Emissions of ammonia, carbon dioxide, and hydrogen sulfide from swine wastewater during and after acidification treatment: Effect of pH, mixing and aeration

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ABSTRACT

This study aimed at evaluating the effect of swine slurry acidification and acidification-aeration treatments on ammonia (NH₃), carbon dioxide (CO₂) and hydrogen sulfide (H₂S) emissions during slurry treatment and subsequent undisturbed storage. The study was conducted in an experimental setup consisting of nine dynamic flux chambers. Three pH levels (pH = 6.0, pH = 5.8 and pH = 5.5), combined with short-term aeration and venting (with an inert gas) treatments were studied. Acidification reduced average NH₃ emissions from swine slurry stored after acidification treatment compared to emissions during storage of non-acidified slurry. The reduction were 50%, 62% and 77% when pH was reduce to 6.0, 5.8 and 5.5, respectively. However, it had no significant effect on average CO₂ and H₂S emissions during storage of slurry after acidification. Aeration of the slurry for 30 min had no effect on average NH₃, CO₂ and H₂S emissions both during the process and from stored slurry after venting treatments. During aeration treatment, the NH₃, CO₂ and H₂S release pattern observed was related to the liquid turbulence caused by the gas bubbles rather than to biological oxidation processes in this study.

1. Introduction

Air pollutants, such as ammonia (NH₃), hydrogen sulfide (H₂S), methane (CH₄), and nitrous oxide (N₂O), emitted from animal wastewater (slurry) can affect human and animal health and the natural environment (Hartung and Phillips, 1994; Erisman et al., 2008). Deposition of NH₃ gas and particulate ammonia can cause eutrophication of surface water and may acidify ecosystems. Ammonia release from animal waste has received much attention from policy makers because of the large contribution of livestock production to the total NH₃ emissions from anthropogenic sources. Approximately 80% of European and US NH₃ emissions come from livestock production (Hutchings et al., 2001; Webb et al., 2005; Erisman et al., 2008). Swine production buildings and slurry storage facilities contribute to 50% of the NH₃ emissions in Denmark, France, and the Netherlands (van der Peet-Schwering et al., 1999).

Hydrogen sulfide has been reported as a main toxic substance associated with swine operations. Acute exposure to such gases emanating from animal manure can cause severe health impairment to farm operators (Donham et al., 1982). The concentration of H₂S above stored swine slurry is usually below 1 ppm (Ni et al., 2010). However, when slurry is agitated (e.g. during emptying of slurry pits), a short-term peak of very high H₂S concentrations occur (Blanes-Vidal et al., 2009a).

Carbon dioxide is a greenhouse gas, although the contribution of CO₂ released from swine wastes to the overall greenhouse effect is very limited. Quantification of CO₂ production from swine slurry is important because the co-release of NH₃ and CO₂ determines the formation of a pH profile at the slurry surface, and so the emission of other acidic (such as H₂S and CH₃COOH) and basic compounds (Blanes-Vidal and Nadimi, 2011).

Reduction of the NH₃ emissions in Europe has become increasingly significant for more than one decade. International regulations include the Gothenburg Protocol on Long-range Transboundary Air Pollution (UNECE, 1999) (stating the necessity of reducing NH₃ emissions by 12% in 2010 relative to 1990) and the EU directives and strategies (EC, 1997, 1999), e.g. the National Emissions Ceilings Directive (NECD). In the Thematic Strategy on Air Pollution (CEC, 2005), the European Commission expressed the environmental objectives for 2020, aimed at reducing 27% of agricultural NH₃ emissions in the EU25 compared to 2000, approximately 23% of the reduction have to be met by introduction of specific abatement measures in agriculture.
In order to reduce NH₃ emissions, different technologies have been developed (Ndewgwa et al., 2008). Among them, one of the effective mitigation strategies is slurry acidification, which has been approved as Best Available Technology (BAT) in Denmark (Kai et al., 2008). Previous studies have reported that about 70–85% of the NH₃ release from swine slurry can be reduced by decreasing the slurry pH to 5.5 through the addition of sulfuric acid (H₂SO₄) (Stevens et al., 1989; Frost et al., 1990; Kai et al., 2008). Acidification also improves the mineral N fertilizer equivalence (MFE) of the slurry by 25% (Sørensen and Eriksen, 2009).

