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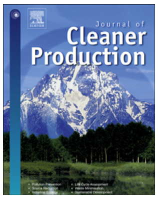

Mitigation of ammonia and greenhouse gas emissions from stored cattle slurry using acidifiers and chemical amendments

I. Kavanagh [a, b], W. Burchill [a, 1], M.G. Healy [b], O. Fenton [a], D.J. Krol [a, *], G.J. Lanigan [a]

[a] Teagasc, Environment, Soils and Land-Use Department, Johnstown Castle, Co., Wexford, Y35 TC97, Ireland
[b] Alice Perry Engineering Building, College of Engineering and Informatics, National University of Ireland, Galway, Co Galway, H91 HX31, Ireland

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ABSTRACT

Cattle and cow slurry storage is a significant source of agricultural greenhouse gas (GHG) and ammonia (NH3) emissions. While acidification has been demonstrated to significantly reduce these emissions, a knowledge gap exists to identify a range of chemical amendments that are safe, suitable and cost effective to mitigate both GHG and NH_3 gases simultaneously. The current study showed that ferric chloride, sulphuric acid, alum and acetic acid were extremely effective at abating emissions, with NH_3 reduced by 96%, 85%, 82% and 73%, respectively. In terms of methane (CH_4), ferric chloride, alum, sulphuric acid and acetic acid reduced emissions by 98%, 96%, 95% and 94%, respectively. Previous studies have found that the reduction of >pH 6 can inhibit the release of these gases; however, the effectiveness can vary depending on each amendment's composition. The cost benefit analysis, assessed the amendments in terms of both gaseous emissions reduction and net cost. Sulphuric acid, acetic acid, ferric chloride and alum ranked best, respectively**.** Currently, the cost of implementing these amendments is, at best, cost neutral. Therefore, incentivising chemical amendments for the abatement of GHG and NH_3 gases from slurry storage is needed. This incubation experiment is an effective means of pre-screening amendments before they are explored at pilot or full scale with subsequent field application. Future research should consider the assessment of cheaper on- and off-farm alternative waste streams as slurry amendment.

1. Introduction

The three principal anthropogenic greenhouse gases (GHGs) comprise carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Globally, total GHG emissions reached 49.3 Gt CO_2-eq in 2016, with agriculture contributing 11.39 Gt (23%) of global emissions (Olivier et al., 2017). Agricultural activities dominate both global CH_4 (52%) and N_2O (75%) emissions (Olivier et al., 2017). Conversely, direct carbon dioxide (CO_2) emissions from agriculture (not including land-use) are small [0.15 Gt CO_2-equivalents (eq) yr^{-1}]).

Ammonia (NH_3) volatilisation is a major loss pathway for nitrogen (N), with agriculture comprising over 90% of global NH_3 emissions (Galloway et al., 2008). The majority of NH_3 emissions originate from livestock waste streams (housing, storage and landspreading of manures; Webb and Misselbrook, 2004; Misselbrook et al., 2005a; Amon et al., 2006; Burchill et al. 2017). Ammonia causes negative environmental impacts by contributing to eutrophication and acidification of water bodies and soils due to release of H^+ during nitrification (Krupa, 2003; Velthof et al., 2011; Fowler et al., 2013). Ammonia also forms secondary aerosols such as ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$), (Warneck, 1999). Furthermore, re-deposition of volatilised NH_3 is an important source of N for the production of N_2O via biological nitrification of ammonium (NH_4^+) (Martikainen, 1985) and subsequent denitrification of nitrate (NO_3^-).

Manure management comprises approximately 12% of global agricultural emissions (Birch, 2014). Methane is emitted during the anaerobic decomposition of organic matter (OM) during storage, especially in liquid waste (slurry), while N_2O is emitted via the nitrification of NH_4^+ and partial (anoxic) denitrification of NO_3^- during storage of solid manure and soil application of both solid and liquid manures.

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[*] Corresponding author.
E-mail addresses: ian.kavanagh@teagasc.ie (I. Kavanagh), William.burchill@teagasc.ie (W. Burchill), mark.healy@nuigalway.ie (M.G. Healy), owen.fenton@teagasc.ie (O. Fenton), dominika.krol@teagasc.ie (D.J. Krol), gary.lanigan@teagasc.ie (G.J. Lanigan).
[1] Present address: Teagasc, Kanturk Local Advisory Office, Percival Street, Kanturk, Co. Cork P51 YR8E, Ireland.

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This study focusses on the abatement of GHG and NH_3 using chemical amendments in slurry during storage. The majority of Ireland and the UK's cattle and dairy cows are housed directly above the slurry storage tanks. This infrastructural reality rules out the majority of mitigation options practiced elsewhere in the world, such as separation of liquid and solids in manure (Dinuccio et al., 2012) or the use of covered storage facilities (Nicolai et al., 2004). A suitable option for this storage configuration may be to reduce the pH of slurry in storage through acidification, a method which has been shown to reduce NH_3 emissions from slurry, while also inhibiting bacterial processes that release GHGs (Sommer and Husted, 1995). Reductions in NH_3 and CH_4 emissions of up to 82% (Stevens et al., 1989) and 87% (Petersen et al., 2012), respectively, have been achieved when chemical amendments such as sulphuric acid (H_2SO_4) and ferric chloride ($FeCl_3$) have been added to dairy and pig slurries to achieve an initial target pH of 5.5 (Table 1). Chemically amending slurry during the storage period may have the added bonus of not only reducing emissions during storage, but also at land application, and may also improve the retention of phosphorus (P) along surface and near surface pathways after land application (Brennan et al., 2011).

