Misselbrook, T. H., Hunt, J., Perazzolo, F. and Provolo, G. 2016. Greenhouse gas and ammonia emissions from slurry storage: impacts of temperature and potential mitigation through covering (pig slurry) or acidification (cattle slurry). *Journal of Environmental Quality.* 45 (5), pp. 1520-1530.

Journal of Environmental Quality

TECHNICAL REPORTS

ATMOSPHERIC POLLUTANTS AND TRACE GASES

Greenhouse Gas and Ammonia Emissions from Slurry Storage: Impacts of Temperature and Potential Mitigation through Covering (Pig Slurry) or Acidification (Cattle Slurry)

Tom Misselbrook,* John Hunt, Francesca Perazzolo, and Giorgio Provolo

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 and NH_3 emissions were measured from pilot-scale cattle slurry (CS) and pig slurry (PS) stores under cool, temperate, and warm conditions (approximately 8, 11, and 17°C, respectively) and including two potential mitigation practices: (i) a clay granule floating cover (PS) and (ii) slurry acidification (CS). Cumulative emissions of both gases were influenced by mean temperature over the storage period. Methane emissions from the control treatments over the 2-mo storage periods for the cool, temperate, and warm periods were 0.3, 0.1, and 34.3 g CH_4 kg^{-1} slurry volatile solids for CS and 4.4, 20.1, and 27.7 g CH_4 kg^{-1} slurry volatile solids for PS. Respective NH_3 emissions for each period were 4, 7, and 12% of initial slurry N content for CS and 12, 18, and 28% of initial slurry N content for PS. Covering PS with clay granules reduced NH_3 emissions by 77% across the three storage periods but had no impact on CH_4 emissions. Acidification of CS reduced CH_4 and NH_3 emissions by 61 and 75%, respectively, across the three storage periods. Nitrous oxide emissions were also monitored but were insignificant. The development of approaches that take into account the influence of storage timing (temperature) and duration on emission estimates for national emission inventory purposes is recommended.

Core Ideas

- Gaseous emissions from livestock slurry storage are strongly influenced by storage temperature.
- Slurry acidification is an effective treatment to reduce CH_4 and NH_3 emissions.
- Covering with a layer of clay granules is effective at reducing NH_3, but not CH_4, emission.
- Methane conversion factors in national inventories should account for storage timing and duration.

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. Livestock slurries are 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.

The current inventories used in the United Kingdom, in common with most countries, use an emission factor 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 realization of B_o for a given set of manure management conditions (Dong et al., 2006). Default values for these parameters are provided according to livestock type and manure management systems. The default IPCC MCF values vary by average annual temperature from 17% for countries/regions with average annual temperatures ≤10°C (applicable to the United Kingdom) to 80% for those with an average annual temperature ≥28°C (Dong et al., 2006). The average annual temperature in the United Kingdom is closer to 8°C, so the MCF might be expected to be lower than the IPCC default value. Additionally, daily CH_4 emissions might be expected to vary throughout the year with ambient temperature, as shown by Rodhe et al. (2012) in a Swedish study, so the duration and temperature for the actual period of slurry storage (rather than annual average) are likely to be important factors influencing total CH_4 emission.

There have been many studies investigating possible 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

J. Environ. Qual. 45:1520–1530 (2016)
doi:10.2134/jeq2015.12.0618

Received 24 Dec. 2015.
Accepted 28 Apr. 2016.
*Corresponding author (tom.misselbrook@rothamsted.ac.uk).

T. Misselbrook and J. Hunt, Sustainable Soils and Grassland Systems Dep., Rothamsted Research, North Wyke, Okehampton, Devon EX20 2SB, UK; F. Perazzolo and G. Provolo, Dep. of Agricultural and Environmental Sciences, Univ. degli Studi di Milano, Via Celoria 2, 20133 Milano, Italy. Assigned to Associate Editor Curtis Dell.

Abbreviations: CS, cattle slurry; GHG, greenhouse gas; IPCC, Intergovernmental Panel on Climate Change; MCF, methane conversion factor; PS, pig slurry; TAN, total ammoniacal nitrogen; VS, volatile solids.

anaerobic digestion plants. Two effective NH_3 mitigation measures that might also be expected to reduce CH_4 emissions are slurry crusting, or covering the slurry surface with a floating material, and slurry acidification.

Ammonia emission occurs from the surface of stored slurry, where equilibria develop between ammonium (NH_4^+) and NH_3 in solution at the slurry surface and NH_3 in the air above the slurry surface (Ni, 1999). Diffusion of NH_3 at the slurry–air interface into the free atmosphere can be a rate-limiting step in the emission process. The presence of a natural crust or layer of floating porous material will greatly increase the diffusion distance compared with the typical laminar boundary layer above a liquid surface, slowing the rate of transfer and thereby increasing the NH_3 concentration in the air at the slurry surface and pushing the equilibria toward retaining more ammonium in the slurry solution. Substantial reductions of up to 80% in NH_3 emissions from slurry storage have been reported with the presence of natural crusts or floating covers (Misselbrook et al., 2005; Portejoie et al., 2003; Sommer et al., 1993; Van der Zaag et al., 2008). Adsorption of ammonium may occur within the covering layer, further decreasing emission but potentially leading to N_2O emissions through the nitrification/denitrification processes (Sommer et al., 2000). Methane emissions arise from anaerobic degradation of organic acids by methanogenic bacteria within the slurry store and transfer to the air above the slurry surface through ebullition. Surface equilibria and diffusion distances are therefore not important rate-limiting steps to CH_4 emissions, but surface crusts and coverings may provide the opportunity for CH_4 oxidation to CO_2, thereby reducing emissions (Husted, 1994; Petersen et al., 2005; Qi et al., 2015; Sommer et al., 2000). Methanotrophs have been identified in slurry surface crusts (Duan et al., 2014), although their presence and level of activity may depend on factors including the age of the crust, crust composition, and inhibition by high concentrations of NH_3 or nitrite (Duan et al., 2013; Hansen et al., 2009; Nielsen et al., 2013; Petersen and Ambus, 2006). In addition, CH_4 arising from ebullition events may pass through the surface covering or by-pass through cracks, minimizing opportunity for CH_4 oxidation to occur (Petersen et al., 2013).

