Greenhouse gas and ammonia emissions from pig and cattle slurry storage: impacts of temperature, covering and acidification

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Abstract

Storage of livestock slurries is a significant source of methane (CH_4) and ammonia (NH_3) emissions to the atmosphere, for which accurate quantification and potential mitigation methods are required. ~~Methane~~ CH4 and NH_3 emissions were measured from pilot scale cattle and pig slurry stores at different temperatures (seasons) including two potential mitigation practices: a) a clay granule floating cover (pig slurry); b) slurry acidification (cattle slurry). Cumulative emissions of both gases were influenced by mean temperature over the storage period and daily flux values were influenced by fluctuations in daily temperature. ~~Methane~~ CH4 emissions from the control treatments over the two month storage periods were 0.3, 0.1 and 34.3 g CH_4 kg^{-1} slurry volatile solids for the cattle slurry and 4.4, 20.1 and 27.7 g CH_4 kg^{-1} slurry volatile solids for the pig slurry for the winter, spring/autumn and summer periods, respectively. Respective ammonia emissions for each season were 4, 7 and 12 % of initial slurry N content for the cattle slurry and 12, 18 and 28 % of initial slurry N content for the pig slurry. Covering pig slurry with a floating layer of clay granules reduced NH_3 emissions by 77% across the three storage periods, but had no impact

on CH_4 emissions. Acidification of cattle slurry reduced CH_4 and NH_3 emissions by 61 and 75%, respectively, across the three storage periods. The development of approaches that take into account the influence of storage timing (season) and duration on emission estimates for national emission inventory purposes is recommended.

Introduction

Manure management is an important source of emissions to the atmosphere of the ~~greenhouse gases~~ (GHG) ~~methane (~~CH_4~~)~~ and nitrous oxide (N_2O) (Chadwick et al., 2011), although the latter is of much less importance from the storage of livestock slurries, which is the focus of this study~~,~~; ~~and~~ it is also a source of the atmospheric pollutant ammonia (NH_3) (Sommer et al., 2006). Accurate quantification of these emissions is required for national GHG and air quality emission inventory compilation purposes (for international reporting obligations) and as a baseline against which to assess potential mitigation methods.

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The current UK inventories, in common with most countries, employ an emission factor (EF) approach to estimating these emissions from manure storage. For CH_4 emissions from manure storage, inventory compilation guidelines given by the Intergovernmental Panel on Climate Change (IPCC) relate the emission to the volatile solids (VS) content of the manure, the biological potential for CH_4 production (B_o) from those VS and a methane conversion factor (MCF), which is the percentage realisation of B_o for a given set of manure management conditions (Dong et al., 2006) and default values for these parameters are provided according to livestock type and manure management systems. The default MCF values vary by average annual temperature, with a value of 17 % for temperatures ≤ 10°C being applicable to the UK. The average annual UK temperature is closer to 8°C, so the MCF might be expected to be lower than the IPCC default value. Additionally, CH_4 emissions might be expected to vary throughout the year, as shown by Rodhe et al. (2012) in a Swedish study, so the duration and time of year of slurry storage are likely to be important factors influencing total CH_4 emission.

There have been many studies investigating possible ~~ammonia (~~NH_3~~)~~ mitigation techniques for slurry storage but less emphasis to date on methods to mitigate CH_4 emissions, with the exception of the deliberate promotion and capture of CH_4 in purpose-built anaerobic digestion plants. Two effective NH_3 mitigation measures which might also be expected to reduce CH_4 emissions are slurry crusting, or covering the slurry surface with a floating material, and slurry acidification. Petersen et al. (2005) reported CH_4 oxidation through the presence of a slurry crust, and the presence of a floating layer of inert clay granules might be expected to have a similar effect by allowing a more aerobic surface layer in which methanotrophic activity can occur as the CH_4 generated within the stored slurry passes through. Slurry acidification to pH values <6 can be very effective at reducing NH_3 emissions, but has also been shown to inhibit methanogenic activity (e.g. Berg et al., 2006).

The objectives of this study were to assess the impact of temperature on CH_4 and NH_3 emissions from slurry storage and to assess two potential mitigation practices: a) adding a clay granule floating cover; and b) slurry acidification. Emissions of N_2O and carbon dioxide (CO_2) were also measured.

Materials and methods

Experimental design

The experiment was conducted using six 1.1 m^3 storage tanks (1.0 m height by 0.6 m radius) at the Rothamsted Research North Wyke site. The tanks were fitted with specially adapted lids for gaseous emission measurement, as described below, and were housed in a polytunnel to exclude rainfall. A total of 6 experimental runs were conducted (Table 1), each of 2 months duration, covering 2 slurry types (pig and cattle), 3 temperature regimes (winter, summer, spring/autumn) and 2 potential mitigation practices (covering with floating clay granules or acidification).

Slurry was obtained locally, from the below slat storage on a finishing pig farm and the slurry pit reception area of a dairy farm to ensure that the slurry had not been previously stored for very long. The slurry was well mixed and then the 6 storage tanks were filled to a depth of approximately 0.8 m. A subsample of slurry was taken for analysis during the filling of each tank. Three tanks were randomly allocated as ‘controls’ and three as ‘treatment’ tanks to which the cover or acidification treatment were applied.

For the floating cover treatment, a layer of 2 cm diameter expanded clay granules was applied to the slurry surface to a depth of 7 cm. For the acidification treatment, 5 L of concentrated sulphuric acid was added to each tank during the filling process for the first cattle slurry experiment (Experiment 3). This proved to be too much, lowering the slurry pH dramatically to approximately 5 and causing excessive foaming during addition. For subsequent Experiments 4 and 6, 2.5 and 3.5 L, respectively, were added to each tank.

