

Emissions of CH₄, N₂O, NH₃ and odorants from pig slurry during winter and summer storage

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Abstract Manure storage contributes significantly to greenhouse gas (GHG), NH₃ and odour emissions from intensive livestock production. A pilot-scale facility with eight 6.5-m³ slurry storage units was used to quantify emissions of CH₄, N₂O, NH₃, and odorants from pig slurry during winter and summer storage. Pig slurry was stored with or without a straw crust, and with or without interception of precipitation, i.e., four

treatments, in two randomized blocks. Emissions of total reduced S (mainly H₂S) and *p*-cresol, but not skatole, were reduced by the straw crust. Total GHG emissions were 0.01–0.02 kg CO₂ eq m⁻³ day⁻¹ during a 45-day winter storage, and 1.1–1.3 kg CO₂ eq m⁻³ day⁻¹ during a 58-day summer storage period independent of storage conditions; the GHG balance was dominated by CH₄ emissions. Nitrous oxide emissions occurred only during summer storage where, apparently, emissions were related to the water balance of the surface crust. An N₂O emission factor for slurry storage with a straw crust was estimated at 0.002–0.004. There was no evidence for a reduction of CH₄ emissions with a crust. Current Intergovernmental Panel on Climate Change recommendations for N₂O and CH₄ emission factors are discussed.

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Abbreviations

VS	Volatile solids
TRS	Total reduced sulphur
TN	Total nitrogen
TAN	Total ammoniacal nitrogen
GWP	Global warming potential
GHG	Greenhouse gas
–P–S	No precipitation, no straw crust
–P+S	No precipitation, straw crust present
+P–S	With precipitation, no straw crust
+P+S	With precipitation, straw crust present

Introduction

Livestock manure has been estimated to contribute 17.5 Tg methane (CH₄) and 3.7 Tg nitrous oxide (N₂O) to the atmosphere each year (Steinfeld et al. 2006), corresponding to 31–37 % of non-CO₂ greenhouse gas (GHG) emissions from agriculture (Smith et al. 2007). The magnitude of CH₄ and N₂O emissions differ between livestock categories; pigs are mostly produced in confined systems where manure is handled in liquid form (as a slurry) and stored prior to use.

The slurry environment is anoxic, and degradation of manure organic matter stimulates CH₄ emission compared to solid manure management, but with a strong seasonal variation in emissions (Husted 1994). In some countries, regulations require slurry storage facilities to be covered in order to mitigate NH₃ emissions, but often this is achieved by a naturally forming crust of manure organic matter, or crust formation can be facilitated by admixing of straw or wood chips (Sommer et al. 2006). An organic surface crust will sustain microbial activity and may thus modify emission. It is well established that surface crusts develop a potential for CH₄ oxidation (e.g., Petersen et al. 2005; Ambus and Petersen 2005), and for production of N₂O (e.g., Sommer et al. 2000; VanderZaag et al. 2009), during slurry storage. The Intergovernmental Panel on Climate Change (IPCC) in its latest revision of the methodology for agricultural GHG emissions (IPCC 2006) proposed that 40 % of CH₄ emissions will be offset by an organic crust. Further, an emission factor for N₂O, expressed as a proportion of manure N, of 0.005 was recommended for liquid manure storage in the presence of a crust. However, a crust is exposed to climatic conditions that vary seasonally, and biogenic emissions may be modified by factors such as temperature and rainfall. Therefore, more knowledge is needed on emissions as influenced by slurry storage conditions.

Besides CH₄, N₂O and NH₃, slurry stores are a source of odour emissions that can be a nuisance to neighboring settlements (Schiffman 1998). The most important odorants include volatile sulphur-containing compounds, indoles and phenols (Blanes-Vidal et al. 2009; Eriksen et al. 2010; Hansen et al. 2012). When evaluating effects of storage conditions on GHG emissions, it is important to document also any effects on odour.

In the present study, emissions of CH₄, N₂O, NH₃ and odorants from pig slurry during summer and winter storage were quantified, and effects of a straw crust and of rainfall were evaluated by manipulation of storage conditions. We expected a crust to modify emissions mainly during summer where storage temperature and thus microbial activity is high. Specifically, we hypothesized that a straw crust would reduce CH₄ emissions from pig slurry in accordance with the observations made with cattle slurry, and that rainfall would reduce effects of a crust by shifting the balance between aerobic and anaerobic microbial activity.

Materials and methods

Pilot-scale storage facility

Full technical documentation of the pilot-scale storage facility was presented by Petersen et al. (2009). It includes eight cylindrical 6.5-m³ units (2 m diam. 2 m height incl. 70 cm above-ground) with a wall of 40 mm HDPE. Each unit has eight air inlets and a single outlet (all 160 mm in diameter), to enable forced ventilation in the presence of a removable cover. All openings may be capped if using the stores as static enclosures during emission measurements. Outlets are connected to a main ventilation duct; a flow restrictor on each connecting tube is connected to a differential pressure transmitter monitoring the air flow.

Storage treatments

Slurry for winter and summer storage experiments was collected at a farm with finishing pigs. Slurry was pumped from a pre-storage reservoir, to which slurry from the housing facility had been recently pumped, hence slurry age was <1 month. Portions of 4 m³ slurry were added to each experimental store; exact volumes were calculated by recording the distance to the liquid surface after filling. Slurry samples were collected from each store for analyses at the beginning, and again at the end of each storage period, after thorough mixing.