The equilibrium between aqueous NH_4^+ and NH_3 in slurry, and hence NH_3 emissions from the slurry surface, is strongly dependent on pH (Ni, 1999). Slurry acidification to pH values <6 (either through direct acid addition or encouragement of microbial production of organic acids in the slurry) can be very effective at reducing NH_3 emissions, with reductions of greater than 90% compared with untreated slurries with typical pH of between 7 and 8 (e.g., Kai et al., 2008; Petersen et al., 2014). A similar reduction in slurry pH has also been shown to reduce CH_4 emissions, presumably through direct inhibition of methanogenic activity (Berg et al., 2006; Petersen et al., 2014).

The objectives of this study were to test the hypotheses that (i) total GHG (CH_4 and N_2O) and NH_3 emissions over a 2-mo period of slurry storage will increase with increasing average temperature, (ii) adding a clay granule floating cover to stored pig slurry (PS) will decrease GHG and NH_3 emissions, and (iii) acidification of stored cattle slurry (CS) will decrease GHG and NH_3 emissions. Carbon dioxide (CO_2) emissions were also measured because these can give insight to the efficiency of anaerobic decomposition processes.

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 six experimental runs were conducted, each of 2 mo duration, using either PS or CS at one of three temperature regimes: cold (_C), temperate (_T) or warm (_W) (Table 1). Two potential mitigation practices were also trialed: covering with floating clay granules for the PS and acidification for the CS. Unfortunately, there were insufficient resources within the project to test all combinations. We wanted information on both manure types and on both potential mitigations, so we decided that the best use of resources was to use the floating covering on PS, where a natural crust was less likely to develop on the control treatment. Within each experiment there were three replicate tanks each of the control and mitigated slurry storage.

Slurry was obtained locally from the below-slat storage on a finishing pig farm and from 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 six 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 (supplied by Ameram Ltd.) was applied to the slurry surface to a depth of 7 cm. For the acidification treatment, 5 L of concentrated sulfuric acid was added to each tank during the filling process for the first CS experiment (CS_T) with the aim of acidifying to pH 5.5. This proved to be too much, lowering the slurry pH dramatically to approximately 5.0 and causing excessive foaming during addition. For subsequent CS experiments (CS_C and CS_W), 2.5 and 3.5 L, respectively, were added to each tank.

After tank filling and treatment addition, tank lids were fitted for commencement of measurements. Temperature probes at 25

Table 1. Slurry storage experiments with pig slurry or cattle slurry stored under cool, temperate, or warm conditions.

Exp.†	Time of year	Mean air temperature	Duration	Mitigation
		°C	d	
PS_C	Feb. –Apr.	9.2 (1.9, 17.3)‡	70	floating cover
PS_T	Apr.–June	11.1 (1.0, 21.1)	70	floating cover
PS_W	June–Aug.	17.1 (6.7, 28.9)	61	floating cover
CS_C	Dec.–Feb.	7.3 (0.3, 14.2)	62	acidification
CS_T	Sept.–Nov.	11.0 (−1.5, 20.4)	71	acidification
CS_W	July–Sept.	17.2 (8.0, 30.7)	72	acidification

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ Values in parentheses show minimum and maximum temperatures during the storage period.

cm depth recorded slurry temperature every 5 min, with two additional probes recording ambient air temperature.

Slurry Characteristics

Slurry samples taken at the start of each storage period were analyzed 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 h. Volatile solids content was determined on a subsample of the total solids by measuring the mass loss on ignition at 550°C. Total N content was determined by Kjeldahl digestion (Gerhardt TT125 infrared digester, Gerhardt Vapodest 40 distillation unit and Metrohm 716 DMS Titrino autotitrator). Ammonium-N was determined by automated colorimetry after extraction with 2 mol L^{-1} KCl. For the CS experiments, 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).

The B_o of the slurry at the start of storage was determined using a purpose-designed laboratory system (Bioprocess Control). Slurry samples were incubated at 37°C with an inoculum, using the recommended ratio of two parts inoculum to one 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 3 mol L^{-1} 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 were continually monitored by a PC controlling the system and normalized 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 approximately 10 cm diameter to which a fan was fitted to draw air from the tank headspace (Fig. 1). Air was drawn into the tank headspace via 10 holes around the outer edge of the lid each of approximately 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 is the air volume flow rate ($m^3\ s^{-1}$), and C_o and C_i are the outlet and inlet gas concentrations ($\mu g\ m^{-3}$), respectively. Methane and CO_2 concentrations were measured using a Los Gatos Ultra-Portable Greenhouse Gas Analyzer (Los Gatos Research) based on cavity enhanced absorption spectroscopy with a multiport inlet sampler. Sampling was on a semi-continuous basis with measurements from each sampling position (six tank duct outlets and two ambient air sampling positions) for 5 min and cycled continuously around the eight sampling positions. The instrument measured gas concentrations every 20 s, 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 three concentration readings.

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

Ammonia concentration measurements were made over a 1-h period twice per week by subsampling the air flow from the tank outlet ducts or from the ambient sampling points and passing the samples through acid absorption flasks (100 mL of 0.01 mol L^{-1} orthophosphoric acid per flask). 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.

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 analyzing by gas chromatography (Clarus 500, PerkinElmer) in the laboratory. Samples were taken on two occasions per week. The same samples were also analyzed for CH_4 and CO_2 concentration by gas chromatography, which provided data for periods when the Greenhouse Gas Analyzer was unavailable or not functioning.

Statistical Analysis

One-way ANOVA (Genstat 16.0, VSN International) was used to test for treatment effects on cumulative gas emissions within each experiment. Two-way ANOVA was used to test for the effects of slurry type and storage temperature regime (cool, temperate, warm) and interactions between those on cumulative gas emissions across all experiments within either the control or treated (combining acidified and covered as "treated") slurries, using the least significant difference option set to 5% to determine significant differences.

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, and pH of typical slurries from dairy and finishing pig production systems in the United Kingdom (Table 2), although it was notable that the pH for PS_C was similar to that of the cattle slurries and approximately 1 pH unit lower than for PS_T and PS_W. Average B_o values were determined as 0.37 ± 0.01 (SE) and 0.20 ± 0.01 m^3 CH_4 kg^{-1} VS for PS and CS, respectively; that for PS is lower than the IPCC default value of 0.45 m^3 CH_4 kg^{-1} VS, whereas 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 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 slurry temperature that was higher by 0.3, 1.0, and 1.5°C compared with the control for PS_C, PS_T, and PS_W, respectively, presumably because of lower evaporative losses (see below), and further reduced diurnal variation when compared with the control slurry. There was no significant difference between ambient air, control slurry, and the acidified CS temperatures.

