Relationships between Dairy Slurry Total Solids, Gas Emissions, and Surface Crusts

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Livestock slurry storages are sources of methane (CH₄), nitrous oxide (N₂O), and ammonia (NH₃) emissions. Total solids (TS) content is an indicator of substrate availability for CH₄ and N₂O production and NH₃ emissions and is related to crust formation, which can affect these gas emissions. The effect of TS on these emissions from pilot-scale slurry storages was quantified from 20 May through 16 Nov. 2010 in Nova Scotia, Canada. Emissions from six dairy slurries with TS ranging from 0.3 to 9.5% were continuously measured using flow-through steady-state chambers. Methane emissions modeled using the USEPA methodology were compared with measured data focusing on emissions when empty storages were filled, and retention times were >30 d with undegraded volatile solids (VS) remaining in the system considered available for CH₄ production (VS carry-over). Surface crusts formed on all the slurries. Only the slurries with TS of 3.2 and 5.8% were covered completely for ~3 mo. Nitrous oxide contributed <5% of total greenhouse gas emissions for all TS levels. Ammonia and CH₄ emissions increased linearly with TS despite variable crusting, suggesting substrate availability for gas production was more important than crust formation in regulating emissions over long-term storage. Modeled CH₄ emissions were substantially higher than measured data in the first month, and accounting for this could improve overall model performance. Carried-over VS were a CH₄ source in months 2 through 6. The results of this study suggest that substrate availability regulates emissions over long-term storage and that modifying the USEPA model to better describe carbon cycling is warranted.

Manure management is an important source of greenhouse gases (GHG) (Smith et al., 2007b) and ammonia (NH₃) (McGinn et al., 2008). In addition to the environmental impacts associated with GHG and NH₃ emissions, a loss of nitrogen (N) during storage reduces the value of manure as a fertility amendment. Livestock manure is often handled as a liquid or slurry to improve the ease of handling (Chastain et al., 2001b). The anaerobic environment of slurry storage is, however, conducive to methane (CH₄) production (Kebreab et al., 2006). Mineralization of organic N can be an important source of ammoniacal N when slurry is stored for extended periods (Sommer et al., 2006). Although nitrous oxide (N₂O) is not typically produced in slurries, it may be produced if surface crusts form (Berg et al., 2006; Petersen and Miller, 2006). The concerns related to N₂O production in crusts highlight the need for multi-gas monitoring to identify potential NH₃–N₂O and CH₄–N₂O emission tradeoffs when evaluating possible beneficial management practices.

The slurry total solids (TS) content influences GHG and NH₃ emissions from storages. The TS is an indicator of the volatile solids (VS) content and thus of the quantity of degradable organic matter that may lead to CH₄ production. More concentrated slurries will also tend to be higher in N and thus will be a greater source of NH₃. Therefore, TS can be considered a proxy for the VS and N content (i.e., slurry concentration). Volatile solids content is the main variable driving CH₄ production in anaerobic systems (Dong et al., 2006; Sommer et al., 2004). Storage time and temperature also regulate the magnitude of CH₄ production within the slurry (Hashimoto et al., 1981). It is possible that crust formation, which appears to be more prevalent for high-TS slurries, may mitigate emissions (Misselbrook et al., 2005; Smith et al., 2007a; VanderZaag et al., 2009, 2010). Crusts impart additional resistance to mass transfer (Olesen and Sommer, 1993), and there is evidence that CH₄ oxidation may occur within the crusts due to the presence of methanotrophic bacteria (Ambus and Petersen, 2005; Petersen et al., 2005). Due to the complex and poorly understood processes contributing to crust formation (Misselbrook et al., 2005), particularly as they pertain to the capacity for crusts to

Abbreviations: BLS, bivariate least squares; GHG, greenhouse gas; MCF, methane conversion factor; MDP, management and design practice; TAN, total ammoniacal nitrogen; TS, total solids; VS, volatile solids.
act as N₂O sources or CH₄ sinks over long-term storage, nonlinear responses in total emissions to TS might be expected.

