurry and slurry fermented at a biogas plant. J. Environ. Qual. 29, 744–751.

Sommer, S.G., Génermont, S., Cellier, P., Hutchings, N.J., Olesen, J.E., Morvan, T., 2003. Processes controlling ammonia emission from livestock slurry in the field. Eur. J. Agron. 19, 465–486.

Sommer, S.G., Hjorth, M., Leahy, J.J., Zhu, K., Christel, W., Sutaryo, S., Sørensen, C.A.G., 2014. Pig slurry characteristics, nutrient balance and biogas production as affected by separation and acidification. J. Agric. Sci. available on CJO2014 http://dx.doi.org/10.1017/S0021859614000367.

Sørensen, P., Amato, M., 2002. Remineralisation and residual effects of N after application of pig slurry to soil. Eur. J. Agron. 16, 81–95.

Sørensen, P., Eriksen, J., 2009. Effect of slurry acidification with sulphuric acid combined with aeration on the turnover and plant availability of nitrogen. Agric. Ecosyst. Environ. 131, 240–246.

Stevens, R.J., Laughlin, R.J., Frost, J.P., 1989. Effect of acidification with sulphuric acid on the volatilization of ammonia from cow and pig slurries. J. Agric. Sci. Camb. 113, 389–395.

Stevens, R.J., Laughlin, R.J., Frost, J.P., 1992. Effects of separation, dilution, washing and acidification on ammonia volatilization from surface-applied cattle slurry. J. Agric. Sci. 119, 383–389.

Stevens, R.J., Laughlin, R.J., O'Bric, C.J., 1995. The fate of nitrate in cattle slurry acidified with nitric acid. J. Agric. Sci. 125, 239–245.

Sutaryo, S., Ward, A.J., Møller, H.B., 2012. Thermophilic anaerobic co-digestion of separated solids from acidified dairy cow manure. Bioresour. Technol. 114, 195–200.

Sutaryo, S., Ward, A.J., Møller, H.B., 2013. Anaerobic digestion of acidified slurry fractions derived from different solid-liquid separation methods. Bioresour. Technol. 130, 495–501.

Tran, M.T., Vu, T.K.V., Sommer, S.G., Jensen, L.S., 2011. Nitrogen turnover and loss during storage of slurry and composting of solid manure under typical Vietnamese farming conditions. J. Agric. Sci. 149, 285–296.

Vandre, R., Clemens, J., 1997. Studies on the relationship between slurry pH,volatilization processes and the influence of acidifying additives. Nutr. Cycl. Agroecosys 47, 157–165.

Velthof, G., Oenema, O., 1993. Nitrous oxide from nitric-acid-treated cattle slurry applied to grassland under semi-controlled conditions. Neth. J. Agri. Sci. 41, 81–93.

Webb, J., Pain, B., Bittman, S., Morgan, J., 2010. The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response-A review. Agric. Ecosyst. Environ. 137, 39–46.

Wenzel, H., Petersen, B.M., 2009. Life Cycle Assessment of Slurry Management Technologies. Environmental Project No. 1298. Danish Ministry of the Environment, Environmental Protection Agency, Copenhagen, Denmark.

Wesnæs, M., Wenzel, H., Petersen, B.M., 2009. Life Cycle Assessment of Slurry Management Technologies. Danish Ministry of the Environment, Environmental Protection Agency, Copenhagen, Denmark, p. 266.

Witter, E., Kirchmann, H., 1989. Effects of addition of calcium and magnesium salts on ammonia volatilization during manure decomposition. Plant Soil 115, 53–58.

Zhang, Z., Zhu, J., 2005. Effectiveness of short term aeration in treating swine finishing manure to reduce odour generation potential. Agric. Ecosyst. Environ. 78, 93–106.

Zhang, D., Yuan, X., Guo, P., Suo, Y., Wang, X., Wang, W., Cui, Z., 2011. Microbial population dynamics and changes in main nutrients during the acidification process of pig manures. J. Environ. Sci. 23, 497–505.

Zhu, H.F., Zhou, L.X., Wang, D.Z., 2012. Effect of acidification on the dewaterability of sewage sludge in bioleaching. Environ. Sci. 33, 916–921.