In both winter and summer storage experiments, four treatments were represented in two randomized

blocks each with four storage units. The four treatments were: Admixing of 2.5 kg Mg⁻¹ chopped wheat straw to produce a surface crust (+S), or no straw amendment (-S). This was combined with sheltering to intercept precipitation as rainfall or snow (-P), or open storage conditions except during emission measurements (+P). Hence, the four treatments were: -P-S, -P+S, +P-S and +P+S. The winter storage period lasted from 27 Nov 2007 to 11 Jan 2008 (45 days), while the summer storage period lasted from 16 Jun to 13 Aug 2008 (58 days).

Precipitation was eliminated by permanently applying the removable covers on relevant stores, but with continuous ventilation to simulate open storage conditions. Ventilation rates were 175 and 94 m³ h⁻¹ in winter and summer experiments, respectively, in accordance with the difference in average wind speed for these periods the previous year, 5.3 and 3.7 m s⁻¹, respectively (based on data from a nearby climate station). Inside the stores, wind velocities were always <1 m s⁻¹ as determined by a hot-wire anemometer, and declining towards the surface of the stored slurry (data not shown). Treatments representing open storage, i.e., with precipitation reaching the stored slurry, were covered only during gas sampling (see next section).

Gas sampling

Emissions were as a rule determined weekly during 24-h periods, resulting in six and seven sampling occasions in the winter and summer experiment, respectively. During gas sampling, all eight stores were covered, and the ventilation air from each store was sub-sampled at 15 mL min⁻¹ via a 3-mm inner diam. FEP tubing from a position immediately after the flow restrictor where the gas was well-mixed. Gas washing bottles with 20 mM H₃PO₄ for trapping NH₃ were inserted near the point of sub-sampling. From the acid traps, the gas was transported in an insulated and heated sheath, via water traps and a peristaltic pump, to a manifold with three-way solenoid valves where sub-samples for GHG analysis were collected in 3-L Tedlar gas sampling bags during 0.5 min in every 5-min period; this gave a 2.16-L composite gas sample in 24 h. All settings and readings were recorded by LabView and stored in a log file with automated daily backup.

Selected odorants and total reduced sulphur (TRS) were monitored in six separate campaigns during the summer storage experiment. Since concentrations of odorants in the ventilation air were diluted to below the detection limits, the stores were used as static enclosures, i.e., after the 24-h period used for GHG and NH₃ emission measurements, all eight air inlets and the outlet of each store were capped and a fan activated for mixing of the headspace as described by Petersen et al. (2009). After 3–3.5 h, headspace air was sampled and analyzed. Odorants were analyzed using membrane inlet mass spectrometry (MIMS) as previously described (Feilberg et al. 2010). Gas was pumped from each store via a multi-position valve to the instrument via a separate line of insulated tubing. Reference air for baseline correction was produced on-site by pumping outside air through an activated charcoal gas trap (Supelco, St. Louis, Missouri, USA). Tubings used were PTFE (o.d., 3.2 mm; i.d., 1.6 mm). Results for two mass-to-charge values (m/z), m/z 107 and m/z 130, are shown, i.e., 4-methylphenol (*p*-cresol) and 3-methylindole (skatole) (Feilberg et al. 2010; Feilberg et al. 2011), which were consistently detected above the baseline levels. At m/z 107 there is also a contribution from 4-ethylphenol, which is typically present at levels of ~10 % of *p*-cresol. TRS was measured with a portable Jerome Hydrogen Sulfide Analyzer (Model 631-X, Arizona Instruments; Phoenix, AZ).

Analyses

Climate data were obtained from a nearby (<1 km) meteorological station. Slurry pH was analyzed with a Sentron 3001 pH-meter (Roden, The Netherlands), and electrical conductivity (EC) with a Radiometer conductivity-meter (Copenhagen, Denmark). Slurry dry matter (DM) was determined after drying at 105 °C for 24 h, and volatile solids (VS) after an additional 3 h at 550 °C. Total and ammoniacal N was determined by Kjeldahl digestion (Kjeltec 1030, Höganäs, Sweden). Ammonia trapped in 20 mM H₃PO₄ was determined colorimetrically (Keeney and Nelson 1982) after adjustment to known volume.

Concentrations of CH₄ were analyzed manually on a Shimadzu 14B gas chromatograph (Petersen et al. 2005), and N₂O on a Chrompack 9001 gas chromatograph (Mutegi et al. 2010). MIMS measurements were carried out as described by Feilberg et al. (2010).

In short, a quadrupole mass spectrometer (QMG 422, Balzers; Liechtenstein) was equipped with a custom-built membrane inlet (Mikrolab, Denmark) holding a poly-(dimethylsiloxane) (PDMS) sheet membrane (130 μm thickness, Techn. Products, Georgia). An inlet temperature of 50 $^{\circ}\text{C}$ was used. During operation a continuous flow of sampling air passes the membrane.

Data analysis

Air exchange was calculated from differential pressure readings using an algorithm given for the flow restrictor (Petersen et al. 2009). The precision of calculated air flows was $\pm 5\%$. Effects of storage conditions on changes in slurry composition were analyzed with a mixed model for the winter and the summer storage experiment separately using SAS 9.2. Treatment effects on cumulated emissions were identified by one-way ANOVA and Tukey HSD tests for each storage experiment.

The dependency of net CH_4 production on slurry temperature was characterized using the Arrhenius equation:

$$\ln(F_{\text{CH}_4}) = \ln(A) - E_A/RT,$$

where F_{CH_4} is the CH_4 flux ($\text{g CH}_4 \text{ kg}^{-1} \text{ VS h}^{-1}$), A is the pre-exponential factor ($\text{g CH}_4 \text{ kg}^{-1} \text{ VS h}^{-1}$), E_A is the apparent activation energy (J mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute slurry temperature (K). It was assumed that 80 % of VS in the pig slurry was available for fermentative degradation (Sommer et al. 2004).

