



Response Curves for Ammonia and Methane Emissions From Stored Liquid Manure Receiving Low Rates of Sulfuric Acid

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Addition of sulfuric acid (H₂SO₄) to liquid dairy manure (slurry) reduces methane (CH₄), nitrous oxide (N₂O), and ammonia (NH₃) emissions. There is interest in understanding how gaseous emissions respond to decreasing rates of acidification, to determine economically optimum application rates. Acidification rates were tested ranging from 0 to 2 g sulfuric acid (H₂SO₄) L⁻¹ slurry in six meso-scale outdoor storage tanks, each filled with 10.6 m³ slurry and stored for 114 d. Results showed that the rate of acidification for maximum inhibition of CH₄ and NH₃ emissions varied markedly, whereas N₂O reductions were modest. Reductions of CH₄ increased with acid rate from 0 to 1.2 g L⁻¹, with no additional response beyond > 1.2 g L⁻¹. In contrast to CH₄, inhibitions of NH₃ showed a linear response across all rates, although reductions were ≤30%. Thus, higher acidification rates would be required to achieve greater NH₃ emission reductions. Our findings indicate that achieving >85% NH₃ emissions reductions would require 4 × more acid than achieving >85% CH₄ reductions. Decisions on optimum H₂SO₄ rates will depend on the need to mitigate CH₄ emissions (the primary greenhouse gas emitted from stored liquid manure) or reduce NH₃ emissions (which is regulated in some regions). These results will help develop guidelines related to the potential costs and benefits of reducing emissions through acidification.

Keywords: manure acidification, methane, ammonia, manure management, greenhouse gases

INTRODUCTION

Storage of liquid manure is a potential hotspot for methane (CH₄), nitrous oxide (N₂O), and ammonia (NH₃) emissions (Petersen, 2018). Current estimates suggest that 0.36 Gt CO₂eq y⁻¹ greenhouse gases (GHG) are emitted globally annually from manure storages (IPCC, 2014). Ammonia emissions have significant environmental implications and reduce the fertilizer value of the slurry, while methane and N₂O are potent greenhouse gases (Amann et al., 2013; IPCC, 2013). Methane is the predominant GHG emitted and has a warming potential of 34× that of CO₂ over 100 years. Nitrous oxide, on the other hand, has lower emittance, but is a potent GHG with 298× the warming potential of CO₂ over 100 years. Owing to their significant impacts on environmental

quality and climate change, CH₄, N₂O, and NH₃ emission reductions from these point sources has been greatly studied (Hörnig et al., 1999; Smith et al., 2007; Montes et al., 2013; Petersen, 2018).

Acidification of slurry is gaining attention as an emission mitigation practice due to its low cost and relative efficiency for reducing multiple gases (Kavanagh et al., 2019). Reducing slurry pH by adding sulfuric acid (H₂SO₄) to stored dairy slurries has led to a range of CH₄ and NH₃ reduction efficiencies (Habtewold et al., 2018; Sokolov et al., 2019b, 2020). Sommer et al. (2017) reported 62 and 68% reductions in NH₃ and CH₄ emissions, respectively, with 0.27 g H₂SO₄ L⁻¹ slurry (pH 5.2). Similarly, Petersen et al. (2012) reported reduction of 87% CH₄ and 95% NH₃ emissions, by reducing slurry pH from 7 to 4.5. Lastly, Misselbrook et al. (2016) reported up to 61 and 75% reductions in CH₄ and NH₃ emissions, respectively, for rates up to 6.9 g H₂SO₄ L⁻¹ slurry. Our previous research (Habtewold et al., 2018; Sokolov et al., 2019b, 2020) had 84 and 90% CH₄ reductions using 1.5–2.7 g L⁻¹ H₂SO₄ (pH ~6). Although H₂SO₄-based acidification of dairy slurry is the most tried-and-true measure in reducing CH₄ and NH₃ emissions during slurry storage, the sensitivity of these emissions to different rates of H₂SO₄ addition and the optimal rate for reduction of emissions have not been evaluated.

Simultaneous reductions of GHG and NH₃ emissions have significant environmental benefits, yet regulatory and policy considerations differ across countries. For instance, several European countries (e.g., Denmark) have established legislation for the reductions of GHGs and NH₃ emissions (Jacobsen, 2015) whereas other countries, including Canada, have only GHG reduction targets. Therefore, it is desirable to further determine the optimal application rate to reduce the cost and volumes of acid required, depending on which gas(es) are the target for mitigation. To address these issues and successfully adapt manure acidification to full-scale systems, dose-response evaluation of acidification rates and the resulting reductions in CH₄, N₂O, and NH₃ emissions, particularly on a larger scale, is desirable. Previous research has shown that reductions in CH₄ emissions have greater sensitivity to H₂SO₄ addition than NH₃ emissions (Habtewold et al., 2018; Sokolov et al., 2019b), and hence it may be possible to optimally reduce CH₄ emissions at a lower rate of acid than NH₃ emissions.