To date, few studies have assessed the impact of amending stored cattle slurry of differing dry matter (DM) content under temperate climate winter conditions on GHG and NH_3 emissions. The identification of a single amendment capable of simultaneously reducing GHG and NH_3 emissions from slurry in storage has practical and economic implications for the farmer. Most studies have concentrated on a particular organic fertiliser and a single amendment focusing on the emissions of a single gas (Table 1). Furthermore, studies that have examined the impact of acidification of slurries using different amendments have been conducted at higher temperatures than those measured in Irish conditions (Fangueiro et al., 2008), as well as using differing dosing rates and amendments, (Petersen et al., 2012; Misselbrook et al., 2016), The amendments used in this experiment were chosen primarily due to their impact on reducing gaseous emissions, either GHG or NH_3 demonstrated in previous studies (Meisinger and Jokela, 2000; Panetta et al., 2005; Petersen et al., 2012; Brennan et al., 2012). Additionally, ferric chloride and alum have previously been used in studies focusing on one response parameter, therefore their combined effect on both GHG and NH_3 emissions was of interest here. Moreover, these two amendments have demonstrated potential benefit to restrict P movement in the soil upon land application (Brennan et al., 2015). Secondary consideration guiding the choice of amendments was the cost associated with using various treatments in order to conduct cost-benefit analysis, i.e. acetic acid was chosen as a cheaper acidifying alternative to sulphuric acid.

Thus, the objectives of this study were to (1) assess the efficacy of various chemical amendments to slurries of different DM content (4% and 7%) in the reduction of GHGs and NH_3, and (2) evaluate the cost of using these amendments to achieve greatest reductions. Controlled laboratory experiments simulating winter slurry storage in a temperate climate were conducted over an 84-day period.

2. Materials and methods

2.1. *Incubation study – experimental set up*

Slurry was collected from an underground storage tank, with a total capacity of $20\ m^3$, on a commercial dairy farm in the south-east of Ireland. The dairy cow and cattle diet consisted predominantly of grass silage. Prior to collection from the storage tank, the slurry was thoroughly mixed using a mechanical agitator. Eighty litres of slurry was sampled and immediately sieved through a 9.5 mm-sized mesh to ensure homogeneity. Two DM slurries (4% and 7%) were used in the experiment to represent different types of slurry typically found on beef and dairy farms in Ireland (Coulter and Lalor,. 2008) Slurry from beef farms typically has a higher DM due to the high protein content of the diet, whereas dairy cattle typically have a higher utilisation of feed as it is being processed for milk production, resulting in less of the available nutrients being expelled, and consequently has a lower DM slurry (Shalloo et al., 2011; Niu et al., 2017). In addition, waste water from yard washings further diluted the slurry. To achieve a 4% DM slurry, a 7% DM slurry was diluted with water.

A laboratory-scale incubation experiment was conducted in a temperature-controlled growth chamber (Temperature Applied Science Ltd., West Sussex, U.K.) over a period of 84 days. Temperature (8.6 °C) and humidity (60%) were controlled to replicate conditions found on Irish farms during winter (Met Éireann, 2017). The experimental treatments (all at $n = 3$ per treatment) used for each slurry DM were: 95–97% sulphuric acid (H_2SO_4, Sigma-Aldrich), 95–98% acetic acid (CH_3COOH, Sigma-Aldrich), alum 98% ($AIK(SO_4)2.12H_2O$; Sigma-Aldrich), ferric chloride iron (III) hexahydrate ($FeCl_3$; Alphy), and a slurry control. The amendments were laboratory-grade chemicals. Thirty containers in total were used in this experiment.

Six kg of both DM slurries were poured into 15 L-capacity containers. The four chemical amendments were added incrementally to the containers over a period of 2–4 h until a pH of 5.5 was attained. Details of all experimental treatments can be found in Table 2. The slurries were stirred continuously during chemical addition to limit foaming and to achieve a homogenous mix. Following this procedure, 1.6 kg of treated or control slurry was transferred to 2 L-capacity containers and placed in the temperature and humidity-controlled room in a randomised block design. Due to the relatively long experimental period, 1.6 L of slurry was chosen as the maximum amount that could be incubated in the

Table 1
Summary of previous studies investigating the potential to reduce ammonia (NH_3) and methane (CH_4) emissions from stored slurries through addition of chemical amendments.