A theoretical water balance for the summer storage period was calculated from precipitation and potential evaporation data obtained from a nearby climate station as previously described (Sommer et al. 2000). Here it was assumed that evaporation from actively ventilated stores with a cover was identical to that of open stores without cover except during measurements.

Results

Changes in slurry composition

Daily mean temperature during the winter storage period ranged from -3 to 9°C , and summer temperatures from 10 to 23°C (Fig. 1). Precipitation during

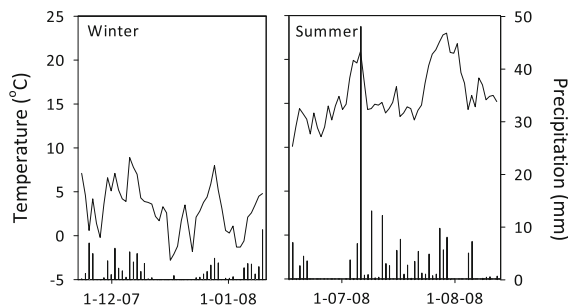


Fig. 1 Temperature and precipitation during the periods of the winter and summer experiments to determine effects of cover strategy

winter and summer periods were 82 and 174 mm, respectively. Considering that interception of precipitation was included as an experimental treatment, a wide range of weather conditions were represented.

Table 1 presents selected slurry characteristics for the batches of pig slurry used for winter and summer storage experiments. Although the same farm supplied the slurry for both storage periods, the material obtained for the summer experiment was clearly more concentrated, as reflected in higher EC, DM, and nitrogen concentrations, and there was a tendency for differences in DM and VS, but not in TN or TAN, between four loads of slurry collected sequentially, as indicated by standard errors. The relatively high DM content resulted in some DM accumulating at the surface during summer storage, even in the $+P-S$ treatment.

Changes during storage, as indicated by a mixed model, are shown at the bottom of Table 1. Slurry pH declined slightly during winter, but increased in all treatments during summer storage. The increase in TN and TAN during winter without precipitation could be due to some evaporative loss of water. During summer storage, there were substantial losses of TN and TAN with open storage conditions ($+P$), especially without the straw crust ($-S$); a decline of 0.8 kg Mg^{-1} TN versus 0.4 kg Mg^{-1} TAN indicated that losses during storage were substantial. There were no overall changes in EC during storage, but significant changes at the treatment level which reflected changes in TAN (Table 1).

Emissions of CH_4 , N_2O and NH_3

Cumulated CH_4 emissions were 100-fold higher during summer compared to winter storage (Table 2),

Table 1 Selected properties of pig slurry used in the storage experiments conducted in a winter and a summer period

Experiment	Time	Precip.	Straw	pH	EC (dS m ⁻¹)	DM		VS		TN		TAN	
						kg Mg ⁻¹ fresh wt.							
Winter (W)	22-Nov-07	+	+	7.8 (0.03)	15.8 (2.0)	28.8 (2.2)	20.6 (1.4)	2.9 (0.4)	2.0 (0.2)				
		-	+	7.9 (0.04)	19.3 (0.7)	35.9 (4.5)	25.7 (4.0)	3.7 (0.0)	2.5 (0.04)				
		+	-	7.4 (0.28)	16.5 (0.6)	34.7 (4.7)	25.8 (4.8)	3.1 (0.1)	2.0 (0.1)				
		-	-	7.5 (0.04)	20.4 (1.3)	29.5 (3.8)	21.1 (2.6)	3.5 (0.1)	2.4 (0.01)				
Winter (W)	22-Jan-08	+	+	7.5 (0.13)	16.9 (2.0)	26.7 (5.5)	18.7 (4.5)	3.2 (0.5)	2.2 (0.4)				
		-	+	7.4 (0.06)	19.6 (0.6)	32.5 (2.1)	21.6 (0.4)	3.7 (0.03)	2.5 (0.1)				
		+	-	7.3 (0.11)	18.1 (1.0)	32.4 (0.4)	22.9 (0.4)	3.4 (0.2)	2.2 (0.1)				
		-	-	7.4 (0.04)	19.1 (0.3)	31.2 (1.7)	20.7 (0.9)	3.6 (0.1)	2.5 (0.0)				
Summer (S)	16-Jun-08	+	+	7.2 (0.07)	28.0 (0.3)	96.8 (13.6)	77.4 (11.9)	6.2 (0.00)	4.22 (0.03)				
		-	+	7.2 (0.01)	27.3 (0.4)	91.1 (19.5)	71.3 (17.7)	6.3 (0.05)	4.27 (0.02)				
		+	-	7.2 (0.07)	29.0 (0.2)	74.0 (22.2)	56.4 (20.6)	6.2 (0.23)	4.20 (0.04)				
		-	-	7.2 (0.08)	29.2 (0.2)	84.6 (12.2)	66.6 (10.7)	6.3 (0.04)	4.32 (0.04)				
Summer (S)	14-Aug-08	+	+	7.6 (0.01)	27.7 (0.4)	88.6 (11.1)	69.4 (10.3)	5.9 (0.1)	3.97 (0.04)				
		-	+	7.6 (0.02)	29.3 (0.1)	85.1 (22.0)	65.6 (19.5)	6.2 (0.1)	4.36 (0.03)				
		+	-	7.6 (0.03)	26.9 (0.7)	74.4 (24.8)	56.7 (20.9)	5.4 (0.3)	3.81 (0.00)				
		-	-	7.6 (0.01)	29.8 (0.4)	83.5 (5.7)	62.9 (6.2)	6.1 (0.1)	4.18 (0.02)				
Experiment				W	S	W	S	W	S	W	S	W	S
Time				*	***					**	***	*	***
Precipitation						*							**
Straw													*
Time × precip.						**				*	**		***
Time × straw						**					*		
Precip. × straw													
Time × precip. × straw											*		