Evaporative losses as estimated by loss of slurry volume were not measured for all experiments but increased with storage temperature from <2% of initial volume for the CS_C to 13% of initial volume for CS_W. There was some evidence that losses were greater from the control pig slurries than for the cattle slurries, as would be expected with the greater propensity for cattle slurries to form a crust, and that the covering of clay granules reduced evaporative losses from the pig slurries by approximately 30%. There was no apparent effect of acidification of the cattle slurries on evaporative loss.

Cattle Slurry pH Evolution

The pH of the control cattle slurries remained relatively constant throughout the storage period (Fig. 2; 10 cm depth values), with a slight increase in that for CS_W (from pH 7.3 to 7.6). The surface pH was generally between 0 and 0.1 pH units greater than that measured at 10 cm depth (data not shown). For the acidified treatments, the pH of CS_C, which had the greatest volume of acid addition, remained below pH 5 throughout the duration of measurement. For CS_T and CS_W, where less acid was added, pH increased throughout the storage period from an

Table 2. Slurry characteristics at the start of each experiment.

Experiment †	Total solids	Volatile solids	B_o ‡	Total N	Ammonium-N	pH
	g kg^{-1}		m^3 CH_4 kg^{-1} VS§	g kg^{-1}		
PS_C	61.5 (0.25)¶	49.6 (0.07)	0.38 (0.00)	5.62 (0.03)	3.69 (0.03)	7.1 (0.01)
PS_T	81.1 (1.91)	64.3 (0.75)	0.37 (0.02)	6.32 (0.17)	2.83 (0.12)	8.1 (0.03)
PS_W	61.7 (1.37)	50.1 (3.02)	0.35 (0.04)	5.74 (0.02)	2.88 (0.09)	7.9 (0.02)
CS_C	54.2 (0.38)	43.3 (0.04)	0.19 (0.02)	2.49 (0.06)	0.78 (0.01)	7.3 (0.17)
CS_T	66.2 (2.98)	49.4 (0.75)	0.21 (0.03)	2.76 (0.04)	0.84 (0.06)	7.1 (0.01)
CS_W	60.5 (0.37)	51.1 (1.73)	0.21 (0.00)	2.76 (0.02)	0.95 (0.02)	7.3 (0.08)

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ Biological potential for CH_4 production.

§ VS, volatile solids.

¶ Values in parentheses are SEM (*n* = 3).

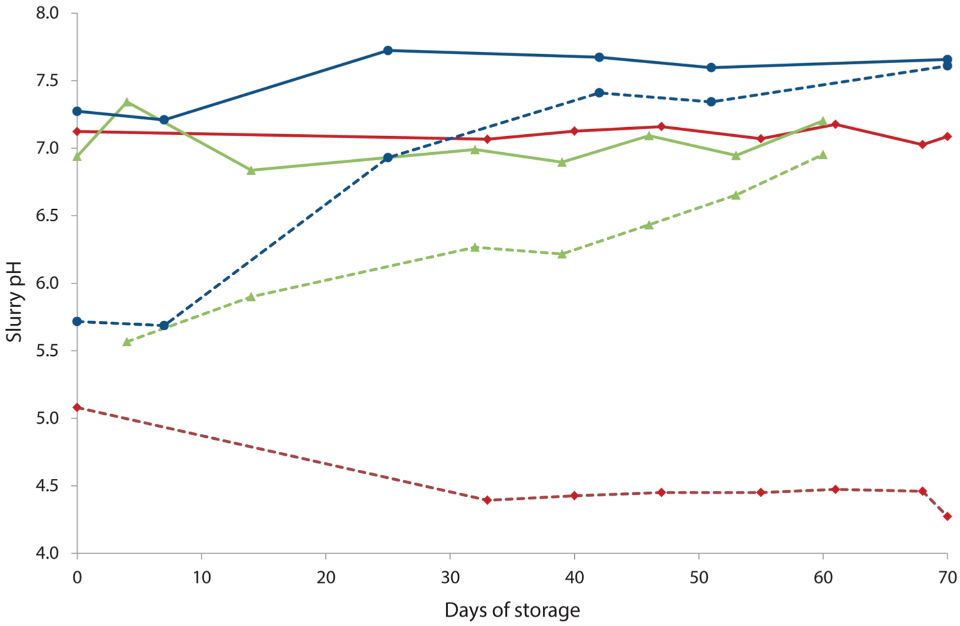

Fig. 2. Evolution of cattle slurry (CS) pH (at 10 cm depth) during storage under cool (_C), temperate (_T), or warm (_W) conditions. Solid lines represent control treatments; dashed lines represent acidification treatments. Green lines (triangles), CS_C; red lines (diamonds), CS_T; blue lines (circles), CS_W.

initial value of approximately 5.5. The increase occurred more rapidly for CS_W, for which pH was effectively the same as in the control treatment after 40 d. The more rapid return of pH in the acidified CS_W treatment despite having more acid added than CS_C may have been due to the higher temperature and increased microbial and chemical activity for that treatment; loss of CO_2 will increase slurry pH, and the difference in CO_2 loss was greater between control and acidified treatment for CS_C than CS_W. Further acid addition throughout storage may therefore be required to maintain pH values at or below pH 6.0.

CH_4 Emissions

Daily CH_4 fluxes were greatest from CS_W, 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 PS_W (Fig. 3). Fluxes from the CS at the lower storage temperatures were consistently below 5 g CH_4 m^{-3} d^{-1} and were also low from PS_C, but fluxes from PS_T were similar to those from PS_W. Sommer et al. (2000) reported relatively low emission rates from stored CS (0–22 g CH_4 m^{-3} d^{-1}), and Wood et al. (2012) reported a lag of 50 to 70 d before the onset of increased CH_4 fluxes from stored CS, 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. There was a significant interaction between slurry type and average storage temperature on