National GHG inventory methodologies account for these factors when predicting emissions from manure management systems (Dong et al., 2006; USEPA, 2011). Inventory models were developed because of the complexity and cost associated with physically measuring GHG emissions from farms. The inputs for these models are readily available farm data, including animal type, herd size, feed rations, air temperature, and the type of manure management (Dong et al., 2006; Mangino et al., 2001; USEPA, 2011). The USEPA model for CH₄ emissions from slurry storages is based on the work of Mangino et al. (2001), who developed equations for anaerobic lagoons. The same model is applied for manure storages, assuming that the retention time is <1 mo and that there is no VS carry-over (USEPA, 2011). When calculating CH₄ emissions using the model, VS carry-over refers to the practice of adding the undegraded VS remaining in the storage to the newly loaded VS to determine the VS available for CH₄ production. Assuming retention times of <1 mo and no VS carry-over may be inappropriate for storage systems when manure is stored for longer than 1 mo, especially in cooler climates (VanderZaag et al., 2011). Lory et al. (2010) criticized the USEPA CH₄ model for anaerobic lagoons, arguing that (i) the effect of climate has been accounted for in anaerobic lagoon design (i.e., lagoons must be larger in colder climates) and therefore temperature corrections should not be applied in the methane conversion factor (MCF) calculation and (ii) that the MCF should be based on degraded VS rather than the VS loaded. However, because slurry storages are not designed for manure management and design practices (MDP) factor, low temperature cut-off, and whether undegraded VS should be carried over, produce drastically different CH₄ emission predictions (Park et al., 2006; VanderZaag et al., 2011). Another issue highlighted in VanderZaag et al. (2011) is that the USEPA model greatly overestimates emissions in the month when slurry is first added to an empty storage. Verifying modeled emissions is further complicated due to uncertainties with the equations that predict VS produced by the livestock. It would be useful to compare measured and modeled CH₄ emissions from systems where VS loading is controlled and thus uncertainty induced by the VS-produced algorithms and the MDP factor is eliminated.

In Canada, slurry is often stored for at least 4 to 6 mo because the land cannot support continuous application or because winter conditions do not permit spreading, often resulting in a warm and a cold storage season each year. This research focused on the warm-season storage (May–Nov.). The objectives of this study were (i) to quantify the relationships between TS and crust formation and their combined effects on CH₄, N₂O, and NH₃ emissions from dairy slurry during undisturbed storage and (ii) to compare measured CH₄ data with emissions predicted by the USEPA model.

Materials and Methods

Site Description

The study was conducted from 20 May through 16 Nov. 2010 using a gas emissions monitoring system at the Bio-Environmental Engineering Center in Truro, Nova Scotia, Canada (45°45’ N, 62°50’ W). Six pilot-scale manure storages were batch filled with ~10.4 m³ of dairy slurry, each with a different initial TS level. Each rectangular storage tank was 1.75 m wide, 3.90 m in length, and 1.80 m deep. The depth of the slurry in each tank was ~1.6 m. The raw slurry was obtained from the Nova Scotia Agricultural College Experimental Farm and had a TS content of ~9.5% and was a mix of manure ranging in ages of 2 to 21 d. The farm has 40 milking cows housed in a tie-stall barn. The cows were pastured for 19 h d⁻¹ and were fed 5 kg d⁻¹ of feed ration when in the barn. The main ingredients of the feed mix were corn (31%), wheat (12%), barley (15%), soyameal (12%), soyhulls (18%), and top soy (2%). Raw slurry was added to each tank and then diluted with well water to give slurries with initial TS levels of approximately 0.3, 1.3, 3.2, 5.8, and 8.2%. One tank was filled with raw slurry (~9.5% TS) and not diluted. Dilution water was added to the tanks using a fire hose, and the slurries were mixed as well as possible. This approach was used to prevent dilution water from resting on top of the slurry. The slurries were stored undisturbed from 20 May through 16 November.

Flux Density Quantification

Gas flux densities were quantified using previously described flow-through steady-state chambers (VanderZaag et al., 2008, 2009, 2010). Each storage tank was permanently fitted with a chamber that was covered with 6-mm greenhouse plastic. Air was continuously drawn through each chamber by a fan situated in exhaust ventilus at a nominal airflow rate of 0.5 m³ s⁻¹. This airflow rate exchanged the chamber air volume 1 or 2 times per minute. Flux densities, \( F (\mu g m^{-2} s^{-1}) \), were calculated according to:

\[
F = \frac{(C_{out} - C_{in})}{A_i} \times Q
\]

where \( C_{out} \) and \( C_{in} \) are the outlet and inlet target gas concentrations (\( \mu g m^{-3} \)), respectively; \( A_i \) is the surface area of the storage tank (m²); and \( Q \) is the airflow rate (m³ s⁻¹). Outlet concentrations were measured in each of the exhaust ventilus. The \( C_o \) was the average of two ambient measurements made 0.3 m upstream of the chamber inlets of chambers 2 and 5. The ambient measurements were made at a height of 1.7 m. It was assumed that the air outside of the chambers was well mixed and that this average concentration was representative of the six chamber inlets. To test this assumption, the running standard deviation (rank = 5) was computed for the differences in ambient concentrations as in VanderZaag et al. (2010). If a difference was more than twice the running standard deviation, the data were rejected. Methane and N₂O flux densities were measured continuously. Ammonia flux densities were measured three times per week.