The batches of slurry stored in each of the eight pilot-scale stores was sub-sampled after mixing. Data represent mean with SE in parentheses. The statistical results were obtained with a mixed model

EC electrical conductivity, DM dry matter, VS volatile solids, TN total N, TAN total ammoniacal N

presumably as a result of the different storage temperature regimes. There was an exponential relationship between slurry temperature and CH₄ emissions across the two storage periods, which was similar for stores without (Fig. 2a) and with a straw crust (Fig. 2b), although emissions from stores with a crust were much more variable. The values derived for ln(A) with and without added straw were 70.5 and 83.0, respectively, whereas apparent E_A were 21.5 and 25.3 kJ mol⁻¹.

No N₂O emissions were observed during winter, whereas in the summer experiment significant emissions developed, but only from stores with a straw crust (Fig. 3). Emissions of N₂O from both stores without precipitation, -P+S, and with precipitation, +P+S, increased following an extended lag phase, although temporal dynamics were very different. In -P+S, the emission of N₂O stabilized around

1 g N₂O m⁻² day⁻¹, whereas in +P+S the N₂O emissions peaked after 3 weeks, followed by a sharp decline in response to decreasing temperatures and rainfall (Fig. 1).

Also shown in Fig. 3 are theoretical water balances for -P+S and +P+S treatments. With permanent sheltering to intercept precipitation, a water deficit of -200 mm during storage was calculated, whereas the water balance dropped more slowly in +P and, following heavy rainfall in early August, returned to zero, i.e., saturation. Registrations at the end of the storage experiment suggested a water loss closer to 100 mm in stores with a permanent cover, i.e., the theoretical water balance was probably overestimated and should be taken mainly as a proxy for crust aeration status. With both -P and +P treatments, the peak in N₂O emissions occurred when the theoretical water balance was -50 to -100 mm, and the dramatic

Table 2 Cumulated fluxes of CH₄, N₂O and NH₃, as well as total GHG emissions expressed as CO₂ equivalents, in the winter (45 days) and summer experiment (58 days)

	Winter				Summer			
	CH ₄ g m ⁻³	N ₂ O g m ⁻²	NH ₃ g m ⁻²	GHG kg CO ₂ eq m ⁻³	CH ₄ g m ⁻³	N ₂ O g m ⁻²	NH ₃ g m ⁻²	GHG kg CO ₂ eq m ⁻³
– Precip. + straw	20.4	ND	19.8b	0.4	2,520	39.7a	20.0b	72.4
+ Precip. + straw	23.7		8.0b	0.7	2,223	20.6b	18.0b	60.5
– Precip. – straw	28.7		39.9a	0.7	2,760	0.1c	180.2a	69.7
+ Precip. – straw	13.5		22.0ab	0.9	2,737	–0.3c	114.7a	74.1

Pig slurry was stored with or without sheltering to intercept precipitation, and with or without straw amendment ($n = 2$). Significant treatment effects ($P < 0.05$) are indicated by different letters within a column

drop in N₂O emissions from $-C + S$ coincided with a re-wetting of the crust. Cumulated N₂O emissions during storage are shown in Table 2.

Ammonia emissions were reduced by the straw crust, especially during summer storage. For the treatment with precipitation and without straw amendment, $+P-S$, 75 % of the loss in TAN during summer storage (Table 1) could be accounted for by the observed NH₃ loss. However, as mentioned above, the TN loss from this treatment was higher than TAN loss, suggesting that there were N losses not accounted for by the NH₃ emissions.

Total GHG balances, as represented by CH₄ and N₂O, and indirect N₂O emissions derived from NH₃, were calculated assuming GWP_{100 year} values for CH₄

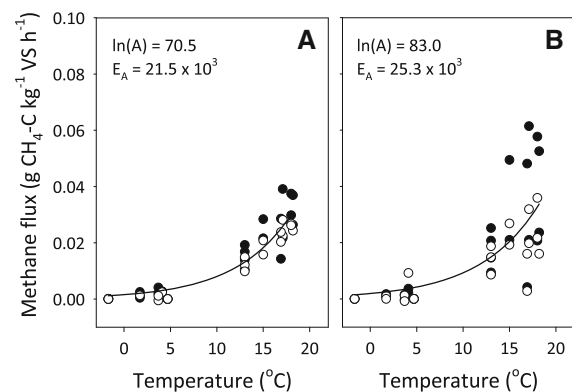


Fig. 2 Relationships between CH₄ flux and pig slurry storage temperature during winter and summer storage conditions without (a) or with a surface crust (b) were modelled with an Arrhenius relationship. Black and white symbols represent stores without and with precipitation, respectively. Inserted are the values derived for the Arrhenius constant, $\ln(A)$, and apparent activation energy, E_A

and N₂O of 25 and 298 (Forster et al. 2007), and indirect N₂O emissions corresponding to 1 % of NH₃ emissions. The balance was always dominated by