MATERIALS AND METHODS

Experimental Site and Manure Acidification

This research was conducted from May 25 through September 15, 2019 using a meso-scale facility located at the Dalhousie University's Bio-Environmental Engineering Centre in Truro, NS, Canada (45°45' N, 62°50' W). Six concrete rectangular outdoor slurry tanks (1 × w × h, 3.8 m × 1.73 m × 1.80 m), which were covered by flow-through steady-state chambers (**Figure 1**), were filled with dairy manure (10.6 m³ per tank). Details about the experimental site, storage tanks, and chambers were described by Wood et al. (2012). This experimental site has been used in the past to assess a range of dry matter content (Wood et al., 2012), manure types (Le Riche et al., 2017), residual manures

(Wood et al., 2014; Sokolov et al., 2019a), and surface covers (VanderZaag et al., 2009, 2010).

Manure was obtained from a manure storage from a local commercial dairy farm. To make sure the tanks received similar compositions of manure, each load of the fresh manure collected from the farm was equally distributed. The farm used sand bedding which can inflate the dry matter content of the manure. The fresh manure collected had a dry matter content of up to 23.5%. This was markedly higher than in previous research and caused a breakage of the pumping mechanism on the tankard used. The high dry matter was likely due to poor timing of manure collection with farm activities (tank emptying, manure addition, etc.). To avoid further issues and to simulate more typical liquid dairy manure storage conditions (i.e., dry matter content <10%) we diluted the manure using lake water prior to the start of monitoring. This may have changed the sand settling, although prior researched (Sokolov et al., 2019a) observed sand settling occurred rapidly, therefore it likely had a very minimal effect.

For acidification, we used different volumes of 95% H₂SO₄ solution (Bebington Industries, Dartmouth, NS, Canada) resulting in H₂SO₄ addition rates of 0, 0.4, 0.8, 1.2, 1.6, or 2.0 g L⁻¹. This experimental design was modified from Ngwabie et al. (2016). Instead of treatment replications this study focused on continuous sampling over a full season of monitoring at the meso-scale. Although the results cannot be directly applied to on-farm manure storages, the results will be important in comparison with previous meso-scale research and understanding the mechanism of H₂SO₄ reduction of GHG and ammonia production. In our previous studies, the addition of 1.6 or 2.7 g H₂SO₄ L⁻¹ slurry reduced CH₄ emissions by ≥85% but no significant difference was observed for the two rates (Habtewold et al., 2018; Sokolov et al., 2019b). Thus, our goal for this study was to test the effects of lower rates of H₂SO₄ addition (i.e., ≤2 g L⁻¹) on emissions, given that the resulting pH does not seem to be a determining factor in CH₄ reductions. The acid was pumped into the manure using a peristaltic pump with acid resistant tubing. The acid was simultaneously mixed into the manure for an even distribution. Gas sampling started immediately following acidification. Previous research (Sokolov et al., 2019b) observed that due to the large scale of the tanks, our mixing was not enough to fully homogenize the manure and pockets of more acidic manure were observed. Therefore, waiting ~2 weeks (June 10) prior to manure sampling allowed for the manure to fully homogenize.

Gas Measurements

During storage, air samples from the inlet (i.e., ambient air) and outlet of each tank's chamber were continuously collected through long polyethylene tubing connected to two tunable diode laser trace gas analyzers in an adjacent trailer (**Figure 1**). The gas analyzers measure the concentration of CH₄ and N₂O in gas subsamples every 30 s, while a CR5000 datalogger (Campbell Scientific Inc., Edmonton, AB, Canada) controls the air sampling system and records gas concentrations. Methane concentrations (μg m⁻³) were computed from the measured mixing ratios (i.e., relative abundance of gas components in the gas samples)



FIGURE 1 | The mesoscale study site indicating manure source, storage tanks, and slurry acidification.

using chamber air temperatures and atmospheric pressure (i.e., 101.3 kPa).

Gas fluxes ($\mu\text{g m}^{-2} \text{s}^{-1}$) were calculated based on Wood et al. (2012):

$$F = \frac{C_{\text{out}} - C_{\text{in}}}{SA} \times Q \quad (1)$$

where C_{out} and C_{in} are measured gas concentrations ($\mu\text{g m}^{-3}$) from the outlet and inlet gas samples, respectively; SA is the surface area of the storage tank (m^2); and Q is the airflow rate ($\text{m}^3 \text{s}^{-1}$).

Ammonia concentrations, measured periodically during the incubation (49 times during the 114 d of incubation), were measured with 24-h deployment intervals using gas washing technique as described by VanderZaag et al. (2010). Details about gas sampling and analysis for NH_3 concentrations are provided by Sokolov et al. (2019b). Ammonia concentrations ($\mu\text{g m}^{-3}$) were calculated as:

$$CNH_{3,\text{air}} = \frac{CNH_{3,\text{aq}} \times V_1}{V_{\text{air}}} \times Q \quad (2)$$

where $C_{\text{NH}_{3,\text{air}}}$ ($\mu\text{g m}^{-3}$) is the concentration of NH_3 -N in the air subsample, $C_{\text{NH}_{3,\text{aq}}}$ is the aqueous NH_3 concentration ($\mu\text{g m}^{-3}$), V_1 is the volume of the trapping solution (m^3), and V_{air} is the volume of sample air that passed through the trap during the deployment (m^3). The NH_3 flux was then calculated using (Equation 1).

The indirect N_2O emissions from volatilized NH_3 were calculated by using the default emission factor (i.e., 0.01) suggested for manure management systems (Dong et al., 2006). The total GHG emitted (100 y global warming potential) from each tank was calculated after converting CH_4 and N_2O to carbon dioxide equivalents ($\text{CO}_2\text{-eq}$) by multiplying emissions by 34 and 298, respectively (IPCC, 2013).