Following tank filling and treatment addition, temperature probes were installed at approximately 25 cm slurry depth and tank lids fitted for commencement of measurements. At the end of the storage period, for Experiments 3 – 6, the slurry in each tank was thoroughly mixed and a subsample taken for analysis.

Slurry characteristics

Slurry samples taken at the start of each storage period were analysed for total solids and volatile solids content, total N, ammonium-N, and pH. Total solids content was determined by measuring the mass loss after drying at 85 °C for 24 hours. Volatile solids content was determined by measuring the mass loss of a subsample of the total solids after further drying for 4 hours at 550 °C. Total N content was determined by Kjeldahl digestion. Ammonium-N was determined by automated colorimetry following extraction with 2M KCl. For Experiments 1 and 4 – 6, slurry pH was monitored twice per week throughout the storage period at the slurry surface and at a depth of 10 cm using a portable meter with pH probe (HI 9025, Hanna Instruments, Leighton Buzzard, UK).

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In addition, the CH_4 producing potential (B_o) of the slurry at the start of storage was determined using a purpose-designed laboratory system (Bioprocess Control, Lund, Sweden). Slurry samples were incubated at 37 °C with an inoculum, using the recommended ratio of 2 parts inoculum to 1 part sample based on volatile solids content. The inoculum used was a sample of digestate from a local anaerobic digestion plant and was prepared in advance by incubating for approximately 10 d. Gas generated from the incubation vessels was passed through a solution of 3M NaOH (with pH indicator) to remove CO_2 and H_2S gas, leaving only CH_4 to pass through the gas volume measuring device, which operates on a principal of buoyancy and displacement. Blank samples consisting of just inoculum and water were included. The gas flow rate and cumulative gas volume from each vessel was continually monitored by a PC controlling the system and normalised accounting for temperature and pressure.

Gaseous emission measurements

The slurry storage tanks were fitted with specially adapted lids, which had a central circular hole of c. 10 cm diameter to which a fan was fitted to draw air from the tank headspace. Air was drawn into the tank headspace via ten holes around the outer edge of the lid each of c. 3 cm diameter. The air was vented, via the fan, through a duct to an area outside the polytunnel. The lids were left in-situ throughout the storage period with fans running continuously. Air flow rate was nominally 0.04 $m^3 s^{-1}$, but was measured at the duct outlet for each tank twice per week. The tanks with lids therefore effectively acted as large dynamic chambers for emission measurements. Gas concentration measurements were made via a cross-sectional sampling tube within the outlet duct of each tank and at two places within the polytunnel as proxy for inlet concentrations. Estimates of flux for each gas (F, $\mu g\ s^{-1}$) could therefore be made according to:

$$F = V(C_o - C_i)$$

where V ($m^3\ s^{-1}$) is the air volume flow rate and C_o and C_i the outlet and inlet gas concentrations ($\mu g\ m^{-3}$), respectively.

~~Methane~~ CH4 and CO_2 concentrations were measured using a Los Gatos Ultra-Portable Greenhouse Gas Analyser (Los Gatos Research, California) based on cavity enhanced absorption spectroscopy, with a multiport inlet sampler. Sampling was on a semi-continuous basis with measurements from each sampling position (6 tank duct outlets and 2 ambient air sampling positions) for 5 minutes and cycled continuously around the eight sampling positions. The instrument sampled every 20 seconds and equilibration of the concentration reading when switching between sampling points was very fast. The mean concentration at each sampling point for a given cycle was derived from the last 12 concentration measurements at each sampling point, discarding the initial 3 concentration readings.

Ammonia concentration measurements were made twice per week by subsampling the air flow from the tank outlet ducts or from the ambient sampling points and passing through acid absorption flasks. The quantity of ammonia-N trapped in the absorption flasks was determined by automated colorimetry and was divided by the volume of air passing through the flask to derive the concentration in the sampled air. For Experiments 5 and 6, a Los Gatos Economical Ammonia Analyser (Los Gatos Research, California) was also used together with a multiport inlet sampler to provide semi-continuous NH_3 concentration measurements. As NH_3 is a notoriously 'sticky' gas, a longer equilibrium time was required when switching between sampling positions than for the CH_4 and CO_2 sampling, so measurements were made at each sampling position for a period of 10 minutes. The instrument sampled every 20 seconds and the final 5 readings for each sampling position were used to derive mean concentration for that sampling point for a given cycle. A calibration function was derived from the periods when both the Ammonia Analyser and acid absorption flasks were used and was applied to the Ammonia Analyser concentration data.

Nitrous oxide concentration measurements were made by manually taking gas samples from the tank outlet ducts and ambient sampling points, storing in evacuated glass vials and analysing by gas chromatography (GC) in the laboratory. Samples were taken on two occasions per week. The same samples were also analysed for CH_4 and CO_2 concentration by GC, which provided data for periods when the Greenhouse Gas Analyser was unavailable or not functioning.

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Statistical analysis

Analysis of variance (Genstat 16.0, VSN International) was used to test for treatment effects within each experiment and on storage temperature (season) effects within treatment on cumulative gaseous emission over the storage period.

Results and discussion

Initial slurry characteristics

The slurries used in the experiments were representative in terms of total solids content, total nitrogen and ammoniacal nitrogen content of typical slurries from UK dairy and finishing pig production systems (Table 2). Average B_o values were determined as 0.37 and 0.20 m^3 CH_4 kg^{-1} VS for pig and cattle slurry, respectively; that for pig slurry is lower than the IPCC default value of 0.45 m^3 CH_4 kg^{-1} VS, while that for cattle compares well with the IPCC default values of 0.24 and 0.18 m^3 CH_4 kg^{-1} VS for dairy and other cattle, respectively (Dong et al., 2006).