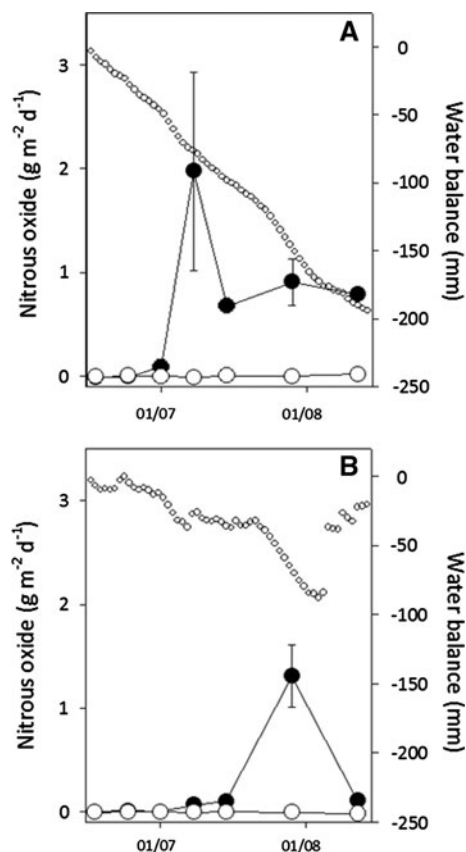


Fig. 3 Nitrous oxide emissions during the summer experiment with storage of pig slurry without (a) or with precipitation (b) in combination with a straw crust (black) or no straw crust (white). Also shown are water balances for stores without and with precipitation, calculated as described by Sommer et al. (2000). For emission data mean \pm standard errors are shown

CH₄, which accounted for 80 % or more of GHG emissions (data not shown). During winter and summer storage periods, GHG emissions were 0.01–0.02 and 1.1–1.3 kg CO₂ eq m⁻³ day⁻¹.

Emission of odorants

Total reduced sulphur, which is dominated by H₂S (Gay et al. 2003), showed a maximum within 2 weeks of storage, possibly reflecting sulphate reduction or S mineralization from slurry organic matter (Fig. 4, top panel). Evidently, a straw crust reduced these emissions.

For skatole, the time course and concentration range was largely the same irrespective of storage conditions, i.e., there was little retention of this compound in the straw crust (Fig. 4, centre panel). In most stores a peak in skatole was observed at the second sampling, suggesting that the compound was produced during slurry organic matter decomposition.

p-Cresol exhibited a clear effect of Straw addition, i.e., a straw crust effectively reduced emissions in both $-P+S$ and $+P+S$ (Fig. 4, bottom panel). In most cases, a peak in *p*-cresol was observed at the second sampling in $-S$ treatments, but in one replicate of $-P-S$ this peak was apparently delayed.

Discussion

Emissions from livestock manure are difficult to quantify under practical storage conditions (Hensen et al. 2006; Sneath et al. 2006), and comparative studies are nearly impossible to conduct because of unique features with respect to feeding, management, and site-specific conditions complicating measurements. Pilot-scale storage facilities offer a possibility for side-by-side comparison of contrasting storage conditions. In the present study, pig slurry was stored summer and winter with or without admixing of straw and interception of precipitation to establish a wide range of storage conditions. Storage with a permanent cover and active ventilation was used to simulate open storage while avoiding precipitation, not as an example of practical storage conditions.

Emission of odorants

Many sulphur-containing volatile organic compounds rank high with respect to malodour (O'Neill and Phillips 1992), but in a storage experiment with 24 pig slurry materials, H₂S explained 68 % of the total variability in odour emissions (Blanes-Vidal et al. 2009). Similarly, a recent study of emissions from a finishing pig production facility found that H₂S and

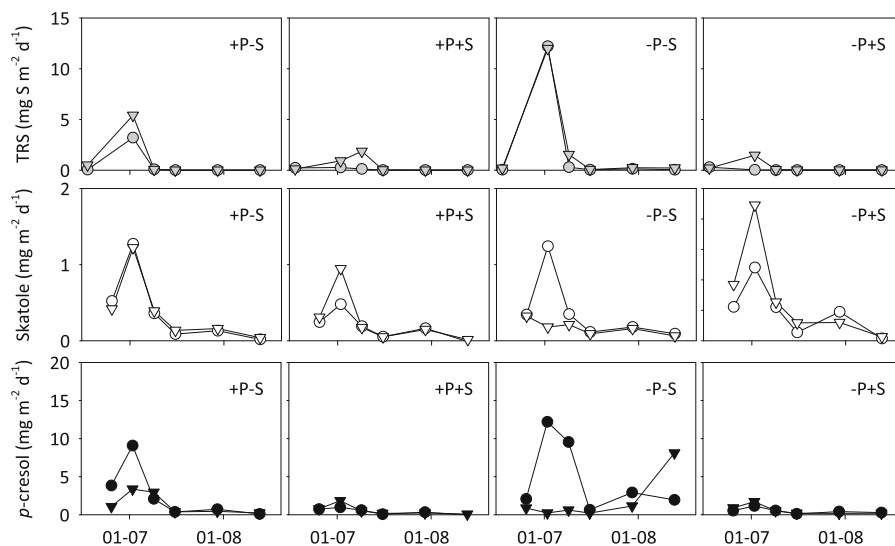


Fig. 4 The three panels show emissions of TRS (top), skatole (middle) and *p*-cresol (bottom) during the summer storage experiment investigating four sets of storage conditions (with or without interception of precipitation (*P*), and with or

straw amendment (*S*). Due to different temporal dynamics of odorant emissions in some treatments, data from each replicate store is presented rather than averages

Table 3 A compilation of apparent activation energies (kJ mol^{-1}) observed in contrasting environments