Methane and Nitrous Oxide Concentrations

Sample air was continuously drawn from all sample intakes through separate 25-m lengths of polyethylene tubing (6.4 mm o.d.; 3.2 mm i.d.) by a vacuum pump (Busch Vacuum Pumps and
Ammonia concentrations were measured using a gas washing method similar to VanderZaag et al. (2008). During each 24-h deployment, unfiltered sample air was drawn from each site through separate lengths of 25-m polyethylene tubing. There were four air pumps (Thomas Pumps and Compressors), each of which drew sample air from two of the intakes through the system. There was an airflow meter (Actaris Metering Systems) for each site that measured the air volume sampled during the deployment. The airflow rate was set by critical orifices (O’Keefe Controls) at 1.5 L min⁻¹. Air from each site was diffused into 125 mL of 0.005 mol L⁻¹ phosphoric acid using dispersion tubes with fritted cylindrical ends (Ace Glass). The trapping solution volume was standardized to 125 mL after the deployment. The NH₃-N concentration in the trapping solution was quantified using the standard phenate method, 4500-NH₃-F (Clesceri et al., 1998). Gaseous NH₃ concentrations, C_{NH₃,air} (μg m⁻³), were calculated according to Eq. [2]:

\[ C_{NH₃,air} = \frac{C_{NH₃,aq} \times V'_1}{V'_{air}} \]  

where \( C_{NH₃,aq} \) is the aqueous NH₃ concentration (μg L⁻¹), \( V'_1 \) is the normalized volume of the trapping solution (L), and \( V'_{air} \) is the volume of sample air that passed through the trap during the deployment (m³). Ammonia is a challenging gas to measure because it can adsorb to the walls of the sampling system (Shah et al., 2006). Steps were taken to minimize the biases introduced by the sampling system. Before use, all tubing was conditioned by sampling the headspace of ammonium chloride solution (NH₄Cl; pH 12) for 48 h. Deployment times of 24 h were used to allow a tubing-NH₄⁺ equilibrium to establish, thus minimizing the effect of the tubing on the mean concentration over the deployment. It is possible that NH₄⁺ adsorption varied on a day-to-day basis; however, each experimental unit was fitted with the same chamber and tubing (used to sample exhaust air) for the duration of the experimental period. Thus, if there was greater NH₄⁺ adsorption on 1 d, on later desorption it would be sampled by the acid trap associated with the same experimental unit.

In addition to these operational considerations, recovery tests were performed to ensure similarity in sampling system biases for ambient and exhaust intakes. There were solutions of NH₄Cl at 2 and 10 mg N L⁻¹ for simulating ambient and exhaust air, respectively. Sodium hydroxide (10 mol L⁻¹) was added to the solutions to raise the pH to 12, and the sampling system was deployed to sample the headspace for 24 h. Three intakes measured each concentration level. The aqueous NH₄⁺ concentration and volume of the solutions was measured before and after the deployment, and a mass balance was performed to calculate the emitted NH₃. Aqueous NH₄⁺ was determined according to the standard phenate method. This procedure was performed three times, with fresh emitting solutions being used for each replicate. The recoveries were 95 (SE, 4.1%) and 103 (SE, 6.2%) for the tubing sampling the headspace of the high and low NH₄Cl solutions, respectively. A t test confirmed that the mean recoveries were not significantly different (\( p = 0.3477 \)).

With these precautions in mind, it was decided that potential errors introduced by the sampling system were systematic and that the comparison of NH₃ emissions from the different slurries was not affected by sampling system biases. Due to the challenges associated with quantifying short-term variability in NH₃ flux densities, this paper focuses on long-term emission trends and total integrated emissions.

Environmental Conditions

Air and manure temperatures were measured using copper-constantan thermocouples manufactured in house using wire obtained from Omega Engineering Inc. The air temperature in each chamber was a spatial average of three measurement junctions suspended along the length of the chamber. Each measurement junction was shielded from radiation and was 50 cm above the manure surface. In each tank, the manure temperature was a spatial average of three measurement junctions, each located 10 cm from the bottom of the tank. Net radiation was measured in two of the chambers using net radiometers (model Q-7.1, Radiation and Energy Balance Systems Inc.). One-minute averages were recorded for all environmental variables by a datalogger (CR3000, Campbell Scientific Canada Corp.) set at a scan rate of 15 s.

The chamber covers excluded rainfall from the tanks. Rainfall inside the chambers was simulated using lawn sprinklers attached to a flow meter. Each week, the equivalent depth of water applied to each tank was the 30-yr weekly normal precipitation for Truro, Nova Scotia. Water was applied to each tank on 2 d per week. Simulated rainfall was ceased on 15 October.

Crust thickness was measured weekly using a rod fitted with a wing at the bottom. The winged-end of the rod was inserted until completely penetrating the crust. The rod was then turned 90° and pulled up until the wings butted against the underside of the crust. The distance from the crust surface to the end of the rod was measured and subtracted from the length of the rod-end to the wings to give the crust depth. At each sampling, the crust...
depth was measured at five locations in each tank. Crust thickness measurements disturbed <0.1% of the tank surface area. The fraction of the surface covered by the crust is another important metric; however, it is difficult to accurately quantify and was therefore not done. It was possible to gauge when the surface of slurries were completely encrusted, and this presence or absence was recorded at each crust sampling.