Reference	Scale	Duration	Temp	Dry matter	pH	Amendment	Addition rate	% reduction	
		days	°C	%				NH_3	CH_4
Meisinger and Jokela (2000)	Lab	14	14	9–11	4.7	Alum	2.5%	60	
Smith et al. (2004)	Lab	2	20	–	–	Alum	6%	52	
Shi et al. (2001)	Field	12	20	9	5.9	Sulphuric acid	8.5%	92	
Panetta et al. (2005)	Pot	3	18	–	5.3	Sulphuric acid	–	89	
Regueiro et al. (2016)	Pot	60	15	24	5.5	Sulphuric acid	165 meq/kg	81	64
Kia et al. (2008)	Lab	14	N/A	4.3	5.8	Sulphuric acid	5%	70	
Brennan et al. (2015)	Lab	3	18–20	–	6.7	Ferric chloride	1.3%	56	
Brennan et al. (2012)	Lab	54	20	10.5	5.4–12.2	Ferric chloride	3%	99	
Petersen et al. (2012)	Feld	95	12	9	4.5	Acetic acid	16%		87
Regueiro et al. (2016)	Lab	60	20	8	5.5	Acetic acid	~122 meq/kg	50	

container while still maintaining an adequate head space for accurate gas sampling.

In order to replicate field conditions, each container was covered with a lid perforated with twelve 2 mm-diameter holes. These holes simulated air flow in large-scale slatted storage tanks used on commercial livestock farms. A preliminary test was carried out in the growth chambers prior to starting the experiment, which compared open containers (containing slurry of 4% and 7% DM) to containers instrumented with perforated caps. There was a 67% reduction in evaporation from the containers with the perforated caps compared to open containers over a 14-day period.

2.2. Sample collection

Daily measurements of NH_3 and GHG emissions were conducted for the first eleven days of the experiment, followed by measurements every second or third day until the end of the experiment (Day 84). Measurements of pH were taken on days 0, 1, 2, 3, 4 and 5 using a JENWAY 1510 pH meter (Straffordshire, U.K.) and then once-a-week until the end of the experiment. The weight of the containers and slurry volume were measured every seven days and DM was measured at the start and end of the experiment. The slurry was also characterised at the beginning and end of the experiment for total nitrogen (TN), total phosphorus (TP) and total ammonical nitrogen (TAN). Total ammonical nitrogen was analysed using $CaCl_2$ extractions at a dilution rate of 1:25, centrifuged for 10 min, filtered through a 0.5 μm sieve, and tested using an Aquakem 600 discrete analyser (Aquachem, Sweden). Slurry was tested for TN on a Leco elemental analyser (Anzier2, Sweden). To obtain DM of the slurry, a sub-sample was dried in an oven at 105 °C for 24 h.

2.3. Analytical methods and calculations

Ammonia emissions for all treatments were monitored using a dynamic chamber system similar to that described by Dinuccio et al. (2008). Concentrations of NH_3 in the air entering and leaving each container, over a period of 16 min per sampling, were monitored using a photoacoustic INNOVA 1412 field gas-monitor (LumaSense Technologies, Denmark) coupled to a Gasmux multiplexer GM3000 (IMT Vohenstrauss, Germany). Glass wool soaked with oxalic acid (0.05 M) was used to strip moisture from the background air entering the photoacoustic monitor.

Gas Fluxes (F_j in mg m^{-2} h^{-1}) for NH_3 were calculated according to (Dinuccio et al., 2008):

$$Fj = Q\,\frac{(Cex.j - Cin.j)}{A} \qquad (1)$$

where $Cex.j$ is the NH_3, N_2O, CH_4 or CO_2 concentration of air outlet from the chamber (mg m^{-3}), $Cin.j$ is the NH_3, N_2O, CH_4 or CO_2 concentration of air into the chamber (mg m^{-3}), Q is the airflow rate through the chamber (m^3 h^{-1}), and A is the area of emitting surface covered by the chamber (m^2). Carbon dioxide equivalents were determined after Birch (2014) to enable comparison of results.

Methane emissions were measured using a retro-fitted static chamber technique, whereby the containers were sealed with a screw-cap lid modified with a rubber septum (Becton Dickinson, Oxford, U.K.). Gas samples (10 ml) were extracted at 0, 5 and 10 min after the container was closed using a polypropylene syringe (BD Plastipak, Oxford, U.K.) fitted with a hypodermic needle (BD microlance 3; Becton Dickinson). The samples were then injected into pre-evacuated (−1000 mbar) 7 mL screw cap septum glass vials (Labco, High Wycombe, U.K.). The resulting gas samples were analysed for CH_4 concentrations using gas chromatography (GC) (Varian CP3800 GC; Varian, Walnut Creek, CA USA) and Bruker SCION 456 GC, with high-purity helium used as a carrier gas. Samples were introduced to the GC system by a Combi-PAL automatic sampler (CTC Analytics, Zwingen, Switzerland). The increase in CH_4, CO_2 and N_2O concentrations in the containers over time was used to determine the gas flux. Daily fluxes were calculated for each gas and each treatment from the increase in headspace concentration over three sampling times (0, 5 and 10 min after enclosure) following Eqn. (2), adapted from Kelliher et al. (2013):

$$F(daily) = \left(\frac{\partial C}{\partial T}\right) \times \frac{M \times P}{R \times T} \times \left(\frac{V}{A}\right) \qquad (2)$$

where ∂C is the change in gas concentration in the chamber headspace during the enclosure period in ppbv or μll^{-1}, ∂T is the enclosure period expressed in days, M the molar mass of the gas element, P is the atmospheric pressure in Pa, and T is the temperature in Kelvin.