Although effect of acidification on NH₃ emissions has been known for many years, its implications on the emission of other compounds, such as CO₂ and H₂S, has not been fully documented in the literature. The release of dissolved gases from slurry is a function of the concentration of gas present in the slurry surface in a non-ionized form, which will be affected by the slurry surface pH. Therefore, a reduction of slurry pH favors the emission of weak acid forming gases such as CO₂ and H₂S. Furthermore, acidification by addition of H₂SO₄ may increase the concentration of inorganic sulfates in the slurry, which could potentially result in an increase of H₂S emission as a result of the additional sulfate provided as substrate to sulfate-reducing bacteria. However, acidification caused low pH may also inhibit the bacterial activities in slurry and limit the sulfate reduction (Eriksen et al., 2008).

Aeration has been applied to stored slurry to create aerobic environment to reduce odor potential via biological degradation of volatile fat acid (VFA) (Zhang and Zhu, 2005). However, the decrease of VFA in slurry results in an increase of slurry pH and shifts the NH₄⁺ = NH₃ + H⁺ equilibrium, which may contribute to increased NH₃ volatilization losses (Paul and Beauchamp, 1989; Zhang and Zhu, 2005). By contrast, Clark et al. (2005) proposed a low-level of bubbling air, being intent to promote the gradual release of gases (i.e. H₂S) generated in anaerobic condition at innocuous rates throughout the storage rather than to oxidize the volatile compounds in the slurry.

A new slurry acidification technology, which combines acidification with aeration, has been recently introduced in Denmark and is currently in use in more than eighty Danish fattening pig farms (Eriksen et al., 2008; Kai et al., 2008; Sørensen and Eriksen, 2009). The use of this acidification technology is expected to increase in the coming years, as it has been estimated that in 2020 between 16 and 28% of the Danish commercial fattening pig farms will use a commercially available slurry acidification technology (Aaes et al., 2008).

In this acidification-aeration technology, slurry from the in-barn storage pit is transported to a process tank, where it is acidified to a pH of 5.5 by controlled addition of concentrated sulfuric acid (H₂SO₄), the acidified slurry is then pumped back to the barn pit, resulting in a reduction of slurry pH to 6.0 shortly after excretion (Sørensen and Eriksen, 2009). During acidification treatment, low-level aeration is also applied, as observation and practical experience has shown that it helps to decrease the formation of foam during the addition of acid (Kai et al., 2008; Sørensen and Eriksen, 2009).

The effect of this combined acidification/aeration treatment needs to be evaluated from a wider perspective, including emissions during treatment and storage, and considering not only the targeted gas (NH₃), but also other important gases (CO₂ and H₂S) whose emission can be affected by the treatment.

The objectives of the study were: (1) to investigate the effect of different pH levels on the emission of NH₃, CO₂ and H₂S from swine slurry during and after acidification treatment; and (2) to compare the contribution of aeration to the efficacy of the acidification process (reduction of pH and NH₃ emission) and its effect on the emission of other compounds (CO₂ and H₂S).

2. Materials and methods

2.1. Experimental setup and procedure

The study was conducted in a laboratory using nine dynamic flux chambers, each with a volume of 30 L and a height of 51 cm (Fig. 1S). An air inlet and an exhaust air outlet were installed in the top cap. At the center of the top cap, five other ports were installed for headspace NH₃, CO₂ and H₂S concentration measurement, pH measurement, slurry stirring, addition of fresh slurry and acid, and slurry aeration. The inlet and outlet air ducts and the sampling points were located 3 cm below the top cap. All the ports were closed by plugs to make the chamber interface airtight during the storage. A water tap was installed in the middle of the side of each chamber for slurry sampling. Slurry was collected from under-floor deep pits of a fattening pig barn after 6–7 days accumulation from last empty. Four days before starting the first treatment, each flux chamber was filled with 20 L of homogenized swine slurry to a depth of 35 cm. During the experimental period the chambers were ventilated at a constant airflow rate of 1.9 L/min, which was maintained by a critical orifice inserted in the outflow tube, between a filter and the air pump.