Environment	E_A	References
Pig slurry	22–25	This study
Cattle slurry	80–230	Sommer et al. (2000)
Cattle slurry	234	Khan et al. (1997)
Digested slurry	133–283	Sommer et al. (2000)
Psychrophilic digester	64	Safley and Westerman (1990)
Cellulose-degrading cultures	120–122	Chin et al. (1999)
Peat materials	123–271	Dunfield et al. (1993)

methanethiol (CH_3SH) accounted for a significant part of the odour, although also *p*-cresol and trimethylamine were important (Hansen et al. 2012). TRS, including both organic and inorganic sulphur-compounds, thus appears to be a useful indicator of odour from pig slurry. Emissions of TRS were transient, and were clearly mitigated by straw addition. In the last part of the storage period, emissions of TRS dropped to 0 irrespective of storage conditions, probably because oxygen penetration at the slurry-air interface enabled sulphide oxidation (Millero et al. 1987) and sustained aerobic microbial degradation of organic sulphur compounds at the slurry-air interface.

Concentrations of skatole were considerably lower than those of *p*-cresol. The transient increase in emissions of both skatole and *p*-cresol from fresh pig slurry was also observed by Eriksen et al. (2010), and by Wu et al. (1999) monitoring skatole in untreated pig slurry. Both *p*-cresol and skatole can be degraded under aerobic or anaerobic conditions (Bossert and Young 1986; Yin and Gu 2006), but a potential for retention of *p*-cresol apparently developed more rapidly than that for skatole retention, indicating that biodegradation was involved.

GHG emissions

Storage of pig slurry resulted in total GHG emissions of up to $1.3 \text{ kg CO}_2 \text{ eq m}^{-3} \text{ day}^{-1}$ during summer storage, whereas GHG emissions during winter storage were negligible. Clemens et al. (2006) stored untreated and digested cattle slurry with different cover strategies during summer and winter and found similar seasonal effects, but a maximum emission of $0.65 \text{ kg CO}_2 \text{ eq m}^{-3} \text{ day}^{-1}$. In their study, total GHG emissions were also dominated by CH_4 emissions during summer storage.

Methanogenesis in livestock slurry is highly sensitive to temperature (Husted 1994; Sommer

et al. 2007). In Table 3, apparent E_A values are compiled for methanogenesis in manure and other environments, including the results from the present study. Apparent E_A values from this study were low, corresponding to a moderate response to temperature, also when compared to other results for slurry materials. The proportion of readily degradable VS in pig slurry is high (Møller et al. 2004), and the most likely explanation for the moderate temperature response is therefore that degradable VS in the pig slurry was depleted at the higher temperatures, i.e., during the summer storage experiment. There was no evidence for an effect of a straw crust on CH_4 emissions from the stored pig slurry, in contrast to the study of Sommer et al. (2000). Possible reasons are discussed in the next section.

Ammonia emissions were $2.0\text{--}3.1 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$ without straw addition (Table 2), and ten-fold lower with a straw-enforced crust during summer storage. Other pilot-scale storage experiments have reported NH_3 emissions from uncovered cattle slurry of 1.6 (Clemens et al. 2006) and $2 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$ (VanderZaag et al. 2009). Sommer (1997), using a micrometeorological mass balance method, observed NH_3 emissions from practical-scale storage tanks with digested slurry (pH 7.9–8.1) of up to $30 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$ (average $11 \text{ g NH}_3 \text{ m}^{-2} \text{ day}^{-1}$). Further, he found significant effects of incoming solar irradiance and temperature, but not wind speed, on NH_3 emissions. It implies that the coverage of stores during measurement of NH_3 emission, as was practiced in this study, could lead to underestimation of true fluxes during summer storage by intercepting solar irradiation. As a consequence, NH_3 losses measured in treatment +*P*–*S* could have been lower than NH_3 losses between measurements, possibly explaining the TN loss in this treatment (Table 1) not accounted for by NH_3 emission.

As expected from previous studies, a potential for N_2O emissions developed only in the presence of a crust. The highest N_2O emissions observed in the present study corresponded to *c.* $80 \text{ mg m}^{-2} \text{ h}^{-1}$, which was higher than maximum emissions of $55 \text{ mg N}_2\text{O m}^{-2} \text{ h}^{-1}$ observed by Sommer et al. (2000) and *c.* $30 \text{ mg N}_2\text{O m}^{-2} \text{ h}^{-1}$ reported by VanderZaag et al. (2009). Straw was actively mixed with the slurry prior to storage, in accordance with local regulations, and therefore oxygen demand and water content of the developing crust was initially high. Sommer et al. (2000) found a significant relationship between N_2O emissions during summer storage of cattle slurry and the water balance, as calculated from a theoretical balance between precipitation and potential evaporation. Nitrous oxide emissions in this earlier study peaked at -60 mm , which is consistent with the results of the present study (Fig. 2). As mentioned, the calculated water balance does not represent the true water loss from the store, but still is a useful proxy for temporal dynamics in crust wetness during storage. Saturation of the crust due to rainfall in the $+P+S$ treatment coincided with an elimination of N_2O emissions, indicating that gas exchange is a key factor in the regulation of microbial activity in surface crusts and hence emissions during storage.