Slurry temperature

The temperature profiles throughout the storage duration differed across the Experiments (Fig. 2). For Experiment 1, temperature was relatively stable between 10 and 15 °C until the final 15 d of storage when there was a rise in temperature. For Experiment 2, temperature started at about 15 °C, rose to 20-25 °C and then declined again. For Experiment 3, temperature declined throughout the storage period from an initial 15 °C to a final temperature approaching 0 °C. Experiment 4 showed the most stable temperature profile, remaining between 5 and 10 °C throughout the storage period. In Experiment 5, temperature was between 5 and 10 °C for the first 40 d of storage and then rose to just above 10 °C for the remaining 30 d. In Experiment 6, temperature rose to a peak of c. 24 °C at 20 d and then declined to 15-17 °C from 40 d to the end of storage. The diurnal variation in slurry temperature was much less than that for ambient air temperature, as would be expected. The clay granule floating cover treatment resulted in a higher slurry temperature and also further reduced diurnal variation when compared with the

Commentato [p5]: is all this description necessary control slurry (Fig. 2 a, b and e). There was no significant difference between ambient air, control slurry and the acidified slurry temperatures (Fig. 2 c, d and f).

Methane emissions

Daily CH_4 fluxes were greatest from the summer storage of cattle slurry, with the emission rate peaking at 110 g CH_4 m^{-3} d^{-1}, compared with a peak of 55 g CH_4 m^{-3} d^{-1} from the pig slurry at a similar storage temperature (Fig. 3). Fluxes from the cattle slurry at the lower storage temperatures were consistently below 5 g CH_4 m^{-3} d^{-1} and were also low from pig slurry at the lower storage temperature (Experiment 5), but fluxes from pig slurry at the medium storage temperature were similar to those at the higher temperature (Experiments 1 and 2). Sommer et al. (2000) reported relatively low emission rates from stored cattle slurry (0 – 22 g CH_4 m^{-3} d^{-1}), and Wood et al. (2012) reported a lag of 50 – 70 d before the onset of increased CH_4 fluxes from stored cattle slurry which they thought might have been associated with the time required for the establishment of sufficient methanogenic population. This is less likely to be the case in our study where slurry was taken from a reception pit in which methanogenic bacteria would be expected to be present. For the experiments showing the higher fluxes, particularly Experiments 2 and 6, there was a good correlation between daily flux and temperature.

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Slurry acidification effectively stopped CH_4 emissions after the first few days of storage in Experiments 3 and 4, but in Experiment 6, while much lower than for the control slurry, the flux rate did increase from the acidified slurry over the first 30 d and then decreased again and stayed low even though that from the control slurry subsequently increased again with temperature (Fig. 3). This latter reduction in daily flux may have been associated with the formation of a hard, dry in-tact crust on this treatment. There was a significant effect of acidification on cumulative CH_4 emissions from cattle slurry, with emission reductions of 91, 86 and 63% from Experiments 3, 4 and 6, respectively (Table 3). This agrees well with Petersen et al. (2012) who reported emission reductions of between 67 and 87% when acidifying cattle slurry to pH 5.5.

There was no significant effect of the floating clay granule cover on cumulative CH_4 emissions from pig slurry (Table 3). The literature evidence is mixed for the effect of floating covers on CH_4 emissions. Petersen et al. (2005) demonstrated methanotrophic activity within crusts forming on slurry stores and hypothesised that this might be an effective CH_4 emission reduction measure. However, more recent evidence suggests that crusts or floating covers may be ineffective in this respect as the majority of CH_4 emissions occur as ebullition events which either by-pass any crust or cover or pass through it at too high a rate for effective methanotrophic activity to occur (Petersen et al., 2013). Sommer et al. (2000) reported a 40% reduction in emissions from stored cattle slurry with either a crust, straw or clay granules cover. Wulf et al. (2002) reported increases in CH_4 emission with straw covering and suggested that this was because of the addition of easily degradable carbon in the straw to the slurry. Rodhe et al. (2012) reported no significant effect of straw cover, but a 40% reduction with a floating plastic cover. Guarino et al. (2006) reported no significant effect of floating cover materials on CH_4 emissions when used on pig slurry storage, but did report significant reductions in CH_4 emissions of 32 and 16% for wood chip and expanded clay, respectively, when used on cattle slurry storage. Successful mitigation though the use of floating covers most likely depends therefore on the establishment of an active methanotroph population within the cover matrix. This may not have occurred in our current study which was of relatively limited duration.

Methane conversion factor

Following the IPCC Guidelines approach to estimating CH_4 emissions form manure management (Dong et al., 2006), we can define the MCF (%) according to:

$$MCF = \frac{cumulative\ CH_4\ emission}{VS \times B_o \times 0.67}$$

Where the cumulative CH_4 emission is expressed as kg CH_4 m^{-3} slurry, VS as kg m^{-3} slurry, B_o as m^3 CH_4 kg^{-1} VS and 0.67 is a conversion factor of m^3 CH_4 to kg CH_4. From the measured VS, B_o and cumulative CH_4 emission in the present study, we derived MCF values for the 2-month storage periods (Table 4). Slurries are typically stored for longer than two months in the UK, but based on these results we can estimate an average 6-month storage MCF for pig slurry of 21%, assuming storage may be at any time of year, which compares favourably with the IPCC 2006 Guidelines default value of 17% appropriate for UK temperatures. For cattle slurries, storage is generally through the autumn, winter and spring months, giving an MCF based on this study of c. 2%, much lower than the IPCC default value and in agreement with the observations of Rodhe et al. (2012) for pig slurry storage in Sweden. However, any storage over summer months would greatly increase this value. Further measurements are required for a range of slurries across the range of typical storage temperatures to develop robust MCF values, but results from this study would suggest that the current value of 17% for cattle slurry used in the UK GHG inventory is too high. While only of relatively short duration, our measurements from pig slurry covered with floating clay granules would not support implementing the 40% reduction in MCF as applied for crusted slurries in the IPCC 2006 Guidelines (Dong et al., 2006).