The experimental design included four pH levels: non-acidified slurry (pHn), and slurry acidified to pH = 6.0 (A6.0), pH = 5.8 (A5.8), and pH = 5.5 (A5.5). Acidification has been performed by addition of concentrated sulfuric acid while mixing with a portable paddle mixer at 500 rpm in the center of the slurry chamber. Besides, the effect of two types of venting gases: air (Ga) (for the aeration treatment) and nitrogen gas (Gn) (an inert gas that creates slurry agitation with no oxidation effects) with comparison to no venting treatment (Go) were studied (Table 1). The pH level 5.5 was selected according to previous literature (Eriksen et al., 2008; Kai et al., 2008; Sørensen and Eriksen, 2009), while levels pH = 6.0 and pH = 5.8 were selected to assess the gas emission reduction achieved with a less severe acidification treatment (which involves less economical expenses related to acid addition). Aeration of 30 min at a ratio of 0.04 L s⁻¹ was applied following the velocity used in practice and our pre-test in the fresh swine manure (DM content of 5.4%) to have homogeneous bubbles coming out to the surface. The total duration of the experiment was 155 days. Slurry treatments were applied three times (days 5–8: T0, days 26–27: T1 and days 56–57: T2) during the experiment. The first treatment (T0) was performed to create acidified slurry, while, the subsequent treatments (T1 and T2) correspond to two repetitions of the acidification-aeration treatment performed on the mixture of acidified slurry and non-acidified slurry added to the flux chamber (which corresponds to the slurry added to the pit by animal excretion in commercial farms). After each acidification treatment, slurries in all flux chambers (acidified and non-acidified slurries) were stored under undisturbed conditions. The experimental procedure for each slurry chamber is summarized in Table 1.

2.2. Slurry pH and characteristics

Surface pH measurements at three different depths (0.5–1 cm, 4 cm and 6 cm from the slurry surface) were measured by a pH meter (model PHM210, Meterlab Radiometer Analytical, Lyon, France, accuracy ±0.01 pH units), at the same location at the beginning of the experiment, before each treatment, during each acidification, and 30 min after acidification. Two slurry samples per chamber were collected immediately after filling and analyzed for dry matter (DM), total nitrogen (TN), total ammonium nitrogen (TAN), total inorganic carbon (TIC), and total sulfide (TS). Slurry subsamples were evaporated to dryness...
with a constant weight in an oven at 105 °C for 24 h, and the remaining mass was recorded as DM. TN was analyzed by Kjeldahl method, and TAN was determined using titration with hydrochloric acid (HCl, 1 mol L⁻¹) as described by Sommer (1997). TS were determined by titration (T50 Titrator, Mettler Toledo, Columbus, USA) with 100× dilution. TIC was determined using titration with hydrochloric acid (HCl, 1 mol L⁻¹) as described by Sommer (1997). DM was recorded as the remaining mass. TN was analyzed by Kjeldahl method, and TAN was determined using ammonium cuvette test (E, mg m⁻² d⁻¹). The differences on the initial slurry conditions (pH and concentrations) from different flux chambers and the effects of pH level and mixing on NH₃ and H₂S emissions during and after slurry treatments were studied by analysis of variance (ANOVA) at a significance level of 0.05 and Tukey's honestly significant difference test were used for subsequent multiple comparisons. The statistical analyses were performed in Matlab version 7.11.0 (R2010b, Mathworks Inc. Natick, MA, USA).

2.3. Gas concentrations and emissions

Headspace NH₃ and CO₂ concentrations were continuously measured during the 155 days experimental period using an infrared 1412 photoacoustic multi-gas analyser and a multiplexer 1009 (Innova Air Tech Instruments A/S, Denmark), compensated for gas and water interferences. The detection limits for NH₃ and CO₂ were 0.2 ppm and 1.5 ppm respectively (1 atm, 20 °C). The sampling rate was 45 s, so a gas emission data from each chamber was obtained every approximately 10 min. For each of the treatment process, the NH₃ and CO₂ concentration observations were one (during mixing), three to five (during acidification) and two to three data points (during venting). Concentrations of H₂S were measured during acidification treatments (at three moments: right after slurry addition, slurry mixing and aeration) and once per day (three measurements at the same location) during undisturbed storage after treatment, using a H₂S analyzer (Arizona Instrument LLC, model Jerome 631-X, measurement range 0.001 ppm–50 ppm). A Teflon tube was used to connect the analyzer to the inlet and outlet connections. During the acidification treatment, the concentrations of H₂S exceeded the analyzer's detection limit, and therefore precision gas detector tubes (kitagawa, Japan; range from 0.75 to 300 ppm and 0.005%–0.16%) were used.