The methane conversion factor was calculated for each H_2SO_4 rate using the starting loss on ignition (LOI) (kg) and maximum potential CH_4 production ($B_0 = 0.24 \text{ m}^3 \text{ CH}_4 \text{ kg}^{-1} \text{ LOI}$) following the IPCC methods (Dong et al., 2006). Additionally,

cumulative CH_4 emissions for each rate were scaled by starting LOI, while N_2O and NH_3 -N emissions were scaled by starting total nitrogen (TN) and total ammoniacal nitrogen (TAN).

Analysis of Manure Properties

Manure samples were taken at the trial start (May 25, 2019), as well as before (June 10, 2019), during (August 19, 2019), and after (November 2, 2019) peak CH_4 fluxes. Samples were collected with a long sampling rod with a manually operated opening to avoid mixing between layers and samples were frozen until analysis. To reduce spatial variability in manure properties, a composite sample per tank was obtained after mixing samples from nine different locations (on coordinates of a grid) and depth profiles. Only one sample ($2 \times 1 \text{ L}$) was taken per tank in order to make scheduling easier and ensure timely alignment with CH_4 flux emissions. Several manure properties including pH using an electrode (American Public Health Association method 4500- H^+), dry matter (DM) and loss on ignition (LOI) (American Public Health Association method 2540 B), total carbon (TC), TN (combustion method AOAC 990.03-2002), ammonium-N (NH_3 -N) (American Public Health Association method 4500- NH_3 B), and total phosphorous (TP) contents were determined at the Nova Scotia Department of Agriculture's Laboratory Services (Harlow Institute, NS, Canada) using standard methods (Clesceri et al., 1998).

Data Analysis

Unlike CH_4 and N_2O , NH_3 emissions were measured periodically (46 measurements over 114 d). Therefore, interpolations were used to obtain a complete data set for the 114 d. Acidification-induced changes in manure characteristics and gaseous emissions were compared to the control (untreated) slurry. To assess how rates of acidification were numerically related to differences in manure characteristics (pH, LOI, and NH_4 -N) or reductions in emissions (CH_4 and NH_3), response-curves were plotted by applying a linear regression model. For changes in CH_4 and total GHG emissions, the low rate ($0\text{--}1.2 \text{ g L}^{-1}$) and high rate ($1.2\text{--}2.0 \text{ g L}^{-1}$) were analyzed separately. This was done to highlight the difference in response between

the low and high rates. Additionally, a higher rate from our previous research, 2.7 g L^{-1} , for the same site and manure source (Habtewold et al., 2018; Sokolov et al., 2019b) was added to the regression analyses to extrapolate the regression and test its fit in the models. This made the high rate $1.2\text{--}2.7 \text{ g L}^{-1}$, while the low rate stayed $0\text{--}1.2 \text{ g L}^{-1}$. Regression analyses were performed using the function “lm” in R version 3.6.3 [(R Core Team, 2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <https://www.R-project.org/>]. In addition to the coefficient of determination (i.e., R^2 ; explained/total variation of the model), residuals (i.e., differences between the observed and predicted reductions in CH_4 or NH_3 emissions) were assessed to the test whether the regression fits were good (Law and Jackson, 2017). When $P < 0.05$, we considered the changes in the manure characteristics, CH_4 , or NH_3 emissions have significant relations with changes in H_2SO_4 rates.

RESULTS

Slurry Characteristics Vary With Acidification Rate

The pH of dairy slurry used for this research was 8.2. At the start of the experiment, addition of 0.4 or 0.8 g L^{-1} had no significant effect ($P = 0.164$; **Figure 2**) on slurry pH while the higher rates (i.e., $\geq 1.2 \text{ g L}^{-1}$) reduced the slurry pH to 7.4. Although not significant, rates of H_2SO_4 addition and slurry pH had a negative relationship at all sampling periods throughout the trial (**Figure 2**).

There were no clear impacts of acidification on nutrient mineralization, as expressed by manure contents of DM, LOI, TN, TC, $\text{NH}_4\text{-N}$, and TP (**Table 1**). Differences between

treatments were minor over all sampling periods. However, there was a general trend in all tanks for DM, LOI, TN, and TC to decrease over time, especially early in the storage period (June 10–August 19, **Table 1**). This was expected as the early stage (i.e., lag phase) is typically characterized by rapid solids settling and higher rates of microbial hydrolysis and acidogenesis which supply substrates for more rapid gaseous production in the later stages.

With few exceptions, slurry pH generally increased with storage time, which is consistent with our previous research and other studies (**Table 1**; Petersen et al., 2012; Wang et al., 2014; Regueiro et al., 2016; Sommer et al., 2017; Habtewold et al., 2018; Kavanagh et al., 2019). Microbial utilization of accumulated volatile fatty acids has often been used to explain gradual increases in slurry pH, although the process may be affected by H_2SO_4 through lower pH and/or SO_4^{2-} toxicity.