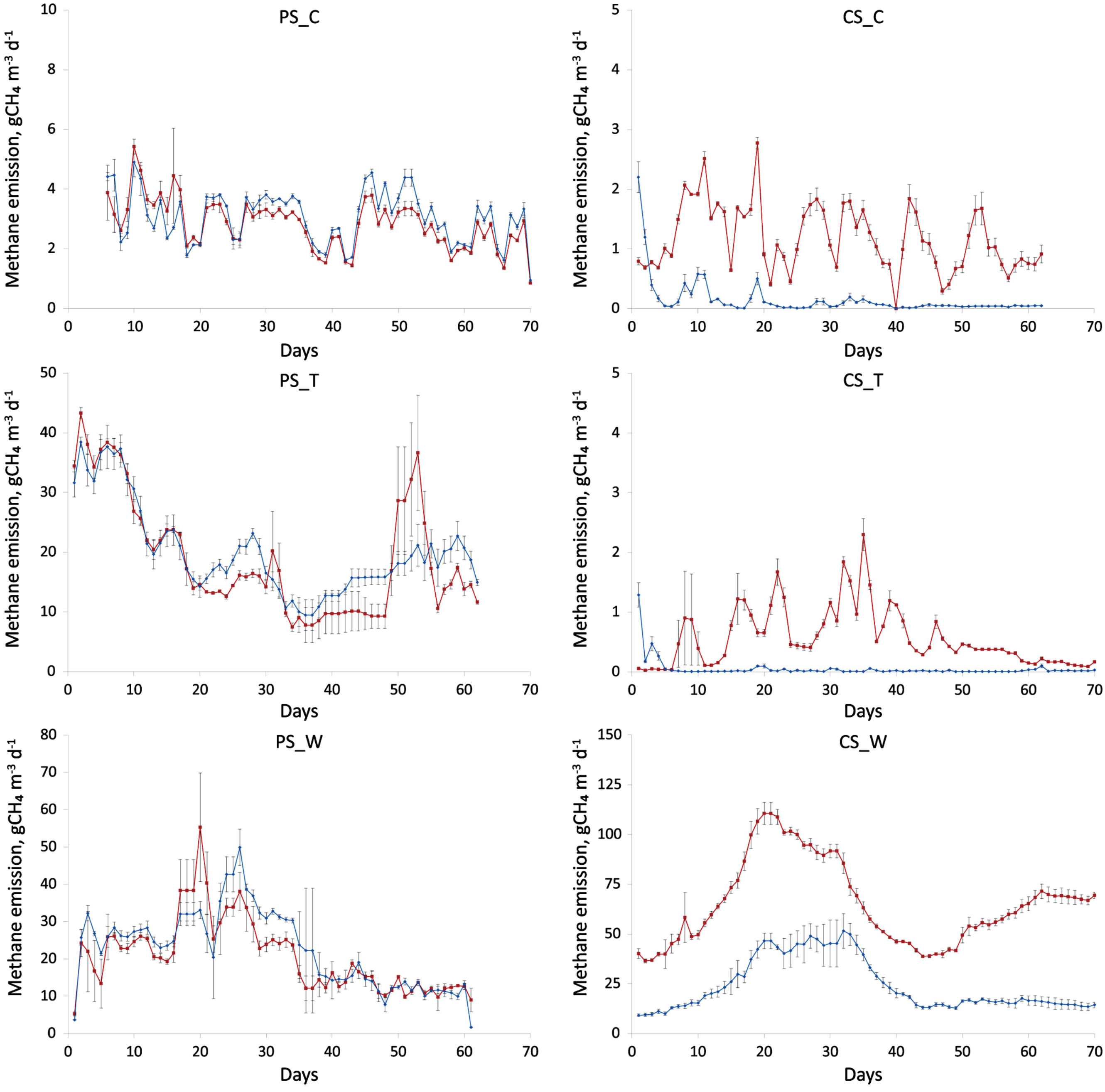

Fig. 3. Methane flux during the slurry storage experiments (error bars show ± SEM). Pig slurry (PS) and cattle slurry (CS) under cool (_C), temperate (_T), or warm (_W) conditions. Red line represents the control; blue line represents the mitigation treatment (clay granule covering for PS and acidification for CS).

cumulative CH_4 emissions from the control slurries, expressed per kg VS (Table 3). For CS, cumulative emission was much greater ($P < 0.05$) from CS_W than either CS_C or CS_T, which were not significantly different. For PS, emissions from PS_T and PS_W were not significantly different but were significantly greater than from PS_C ($P < 0.05$) but not as large as from CS_W. Mean storage temperatures were very similar for both slurry types under temperate and warm conditions, although the dynamics of temperature variation through the storage period were different for the temperate storage periods; for CS_T, temperature declined throughout storage from an initial 16°C to approximately 3°C at the end. For PS_T, temperature remained stable at approximately 10°C for most of the storage period, with an increase to 15°C over the last 10 d. Temperature profiles during storage of CS_W and PS_W were very similar. The relationship between slurry temperature and methanogenic activity is almost certainly nonlinear, but further controlled temperature studies are required to determine if there is a temperature threshold above which activity increases rapidly and whether slurry composition influences this threshold temperature.

Slurry acidification effectively stopped CH_4 emissions after the first few days of storage in CS_C and CS_T. However, in CS_W, although much lower than for the control slurry, the flux rate did increase from the acidified slurry over the first 30 d (in line with increasing slurry pH for the acidified CS_W treatment) (Fig. 2) 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 intact crust on this treatment (visual observation). There was a significant effect of acidification on cumulative CH_4 emissions from CS, with emission reductions of 86, 91, and 63% from CS_C, CS_T, and CS_W, respectively, when expressed per m^3 slurry and 82, 88, and 60% reductions when expressed per kg initial VS (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. The reduction efficiency of acidification was least under the warm storage conditions, but because the quantity of acid addition and storage temperature are confounded in our study it is difficult to interpret this; certainly the increase in pH subsequent to acidification was greatest and occurred more quickly for CS_W than for either CS_C or CS_T (Fig. 2).

There was no significant effect of the floating clay granule cover on cumulative CH_4 emissions from PS (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 hypothesized 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 because the majority of CH_4 emissions occur as ebullition events that 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 CS 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 reported 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 PS storage but did report significant reductions in CH_4 emissions of 32 and 16% for wood chip and expanded clay, respectively, when used on CS storage. Successful mitigation through 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.

CH_4 Conversion Factor

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

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

where cumulative CH_4 emission is expressed as kg CH_4 m^{-3} slurry, VS is expressed as kg m^{-3} slurry, B_o is expressed 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-mo storage periods (Table 4). Slurries are typically stored for longer than 2 mo in the United Kingdom, but based on these results we can estimate an average 6-mo storage MCF for PS of 21%, assuming storage may be at any time of year, which compares favorably with the IPCC 2006 Guidelines default value of 17% appropriate for temperatures in the United Kingdom. For cattle slurries, storage

Table 3. Cumulative methane emissions from the control and treated slurries (covering with clay granules for pig and acidification for cattle) in each experiment.

Experiment †	CH_4 emissions					
	Control	Treatment	*P* value	Control	Treatment	*P* value
	——g CH_4 m^{-3} slurry ——			——g CH_4 kg^{-1} volatile solids ——		
PS_C	203a‡	221a	0.175	4.1a	4.4a	0.177
PS_T	1314b	1349b	0.799	21.5b	20.1b	0.644
PS_W	1346b	1389b	0.686	27.1b	27.7c	0.864
CS_C	74a	12a	<0.001	1.7a	0.3a	<0.001
CS_T	40a	4a	<0.001	0.8a	0.1a	<0.001
CS_W	4558c	1681c	<0.001	86.7c	34.3d	0.002

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ Values followed by different letters within columns are significantly different ($P < 0.05$).