Gas emissions from the slurry during the experiments (E, mg m⁻² s⁻¹) were calculated as follows (Eq. (1)):

\[ E = \frac{(C_{o} - C_{i}) \cdot Q}{S} \]  

where \( C_{o} \) and \( C_{i} \) are the gas concentrations (mg m⁻³) at the outlet and inlet, respectively, \( Q \) is the airflow rate (m³ s⁻¹), and \( S \) is the emitting surface area (m²).

2.4. Statistical analysis

The differences on the initial slurry conditions (pH and compositions) from different flux chambers and the effects of pH level and aeration on NH₃, CO₂ and H₂S emissions during and after slurry treatments were studied by analysis of variance (ANOVA) at a significance level of 0.05 and Tukey's honestly significant difference test were used for subsequent multiple comparisons. The statistical analyses were performed in Matlab version 7.11.0 (R2010b, Mathworks Inc. Natick, MA, USA).

3. Results and discussion

3.1. Slurry characteristics

Measured slurry pH, DM, TN, TAN, TS, TIC at day 0 were on average of 6.31 ± 0.08 pH units, 53.49 ± 2.99 g kg⁻¹, 4.94 ± 0.04 g kg⁻¹, 3.15 ± 0.06 g kg⁻¹, 1.86 ± 0.04 g kg⁻¹, 4.79 ± 0.14 g kg⁻¹ (mean ± standard deviations, \( n = 9 \)), respectively. In Table 2 the measurements for each individual flux chamber are shown. Slurry composition and pH values were in agreement with data reported in previous studies (Sanchez and Gonzalez, 2005; Fangueiro et al., 2009; Sorensen and Eriksen, 2009).

No statistical differences regarding pH and slurry characteristics at day 0 were found among the different flux chambers, indicating that any eventual differences in the gas measurements cannot be attributed to slurry composition differences.
3.2. Gas emissions during slurry addition, mixing, acidification treatment and venting treatment

The emissions of NH$_3$ and CO$_2$ during slurry addition, slurry mixing, addition of acid while mixing, and venting treatment (with air or N$_2$ bubbles) are shown in Fig. 1. Differences of NH$_3$ and CO$_2$ emissions among the flux chambers (during each treatment step) were not significant ($P > 0.05$). This indicates that the measurements from the different chambers can be considered as replicates and that descriptive statistics can be performed on these. Average NH$_3$ and CO$_2$ emissions during slurry addition were 3.09 ± 0.96 mg m$^{-2}$ min$^{-1}$ and 146 ± 69 mg m$^{-2}$ min$^{-1}$, respectively (averaged from pHn; as data in acidified slurry were not obtained because slurry mixing was performed shortly after slurry addition). Average NH$_3$ and CO$_2$ emissions during slurry mixing were 1.01 ± 0.28 mg m$^{-2}$ min$^{-1}$ and 621 ± 194 mg m$^{-2}$ min$^{-1}$, respectively. Average NH$_3$ emissions during acidification treatment were 0.56 ± 0.17 (for A6.0), 0.63 ± 0.08 (for A5.8), 0.51 ± 0.06 (for A5.5) mg m$^{-2}$ min$^{-1}$, respectively (averaged for all chambers containing slurry acidified at the same pH level: 6.0, 5.8 or 5.5). These NH$_3$ emissions during acidification, from slurries acidified at different pH levels were not significantly different ($P > 0.05$). Average CO$_2$ emissions during acidification were 1029 ± 211 (A6.0), 1348 ± 390 (A5.8), 1328 ± 122 (A5.5) mg m$^{-2}$ min$^{-1}$, respectively. Although the results showed higher CO$_2$ emissions at pH = 5.5 and 5.8 than at pH = 6.0 during acidification, but no statistical differences were found ($P > 0.05$). This can be explained by the fact that, the lower the pH, the longer the time required for acidification and the higher the disturbance of the slurry. Higher levels of disturbance result in more CO$_2$ release. Ammonia emissions averaged from treatments with venting air (Ga) and venting using N$_2$ (Gn) were 0.52 ± 0.12 and 0.60 ± 0.25 mg m$^{-2}$ min$^{-1}$, respectively, while average CO$_2$ emissions were 1034 ± 410 and 1202 ± 433 mg m$^{-2}$ min$^{-1}$, respectively. Although the averaged NH$_3$ and CO$_2$ emissions of treatments with aeration appeared to be lower than those of treatments with venting N$_2$, no significant difference was found between them ($P > 0.05$). During the entire treatment, average CO$_2$ emissions from slurry acidified to pH = 5.8 (A5.8) and 5.5 (A5.5) were significantly higher than from non-acidified slurry (Table 3). Averaged NH$_3$ emissions of the treatment with only slurry addition (pHnG0) were significantly higher than all other treatments including slurry mixing, acidification, and venting treatment (Table 3). Slurry disturbance caused by addition, mixing or other agitation (e.g. venting) resulted in a breakage of surface buffer equilibrium and a reduction of surface pH (Blanes-Vidal et al., 2012). The higher emission of NH$_3$ from pHnG0 treatment was because of less pH reduction caused by agitation (only slurry addition) during the treatment process, and higher pH level favors higher NH$_3$ emissions.