**Slurry Analysis**

Manure samples were collected at the start and end of the storage period. At the end of the storage period, samples were collected at 5 cm below the crust–slurry interface and 20 cm from the bottom of the tank using a sampler with a spring-loaded lid. The TS and VS were determined according to standard American Public Health Association (APHA) methods 2540 B (total solids dried at 103–105°C) and 2450 E (fixed and volatile solids ignited at 550°C), respectively (Clesceri et al., 1998). Total ammoniacal N (TAN) was measured by distillation (APHA 4500-NH, B) and titration (APHA 4500-NH, D). Total N and total C were quantified by combustion using a CNS analyzer (model 1000, LECO Corp.). Results for the above analytes were measured using an electrode (APHA 4500-H+).

All GHG budget, global warming potentials of 25 and 298 were used for CH4 and N2O, respectively (Forster et al., 2007). Cumulative emissions on the last day of storage represented the cumulative emissions for each gas were determined by integrating daily flux densities over time. The climate factor is used to calculate the amount of VSA that is degraded based on the van’t Hoff–Arrhenius relationship and was computed using monthly average chamber air temperatures (Mangino et al., 2001). Emissions were also modeled using monthly average slurry temperatures. The climate factor is used to calculate the amount of VSA that is degraded based on the van’t Hoff–Arrhenius relationship and was computed using monthly average chamber air temperatures (Mangino et al., 2001). Without carry-over there would have been no source of available VS for CH4 production in months 2 through 6, and the model would only predict CH4 emissions in the first month of storage. The model also assumes that B0 is constant over time, which for this case could exacerbate errors during months 2 through 6 because no fresh manure was loaded into the tanks. Uncertainties in the modeled emissions were estimated using measurement error propagation theory based on errors in VS and temperature measurements. The response of modeled CH4 to measured emissions was analyzed using BLS regression.

**Methane Emission Modeling**

Methane emissions were modeled by adapting the USEPA inventory methodology for manure management (USEPA, 2011). Adaptation of the model was necessary because the storage component of the manure management system was being examined in isolation in this present study. Monthly CH4 emissions were calculated according to Eq. [3]:

\[ E_M = VSA \times f \times B_0 \times 0.662 \]  

where \( E_M \) is the monthly CH4 emissions (kg), VS A is the VS available for degradation (kg), \( f \) is the climate factor (dimensionless), \( B_0 \) is the ultimate CH4 yield (m^3 CH4 kg^{-1} VS), and 0.662 is the density of CH4 (kg m^{-3}). The climate factor is used to calculate the amount of VSA that is degraded based on the van’t Hoff–Arrhenius relationship and was computed using monthly average chamber air temperatures (Mangino et al., 2001). Without carry-over there would have been no source of available VS for CH4 production in months 2 through 6, and the model would only predict CH4 emissions in the first month of storage. The model also assumes that B0 is constant over time, which for this case could exacerbate errors during months 2 through 6 because no fresh manure was loaded into the tanks. Uncertainties in the modeled emissions were estimated using measurement error propagation theory based on errors in VS and temperature measurements. The response of modeled CH4 to measured emissions was analyzed using BLS regression.

**Results and Discussion**

**Slurry and Climate Data**

Slurry TS ranged from 0.3 to 9.5%, representing a range of conditions from concentrated wastewater to thick slurries. A gradient in VS content was also achieved where levels were consistently ~83% of the TS. The TAN levels were similar for the 0.3 through 5.8% TS slurries (Table 1). It is possible that NH3 stripping occurred during the dilution process. The two most concentrated slurries did not lose as much TAN because there was little to no mixing during dilution for these storages. All slurries stratified during the storage period with respect to TS and VS, with solids accumulating at the bottom of the storage (Table 1) due to settling.
Monthly air temperatures were similar for all chambers (SD ≈ 0.2°C) and increased during the first 60 d and then decreased through the end of undisturbed storage (Fig. 1a). There was a decreasing trend in net radiation from 90 d through the end of undisturbed storage as the season changed from the summer through the autumn (Fig. 1b). Manure temperatures increased until stabilizing between 90 and 120 d, after which they decreased through the autumn (Fig. 1a).

Gas Emissions

For each slurry, there was a period where cumulative NH₃ emissions increased linearly (Fig. 2a). Flux densities were higher from the TS > 8% slurries, and the duration of the linear increase in cumulative emissions was longer at ~130 d. Cumulative NH₃ emissions from the slurries with TS of 3.2 and 5.8% increased linearly until ~90 d. After 90 d, emissions from these slurries were low and were a minor contributor to the total NH₃ budget over the undisturbed storage period. The capping of emissions at 90 d for the 3.2 and 5.8% TS slurries was due to the presence of natural surface crusts. Lower fluxes during the entire storage period for the 0.3 and 1.3% TS slurries were possibly due to the lower N content (Table 1).