Nitrous oxide emissions

No significant N_2O emissions were detected from any of the control or treated slurries across all experiments. The dynamic open chamber technique as used in this study is less sensitive than closed chamber techniques which rely on headspace accumulation to enable detection of concentration increases, and it is possible that emission rates and differences between treatments may have been detected with such a closed chamber technique. Some authors have measured N_2O emissions from slurry storage (van der Zaag et al., 2008), particularly where crusts or floating covers are put in place, but these tend to be very low emissions and do not contribute significantly to the overall GHG emission from slurry storage.

Carbon dioxide emissions

Carbon dioxide fluxes showed some correlation with temperature for Experiments 1, 2, 5 and 6 (Fig. 4). Emission rates tended to be lower from the clay granule covering treatment (Experiments 1, 2 and 5), suggesting that the increased anaerobicity of the slurry due to covering was more influential on emission rate than the small increase in slurry temperature.

For the cattle slurry (Experiments 3 and 4, Fig. 4), there was a large initial peak emission which declined rapidly. Subsequent emission rates were in the range 0 – 90 g CO_2 m^{-3} d^{-1} for Experiment 3 and 10 – 30 g CO_2 m^{-3} d^{-1} for Experiment 4. This large initial peak was not observed in Experiment 6 and rates were generally much greater (50 – 300 g CO_2 m^{-3} d^{-1}) in line with the higher temperature. With the exception of lower emissions from the acidified slurry for a few days following the initial high peak event, there were no significant differences in fluxes between treatments. However, the initial high emission rate of CO_2 on addition of acid to the slurry may not have been fully captured in the measurements, as there was some delay between filling of the slurry tanks, acid addition, lid installation and the commencement of measurements.

Cumulative CO_2 emissions over the 2-month storage period were of a similar order of magnitude ($P>0.05$) for the control cattle and pig slurries (Table 5). Carbon loss was generally greater in the form of CO_2 than CH_4 from all control slurries, by two- to seven-fold for the pig slurries, and by 12- to 27-fold for the cattle slurries, with the exception of Experiment 6 where losses were of the same magnitude. There was a significant effect of season on cumulative emission ($P<0.05$), related to storage temperature with emissions being greatest from summer storage and least from winter. Covering of pig slurry with a layer of floating clay granules gave a significant emission reduction ($P<0.05$) of c. 30% across all timings, with respective reductions of 40, 23 and 29% for Experiments 1, 2 and 5, respectively. Acidification of the cattle slurry resulted in a significant reduction ($P<0.05$) in cumulative emission of 26% when averaged across all timings and significant reductions of 28 and 31% for Experiments 4 and 6 but no significant difference for Experiment 3, which could be related to the much lower pH maintained in the acidified slurry throughout Experiment 3.

Ammonia emissions

Ammonia emissions from the control pig slurry stores (Experiments 1 and 2) were in the range 5 – 35 g NH_3-N m^{-3} d^{-1} (Fig. 5), and changes in emission rate correlated well with temperature changes. Covering the slurry with a layer of floating clay granules significantly reduced the emission rate throughout the measurement period. Emission rates from the control cattle slurry stores were very much lower, in the range 1 – 8 g NH_3-N m^{-3} d^{-1} (Fig. 5). Acidification significantly reduced the emission rate; in Experiment 3 the slurry pH remained below 5 throughout the measurement period (Fig. 6) and the emission rate from the acidified treatment remained at or below zero throughout. In Experiments 4 and 6, where less acid was added, pH started at 5.5 but increased over the storage period (Fig. 6). Ammonia emission from the acidified slurries in these experiments increased as the pH value increased until day 30 and then remained at a rate just below that of the control treatment in

Experiment 4 but decreased again as a solid crust formed on the acidified slurry in Experiment 6.

Daily fluxes determined using the Los Gatos Economical Ammonia Analyser for Experiments 5 and 6 did not always follow the same pattern as those measured using the absorption flask, although generally showed a similar order of magnitude difference between control and treated slurries. A comparison of flux rates determined using the two methods is given in Figure 7, showing results from two of the storage tanks for Experiment 5, one control and one treated slurry. The fluxes follow a similar pattern for the first part of the storage period, but the Los Gatos does not show an increase in flux in the latter part of the storage period which is clearly seen from the absorption flask measurements. As regular calibration against an ammonia gas standard was not included for the Los Gatos, fluxes derived using the acid absorption flasks are considered more robust in this study.

Cumulative NH_3 emissions were greater from the pig slurries than the cattle slurries (control treatments) both in absolute terms and as a percentage of the initial slurry N content (Table 6). For comparison, cumulative values determined from the Los Gatos Ammonia Analyser data were 308 and 128 g NH_3-N m^{-3} slurry for the control and treated slurry, respectively, in Experiment 5 and 250 and 71 g NH_3-N m^{-3} slurry for the control and treated slurry, respectively, in Experiment 6. Losses expressed as a percentage of initial total ammoniacal N (TAN) content are high compared with the current UK emission factor for slurry tanks of 10 and 13% for cattle and pig slurries, respectively, but comparable with the currently-used value for slurry lagoons (cattle and pig slurry) of 52% (Misselbrook et al., 2015), perhaps reflecting the relatively low depth to surface area ratio of the stores used in this experiment in comparison to slurry stores on commercial farms.