Slurry disturbance caused by the treatment had an immediate decrease of NH$_3$ emission (57–83%) and a sharp increase of CO$_2$ emission (279–443%) (Fig. 2), in agreement with Ni et al. (2009) and Blanes-Vidal et al. (2012). In the latter study, it showed a decrease of NH$_3$ emissions by 61–91% and an increase of CO$_2$ emissions by 40–1515% after slurry disturbance (slurry addition or mixing).

Hydrogen sulfide emissions during slurry treatment were more than ten thousand fold higher (by 34,674–233,770%) than the emissions before treatment. Large variations in H$_2$S emissions

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### Table 2

Characteristics of the slurry at day 0.$^a$

<table>
<thead>
<tr>
<th>Flux chambers$^b$</th>
<th>pHnG0</th>
<th>pHnGn</th>
<th>pHnGa</th>
<th>A6.0Gn</th>
<th>A6.0Ga</th>
<th>A5.8Gn</th>
<th>A5.8Ga</th>
<th>A5.5Gn</th>
<th>A5.5Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM (g kg$^{-1}$)</td>
<td>48.81</td>
<td>51.63</td>
<td>50.22</td>
<td>53.44</td>
<td>55.68</td>
<td>58.82</td>
<td>54.14</td>
<td>54.70</td>
<td>53.96</td>
</tr>
<tr>
<td>TN (g kg$^{-1}$)</td>
<td>4.88</td>
<td>4.97</td>
<td>4.92</td>
<td>4.91</td>
<td>4.91</td>
<td>4.96</td>
<td>5.01</td>
<td>5.00</td>
<td>4.94</td>
</tr>
<tr>
<td>TAN (g kg$^{-1}$)</td>
<td>3.10</td>
<td>3.23</td>
<td>3.06</td>
<td>3.21</td>
<td>3.14</td>
<td>3.19</td>
<td>3.09</td>
<td>3.21</td>
<td>3.14</td>
</tr>
<tr>
<td>TS (g kg$^{-1}$)</td>
<td>1.86</td>
<td>1.83</td>
<td>1.86</td>
<td>1.94</td>
<td>1.91</td>
<td>1.83</td>
<td>1.83</td>
<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>TIC (g kg$^{-1}$)</td>
<td>4.74</td>
<td>4.63</td>
<td>4.96</td>
<td>5.02</td>
<td>4.85</td>
<td>4.72</td>
<td>4.83</td>
<td>4.78</td>
<td>4.59</td>
</tr>
</tbody>
</table>

$^a$ Each value was on an average of two measurements.