Implications for N_2O and CH_4 emission factors

In the latest revision of the IPCC methodology (IPCC 2006), an N_2O emission factor of 0.005 (uncertainty range: 0.0025–0.01) was proposed for liquid manure storage with an organic crust, although few measurement data have been published. The N_2O emissions recorded in the present study from untreated pig slurry with a straw crust during 58 days of storage represented 0.0006–0.0012 of total N in $+P+S$ and $-P+S$, respectively. Assuming this emission range is representative for the summer season (180 days) and no emissions occur during the remaining part of the year, in accordance with Fig. 2 and previous studies (Sommer et al. 2000; VanderZaag et al. 2009), then these numbers would correspond to annual N_2O emission factors of 0.002–0.004, which is within the uncertainty range of the IPCC emission factor. However, as indicated by Fig. 2, N_2O emissions depend on the water balance of the crust as well as storage temperature and, accordingly, is subject to inter-annual and regional differences. If a relationship with crust

wetness is confirmed in future studies, then modelling of N_2O emissions based on local climatic conditions should be explored.

Sommer et al. (2000) found that CH_4 emissions from cattle slurry during summer storage were reduced by, on average, 38 % in the presence of floating crust materials. In a subsequent study, Clemens et al. (2006) stored digested cattle slurry with or without a crust during summer and winter storage conditions, but did not find any effect on CH_4 emissions (although a reduction of 15–30 % occurred when stores were covered by a wooden lid). In the present study, simulating open storage conditions by continuous ventilation of stores amended with a cover, no effect of a straw crust on CH_4 emissions was observed. It would thus appear that the proposed 40 % reduction of CH_4 emissions in the presence of a crust on slurry stores (IPCC 2006) has been premature, and that the relationship between storage conditions and CH_4 emissions should be better documented before effects of a crust on CH_4 emissions are assumed in GHG inventories.

Can these apparent disagreements between observations be resolved? Incubation experiments have shown that an increase in CH_4 availability stimulates microbial methane oxidation in surface crust materials (Petersen and Ambus 2006; Duan et al. 2013), with apparent half-saturation constants, K_{app} , that correspond to gas phase concentrations of CH_4 at least 3 orders of magnitude above atmospheric. Sommer et al. (2000) observed a reduction in CH_4 emissions with crust materials while using the stores as static enclosures, and Clemens et al. (2006) when applying a wooden lid during slurry storage. In both cases, CH_4 concentrations were able to build up in the air above the crust. It is thus conceivable that elevated gas phase concentrations of CH_4 are required for a significant stimulation of methanotrophic activity. Supply of CH_4 from the air above the slurry could be important if a large proportion of CH_4 is released to the atmosphere by ebullition rather than diffusive flux.

Conclusions

This study quantified gaseous emissions from pig slurry under a wide range of storage conditions, extending previous studies on cattle slurry storage. The overall GHG balance was similar in all four

experimental treatments, and was dominated by CH₄ emissions during summer storage. Methane emissions were not reduced in the presence of a crust, as hypothesized, possibly because accumulation of CH₄ in the air is required to stimulate methane oxidation. Peak emissions of N₂O coincided with a negative water balance of –50 to –100 mm, and dropped to zero as a result of rewetting after rainfall, probably as a result of a shift towards anaerobic conditions in the crust. A better understanding of the effects of storage environment on emissions of N₂O and CH₄ is needed for more reliable emission estimates, and for identification of effective mitigation measures.