2.4. Cost-benefit analysis of amendments

In order to determine the marginal abatement cost of each measure on both GHG and NH_3, the net cost of each measure was expressed relative to the amount of NH_3 or GHG saved. Net costs were the sum of gross cost (which consisted of the price of amendments and transportation) less net N fertiliser savings. In terms of cost savings for both DM slurries in terms of TAN, the amount of ammonical N per kg saved for each amendment was compared to the current price of €300 per tonne of synthetic fertiliser in the form of calcium ammonium nitrate (CAN), which was equivalent to €1.09 kg^{-1}N. For total GHG, methane emissions were converted to CO_2e by multiplication with its Global Warming Potential (GWP) of 25 (IPCC, 2014). In order to calculate indirect N_2O, it was assumed that all NH_3 emissions would be wet or dry deposited within a 1 km radius of the point of emission (Kelleghan et al., 2019). Subsequently the CO_2-eq associated with this deposition was calculated by assuming that 1% of the deposited N was re-emitted as N_2O and that this was converted to CO_2-eq by multiplying by 298 (IPPC, 2014). Nitrous oxide and CO_2 were not included in the cost benefit analysis, as there was no statistical difference in emissions compared to the control. The floor price of

Table 2
Treatments and amendment rate added to 6 kg of slurry (4% and 7% DM) to achieve a target pH of 5.5.

Treatment	4% DM		7% DM	
	Stoichiometric addition	Amendment added	Stoichiometric addition	Amendment added
	g/g	g	g/g	g
Alum	4.42	53.1	8.85	88.5
Ferric chloride	4.12	41.3	8.25	70.1
Acetic acid	1.04	35.7	4.35	43.5
Sulphuric acid	2.17	20.8	2.01	19.2
Control		0.0		0.0

Table 3
Chemical characteristics of 4% and 7% DM slurry at Day 0 and 83.

Treatment	Time	4% DM slurry			7% DM slurry		
		TN	TP	TAN	TN	TP	TAN
Acetic acid	Start	2.85	0.74	70.5	3.01	0.76	125.8
	End	2.90	0.76	42.6	2.94	0.80	76.5
Alum	Start	3.04	0.69	67.7	3.10	0.71	121.0
	End	3.23	0.69	73.6	3.02	0.68	118.0
Ferric chloride	Start	3.59	0.71	68.3	3.63	0.72	121.2
	End	3.76	0.71	83.8	3.53	0.67	151.5
Sulphuric acid	Start	3.40	0.72	57.2	3.31	0.74	105.1
	End	3.69	0.61	57.3	3.38	0.77	111.7
Control	Start	2.71	0.76	49.9	2.83	0.83	98.8
	End	2.81	0.79	34.2	2.71	0.83	58.0

TN: total nitrogen, TP: total phosphorus.

CO_2-eq was set at €27 per tonne (World Bank Group, 2018). Once this was achieved, the cost of each amendment was subtracted from the savings achieved.

2.5. Statistical analysis

Statistical analyses were carried out using SAS 9.4 (2002–2010) (SAS Institute Inc., USA). Statistical differences in cumulative N_2O, CH_4, CO_2 and NH_3 emissions between the slurry treatments were tested by a two-way analysis of variance (ANOVA) (treatment and slurry DM% were independent variables and replicate was a random term). Slurry NH_4–N, TON and pH were analysed by ANOVA with measurement day included as a repeated measure in the model. Replicates were identified in the repeated measures statement in the model to account for correlations among observations from the same replicate. Post-hoc Turkey tests were carried out to determine differences between treatment means following each ANOVA. A statistical probability of $p > 0.05$ was considered significant for all statistical tests.

3. Results and discussion

3.1. Effect of chemical amendments on slurry characterisation over time

The results of the amended and non-amended slurry (4% and 7% DM) characterisation in terms of TN, TAN, TP concentrations at the beginning and at the end of the experiment are presented in Table 3.

The effects of the treatments on slurry characteristics can be seen in Table 3, there was no significant difference between the TN and TP results for both DM slurry. These results were comparable to other studies (Brennan et al., 2015).

3.2. Effect of chemical amendments on slurry pH over time

The pH of the slurries receiving chemical amendments was set to a target of 5.5 on Day 0 of the experiment, while the control slurries had a pH of approximately 7.2 (Fig. 1). Similar to other studies (SØren et al,. 2012; Brennan et al., 2011; Petersen et al., 2012; Regueiro et al., 2016), the pH of the chemically modified slurries increased over the duration of the experiment (Fig. 1). The pH in the 7% DM slurry increased at a quicker rate than in the 4% DM slurry, which was indicative of the treatments' efficacy reducing at a quicker rate in the higher DM slurry. This was likely caused by the much higher buffering capacity and available nutrients in the 7% DM slurry. The control treatment for both DM slurries remained at a pH of 7.2, with small but not statistically significant ($p > 0.05$) changes over the study duration. The interaction between storage duration and treatments of each DM slurry had a significant ($p < 0.05$) effect on slurry pH.