$^b$ pHn: no acidification; A6.0: acidification to pH = 6.0; A5.8: acidification to pH = 5.8; A5.5: acidification to pH = 5.5; G0: no mixing and venting; Gn: mixing and venting N$_2$; Ga: mixing and venting air.
Table 3
Average ammonia, carbon dioxide and hydrogen sulfide emissions during the treatments (mg m^-2 min^-1).^a,b

<table>
<thead>
<tr>
<th>Gases</th>
<th>Flux chambers</th>
<th>pHnG0</th>
<th>pHnGn</th>
<th>pHnGa</th>
<th>A6.0Gn</th>
<th>A6.0Ga</th>
<th>A5.8Gn</th>
<th>A5.8Ga</th>
<th>A5.5Gn</th>
<th>A5.5Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td></td>
<td>4.52 ± 1.95 a</td>
<td>1.66 ± 0.52 b</td>
<td>0.9 ± 0.08 b</td>
<td>0.80 ± 0.30 b</td>
<td>0.75 ± 0.11 b</td>
<td>0.69 ± 0.11 b</td>
<td>0.75 ± 0.17 b</td>
<td>0.55 ± 0.04 b</td>
<td>0.49 ± 0.06 b</td>
</tr>
<tr>
<td>CO2</td>
<td></td>
<td>143 ± 37 a</td>
<td>348 ± 31 b</td>
<td>483 ± 73 b</td>
<td>861 ± 123b</td>
<td>1009 ± 74 c</td>
<td>1111 ± 223 c</td>
<td>1181 ± 152 c</td>
<td>1091 ± 29 c</td>
<td>1091 ± 33 c</td>
</tr>
<tr>
<td>H2S</td>
<td></td>
<td>2.67 ± 0.54 a</td>
<td>45 ± 3 ab</td>
<td>67 ± 26 ab</td>
<td>195 ± 72 ab</td>
<td>156 ± 43 ab</td>
<td>240 ± 23 ab</td>
<td>268 ± 132 b</td>
<td>68 ± 14 ab</td>
<td>108 ± 45 ab</td>
</tr>
</tbody>
</table>

^a Mean ± standard deviation.
^b Same letters (a, b, c) within rows indicate no significant differences (P > 0.05) between different pH levels and gas bubbling type.
^c pHn: no acidification; A6.0: acidification to pH = 6.0; A5.8: acidification to pH = 5.8; A5.5: acidification to pH = 5.5; G0: no mixing and venting; Gn: mixing and venting N2; Ga: mixing and venting air.
^d Emissions were averaged from slurry addition, mixing and venting.

during acidification were observed in the study. In fact, H2S emissions from the non-acidified slurry during slurry addition were within the range of 0.22 and 2.29 mg m^-2 min^-1, while, H2S levels ranged between 4.49 and 404.07 mg m^-2 min^-1 were measured during slurry mixing, and between 53.88 and 718.35 mg m^-2 min^-1 during air or N2 bubbling. Average H2S emissions during treatment among the different chambers were not significantly different (P > 0.05), except for pHnG0 and A5.8Ga (Table 3). The gas emissions patterns observed during slurry disturbances caused by slurry addition, acid addition, mixing and venting are in agreement with previous studies (Ni et al., 2000, 2009; Blanes-Vidal and Nadimi, 2011). The different gas emission patterns observed for NH3, CO2 and H2S are related to the different gas transport mechanisms governing the release of each gas, which are mainly determined by volatility of each gas and its tendency to form gas bubbles. The immediate decrease in NH3 emissions after disturbance and subsequent increase during transient state conditions after the disturbances could be explained by the formation of a pH profile under the co-release of buffer components such as CO2 (Ni et al., 2009; Blanes-Vidal et al., 2009b, 2010; Blanes-Vidal and Nadimi, 2011). The acidification treatment caused an increase of CO2 and H2S emissions during the treatment process. A closed chamber with an exhaust gases filter could be used in order to minimize the emission of gases such as H2S and CO2 to the atmosphere during treatment.