Responses of Gaseous Emissions to H_2SO_4 Addition Methane

The CH_4 production followed a predictable trend, starting with a production lag (May 25–July 23), followed by a rapid increase peaking mid-summer (July 23–August 23), and ending with a slow decline till the end of the monitoring period (August 23–September 15). Unlike our previous research where daily CH_4 flux started to increase after 35 d of storage (Habtewold et al., 2018; Sokolov et al., 2019b), the current storage had longer lag phase (~ 60 d) before the daily flux started to increase (**Figure 3A**). Daily CH_4 emissions were highest ($52\text{--}68 \text{ g m}^{-2} \text{ d}^{-1}$) between 78 d and 99 d (**Figure 3A**). The total CH_4 production from the control was $2,688 \text{ g m}^{-2}$ and $1,680 \text{ g m}^{-3}$ during the 114-d storage period (**Figure 3B**; **Table 2**). This is

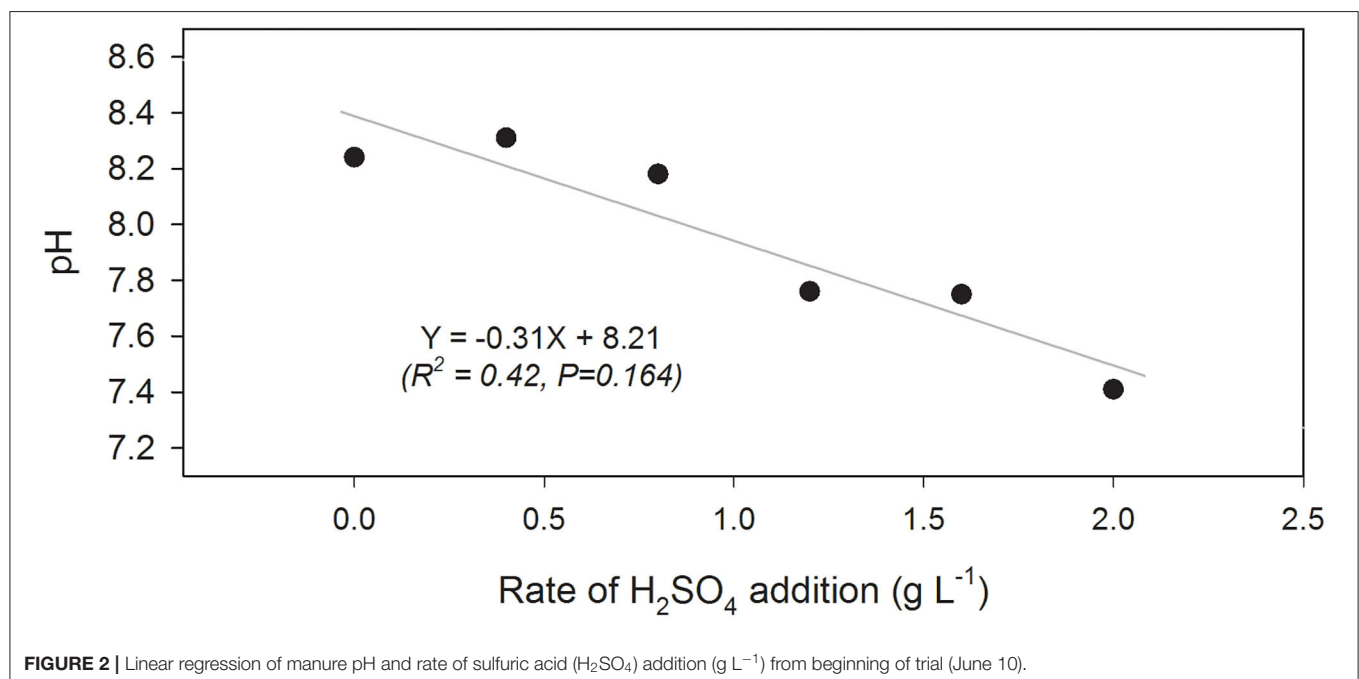


TABLE 1 | Dry matter (DM, %), pH, total nitrogen (TN, %), total carbon (TC, %), ammonia-N (NH₄-N, %), loss on ignition (LOI, %) of dairy slurries at the start of the trial (10 Jun), mid-trial (19 Aug), and end of the trial (02 Nov) in response to different rates of H₂SO₄ (g L⁻¹ slurry) addition.

		H ₂ SO ₄ (g L ⁻¹)					
		0.0	0.4	0.8	1.2	1.6	2.0
DM%	10-June-19	5.10	6.46	7.79	7.43	6.74	6.1
	19-August-19	2.52	2.40	2.68	2.34	2.33	2.48
	02-November-19	2.49	1.58	2.19	1.86	2.16	2.40
pH	10-June-19	8.24	8.31	8.18	7.76	7.75	7.41
	19-August-19	8.19	8.16	7.57	8.13	7.90	7.56
	02-November-19	8.55	8.35	7.58	7.64	8.12	7.97
TN (%)	10-June-19	0.15	0.17	0.20	0.21	0.18	0.17
	19-August-19	0.11	0.12	0.13	0.11	0.13	0.13
	02-November-19	0.11	0.08	0.10	0.09	0.10	0.12
TC (%)	10-June-19	1.00	1.30	1.64	1.66	1.50	1.33
	19-August-19	0.48	0.43	0.40	0.34	0.40	0.41
	02-November-19	0.49	0.26	0.36	0.25	0.33	0.41
NH ₄ -N (%)	10-June-19	0.07	0.06	0.08	0.08	0.07	0.06
	19-August-19	0.07	0.07	0.09	0.07	0.09	0.09
	02-November-19	0.06	0.05	0.07	0.06	0.07	0.08
LOI (%)	10-June-19	2.43	2.77	3.25	3.56	2.94	2.90
	19-August-19	1.47	1.40	1.51	1.39	1.24	1.35
	02-November-19	1.39	0.88	1.20	1.00	1.20	1.36