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

Experiment †	Slurry VS‡	B_o§	Potential CH_4 emission	Measured CH_4 emission	MCF¶
	g kg^{-1}	m^3 CH_4 kg^{-1} VS	kg m^{-3} slurry		%
PS_C	49	0.38	12.5	0.20	1.6
PS_T	61	0.37	15.1	1.31	8.7
PS_W	50	0.35	11.7	1.35	11.5
CS_C	43	0.19	5.5	0.07	1.4
CS_T	49	0.21	6.9	0.04	0.6
CS_W	53	0.21	7.5	4.56	61.1

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ VS, volatile solids.

§ Biological potential for CH_4 production.

¶ MCF, methane conversion factor.

is generally through the autumn, winter, and spring months, giving an MCF based on this study of approximately 2%, which is much lower than the IPCC default value and in agreement with the observations of Rodhe et al. (2012) for PS 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 CS used in the UK GHG inventory is too high. Although our study was of relatively short duration, our measurements from PS 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).

N_2O 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 or if using higher-precision instrumentation. Some researchers 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.

CO_2 Emissions

For the CS experiments, there was a large initial peak emission that declined rapidly, which was not observed for the PS (Fig. 4). Subsequent emission rates for the control CS were similar to those for the control PS, ranging from 10 to 90, from 10 to 150, and from 50 to 300 g CO_2 m^{-3} d^{-1} for cold, temperate, and warm conditions, respectively. Cumulative CO_2 emissions over the 2-mo storage period were of a similar order of magnitude ($P > 0.05$) for the control CS and PS (Table 5). Carbon loss was generally greater in the form of CO_2 than CH_4 from all control slurries by 2- to 7-fold for the PS and by 12- to 27-fold for the CS, with the exception of CS_W, where losses were of the same magnitude. There was a significant effect of mean storage temperature on cumulative CO_2 emission ($P < 0.05$), with emissions being greatest from warm and least from cool storage conditions.

Carbon dioxide emission rates tended to be lower from the clay granule covering treatment in the PS experiments. This was most probably because of an increased resistance to mass transfer of the CO_2 through the covering layer, but there may also have been an effect of increasing the anaerobicity in the slurry surface layer. Covering gave a significant emission reduction ($P < 0.05$) of approximately 30% across all timings, with reductions of 29, 40, and 23% for PS_C, PS_T, and PS_W, respectively.

Fluxes from the acidified CS treatments tended to be lower than from the control for periods throughout storage at all temperatures (Fig. 4). The initial high emission rate of CO_2 on addition of acid to the slurry may not have been fully captured in the measurements because there was some delay between filling of the slurry tanks, acid addition, lid installation, and the commencement of measurements. Acidification of the CS resulted in a significant reduction ($P < 0.05$) in cumulative emission of 26% when averaged across all timings. There were significant reductions of 28 and 31% for CS_C and CS_W but no significant difference for CS_T.

NH_3 Emissions

Ammonia emissions were greater from the control PS than from the control CS, with respective ranges of 5 to 35 and 1 to 8 g NH_3–N m^{-3} d^{-1} across all temperatures (Fig. 5). Cumulative NH_3 emissions were also greater from the control PS than from the control CS in absolute terms and as a percentage of the initial slurry N content (Table 6). Emissions increased significantly ($P < 0.05$) with mean storage temperature for both slurry types. For control CS, cumulative emission expressed as a percentage of initial total ammoniacal N (TAN) content correlated extremely well with ambient temperature ($r^2 = 0.99$), with a slope of 2.0 (i.e., an increase in emission by 2% of initial TAN content for every 1°C rise in mean storage temperature). For control PS, there was a greater temperature effect, with a regression slope of 4.4% ($r^2 = 0.71$).

Acidification of CS significantly reduced the emission rate; in CS_T the slurry pH remained below 5 throughout the measurement period, and the emission rate from the acidified treatment remained at or below zero throughout the measurement period. In CS_C and CS_W, where less acid was added, NH_3 emissions increased as the pH value increased until Day 30 and then remained at a rate just below that of the control treatment in CS_C but decreased again as a solid crust formed on the acidified slurry in CS_W. Acidification of CS gave a significant reduction ($P < 0.05$) in cumulative emissions of 75% across all