3.3. Gas emissions during undisturbed storage after treatment

3.3.1. NH3 emissions

Ammonia emissions from acidified and non-acidified slurry during undisturbed storage after treatment are shown in Fig. 3. Ammonia emissions from acidified slurry were significantly lower than emissions from non-acidified slurry during all stages of storage (first day, seven days and fourteen days after the treatment)
(P > 0.05). Regarding to comparison among acidified slurries (A6.0, A5.8 and A5.5), NH3 emissions were not significantly different during the first day after acidification treatment, but NH3 emissions from slurry acidified to pH = 5.5 (A5.5) were significantly lower than NH3 emissions from slurry acidified to pH = 6.0 (A6.0) during the seven days storage (P < 0.05) (Fig. 3). After fourteen days, there were no significant differences among the acidified slurry treatments (Fig. 3). The effectiveness of slurry acidification in reducing NH3 emission is summarized in Table 4. Some preliminary recommendations can be made based on the results of our study. Both, pH = 5.8 and pH = 5.5 are recommended target pH's for NH3 emission reduction, as they provide similar NH3 emission mitigation. When short-term effects are of interest (i.e. storage time less than seven days), a pH = 5.5 is recommended over a pH = 6.0. More studies, including full-scale studies are needed to confirm the validity of these recommendations. For slurry acidification before land application (Kai et al., 2008) and longtime storage (i.e. 14 days or even more), slurry acidified to pH = 6.0 can be applied by the reason of reducing H2SO4 consumption and energy conservation during acidification process.

After acidification, NH3 emissions remained constant and low for a period of time, and then increased, as shown in Fig. 2. The length of this period of low and stable NH3 emissions was related to the pH. Acidification treatments involving lower targeted pH resulted in longer periods of low and stable NH3 emissions. When the slurry was acidified to pH = 6.0, NH3 emissions were low and stable for 8.5 – 9 h, when they reached a 20% increase compared to emissions measured right after the treatment. However, when the slurry was acidified to pH = 5.5, the time span of low and stable NH3 emissions after acidification ranged between 55 and 58 h. These results suggest that the time between treatments could be of two days (instead of one day, as it is common practice in Denmark). More research (including full-scale experiments) is needed to confirm the appropriateness of this recommendation.

The increase in NH3 emissions can be explained by the formation of a pH profile at the slurry surface (Ni et al., 2009; Blanes-Vidal et al., 2009b; Blanes-Vidal and Nadimi, 2011). In our study a pH profile was also observed in the settled slurry, being the pH at the surface (0.5 – 1 cm from the surface) higher than the pH at deeper layers (Fig. 4).

**Table 4**

<table>
<thead>
<tr>
<th>Reduction in NH3 emissions after acidification to pH = 6.0 (A6.0), pH = 5.8 (A5.8) and pH = 5.5 (A5.5) compared to non-acidified (pHn) slurry.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average NH3 emissions (g m⁻² d⁻¹)²</strong></td>
</tr>
<tr>
<td>pHn</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>One day after treatment</td>
</tr>
<tr>
<td>Seven days after treatment</td>
</tr>
<tr>
<td>Fourteen days after treatment</td>
</tr>
</tbody>
</table>

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² Same letters (a, b) within rows indicate no significant differences (P > 0.05) between different pH levels. Same letters (t, u) within columns indicate no significant differences (P > 0.05) between different acidification times.

³ Averaged from the same pH level and indicated as Mean ± standard deviation.

The reducing efficiency was calculated by: \( R(\%) = \frac{(E_{\text{pHn}} - E_{\text{A6.0}})}{E_{\text{pHn}}} \times 100 \), the Ar in this formula indicate A6.0, A5.8, A5.5.
Previous studies have reported an increase of NH$_3$ emissions during aeration (Zhang and Zhu, 2005; Amon et al., 2006). However, the results of our study suggest that the increase in NH$_3$ emission is mainly caused by the agitation created during aeration rather than the effect of the aerobic conditions in the slurry, as in our study aeration of slurry for 30 min did not have a significant effect on NH$_3$ emissions during storage compared to N$_2$ gas bubbling, which causes bubble formation, but does not contribute to oxidation processes.

### 3.3.2. CO$_2$ emissions

Fig. 3 shows the CO$_2$ emissions from stored slurry after each acidification treatment. Carbon dioxide emissions during storage were not affected by the acidification and the aeration treatments. Carbon dioxide emissions during storage were rather stable if no agitation occurred (Fig. 2). The average emission during entire acidification treatment was approximately 2–10 times higher than that of subsequent storage under undisturbed conditions (Fig. 2). The results approved the inferential conclusion of Fangueiro et al. (2010), who assessed the gas emissions from sandy soil applied with acidified pig slurry and proposed that most of the dissolved CO$_2$ was lost during the acidification process since a significantly decrease of CO$_2$ emission was found during the incubation.