The highest N₂O flux densities from all the slurries occurred between ~40 and 120 d (Fig. 2b). Total emissions were highest for the slurries with TS > 5%. There was a lag of ~40 and ~50 d before the onset of increased N₂O emissions for the TS > 8% and TS = 5.8% slurries, respectively. The lower flux densities after 120 d (Fig. 2b) coincided with decreasing air temperatures and net radiation (Fig. 1a and b), which presumably slowed rates of microbial N₂O production. The higher N₂O emissions from the slurries with TS > 5% may have been due to the higher N content and the fact that these slurries developed crusts during the first week of storage. The nature of the crust may have also contributed to the higher N₂O emissions. The crusts on the TS > 8% slurries were visibly drier than the others, which favors N₂O production (Petersen and Miller, 2006).

There was a lag of ~50 to 70 d before the onset of increased CH₄ fluxes (Fig. 2c). A period of increased CH₄ fluxes was observed between 50 and 70 d for all the slurries, with a second peak in emissions occurring from 90 to 120 d for the TS > 8% slurries. The lag before increased CH₄ fluxes may have been associated with the time required for methanogen populations to establish and for organic matter to be cycled to substrates suitable for methanogenesis.

Crust and Gas Emission Dynamics

The formation of surface crusts was observed on all storages and was influenced by TS content (Fig. 3). Thin crusts began to form within 7 d for the slurries with TS > 5%. For each slurry, there was a period where cumulative NH₃ emissions increased linearly (Fig. 2a). Flux densities were higher from the TS > 8% slurries, and the duration of the linear increase in cumulative emissions was longer at ~130 d. Cumulative NH₃ emissions from the slurries with TS of 3.2 and 5.8% increased linearly until ~90 d. After 90 d, emissions from these slurries were low and were a minor contributor to the total NH₃ budget over the undisturbed storage period. The capping of emissions at 90 d for the 3.2 and 5.8% TS slurries was due to the presence of natural surface crusts. Lower fluxes during the entire storage period for the 0.3 and 1.3% TS slurries were possibly due to the lower N content (Table 1).

The formation of surface crusts was observed on all storages and was influenced by TS content (Fig. 3). Thin crusts began to form within 7 d for the slurries with TS > 5%. In contrast, the mean crust thickness for slurries with TS < 6% increased greatly with the onset of increased CH₄ emissions (Fig. 2c) when bubbles were visible at the surface. The crusts that formed on these slurries varied in thickness and in the fraction of the surface that they covered. The high variability in mean crust thickness for the storages with TS < 4% may have been due to suspended particles being unevenly distributed throughout the slurries. Observations suggested that there were different mechanisms by which the crusts formed. It is possible that crusts on the TS > 8% slurries formed due to evaporation of water from the surface, causing particles near the surface to coalesce, creating a mat (Misselbrook et al., 2005). These crusts were dark in color, relatively dry, hard, and never completely covered the surfaces, as fissures in the crusts on the TS > 8% slurries were visible throughout the undisturbed storage period. Crust formation on the TS < 2% slurries did not occur until the onset of high CH₄ emissions, suggesting that particles were being floated to the surface by gas
Misselbrook et al. (2005) proposed the mechanism whereby crusts are formed by the flotation of neutrally buoyant particles to the surface where they coalesce; this mechanism was subsequently observed by VanderZaag et al. (2009). Crust formation on the slurries with TS of 3.2 and 5.8% appeared to be a combination of the evaporation and particle flotation processes. It is proposed that the crusts on these slurries observed during the first 60 d formed primarily due to the evaporation mechanism, whereas the rapid thickening was caused by particle flotation. The lack of relationship between crust formation and \( \text{CH}_4 \) emissions for the TS > 8% slurries may have been due to particle flotation being inhibited because of higher drag forces associated with the higher viscosity.

The crusts acted as a barrier to \( \text{NH}_3 \) emissions similar to VanderZaag et al. (2009). When a crust is present, the slurry surface is decoupled from the atmosphere, and diffusion through the crust limits mass transport (Olesen and Sommer, 1993; Sommer et al., 1993). The fractional area covered, and not mean thickness, was the more important crust metric responsible for regulating \( \text{NH}_3 \) emissions (Fig. 3c,d vs. Fig. 3a,b,e,f), which supports the finding that thin layers can mitigate \( \text{NH}_3 \) emissions (Misselbrook et al., 2005). After complete encrusting of the surface at ~85 d, only 8 and 11% of total \( \text{NH}_3 \) emissions were measured from the 5.8 and 3.2% TS slurries, respectively. Even though the mean crust thickness was 10 to 20 cm on the 0.3 and 1.3% TS storages after 70 d, they were only completely covered for a short period. Therefore, the capping of emissions observed for the 3.2 and 5.8% TS storages did not occur. The decreased \( \text{NH}_3 \) emissions from the TS < 2% slurries after 90 d (Fig. 2a) were likely due to limited TAN production in the slurry, given that the surface was not completely encrusted (Fig. 3c,d). For the TS > 8% slurries, capping of \( \text{NH}_3 \) emissions did not occur and was due to the crusts not covering 100% of the surfaces because of cracks in the crust. Only the slurries with TS of 3.2 and 5.8% were completely encrusted for an appreciable period (Fig. 3c,d), which is critical if the crust is to mitigate emissions. During the time when the surface was open to atmospheric exchange, the \( N \) content of the slurry was the important factor driving \( \text{NH}_3 \) emissions (Fig. 2a; Table 1).