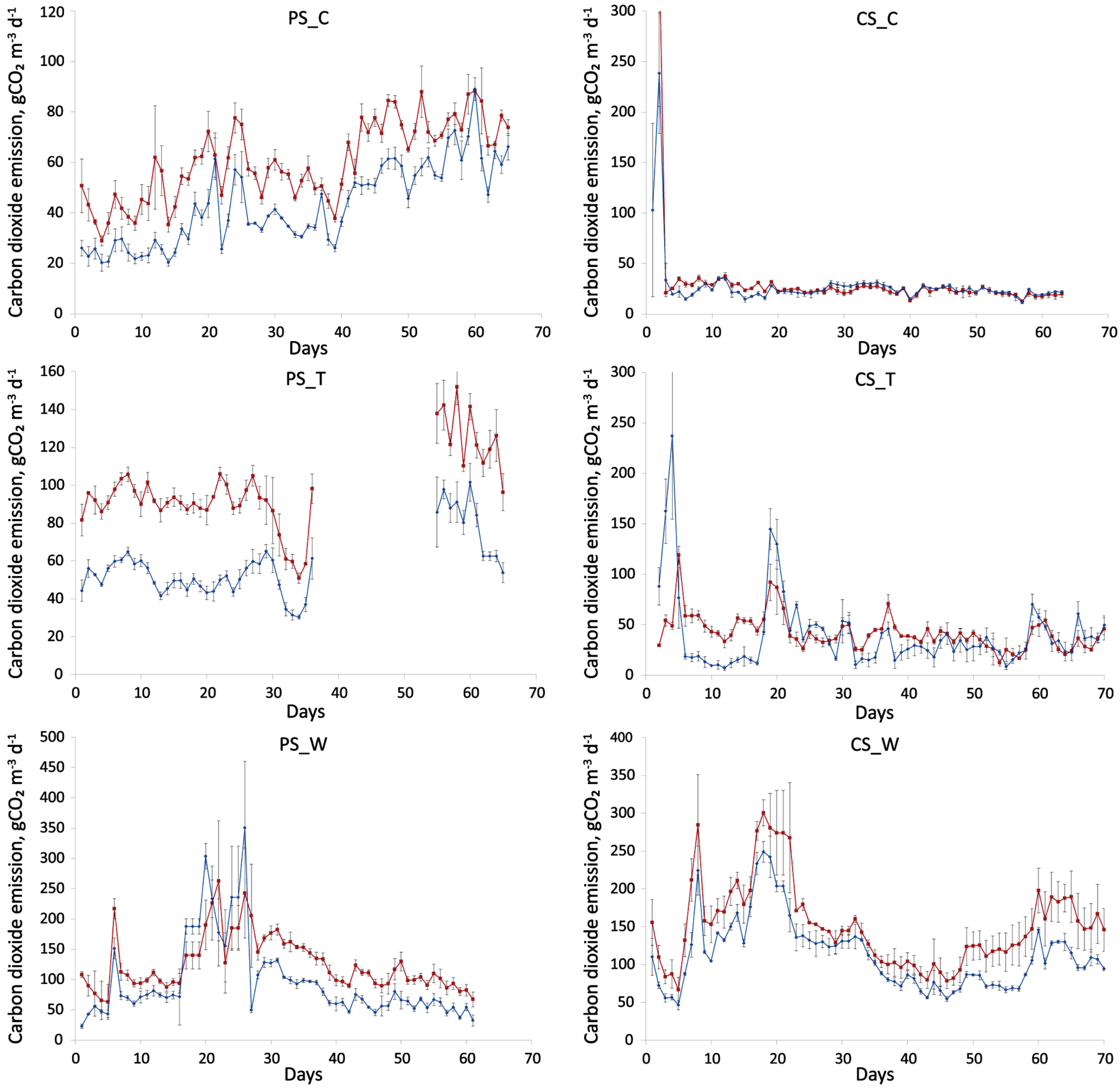

Fig. 4. Carbon dioxide flux during the slurry storage experiments (error bars show ± SEM). Pig slurry (PS) and cattle slurry (CS) under cool (_C), temperate (_T), or warm (_W) conditions. Red line represents the control; blue line represents the mitigation treatment (clay granule covering for PS and acidification for CS).

Table 5. Cumulative CO_2 emissions from the control and treated slurries (covering with clay granules for pig and acidification for cattle) in each experiment.

Experiment†	CO_2 emissions					
	Control	Treatment	*P* value	Control	Treatment	*P* value
	——— g CO_2 m^{-3} slurry ———			——— g CO_2 kg^{-1} volatile solids ———		
PS_C	3,930b‡	2,799b	0.004	79.5ab	56.3ab	0.005
PS_T	6,350c	3,793c	0.002	104.0b	56.7ab	0.003
PS_W	7,647d	5,869d	0.043	154.0c	116.0c	0.048
CS_C	2,490a	1,796a	0.154	59.3a	41.3a	0.067
CS_T	2,989ab	2,893b	0.812	61.6a	59.7ab	0.879
CS_W	11,848e	8,127e	0.002	226.0d	166.0d	0.052

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ Values followed by different letters within columns are significantly different ($P < 0.05$).

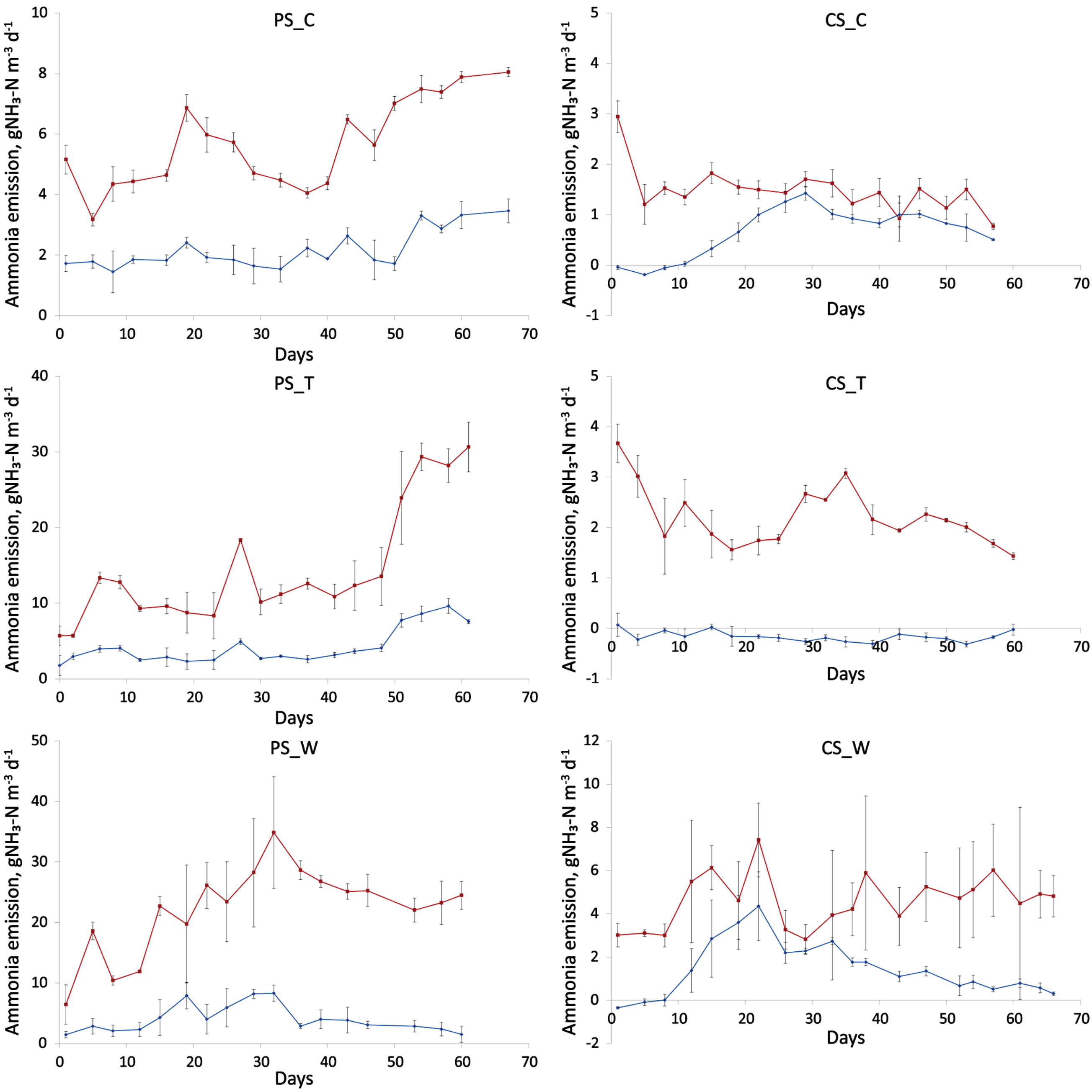

Fig. 5. Ammonia flux during the slurry storage experiments (error bars show ± SEM). Pig slurry (PS) and cattle slurry (CS) under cool (_C), temperate (_T), or warm (_W) conditions. Red line represents the control; blue line represents the mitigation treatment (clay granule covering for PS and acidification for CS).