Covering of pig slurry with the floating layer of clay granules gave a significant reduction ($P<0.05$) in emission of 77% across all experiments, with specific reductions (in emission expressed as % of initial TAN) of 72, 84 and 61% for Experiments 1, 2 and 5, respectively. These reduction efficiencies are at the high end of the range reported in the literature (e.g. Horning et al. 1999; Guarino et al., 2006; Portejoie et al., 2003; van der Zaag et al., 2008). Acidification of cattle slurry gave a significant reduction ($P<0.05$) in emission of 75% across all experiments, with specific reductions (in emission expressed as % of initial TAN) of 99, 56 and 68% for Experiments 3 (where slurry pH remained below 5), 4 and 6, respectively.

Conclusions

Of the slurries used in this study, CH_4 and NH_3 emissions were greater over a 2-month storage period from pig than from cattle slurry. The MCF for pig slurry was of the order of the IPCC 2006 guidelines default value for slurry storage, but that for cattle slurry was much lower if cattle slurry is assumed to be stored mostly over the autumn, winter and spring months; CH_4 emissions were very much greater from cattle slurry during summer storage. The derivation of country-specific MCF values for pig and cattle slurry storage needs to take into account the timing (season) and duration of storage.

Floating clay granules was a very effective NH_3 mitigation technique, giving an average 77% reduction across all storage periods, but had no significant effect on CH_4 emissions from pig slurry. Further assessment of the potential for methanotroph development in floating covers as a CH_4 mitigation measure is recommended. Acidification of cattle slurry was a very effective mitigation technique for both CH_4 and NH_3, with average respective reductions across all storage periods of 61 and 75%. Future research requirements to develop improved approaches to estimating emissions from slurry storage for national inventory purposes include measurements from dynamic slurry storage situations (i.e. where slurry is added to the store on a regular basis), longer term measurements representative of typical slurry storage periods, measurements from a range of pig and cattle slurries to provide robust MCF values and measurements from commercial-scale stores for validation.

Acknowledgements

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Captions for Figures

Figure 1. Pilot scale slurry storage tanks with specially adapted lids for gaseous emission measurements

Figure 2. Slurry and ambient air temperatures for a) Experiment 1, b) Experiment 2, c) Experiment 3, d) Experiment 4, e) Experiment 5, f) Experiment 6

Figure 3. Daily methane flux during the slurry storage experiments (error bars show ± 1 standard error of the mean)

Figure 4. Daily carbon dioxide flux during the slurry storage experiments (error bars show ± 1 standard error of the mean)

Figure 5. Daily ammonia flux measured using acid absorption flasks during the slurry storage experiments (error bars show ± 1 standard error of the mean)

Figure 6. Evolution of cattle slurry pH (at 10 cm depth) during storage

Figure 7. Comparison of daily ammonia flux determined using the Los Gatos Economical Ammonia Analyser (solid lines) and acid absorption flask (crosses) methods for one replicate each of the control (blue) and treated (red) slurry in Experiment 5

Table 1. Slurry storage experiments conducted

Expt	Slurry type	Time of year	Mean air temperature (°C)	Duration (d)	Mitigation
1	Pig	Apr – Jun	11.1	70	Floating cover
2	Pig	Jun – Aug	17.1	61	Floating cover
3	Cattle	Sep - Nov	11.0	71	Acidification
4	Cattle	Dec – Feb	7.3	62	Acidification
5	Pig	Feb - Apr	9.2	70	Floating cover
6	Cattle	Jul - Sep	17.2	72	Acidification

Table 2. Slurry characteristics at the start of each experiment

Experiment	Total solids ($g\ kg^{-1}$)	Volatile solids ($g\ kg^{-1}$)	Methane potential, B_o ($m^3\ CH_4\ kg^{-1}$ VS)	Total N ($g\ kg^{-1}$)	Ammonium-N ($g\ kg^{-1}$)	pH
1 - Pig	81.1 (1.91)	64.3 (0.75)	0.37 (0.02)	6.32 (0.17)	2.83 (0.12)	8.1 (0.03)
2 - Pig	61.7 (1.37)	50.1 (3.02)	0.35 (0.04)	5.74 (0.02)	2.88 (0.09)	7.9 (0.02)
3 - Cattle	66.2 (2.98)	49.4 (0.75)	0.21 (0.03)	2.76 (0.04)	0.84 (0.06)	7.1 (0.01)
4 - Cattle	54.2 (0.38)	43.3 (0.04)	0.19 (0.02)	2.49 (0.06)	0.78 (0.01)	7.3 (0.17)
5 – Pig	61.5 (0.25)	49.6 (0.07)	0.38 (0.00)	5.62 (0.03)	3.69 (0.03)	7.1 (0.01)
6 - Cattle	60.5 (0.37)	51.1 (1.73)	0.21 (0.00)	2.76 (0.02)	0.95 (0.02)	7.3 (0.08)

Values in parentheses are standard errors of the mean (n = 3)

Table 3. Cumulative methane emissions from the control and treated slurries in each experiment