The ability of an additive to decrease the slurry pH depends on the anions that contribute to the pH buffering capacity of the slurry. In slurry, this buffering system is very complex and is mainly composed of NH_4^+, carbonates, phosphates, and volatile fatty acids (VFA) (Sommer and Husted, 1995). This complexity can be seen when comparing the treatment inoculation rates for both DM slurries used in this experiment (Table 2). The 7% DM slurry required between 7% (sulphuric acid) and 70% (ferric chloride) higher inoculation rates than the 4% DM slurry (Kai et al., 2008). The relationship between VFA and an ability to maintain a stable pH indicates that higher DM slurries, with an associated high VFA, results in extra inoculum required for a reduction in pH.

Another consideration when comparing inoculation rates of slurry additives is the composition of the acidifier used. In the current study, acidifiers such as acetic acid and sulphuric acid were in aqueous form, which allowed for immediate and controlled incorporation into the slurry, while alum and ferric chloride were in powder form. When the latter amendments were added to the slurries in the current study, greater homogenisation and mixing were required to ensure the amendments were completely dissolved and a uniform pH was achieved. This should be considered when up-scaling the use of these amendments for farm operations, as greater agitation may be required.

In the current study, a target pH of 5.5 was chosen in order to enable NH_3 abatement to commence immediately. This led to

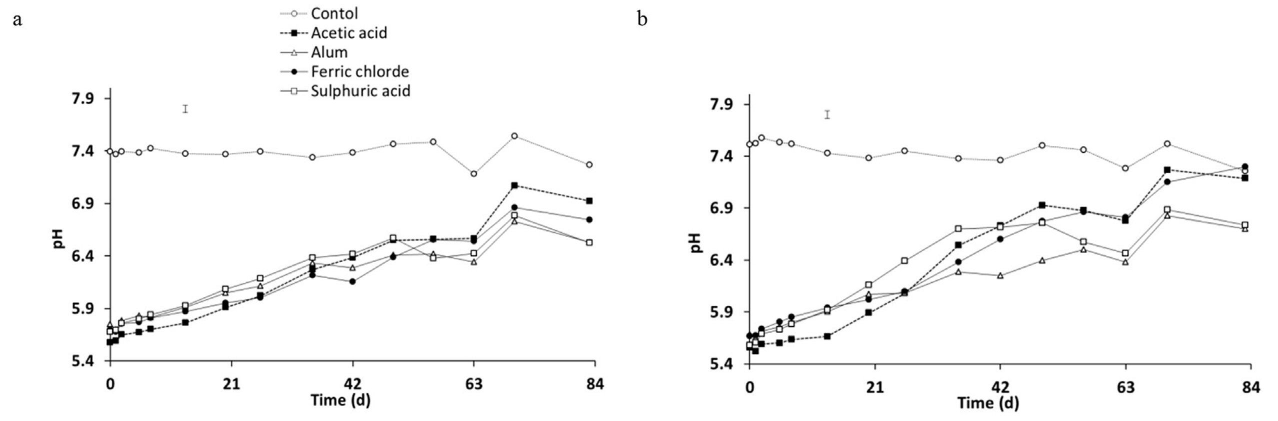

Fig. 1. Changes in slurry pH over time across all chemical amendment treatments for a) 4% DM and b) 7% DM slurry. Error bars indicate pooled standard error of the mean.