slightly lower than observed by Sokolov et al. (2019b) where the daily flux reached 76 g m⁻² d⁻¹, resulting in slightly lower (13%) total emissions. As the manure source and study site were the same in these two studies, the longer lag phase and lower peak emission are likely related to the lower average starting LOI in the current study as a result of the dilution (3.0 and 9.7%) and other environmental factors. Wood et al. (2012) reported lower total CH₄ emissions corresponding with increasing dilution. Additionally, air temperature was lower for more than 1 month in the current study compared to the previous trial (accessed from Environment and Climate Change Canada climate station, ID 8201380, Debert, NS, Canada, ~15 km from the research site). Likely both factors reduced the CH₄ production, therefore it is unclear the extent to which either caused this reduction.

Methane emissions decreased with acidification rate, although not with a simple linear trend. There was a marked difference in CH₄ reductions in high rates of H₂SO₄ (1.2–2.0 g L⁻¹) and low rates of H₂SO₄ (0.0–1.2 g L⁻¹) (Figure 3B). With the high rates of acid (≥1.2 g L⁻¹), the daily CH₄ emissions were consistently ≤5 g m⁻² d⁻¹ throughout the storage period, which resulted in 85–89% reduction in total CH₄ emissions (Figure 3B). This is in line with Sokolov et al. (2019b) where similar reductions were observed using 1.6 or 2.7 g L⁻¹ (Habtewold et al., 2018; Sokolov et al., 2019b). By taking the control slurry as a reference, the relationship between changes in CH₄, NH₃, and total GHG (in CO₂-eq) emissions and H₂SO₄ rates were analyzed using linear regression (Figures 4A–C). Rates of H₂SO₄ and changes in CH₄ emissions showed a strong linear relationship for lower rates of 0–1.2 g L⁻¹ ($R^2 = 0.95$; $P < 0.05$; Figure 4A). At higher rates the linear regression line became nearly flat, showing that the CH₄ emissions were not further reduced at rates of ≥1.2 g L⁻¹

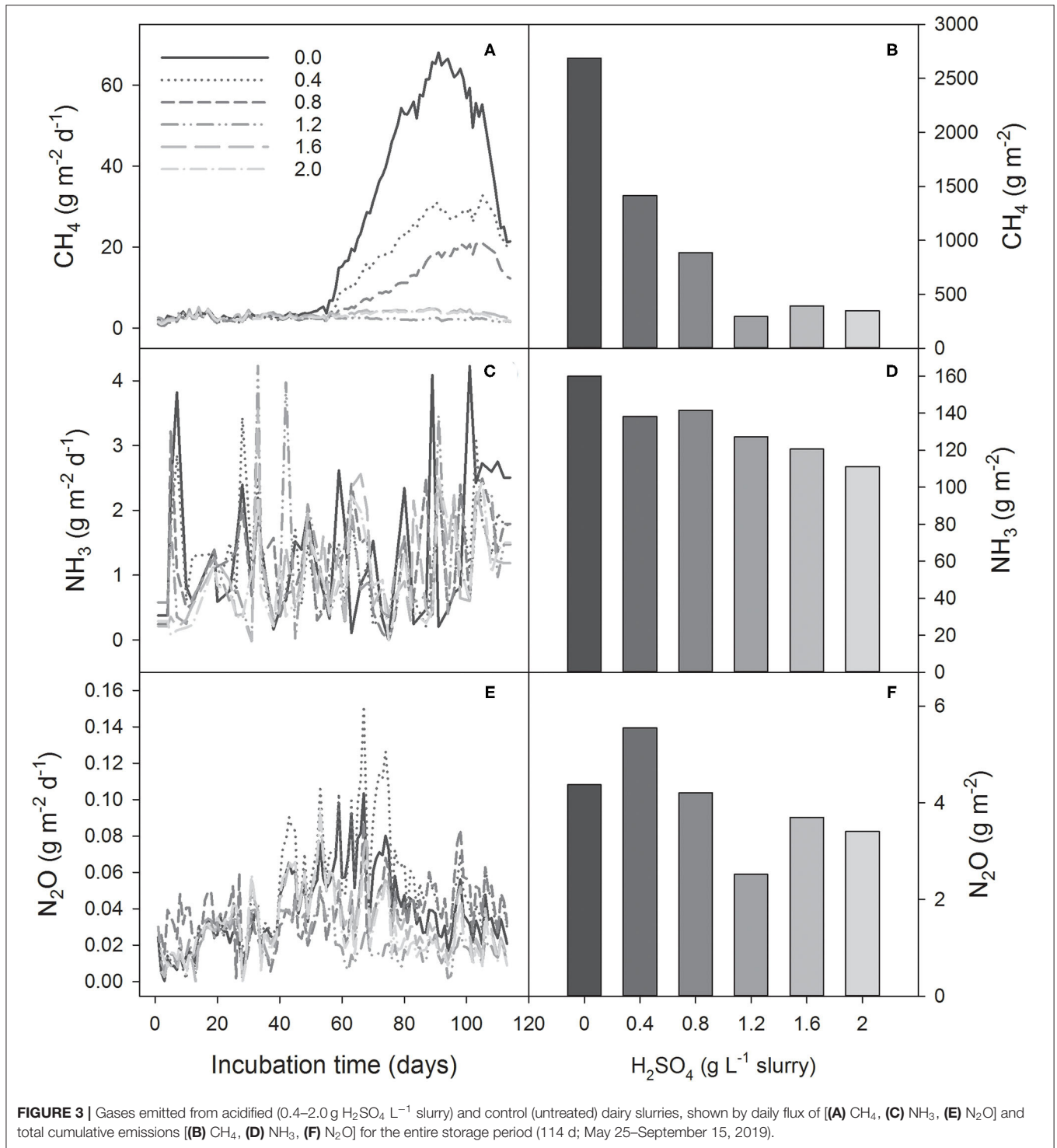
($R^2 = 0.09$; $P > 0.05$). This indicated that rates around 1.2 g L⁻¹ were critical for effective CH₄ emission reductions. Moreover, we observed a good fit of the response data for the higher rate in our previous study (Figure 4A).