Expt.	g CH_4 m^{-3} slurry			g CH_4 kg^{-1} VS		
	Control	Treatment	*P*	Control	Treatment	*P*
1	1314 (99)	1349 (80)	0.799	21.5 (1.9)	20.1 (2.0)	0.644
2	1346 (99)	1389 (13)	0.686	27.1 (2.2)	27.7 (2.2)	0.864
3	40 (2)	4 (0)	<0.001	0.8 (0.0)	0.1 (0.0)	<0.001
4	74 (5)	12 (1)	<0.001	1.7 (0.1)	0.3 (0.0)	<0.001
5	203 (10)	221 (4)	0.175	4.1 (0.2)	4.4 (0.2)	0.177
6	4558 (90)	1681 (165)	<0.001	86.7 (6.6)	34.3 (3.7)	0.002

Values in parentheses are standard errors of the mean (n = 3)

Table 4. Derivation of the methane conversion factor (MCF) for the control slurry in each experiment (2 months storage)

Expt.	Slurry	Ambient temp (°C)	Slurry VS (g kg^{-1})	B_o (m^3 CH_4 kg^{-1} VS)	Potential CH_4 emission (kg m^{-3} slurry)	Measured CH_4 emission (kg m^{-3} slurry)	MCF (%)
1	Pig	11.1	61	0.37	15.1	1.31	8.7
2	Pig	17.1	50	0.35	11.7	1.35	11.5
3	Cattle	11.0	49	0.21	6.9	0.04	0.6
4	Cattle	7.3	43	0.19	5.5	0.07	1.4
5	Pig	9.2	49	0.38	12.5	0.20	1.6
6	Cattle	17.2	53	0.21	7.5	4.56	61.1

Table 5. Cumulative carbon dioxide emissions from the control and treated slurries in each experiment

Expt.	g CO_2 m^{-3} slurry			g CO_2 kg^{-1} VS		
	Control	Treatment	P	Control	Treatment	P
1	6350 (115)	3793 (320)	0.002	104 (3.2)	56.7 (6.7)	0.003
2	7647 (564)	5869 (228)	0.043	154 (13)	116 (3.8)	0.048
3	2989 (222)	2893 (303)	0.812	61.6 (4.8)	59.7 (10.4)	0.879
4	2490 (392)	1796 (46)	0.154	59.3 (7.1)	41.3 (1.1)	0.067
5	3930 (151)	2799 (1080)	0.004	79.5 (3.4)	56.3 (2.3)	0.005
6	11848 (483)	8127 (99)	0.002	226 (22)	166 (3.5)	0.052

Values in parentheses are standard errors of the mean (n = 3)

Table 6. Cumulative ammonia emissions from the control and treated slurries in each experiment

Expt.	g NH_3-N m^{-3} slurry			Emission as % of initial slurry total N		Emission as % of initial slurry TAN	
	Control	Treatment	P	Control	Treatment	Control	Treatment
1	1116 (56)	318 (14)	<0.001	18	5.0	42	11
2	1593 (48)	257 (51)	<0.001	28	4.5	53	9.2
3	166 (8)	2 (2)	<0.001	6.1	0.1	23	0.2
4	104 (12)	46 (1)	0.009	4.1	1.9	13	5.8
5	399 (7)	154 (1)	<0.001	7.1	2.7	10	4.2
6	321 (30)	102 (8)	0.002	12	3.7	33	11

Values in parentheses are standard errors of the mean (n = 3)

Figure 1. Pilot scale slurry storage tanks with specially adapted lids for gaseous emission measurements

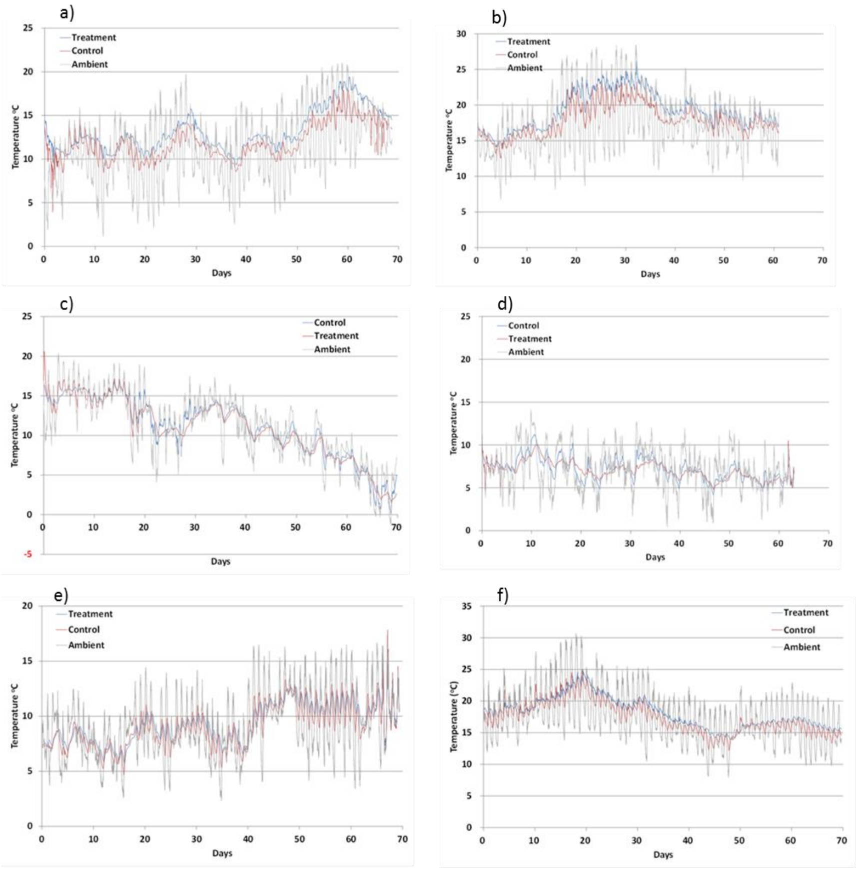

Figure 2. Slurry and ambient air temperatures for a) Experiment 1, b) Experiment 2, c) Experiment 3, d) Experiment 4, e) Experiment 5, f) Experiment 6