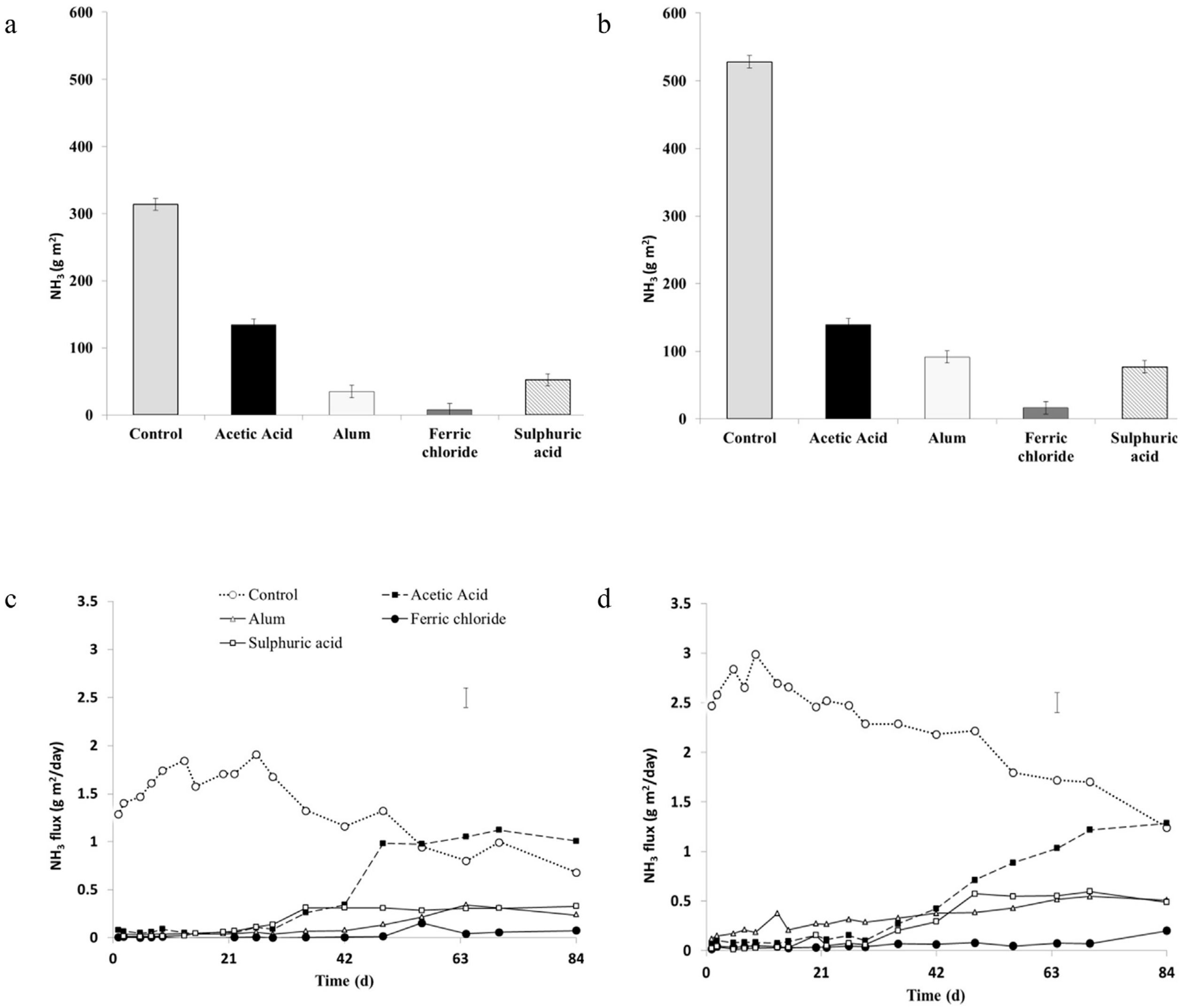

Fig. 2. NH3 cumulative and daily fluxes for 4% (a, c) and 7% (b, d) DM slurries. For a, b error bars indicate standard error of the mean whereas for c, d error bars indicate pooled standard error of the mean.

different rates of amendments compared to other studies. For example, Regueiro et al. (2016) used acetic acid at a significantly higher dosage than used in current study for slurry acidification, and achieved an overall 3% reduction in cumulative NH_3 emissions compared to 54% in the current study. However, the cattle slurry used by Regueiro et al. (2016) had a higher starting pH and ambient temperature, both of which had a dramatic effect on the longevity of the pH decrease.

3.3. NH_3 emissions during slurry storage

In both slurry treatments, daily NH_3 fluxes were similar to those found in other experiments e.g. Regueiro et al. (2016). In the current study, the control treatments emitted 313.69 g NH_3 m^{-2} and 524 g NH_3 m^{-2} over the incubation period (84 days) from 4% to 7% DM slurry, respectively (Fig. 2). These results were similar to those found by Amon et al. (2006) with a cumulative of 226.7 g NH_3 m^{-2}. In the current study, all treatments were effective in reducing the cumulative NH_3 emissions ($p < 0.05$) (Fig. 2 a, b). Over the study period, the largest reduction in both slurry treatments was achieved with $FeCl_3$, with cumulative emissions of 8.03 g NH^3m^{-2} and 16.47 g m^{-2} in the 4% and 7% DM slurries, respectively. These results represented a reduction in cumulative NH_3 emissions of approximately 97% compared with the study controls. Ammonia emissions in the 4% DM slurry treatment were reduced by 89%, 83% and 57% when treated with alum, H_2SO_4 and acetic acid, respectively. In the case of 7% DM slurries, NH_3 emissions were reduced by 83%, 84% and 74% by additions of alum, H_2SO_4 and acetic acid, respectively.

The effect of slurry DM in terms of amendment interaction was significant (<0.05), with amendments performing differently at each DM. The highest cumulative NH_3 emissions were observed from the 7% DM and 4% DM slurry controls 313.69 (±15)gm^2& 528 (±17) gm^2. Acetic acid delivered the smallest cumulative reduction in NH_3 emissions 133 (±2) gm^2 for DM 4; however, it performed better in the higher DM treatment 139 (±10)gm^2. Daily NH_3 fluxes of control slurry at both DMs declined over the experimental period reflecting a reduction in the concentration of NH_4—N over time, while NH_3 from treated slurries gradually increased over the 84-day period (Fig. 2 c, d). The majority of NH_3 loss from amended slurries occurred towards the end of the experimental period. Regardless of time or pH, $FeCl_3$ was the only treatment to remain effective throughout the experimental period (Fig. 2 c, d).

When the slurry TAN content is accounted for, there is a correlation with cumulative NH_3 loss (Table 4). In both slurry DM

Table 4
Total percentage of slurry TAN lost as NH_3 during the course of 83 days of the incubation experiment.