Nitrous Oxide

The effect of H₂SO₄ on N₂O emissions was unclear. While daily N₂O emissions peaked between 40 and 80 d (Figure 3E), with the 0.4 g L⁻¹ rate having the highest daily emissions. Cumulative emissions had an unclear trend, with the lowest rate, 0.4 g L⁻¹, having the highest total emissions (5.55 g m⁻² and 3.47 g m⁻³) and the 1.2 g L⁻¹ rate the lowest (2.52 g m⁻² and 1.57 g m⁻³; Figure 3F, Table 2). Aside for the 0.4 g L⁻¹ rate, all others had rates had lower total emissions than the control, with an average reduction of 21%. Regardless of the treatments, cumulative N₂O emissions were low (<6 g m⁻²), representing <2% of the total CH₄ emitted on a CO₂-eq basis. This is in line with previous research by Sokolov et al. (2019a), who reported insignificant N₂O emissions from stored liquid manure. Given the low emissions, N₂O reductions are less important than CH₄ and NH₃. Therefore, it is more important result is that no increase in N₂O was observed.

Ammonia

Ammonia emissions had an unclear trend over the storage period for all treatments (Figure 3C). Sporadic peaks were observed throughout the study period, likely related to factors other than time and temperature. The control produced the most total NH₃ (160 g m⁻² and 100 g m⁻³) and had the highest daily average emissions (1.40 ± 0.94 g m⁻² d⁻¹; Table 2). Unlike CH₄



emissions, differences in daily NH₃ losses between treatments were small throughout the storage period (Figure 3C). However, the effects of acidification were apparent on the cumulative emissions (Figure 3D). Increasing H₂SO₄ rate appeared to have a linear effect of reducing NH₃ emissions ($R^2 = 0.93$ and $P < 0.01$; Figure 4B). Over the entire storage period (114 d), untreated

slurry and the slurry that received the highest acidification rate emitted 160 and 111 g NH₃ m⁻² (100 and 69.4 g NH₃ m⁻³), respectively. This reduced overall NH₃ emissions by 31% (Figure 3D). This is a significantly lower reduction than reported by others, where $\geq 75\%$ reductions in NH₃ emissions were demonstrated (Petersen et al., 2012; Misselbrook et al., 2016;

TABLE 2 | Methane (CH₄), nitrous oxide (N₂O), and ammonia (NH₃) emissions from stored dairy manure treatments from start of trial (June 10) to trial end (Nov 2) expressed as cumulative (g m⁻² and g m⁻³) and mean daily (g m⁻² d⁻¹ ± SD) emissions, as well as scaled cumulative CH₄ expressed as methane conversion factor (MCF) and scaled cumulative N₂O and NH₃ emissions by total nitrogen (TN, g kg TN⁻¹) and total ammoniacal-nitrogen (TAN, g kg TAN⁻¹).

CH ₄	H ₂ SO ₄ (g L ⁻¹)					
	0.0	0.4	0.8	1.2	1.6	2.0
g m ⁻² d ⁻¹	23.6 ± 23.7	12.4 ± 11.3	7.79 ± 6.86	2.59 ± 0.70	3.46 ± 0.85	3.07 ± 0.85
g m ⁻²	2,688	1,414	888	295	394	350
g m ⁻³	1,680	884	555	184	246	219
kg	17.8	9.40	5.90	2.00	2.60	2.30
m ⁻³	27.2	14.3	8.97	2.98	3.99	3.54
g kg ⁻¹ LOI	65.8	30.4	16.3	4.93	7.98	7.19
LOI, kg	271	309	362	397	327	323
Potential B ₀ × LOI	65	74	87	95	79	78
MCF	0.42	0.19	0.10	0.03	0.05	0.05
N₂O						
g m ⁻² d ⁻¹	0.039 ± 0.02	0.050 ± 0.03	0.038 ± 0.01	0.022 ± 0.01	0.033 ± 0.02	0.030 ± 0.02
g m ⁻²	4.37	5.55	4.21	2.52	3.70	3.41
g m ⁻³	2.73	3.47	2.63	1.57	2.31	2.13
g kg ⁻¹ TAN	3.72	5.50	3.13	1.87	3.14	3.38
g kg ⁻¹ TN	1.74	1.94	1.25	0.71	1.22	1.19
NH₃						
g m ⁻² d ⁻¹	1.40 ± 0.94	1.21 ± 0.68	1.24 ± 0.63	1.12 ± 1.11	1.06 ± 1.06	0.97 ± 0.61
g m ⁻²	160	138	142	127	121	111
g m ⁻³	100	86.4	88.5	79.5	75.4	69.4
g kg ⁻¹ TAN	136	137	105	94.6	103	110
g kg ⁻¹ TN	63.5	48.4	42.1	36.0	39.9	38.9

TABLE 3 | Total greenhouse gas (GHG; kg CO₂-eq m⁻²) emitted from stored liquid dairy slurry per rate of H₂SO₄ (g L⁻¹ slurry) over the 114-d storage period (May 25–September 15, 2019).