Table 6. Cumulative ammonia emissions from the control and treated slurries (covering with clay granules for pig and acidification for cattle) in each experiment.

Experiment†	NH_3–N emissions								
	Control	Treatment	*P* value	Control	Treatment	*P* value	Control	Treatment	*P* value
	— g NH_3–N m^{-3} slurry —			— % initial slurry total N —			— % initial slurry TAN‡ —		
PS_C	399b§	154c	<0.001	7.1b	2.7bc	<0.001	10a	4.2b	<0.001
PS_T	1116c	318e	<0.001	18.0d	5.0e	<0.001	42d	11.0c	<0.001
PS_W	1593d	257d	<0.001	28.0e	4.5de	<0.001	53e	9.2c	<0.001
CS_C	104a	46ab	0.009	4.1a	1.9b	0.012	13a	5.8b	0.014
CS_T	166a	2a	<0.001	6.1ab	0.1a	<0.001	23b	0.2a	<0.001
CS_W	321b	102bc	0.002	12.0c	3.7cd	0.002	33c	11.0c	0.001

† Pig slurry (PS) or cattle slurry (CS) stored under cool (_C), temperate (_T), or warm (_W) conditions.

‡ TAN, total ammoniacal nitrogen.

§ Values followed by different letters within columns are significantly different ($P < 0.05$).

experiments, with specific reductions in emission (expressed as % of initial TAN) of 56, 99, and 68% for CS_C, CS_T (where slurry pH remained below 5), and CS_W, respectively. There was a poor correlation between cumulative emission as a percentage of initial TAN and average storage temperature from the acidified slurries ($r^2 = 0.35$; slope = 0.6). Because of the strong relationship between emission and temperature for the control slurries, this resulted in better reduction efficiency at higher storage temperature. Petersen et al. (2012) reported >90% reduction in NH_3 emission over a 95-d storage period in a laboratory study but reported a gradual increase in pH from acidified slurries over the duration of storage. In a pilot-scale study using PS and sulfuric acid (96%), Petersen et al. (2014) reported reductions in NH_3 emission over an 83-d storage period of 84% where pH was lowered to 5.5 and of 49% where pH was only lowered to 6.5. In their study with acid addition rates of 10 and 6 kg t^{-1} slurry, respectively, pH remained fairly constant throughout the measurement period, unlike in our study where the pH with lower acid addition rates increased during storage for the CS_C and CS_W experiments. Kai et al. (2008) took measurements from a pig farm with a commercially installed acidification unit and reported that acidification during the housing phase (5 kg acid t^{-1} slurry) reduced emissions during a subsequent 13-mo storage period by >90% compared with untreated slurry, with no surface crust development and a pH increase during storage of 1.1 units.

Covering the PS with a layer of floating clay granules significantly reduced the NH_3 emission rate throughout each of the measurement periods (Fig. 5) and gave a significant reduction ($P < 0.05$) in emission of 77% across all experiments, with specific reductions in emission (expressed as percentage of initial TAN) of 61, 72, and 84% for PS_C, PS_T, and PS_W, respectively. As for the acidified slurries, there was a poor correlation between cumulative emission and average storage temperature from the covered slurries ($r^2 = 0.25$; slope = 0.4) and therefore better reduction efficiency at higher storage temperature. These reduction efficiencies are at the high end of the range reported in the literature (Guarino et al., 2006; Hörnig et al., 1999; Portejoie et al., 2003; Van der Zaag et al., 2008).

Conclusions

Mean temperature over the 2-mo storage period had a strong influence on CH_4 and NH_3 emissions from stored PS and CS. This effect was observed more consistently for NH_3 emissions than for CH_4 emissions, where there were indications that there may be a threshold temperature above which emissions increase rapidly. The derived MCF value for PS was of a similar order to the IPCC 2006 guidelines default value for slurry storage, but that for CS was much lower if CS is assumed to be stored mostly over the cooler autumn, winter, and spring months; CH_4 emissions were very much greater from CS under warm storage conditions. The derivation of country-specific MCF values for PS and CS storage needs to take into account the time of year (temperature) and duration of storage.

The use of 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 PS. Further assessment of the potential for methanotroph development in floating covers as a CH_4 mitigation measure is recommended. Acidification of CS 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%, but consideration must be given to maintaining low slurry pH throughout storage duration in the development of practical on-farm systems. Future research requirements to develop improved approaches to estimating emissions from slurry storage for national inventory purposes should 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 PS and CS to provide robust MCF values, and measurements from commercial-scale stores for validation.

Acknowledgments

The authors thank the North Wyke farm laboratory and technical teams for their assistance. This work was supported by the UK Department for Environment, Food and Rural Affairs (Defra); the Department of Agriculture and Rural Development in Northern Ireland; and the Scottish Government and the Welsh Government. Rothamsted Research receives strategic funding from the Biotechnology and Biological Sciences Research Council (BBSRC).

References

Berg, W., R. Brunsch, and I. Pazsiczki. 2006. Greenhouse gas emissions from covered slurry compared with uncovered during storage. Agric. Ecosyst. Environ. 112:129–134. doi:10.1016/j.agee.2005.08.031

Chadwick, D., S. Sommer, R. Thorman, D. Fangueiro, L. Cardenas, B. Amon, and T. Misselbrook. 2011. Manure management: Implications for greenhouse gas emissions. Anim. Feed Sci. Technol. 166-167:514–531. doi:10.1016/j.anifeedsci.2011.04.036

Dong, H., J. Mangino, T. MacAllister, J.L. Hatfield, D.E. Johnson, K.R. Lassey, M.A. de Lima, A. Romanovskaya, D. Bartman, D. Gibb, and J.H. Martin. 2006. Emissions from livestock and manure management. In: S. Eggleston et al., editors, 2006 IPCC guidelines for national greenhouse gas inventories. IGES, Hayama, Japan. p. 10.1–10.87.