It appears as though ebullition contributed to augmented \( \text{NH}_3 \) emissions from the TS > 8% slurries after 90 d; however, the exact mechanism is not clear. Presumably, the lack of complete crusting allowed for higher diffusive fluxes that may have been increased by the higher turbulence in the liquid induced by ebullition, as has been observed in sediments (Chanton and Whiting, 1995). It is also possible that \( \text{NH}_3 \) was present in the bubbles and transported directly to the atmosphere. This is, however, speculative because the composition of the bubbles was not quantified.

Maximum \( \text{CH}_4 \) flux densities from all the storages occurred between 50 and 70 d of storage (Fig. 4), similar to VanderZaag et al. (2010) and Massé et al. (2008). The timing and order of the peaks could not be predicted by TS and may have been associated with natural variability. A second peak in flux densities between 90 and 120 d was observed for slurries with TS > 8%. The duration of the second peak was longer than the first, but maximum flux densities were lower. It is possible that the first and second peaks were associated with easily and slowly degradable organic.

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**Fig. 1.** Average monthly (a) slurry and chamber air temperatures and (b) net radiation (\( Q^* \)) during the undisturbed storage period from 20 May through 16 Nov. 2010. Air temperature data are the mean of measurements from the six chambers. Net radiation data are the mean of measurements made in chambers 3 and 5. Error bars represent 1 SD. Manure temperature data are missing from the last month of storage.

**Fig. 2.** Cumulative (a) ammonia (\( \text{NH}_3 \)), (b) nitrous oxide (\( \text{N}_2\text{O} \)), and methane (\( \text{CH}_4 \)) emissions during 180 d of storage from 20 May through 16 Nov. 2010.
The slurries with TS > 8% were never completely encrusted, and large quantities of bubbles escaping through fissures in the crusts were visible between 90 and 150 d of storage. A second large peak in CH$_4$ emissions was not observed for the other slurries. The greater incidence of crusting and lower VS availability were possibly responsible for the lack of a second peak in CH$_4$ fluxes for TS < 6% slurries.

Although it is evident that the crusts played a role in regulating the magnitude of CH$_4$ flux densities, the exact processes involved remain unclear. Ebuliition is an important mode of gas transfer during periods of high CH$_4$ production (DeSutter and Ham, 2005). If a crust was present at the surface and slurry CH$_4$ transport was due mainly to ebuliition, gas would be forced into the crust to a greater extent than would occur with diffusion from the slurry. In this scenario, the crust would provide additional resistance and slow mass transport to the atmosphere. There is also evidence that the crust may act as a sink for CH$_4$ due to the presence of methanotrophic bacteria (Ambus and Petersen, 2005; Petersen et al., 2005). Thus, when crusts were present, it was possible that CH$_4$ oxidation in the crust decreased net emissions to the atmosphere. From the results presented here, it is not possible to define the role of the crusts in regulating emissions because reduced fluxes could have been due to decreased CH$_4$ production in the slurry, slowed transport, or oxidation in the crust. There is a need to characterize the diversity and activity of the methanotrophic communities in crusts concurrently with flux measurements before conclusions can be drawn relative to the precise role of the crust in mitigating CH$_4$ emissions.

**Effect of Total Solids on Total Emissions**

Total NH$_3$ emissions increased linearly as a function of TS (Fig. 5a) despite a nonlinear increase in initial slurry TAN levels (Table 1). This suggests that mineralization was a source of TAN during storage (Sommer et al., 2006). The non-zero intercept of the regression equation indicates that complete solids removal will not eliminate NH$_3$ emissions from the slurry. Ammonia emissions were a much greater loss of slurry N than N$_2$O emissions were (Fig. 2 and 5).