H ₂ SO ₄	CO ₂ -equivalent GHG emission						Total
	CH ₄		N ₂ O direct		N ₂ O indirect		
	kg m ⁻²	%	kg m ⁻²	%	kg m ⁻²	%	
0.0	91.4	98	1.30	1.4	0.75	0.8	93.4
0.4	48.1	95	1.65	3.3	0.65	1.3	50.4
0.8	30.2	94	1.25	3.9	0.66	2.1	32.1
1.2	10.0	88	0.75	6.6	0.60	5.2	11.4
1.6	13.4	89	1.10	7.3	0.56	3.8	15.1
2.0	11.9	89	1.02	7.6	0.52	3.9	13.4

Values in brackets are per cent (%) of total GHG emissions over a 100-y global warming potential.

Regueiro et al., 2016; Kavanagh et al., 2019; Sokolov et al., 2019b). These studies, however, likely used higher rates of acidification to reduce slurry pH to 4.5–6.5.

The relationship between changes in NH₃ emissions and rates of H₂SO₄ were linear for all rates (Figure 4B). The response data for NH₃ from the previous year was well-correlated with response data from this study ($R^2 = 0.93$; $P < 0.01$). Moreover, the slope of the regression line ($-17\% \text{ g}^{-1} \text{ L}$), indicated the average reduction (%) in NH₃ emissions per gram of H₂SO₄ added. Data extrapolation indicated that $\sim 5 \text{ g L}^{-1}$ may be needed to achieve 85% NH₃ reduction, which is markedly

higher than the rate needed for 85% CH₄ reduction ($4 \times$ more acid needed).

Total Greenhouse Gases

On a CO₂-eq basis, CH₄ accounted for $92 \pm 4\%$ of total GHGs, while direct and indirect N₂O emissions accounted for $5 \pm 2\%$ and $3 \pm 2\%$, respectively (Table 3). Acidification reduced total GHGs by 46–86%. Despite the inconsistent response of N₂O emissions to H₂SO₄ rates, response curves of total GHG emissions (CO₂-eq) and changes in emissions (%) vs. H₂SO₄ rates (Figure 4C) were similar with the observed CH₄ responses.