Treatment	4% DM slurry				7% DM slurry			
	Cumulative NH_3 g/m^2	Average NH_3 g/m^3/hr	% NH_3 loss/TAN[a]		Cumulative NH_3 g/m^2	Average NH_3 g/m^3/hr	% NH_3 Loss/TAN[a]	
Acetic acid	133.78	44.79	22	B	139.1	46.18	12.9	C
Alum	34.69	11.6	6	CD	91.4	30.49	8.7	ED
Ferric chloride	8.03	5.19	1.4	E	16.4	5.49	1.6	E
Sulphuric acid	52.19	17.39	10	CD	76.8	25.6	8.9	CD
Control	313.68	104.56	68	A	528.0	176.1	63.1	A

Means followed by the same letter are not significantly different at $P < 0.05$. Lettering refers to comparisons within rows and columns simultaneously.

[a] TAN: total ammonical nitrogen, %loss: amount of N lost post day 83.

treatments, $FeCl_3$ was associated with the lowest loss of TAN over time in storage. Overall, the statistical analysis showed that slurry DM by treatment interaction was significant and is the main driver of NH_3 emissions. However, in both slurry DMs the effectiveness of the amendments at reducing NH_3 emissions followed a common trend from best to worst i.e. ferric chloride, alum, sulphuric acid and acetic acid.

The percentage of TAN lost as NH_3 was highest in the controls, with losses of between 68% and 63% (Table 4), which are similar to those found by Kai et al (2008) i.e. 53% and Misselbrook et al. (2016) i.e. 50%. Ferric chloride had similar losses of 10% and 9% for both DMs, while alum lost between 8.7% and 11.6%. Brennan et al. (2015) recorded measured losses of 15% for $FeCl_3$ and 4% for alum with a slurry DM of 10.5%. Sulphuric acid had similar losses for both DM with 10% and 8.9%, which were lower than those found by Misselbrook et al. (2016) (13%) and Kai et al (2008) (16%). However, these differences may be accounted for by slightly different inoculation rates.

This gradual increase in NH_3 emissions and subsequent decrease in TAN from the other chemical treatments may be attributed to an increase in slurry pH over time. As the chemical potency of the amendment is neutralized by the OM and bacteria in the slurry, the pH increases leading to more NH_4—N conversion to NH_3 (Kai et al., 2008; Sommer et al., 2017). Based on the temporal trace of pH, which increased periodically (Fig. 1), the increase in pH correlated with the daily increase in NH_3 fluxes (data not shown).

Stevens et al. (1989) and Regueiro et al. (2013) compared acidification pH values of slurry ranging from 3.5 to 8 and found that the effectiveness of acidification is negated once the slurry is above a pH of 6. In the current study, the efficacy of the $FeCl_3$ treatment was unaffected by changes in pH, which, despite a relatively quick rise in pH (>6), did not contribute to any significant increase in daily fluxes. This suggests that $FeCl_3$ creates an unfavorable environment for slurry microbes and is therefore limiting the release of available NH_4—N even once the pH has recovered, potentially due to the ability of the chloride in the slurry to bind to the available H^+ ions (Demirel and Scherer, 2008).

3.4. CH_4 emissions during slurry storage

There was a strong linear correlation between chemical treatment and slurry DM ($p < 0.05$). Emissions are low at slurry DM of 4% due to the dilution effects of the methanogens and the carbon source. Cumulative CH_4 emissions for the 4% DM slurries treated with control, acetic acid, sulphuric acid, alum, ferric chloride, resulted in emissions of, 51 (±8), 19(±3), 16(±4), 12 (±2), 4(±1), g m^2 respectively for 7% DM slurry 801 (±24), 101(±4), 39(±5), 23 (±4), 8(±1) (standard error of the mean in brackets). Treatments were significant when compared to controls ($P > 0.05$).

Wood et al. (2012) found lower DM slurries displayed a "lag" period before emissions increase due to the lack of community size and also for the OM to be cycled into useable substrate to grow these communities; therefore, the efficacy of chemical amendment in the 4% DM slurry is not as pronounced as in the 7% equivalent.

The control slurry had the highest cumulative and daily CH_4 fluxes for both DM slurries throughout the incubation period (Fig. 3 a-d). The daily fluxes in the current study were, on average, 6.6 g CH_4 m^2/day for DM 7%, which were lower than other studies e.g. Brennan et al. (2015), who measured 8.29 g m^2/day This could simply be due to a discrepancy in sampling frequency or a lower inoculation rate. Again, $FeCl_3$ was the most effective in reducing CH_4 emissions from both DM slurries, which were reduced by between 74% (4% DM) and 98% (7% DM). However, similar to NH_3, the proportion of CH_4 released from the 7% DM was almost 14 times higher than that measured from the 4% DM. This is predominately due to the proportion of carbon that was available in the 7% DM slurry (Wood et al., 2012) which is directly affected by DM content, which in turn would mean a higher volatile solid content, which is the main variable driving CH_4 production. This was correlated in the statistical analysis which showed that the DM interaction played a significant role ($p < 0.05$). The pH of both slurries at the beginning of the experiment was similar and therefore had no direct impact on the proportion of CH_4 emitted from the control slurries.