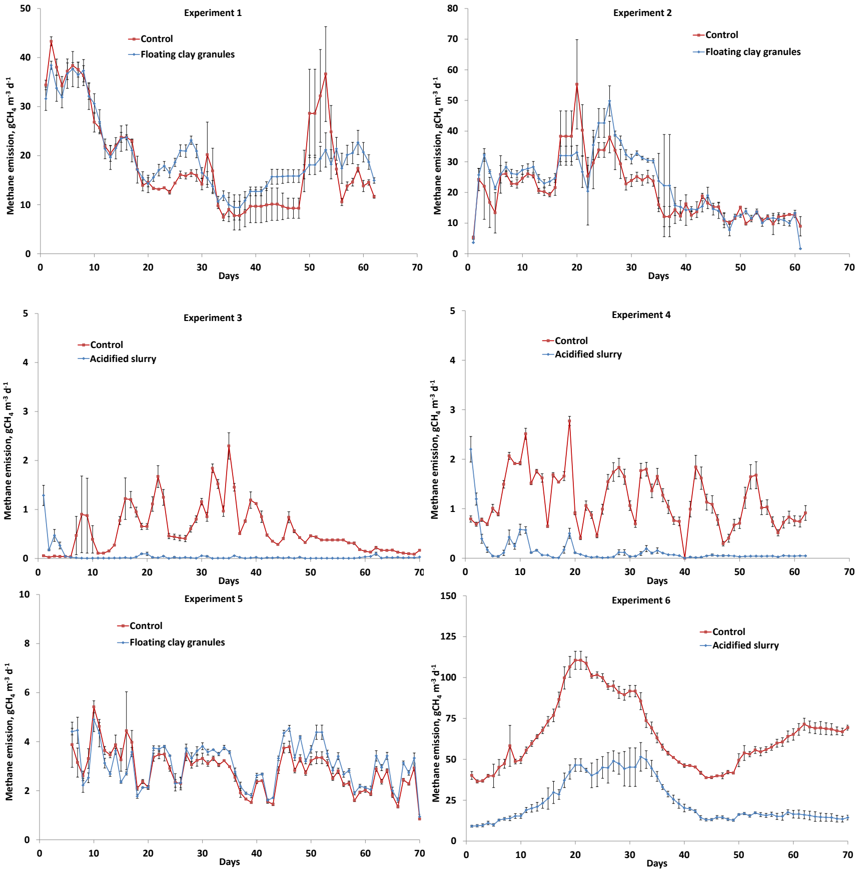

Figure 3. Daily methane flux during the slurry storage experiments (error bars show ± 1 standard error of the mean)

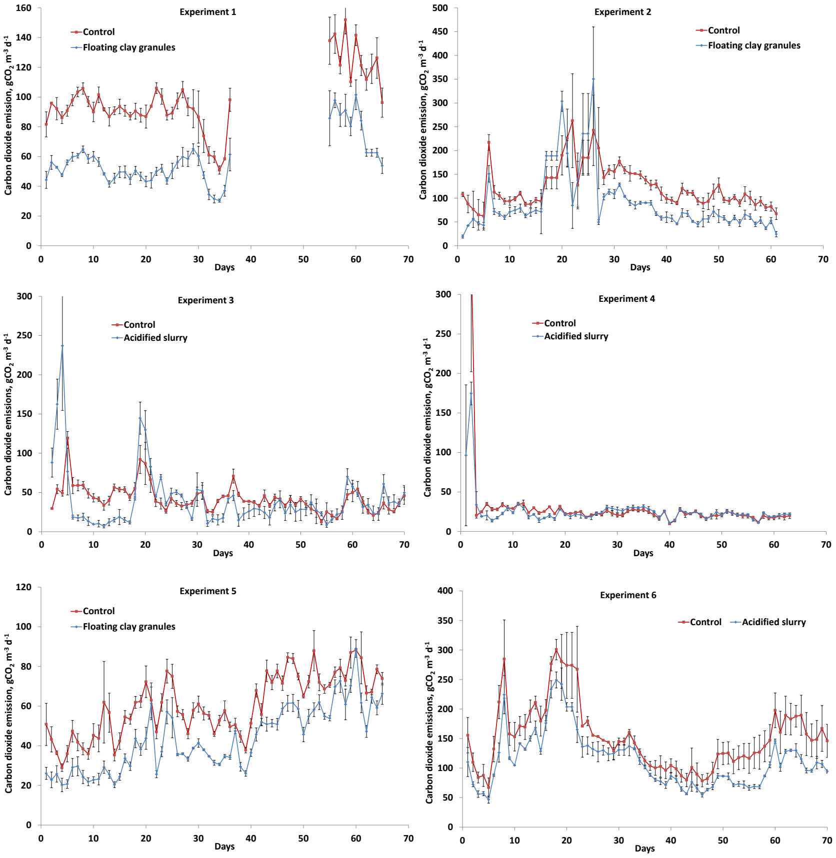

Figure 4. Daily carbon dioxide flux during the slurry storage experiments (error bars show ± 1 standard error of the mean)