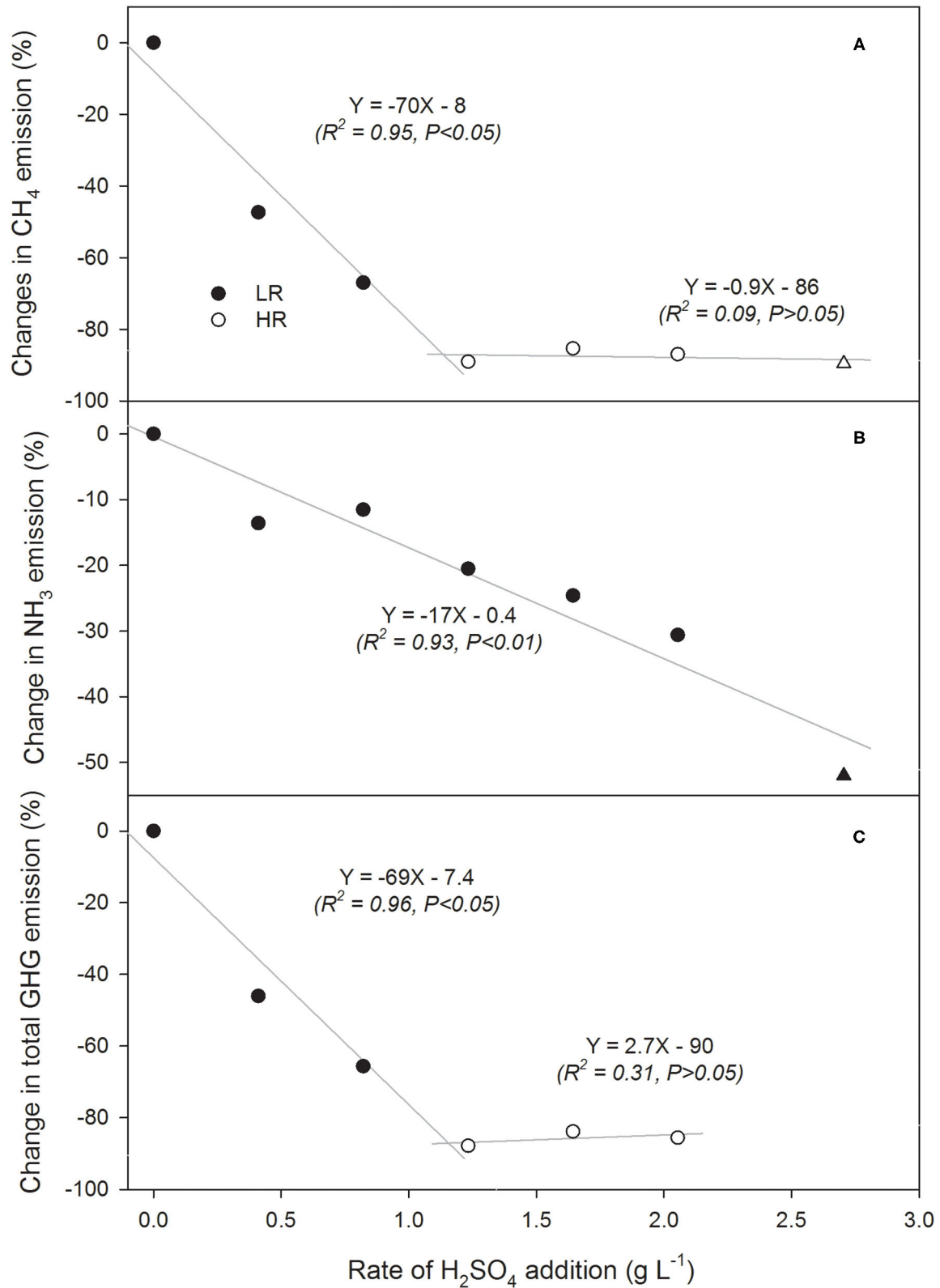


FIGURE 4 | Regression curves showing the relationships between rates of H₂SO₄ addition to stored dairy slurries and the subsequent changes in **(A)** CH₄, **(B)** NH₃, and **(C)** total greenhouse gas emissions (CO₂-eq). Low rate (LR) and high rate (HR) were separated in **(A,C)** to show the differing trends. Data from our previous study (Sokolov et al., 2019b) in **(A,B)** are denoted by Δ and \blacktriangle , respectively. Slopes in the equations indicate expected change (%) in emissions as H₂SO₄ rate increase with 1 g.

Thus, acidification of stored liquid dairy manure with H₂SO₄ appeared to have a stronger influence on the dominant CH₄ than non-CH₄ emissions.

DISCUSSION

Acidification had a non-linear trend of reducing CH₄ emissions and a linear trend for NH₃ emissions. Reducing CH₄ was cost-effective up to 1.2 g L⁻¹ H₂SO₄. At higher acidification rates, the CH₄ reduction become small, while the required quantity of H₂SO₄ continued to increase. This suggests that a low rate of acidification may be enough to make large GHG reductions from liquid dairy manure storages. The NH₃, on the other hand, decreased linearly with acid addition. Therefore, adding more acid would have a corresponding NH₃ reduction. The amount of acidification would, therefore, depend on the target emission and desired result.

Many European countries have regulated NH₃ emissions (Giannakis et al., 2019), and manure acidification is an increasingly common reduction method. Denmark, for example, has adopted strict measures for manure acidification (Jacobsen, 2015). However, in the current study only 30% NH₃ reductions were observed with the highest H₂SO₄ rate of 2 g L⁻¹. This suggests that high rates of acidification may be needed for more marked NH₃ emission reductions. In many countries there are no regulations for direct NH₃ emissions. Instead, strict standards for reducing GHG emissions and the carbon footprint of animal agriculture are enforced. Our findings suggest that total GHG emissions can be reduced at lower rates (i.e., 1.2 g L⁻¹) of acidification by focusing on CH₄ reductions, which is the largest GHG produced. The lower acidification rates for effective reduction of GHG emission also indicate lower cost than previous estimates based on NH₃ reduction. Moreover, decisions for cost-effective rates of acidification may depend on how the policy and regulatory context assigns the relative importance of these gases with respect to GHG emissions.

CONCLUSION

Methane was the dominant GHG from stored liquid dairy manure, contributing >88% of total GHGs (in CO₂-eq m⁻²), whereas NH₃ and N₂O contributed <10 and <5%, respectively. Addition of H₂SO₄ is a common method to reduce CH₄ and NH₃

emissions from stored dairy slurry. However, studies that used different rates of H₂SO₄ acidification (often ≥1.5 g L⁻¹ slurry) achieved comparable reductions. Using meso-scale storage tanks filled with 10.6 m³ of dairy slurry, we show that CH₄ emissions can be effectively reduced at much lower rates of H₂SO₄ compared to NH₃ emissions. A rate of 1.2 g L⁻¹ was sufficient to reduce 89% CH₄ emissions from dairy manure, however, this rate reduced total NH₃ emissions only 20%. This was likely due to different mechanisms for CH₄ and NH₃ inhibitions. Data extrapolation indicated that ≥85% of the reductions in NH₃ emissions may require up to 5 g L⁻¹. Thus, our results suggest differences in the sensitivity of these gases to H₂SO₄ addition may challenge simultaneous inhibition using a single acidification rate. On the other hand, CH₄ (the primary GHG from slurry) can be reduced at relatively low acidification rates, which is promising from a cost-benefit perspective.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

VS was project lead. JH contributed to manuscript writing and data analysis. AV contributed intellectually and financially to overall project, and particularly for GHG emission aspects. KD contributed intellectually and financially to materials and supplies. EG contributed intellectually with manuscript editing and funding. CW-R contributed intellectually and with manuscript editing, and particularly with the GHG emissions aspects. JV contributed intellectually helping with statistical analysis and manuscript editing. RG was major funding holder for this project, contributed intellectually and financially, and particularly with the GHG emission aspects. All authors contributed to the article and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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