A sigmoid response in N$_2$O emissions to TS was observed (Fig. 5b). This may have been due to the influence of TS on crust formation and the higher N content of the more concentrated slurries. It is possible the crusts on the storages having TS > 8% were more suitable for N$_2$O production because they were drier than the crusts that formed on the surface of the other slurries, thus providing a more well defined aerobic–anaerobic interface, which is conducive to nitrification–denitrification (Petersen and Miller, 2006; Sommer et al., 2000). Concerns related to increased N$_2$O production within crusts (Petersen and Miller, 2006; Sommer et al., 2000) were not an issue in this study given the low contribution of N$_2$O to the overall GHG budget (Fig. 2b,c and 5b,c,d). When GHGs were converted to CO$_2$–eq, N$_2$O contributed <5% of the overall budget regardless of TS level.

Total CH$_4$ emissions increased linearly as a function of TS (Fig. 5c). Because the storage time was the same and ambient temperatures were similar for all the slurries, availability of degradable C was the main factor that regulated total CH$_4$ emissions. The presence of volatile fatty acids and other soluble organic matter that can eventually be converted to CH$_4$ may account for the non-zero intercept of the regression equation. The lack of complete crusting on the TS < 2% and TS > 8% slurries (Fig. 3a,b,e,f) while the storages with TS of 3.2 and 5.8% were completely encrusted and the linear relationship between total CH$_4$ emissions and TS indicate that the supply of VS was a more important regulator of emissions than were the crusts. When scaling by VS loaded, emissions decreased exponentially as a function of TS (Fig. 6). This suggests that the supply of degradable C was being exhausted in the storages with TS < 2%. For the TS > 2% slurries, which had higher VS content, time became limiting. Because the TS < 2% slurries were closer to the loading rates experienced in anaerobic lagoons (e.g., 0.048 kg m$^{-2}$ d$^{-1}$), VS conversion to CH$_4$ was perhaps more efficient. Although CH$_4$ emissions scaled by VS decrease in response to TS, it is important to remember that the total mass of CH$_4$ emitted from the TS < 2% tanks was lower than for the TS > 2% slurries.

Total GHG emissions increased linearly with TS (Fig. 5d). The lack of sigmoid character was due to N$_2$O being a minor contributor (<5%) to the overall GHG budget as CO$_2$–eq.
Implications for Management

Reducing the TS content of dairy slurry (Fig. 5) decreased emissions of all gases. A ~50% relative reduction in slurry TS yielded ~50 and ~60% reductions in GHG and NH$_3$ emissions, respectively. Amon et al. (2006) found that a 35% relative reduction in TS reduced emissions of CH$_4$ and NH$_3$ by 54 and 4%, respectively, when comparing raw slurry with the liquid fraction after separation. The low NH$_3$ reductions by Amon et al. (2006) were likely due to the initial total N and TAN contents of the raw slurry and liquid fraction, differing by −1.0 and 5.7%, respectively. Ni et al. (2010) observed a 29% reduction in NH$_3$ emissions for relative reductions in TS and TAN of 44 and 43%, respectively (achieved by dilution). The lower NH$_3$ emission reduction observed by Ni et al. (2010) compared with this study may have been due to the storage period being only 30 d.

This experiment compared emissions from slurries with different TS levels but with each having equivalent volumes. If dilution were used within a farm-scale system to reduce TS levels, the volume of slurry would be increased, having several potential implications. The mitigation potential for NH$_3$ may be reduced due to larger required storage surface areas (Ni et al., 2010). The benefits relative to CH$_4$ may also be limited because VS are not removed from the system. Managing manure as a solid or using solid–liquid separation processes would therefore be preferable. There may, however, be issues with NH$_3$ volatilization during separation (Burton, 2007; Chastain et al., 2001a) and NH$_3$ and GHG emissions while storing or composting the solid fraction (Amon et al., 2006; Chadwick, 2005; Hansen et al., 2006). There does appear to be the potential for GHG mitigation when considering combined emissions from both the liquid fraction and solid manure arising from solid–liquid separation (Amon et al., 2006).

Methane Emission Modeling

Time series of monthly modeled and measured CH$_4$ emissions are provided in Fig. 7. For the TS > 1% slurries, measured emissions were 85 to 96% and 54 to 74% lower than emissions modeled using air temperatures during months 1 and 2, respectively. From 4 to 6 mo of storage, the model using air temperature data always underpredicted CH$_4$ emissions regardless of TS content. The model performed better when emissions were integrated over
the entire undisturbed storage period. The overpredictions in months 1 and 2 were balanced by underpredictions in months 4 through 6. This was due to the model predicting high rates of VS degradation during months 1 and 2, leaving low quantities of VS available for CH₄ production during subsequent months because the tanks were batch loaded. Total modeled CH₄ emissions were related linearly to total measured emissions with a slope of 2.1 (SE, 0.24) and an intercept of −54.3 (SE, 13.04).