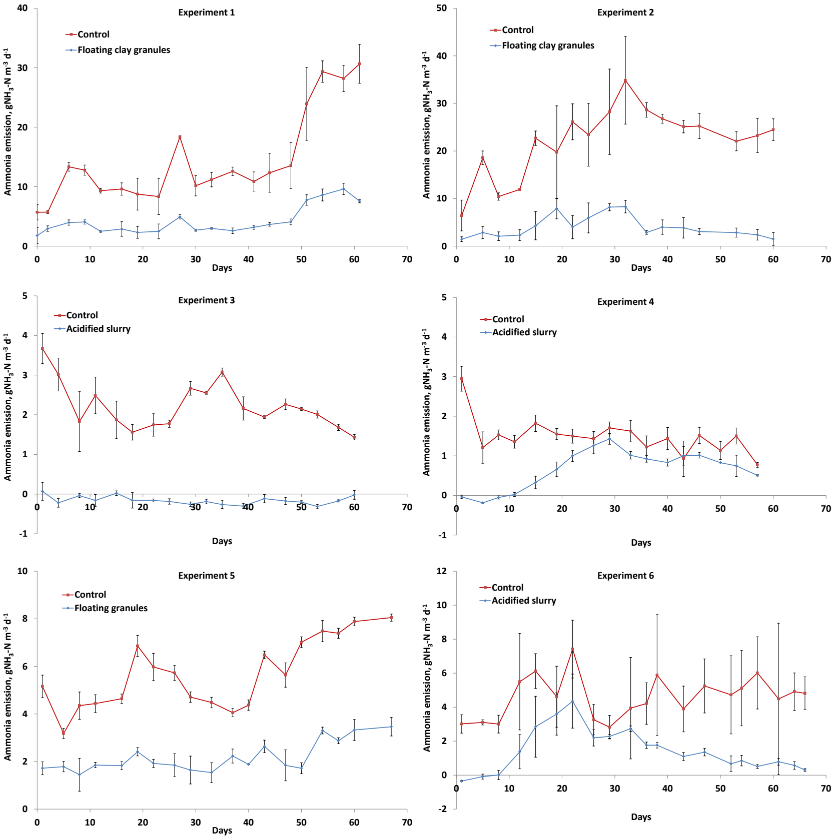

Figure 5. Daily ammonia flux measured using acid absorption flasks during the slurry storage experiments (error bars show ± 1 standard error of the mean)

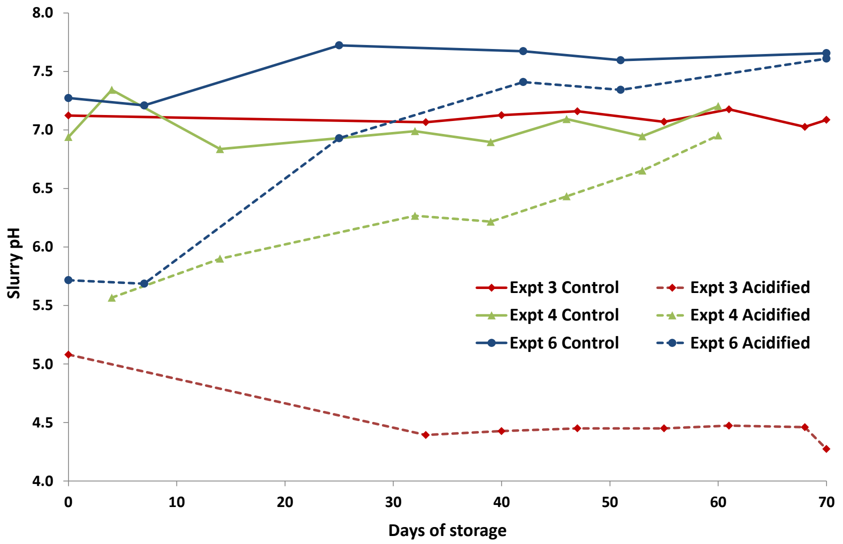

Figure 6. Evolution of cattle slurry pH (at 10 cm depth) during storage

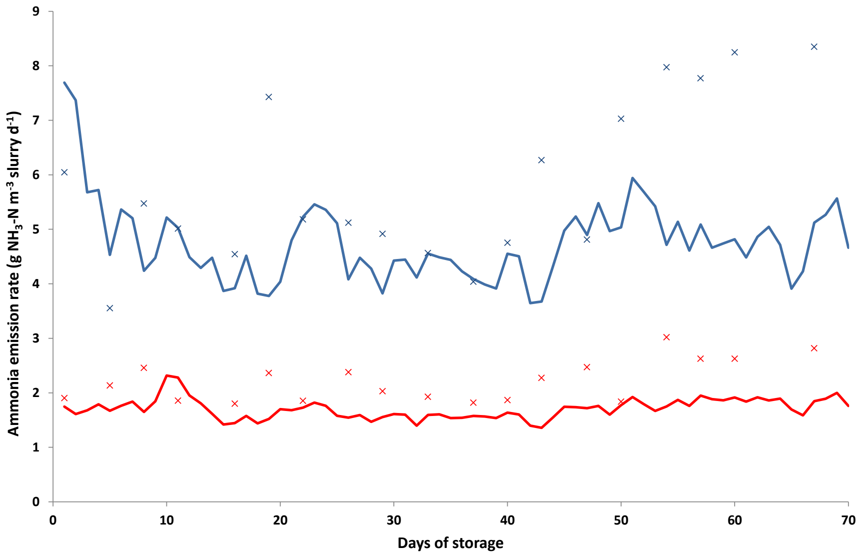

Figure 7. Comparison of daily ammonia flux determined using the Los Gatos Economical Ammonia Analyser (solid lines) and acid absorption flask (crosses) methods for one replicate each of the control (blue) and treated (red) slurry in Experiment 5