During the undisturbed storage after acidification treatment, emission patterns of CO$_2$ were different from those of NH$_3$, which remained low and stable for a period and increased over time. In contrast, CO$_2$ emissions showed an exponential decay during the first 2–4 h after treatment and then reached a stable release in all treatments (Fig. 2). Similar CO$_2$ emission pattern after disturbance was also observed in other studies (Blanes-Vidal et al., 2012; Ni et al., 2009). This pattern of CO$_2$ release can be explained by the CO$_2$ bubble release mechanism, low convective mass transfer and low solubility. With regard to slurry aeration, little attention has been paid to the effect of aerobic treatment on CO$_2$ emissions individually. A previous study (Loyon et al., 2007) reported that aerobic treatment combined with slurry separation of piggery waste can significantly reduce CO$_2$ emissions compared to conventional slurry storage without any treatment. The reason for the lack of research studies in CO$_2$ emissions from slurry is that they are considered negligible compared to CO$_2$ emissions from animals exhalation (Blanes and Pedersen, 2005). However, CO$_2$ emission from slurry plays an important role on the pH buffer system and its emissions significantly affect NH$_3$ emissions during storage (Ni et al., 2009).

#### 3.3.3. H$_2$S emissions

Hydrogen sulfide emissions during undisturbed storage after treatment are shown in Fig. 3. Average H$_2$S emissions during the first day after treatment from non-acidified slurry and slurry acidified to pH = 6.0 (A6.0) were significantly higher than slurry acidified to pH = 5.5 (A5.5) and 5.8 (A5.8) ($P < 0.05$). However, no statistically differences were found during seven days and fourteen days of storage among treatments (Fig. 3). Generally, low slurry pH is in favor of H$_2$S release. However, in our study most of the release of H$_2$S occurs during slurry agitation (acidification treatment process) due to the low volatility of H$_2$S and its bubble formation, ascension and breakage at the surface (Ni et al., 2009; Blanes-Vidal et al., 2012). Lower target pH's resulted in longer acidification treatment times (i.e. the time required to acidify the slurry until target pH increased). As slurry mixing was performed simultaneously, a higher off-gas of H$_2$S contained in the bulk slurry occurred when the slurry was acidified to lower pH's, which may have led to lower H$_2$S emissions during subsequent storage under undisturbed conditions. An alternative mechanism to explain the reduction of H$_2$S during the first day of storage after acidification in treatments A5.5 and A5.8 could be sulfide-reducing bacteria inhibited by accumulated sulfide (Eriksen et al., 2008; Ottosen et al., 2009). Previous research also documented large variations of H$_2$S emission from stored swine slurry when it is disturbed by slurry addition and mixing (Ni et al., 2010). Finally, the results showed that aeration did not have a significant effect on H$_2$S emissions during storage.

### 4. Conclusions

Average NH$_3$ emissions from swine slurry stored after the acidification-aeration treatment, were significantly lower than average NH$_3$ emissions from non-acidified slurry stored under the same conditions. The reductions in NH$_3$ emissions during storage (compared to non-acidified slurry) were of 50%, 62% and 77%, when slurry pH was decreased to 6.0, 5.8 and 5.5, respectively. The acidification treatment had no significant effect on the average CO$_2$ and H$_2$S emissions occurring during storage of slurry after acidification (compared to emissions from non-acidified slurry stored under the same conditions). However, high peaks of CO$_2$ and H$_2$S emissions occurred during the slurry acidification process. Aeration of the slurry for 30 min had no effect on average NH$_3$, CO$_2$ and H$_2$S emissions during the storage of slurries after the treatment. However, an increase of NH$_3$, CO$_2$ and H$_2$S was observed from both venting air and N$_2$ during the treatment. Therefore, the venting air (aeration) caused sudden release of the gases was related to an increase in the liquid turbulence caused by the air bubbles rather than by biological oxidation processes.

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### Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2012.11.019.
References