It has been noted that using air temperatures will likely result in higher CH₄ emission estimates, particularly in the warmer months (Mangino et al., 2001; Park et al., 2006). When emissions were calculated using slurry temperatures, there were still substantial deviations between modeled and measured data (Fig. 7). Temporal trends in monthly data were similar to the air temperature case for TS > 1%, with the highest monthly emissions predicted during months 1 and 2. For TS > 1%, when manure temperatures were used, measured data were lower than monthly modeled emissions by 77 to 94% and 17 to 60% during months 1 and 2, respectively. Total CH₄ emissions modeled using air temperatures were higher on average by 6.3% (SE, 0.47%) compared with when manure temperatures were used. The use of slurry temperature rather than air temperature is clearly more appropriate from a theoretical perspective; however, the improvements in this study were relatively minor. It is important to recognize that air temperature data are more readily available than are slurry temperature data; thus, improving the accuracy of the model for use with air temperatures is a valuable exercise. Furthermore, because in this study total modeled emissions and temporal trends in monthly modeled emissions were similar for the air and slurry temperature cases, other factors must be considered to improve model performance.

Modifications to model calculations to reflect the lag in emissions when filling an empty storage and the carry-over of VS could improve overall emission estimates. The model as applied does not adequately simulate CH₄ emissions when slurry is added to a clean storage. This issue was noted when the model was applied to a farm-scale system and overpredicted emissions in the month after the storage was emptied (VanderZaag et al., 2011); this finding was presumably due to the time required for methanogen and C-cycling bacterial populations to establish. The present research clearly shows a lag period in CH₄ emissions when filling a cleaned-out storage and that the USEPA model is not able to simulate these dynamics (Fig. 7). For example, for slurries with TS > 2% in month 1, measured emissions were on average only 5.6% (SE, 0.75%) and 7.3% (SE, 1.0%) of emissions modeled using air and manure temperatures, respectively. This lag was most likely associated with slurry microbiology and C cycling because uncertainties in predicting the VS produced by the herd and the MDP factor were eliminated from the model calculations. It is possible that applying a scaling factor during the first month to reflect that VS are cycled to substrates suitable for methanogenesis but are not lost to the atmosphere could improve CH₄ emission predictions in the month after emptying the storage. Further research during the autumn is necessary to determine if model overpredictions are as high when emptying and filling during colder conditions.

In the present work, carried-over VS represent the only source of substrates for methanogenesis in months 2 through 6. Measured CH₄ fluxes throughout the entire storage period demonstrated that carried-over VS are a source of CH₄ over...
2 to 6 mo of storage. Whether this organic matter would be degraded if fresh VS with a readily degradable fraction were added is unclear. The results do suggest that the carry-over of undegraded VS needs to be accounted for. The results of Park et al. (2006) and VanderZaag et al. (2011) from operational farms indicated that full VS carry-over causes a significant overprediction of emissions. Overpredictions due to full VS carry-over may be due to storages being overloaded with organic matter and thus not producing CH₄ to their full potential (Park et al., 2006).

Another possible issue is that VS is a bulk quantity used to represent degradable organic matter. In the USEPA model, all constituents of the VS are treated equally and are assumed to degrade in accordance with the van’t Hoff Arrhenius temperature relation. In reality, the degradation of VS constituents is more likely to be described by a distribution of decay constants. When VS are loaded into a slurry storage facility, the more labile fractions are degraded faster, and thus the VS retained in the system are less degradable and are likely to yield less CH₄ per unit mass than fresh manure. This cannot be quantified using the data from the present study because the systems were batch fed, and thus preferential microbial degradation of newly loaded labile VS fractions compared with retained VS cannot be described. Sommer et al. (2004) proposed partitioning the VS into readily and nondegradable fractions in their algorithms for predicting CH₄ emissions from manure slurries; however, they did not address carry-over and how the degradation kinetics of retained VS may change as storage times increase and as fresh VS is added.

Conclusions

Total CH₄, N₂O, and NH₃ emissions from dairy slurry increased with TS despite varying levels of crust formation. Nitrous oxide was a minor contributor to the overall GHG budget. The linear response of CH₄ and NH₃ emissions to TS despite variable levels of crusting indicates that the supply of substrates for production reactions was more important than crusts in regulating emissions over the long-term (i.e., 6-mo) storage period. When crusts are present on the slurry surface, they can reduce NH₃ fluxes, with the greatest emission reductions occurring when there is complete surface coverage. The opportunity for emission mitigation by crusts over long-term storage is limited by the time that is required for the crust to form (~3 mo). When there is incomplete crust coverage, the mitigation potential is reduced. Despite large discrepancies between monthly CH₄ emissions modeled using the USEPA inventory method and measured data, there was a linear relation when CH₄ emissions were integrated over the entire storage period. Scaling predicted emissions in the first month after loading an empty storage may improve CH₄ emission estimates. Carried-over VS was a source of CH₄ throughout the storage period, suggesting that this should be accounted for when performing emission inventories on farms where manure is stored for longer than 1 mo. Further research is needed to identify the best approach for handling VS carry-over. The results of this study also call into question the use of lower MCFs to account for the presence of crusts.

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References