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References

- Ambus P, Petersen SO (2005) Oxidation of ¹³C-labeled methane in surface crusts of pig- and cattle slurry. *Isot Environ Health Stud* 41:125–133
- Blanes-Vidal V, Hansen MN, Adamsen APS, Feilberg A, Petersen SO, Jensen BB (2009) Characterization of odor released during handling of swine slurry: Part I. Relationship between odorants and perceived odor concentrations. *Atmos Environ* 43:2997–3005
- Bossert ID, Young LY (1986) Anaerobic oxidation of *p*-cresol by a denitrifying bacterium. *Appl Environ Microbiol* 52:1117–1122
- Chin K-J, Lukow T, Stubner S, Conrad R (1999) Structure and function of the methanogenic archaeal community in stable cellulose-degrading enrichment cultures at two different temperatures (15 and 30°C). *FEMS Microbiol Ecol* 30:313–326
- Clemens J, Trimborn M, Weiland P, Amon B (2006) Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. *Agric Ecosyst Environ* 112:171–177
- Duan Y-F, Elsgaard L, Petersen SO (2013) Inhibition of methane oxidation in slurry surface crust by inorganic nitrogen. *J Environ Qual* 42 (in press)
- Dunfield P, Knowles R, Dumont R, Moore TR (1993) Methane production and consumption in temperate and subarctic peat soils: response to temperature and pH. *Soil Biol Biochem* 25:321–326
- Eriksen J, Adamsen APS, Nørgaard JV, Poulsen HD, Jensen BB, Petersen SO (2010) Emissions of sulphur-containing odorants, ammonia and methane from pig slurry: effects of dietary methionine and benzoic acid. *J Environ Qual* 39:1097–1107
- Feilberg A, Adamsen APS, Lindholm S, Lyngbye M, Schäfer A (2010) Evaluation of biological air filters for livestock ventilation air by membrane inlet mass spectrometry. *J Environ Qual* 39:1085–1096
- Feilberg A, Nyord T, Hansen MN, Lindholm S (2011) Chemical evaluation of odor reduction by soil injection of animal manure. *J Environ Qual* 40:1674–1682
- Forster P, Ramaswamy V, Artaxo P, Bernsten T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, Van Dorland R (2007) Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) *Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*. Cambridge University Press, Cambridge/New York
- Gay SW, Schmidt DR, Clanton CJ, Janni KA, Jacobson LD, Weisberg S (2003) Odor, total reduce sulfur, and ammonia emissions from animal housing facilities and manure storage units in Minnesota. *Appl Eng Agric* 19:347–360
- Hansen MJ, Adamsen APS, Pedersen P, Feilberg A (2012) Prediction of odor from pig production based on chemical odorants. *J Environ Qual* 41:436–443
- Hansen A, Groot TT, van den Bulk WCM, Vermeulen AT, Olesen JE, Schelde K (2006) Dairy farm CH₄ and N₂O emissions, from one square metre to the full farm scale. *Agric Ecosyst Environ* 112:146–152
- Husted S (1994) Seasonal variation in methane emission from stored slurry and solid manures. *J Environ Qual* 23:585–592
- IPCC (2006) *Guidelines for National Greenhouse Gas Inventories. Agriculture, forestry and other land use, vol 4. Intergovernmental Panel on Climate Change, IGES, Hayama*
- Keeney DR, Nelson DW (1982) Nitrogen—inorganic forms. In: Page AL et al (eds) *Methods of soil analysis. Part 2. Agronomy monographs 9, 2nd edn. American Society of Agronomy and Soil Science Society of America, Madison*, pp 643–693
- Khan RZ, Müller C, Sommer SG (1997) Micrometeorological mass balance technique for measuring CH₄ emission from stored cattle slurry. *Biol Fertil Soils* 24:442–444
- Millero FJ, Hubinger S, Fernandez M, Garnett S (1987) Oxidation of H₂S in seawater as a function of temperature, pH, and ionic strength. *Environ Sci Technol* 21:439–443
- Møller HB, Sommer SG, Ahring BK (2004) Methane productivity of manure, straw and solid fractions of manure. *Biomass Bioenergy* 26:485–495
- Mutegi JK, Munkholm LJ, Petersen BM, Hansen EM, Petersen SO (2010) Nitrous oxide emissions and controls as influenced by tillage and crop residue management strategy. *Soil Biol Biochem* 42:1701–1711
- O'Neill DH, Phillips VR (1992) A review of the control of odour nuisance from livestock buildings: Part 3. Properties of the odorous substances which have been identified in livestock wastes or in the air around them. *J Agric Eng Res* 53:23–50
- Petersen SO, Ambus P (2006) Methane oxidation in pig and cattle slurry storages, and effects of surface crust moisture and methane availability. *Nutr Cycl Agroecosyst* 74:1–11
- Petersen SO, Amon B, Gattinger A (2005) Methane oxidation in slurry storage surface crusts. *J Environ Qual* 34:455–461

- Petersen SO, Skov M, Dröscher P, Adamsen APS (2009) Pilot scale facility to determine gaseous emissions from livestock slurry during storage. *J Environ Qual* 38:1560–1568
- Safley LM, Westerman PW (1990) Psychrophilic anaerobic digestion of animal manure: proposed design methodology. *Biol Wastes* 34:133–148
- Schiffman SS (1998) Livestock odors: implications for human health and well-being. *J Anim Sci* 76:1343–1355
- Smith P, Martino D, Cai Z, Gwary D, Janzen H, Kumar P, McCarl B, Ogle S, O'Mara F, Rice C, Scholes B, Sirotenko O (2007) Agriculture. In: Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA (eds) *Climate change 2007: mitigation. Contribution of working group III to the fourth assessment report of the intergovernmental panel on climate change*. Cambridge University Press, Cambridge/New York
- Sneath RW, Beline F, Hilhorst MA, Peu P (2006) Monitoring GHG from manure stores on organic and conventional dairy farms. *Agric Ecosyst Environ* 112:122–128
- Sommer SG (1997) Ammonia volatilization from farm tanks containing anaerobically digested animal slurry. *Atmos Environ* 31:863–868
- Sommer SG, Petersen SO, Søgaard HT (2000) Greenhouse gas emission from stored livestock slurry. *J Environ Qual* 29:744–750
- Sommer SG, Petersen SO, Møller HB (2004) Algorithms for calculating methane and nitrous oxide emissions from manure management. *Nutr Cycl Agroecosyst* 69:143–154
- Sommer SG, Zhang GQ, Bannink A, Chadwick D, Misselbrook T, Harrison R, Hutchings NJ, Menzi H, Monteny GJ, Ni JQ, Oenema O, Webb J (2006) Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores. *Adv Agron* 89:261–335
- Sommer SG, Petersen SO, Sørensen P, Poulsen HD, Møller HB (2007) Methane and carbon dioxide emissions and nitrogen turnover during liquid manure storage. *Nutr Cycl Agroecosyst* 78:27–36
- Steinfeld H, Gerber P, Wassenaar T, Castel V, Rosales M, de Haan C (2006) *Livestock's long shadow—environmental issues and options*. Food and Agricultural Organization, Rome, Italy. <http://www.fao.org/docrep/010/a0701e/a0701e00.HTM> (verified 18 Nov 2011)
- VanderZaag AC, Gordon RJ, Jamieson RC, Burton DL, Stratton GW (2009) Gas emissions from straw covered liquid dairy manure during summer storage and autumn agitation. *Trans ASABE* 52:599–608
- Wu JJ, Park S, Hengemuehle SM, Yokoyama MT, Person HL, Gerrish JB, Masten SJ (1999) The use of ozone to reduce the concentration of malodorous metabolites in swine manure slurry. *J Agric Eng Res* 72:317–327
- Yin B, Gu J-D (2006) Aerobic degradation of 3-methylindole by *Pseudomonas aeruginosa* Gs isolated from mangrove sediment. *Hum Ecol Risk Assess* 12:248–258