Duan, Y.-F., L. Elsgaard, and S.O. Petersen. 2013. Inhibition of methane oxidation in a slurry surface crust by inorganic nitrogen: An incubation study. J. Environ. Qual. 42:507–515. doi:10.2134/jeq2012.0230

Duan, Y.F., W.A. Al-Soud, A. Brejnrod, S.J. Sørensen, L. Elsgaard, S.O. Petersen, and N. Boon. 2014. Methanotrophs, methanogens and microbial community structure in livestock slurry surface crusts. J. Appl. Microbiol. 117:1066–1078. doi:10.1111/jam.12584

Guarino, A., C. Fabbri, M. Brambilla, L. Valli, and P. Navarotto. 2006. Evaluation of simplified covering systems to reduce gaseous emissions from livestock manure storage. Trans. ASABE 49:737–747. doi:10.13031/2013.20481

Hansen, R.R., D.A. Nielsen, A. Schramm, L.P. Nielsen, N.P. Revsbech, and M.N. Hansen. 2009. Greenhouse gas microbiology in wet and dry straw crust covering pig slurry. J. Environ. Qual. 38:1311–1319. doi:10.2134/jeq2008.0336

Hörnig, G., M. Turk, and U. Wanka. 1999. Slurry covers to reduce ammonia emission and odour nuisance. J. Agric. Eng. Res. 73:151–157. doi:10.1006/jaer.1998.0402

Husted, S. 1994. Seasonal variation in methane emission from stored slurry and solid manures. J. Environ. Qual. 23:585–592. doi:10.2134/jeq1994.00472425002300030026x

Kai, P., P. Pedersen, J.E. Jensen, M.N. Hansen, and S.G. Sommer. 2008. A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. Eur. J. Agron. 28:148–154. doi:10.1016/j.eja.2007.06.004

Misselbrook, T.H., S.K.E. Brookman, K.A. Smith, T.R. Cumby, A.G. Williams, and D.F. McCrory. 2005. Crusting of stored dairy slurry to abate ammonia emissions: Pilot-scale studies. J. Environ. Qual. 34:411–419.

Ni, J.Q. 1999. Mechanistic models of ammonia release from liquid manure: A review. J. Agric. Eng. Res. 72:1–17. doi:10.1006/jaer.1998.0342

Nielsen, D.A., A. Schramm, L.P. Nielsen, and N.P. Revsbech. 2013. Seasonal methane oxidation potential in manure crusts. Appl. Environ. Microbiol. 79:407–410. doi:10.1128/AEM.02278-12

Petersen, S.O., and P. Ambus. 2006. Methane oxidation in pig and cattle slurry storages, and effects of surface crust moisture and methane availability. Nutr. Cycling Agroecosyst. 74:1–11. doi:10.1007/s10705-005-3822-6

Petersen, S.O., B. Amon, and A. Gattinger. 2005. Methane oxidation in slurry storage surface crusts. J. Environ. Qual. 34:455–461.

Petersen, S.O., A.J. Andersen, and J. Eriksen. 2012. Effects of cattle slurry acidification on ammonia and methane evolution during storage. J. Environ. Qual. 41:88–94. doi:10.2134/jeq2011.0184

Petersen, S.O., M. Blanchard, D. Chadwick, A. Del Prado, N. Edouard, J. Mosquera, and S.G. Sommer. 2013. Manure management for greenhouse gas mitigation. Animal 7(Suppl 2):266–282. doi:10.1017/S1751731113000736

Petersen, S.O., O. Højberg, M. Poulsen, C. Schwab, and J. Eriksen. 2014. Methanogenic community changes, and emissions of methane and other gases, during storage of acidified and untreated pig slurry. J. Appl. Microbiol. 117:160–172. doi:10.1111/jam.12498

Portejoie, S., J. Martinez, F. Guiziou, and C.M. Coste. 2003. Effect of covering pig slurry stores on the ammonia emission processes. Bioresour. Technol. 87:199–207. doi:10.1016/S0960-8524(02)00260-2

Qi, X.Y., S.B. Wu, Z.Q. Wang, Z. Zuo, and R.J. Dong. 2015. Seasonal and daily emissions of methane and carbon dioxide from a pig wastewater storage system and the use of artificial vermiculite crusts. Biosystems Eng. 131:15–22. doi:10.1016/j.biosystemseng.2014.12.009

Rodhe, L.K.K., J. Abubaker, J. Ascue, M. Pell, and A. Nordberg. 2012. Greenhouse gas emissions from pig slurry during storage and after field application in northern European conditions. Biosystems Eng. 113:379–394. doi:10.1016/j.biosystemseng.2012.09.010

Sommer, S.G., S.O. Petersen, and H.T. Sogaard. 2000. Greenhouse gas emission from stored livestock slurry. J. Environ. Qual. 29:744–751. doi:10.2134/jeq2000.00472425002900030009x

Sommer, S.G., B.T. Christensen, N.E. Nielsen, and J.K. Schjorring. 1993. Ammonia volatilization during storage of cattle and pig slurry: Effect of surface cover. J. Agric. Sci. 121:63–71. doi:10.1017/S0021859600076802

Sommer, S.G., G.Q. Zhang, A. Bannink, D. Chadwick, T. Misselbrook, R. Harrison, N.J. Hutchings, H. Menzi, G.J. Monteny, J.Q. Ni, O. Oenema, and J. Webb. 2006. Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores. Adv. Agron. 89:261–335. doi:10.1016/S0065-2113(05)89006-6

Van der Zaag, A.C., R.J. Gordon, V.M. Glass, and R.C. Jamieson. 2008. Floating covers to reduce gas emissions from liquid manure storages: A review. Appl. Eng. Agric. 24:657–671. doi:10.13031/2013.25273

Wood, J.D., R.J. Gordon, C. Wagner-Riddle, K.E. Dunfield, and A. Madani. 2012. Relationships between dairy slurry total solids, gas emissions and surface crusts. J. Environ. Qual. 41:694–704. doi:10.2134/jeq2011.0333

Wulf, S., R. Vandre, and J. Clemens. 2002. Mitigation options for CH_4, N_2O and NH_3 emissions from slurry management. In: J. van Ham, A.P.M. Baede, R. Guicherit, J.G.F.M. Williams-Jacobse,, editors, Non-CO2 greenhouse gases: Scientific understanding, control options and policy aspects. Proceedings of the 3rd International Symposium NCGG-3, Maastricht, the Netherlands. 21–23 Jan. 2002. IOS Press, Amsterdam, the Netherlands. p. 487–492.