The daily CH_4 fluxes increased throughout the experimental period for the amended slurries from 0.05 to 3.05 g CH_4 m^2 day. However, elevated CH_4 fluxes occurred earlier in the 4% DM treated slurry compared to the 7% slurry (Fig. 3 c, d). This asynchrony in daily CH_4 emissions positively correlates with temporal changes in slurry pH. This trend has been consistent across all treatments except for $FeCl_3$ which showed no notable increase. It is hypothesized that the reaction between the chloride and the OM of the slurry, has made the micro-environment of the slurry unfavorable for the production of methanogens, primarily acetotrophic methanogens.(Habetwold et al., 2018) Demirel and Scherer (2008) showed that these are the primarily groups affected by pH variances, which in turn limit the production and release of CH_4. In terms of the other GHGs, there were no significant differences between emissions of N_2O and CO_2 and the study controls (data not shown).

3.5. Crust observations

Observations in relation to crust formation were noted once destructive pH sampling frequencies decreased to once a week (after day 5). Although the 4% slurry remained crust free, a light crust was formed on the surface of the 7% DM slurry between sampling periods. These observations were similar to those of Misselbrook et al. (2005b), who found a direct link between crust formation time and thickness versus DM content. Therefore, this implies that the ability of the slurry to form a natural crust is not directly impacted by the amendments. Crust formation, which is a natural barrier to emissions, is not negatively impacted by the chemical amendments used in the current study. Therefore,

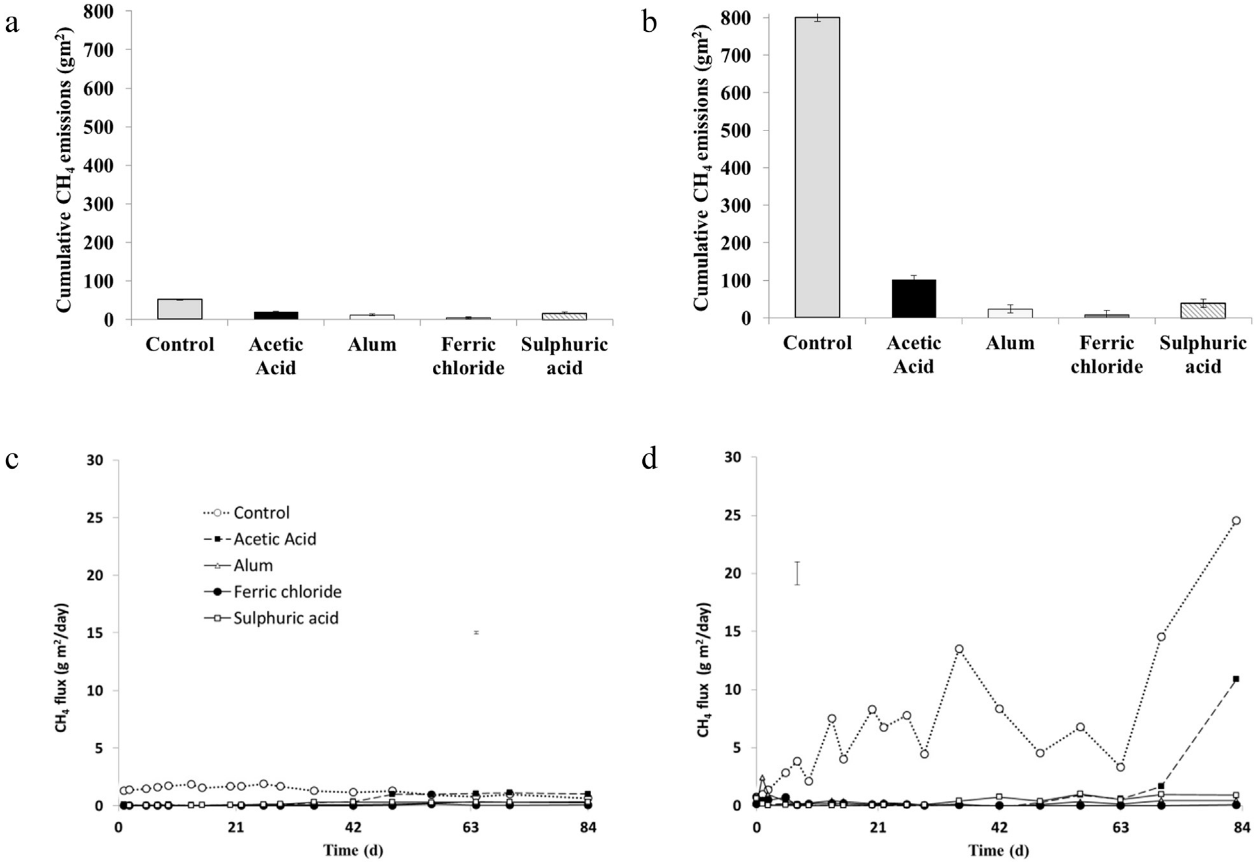

Fig. 3. Cumulative and daily emissions of CH4 for 4% (a, c) and 7% (b, d) DM slurries, respectively. For a, b error bars indicate standard error of the mean whereas for c, d error bars indicate pooled standard error of the mean.

amendment of full-scale slurry storage systems, such as open air lagoons or slurry storage tanks, is viable.

3.6. Cost-benefit analysis of amendments

The marginal abatement cost both in terms of ammonia-N (€ kg^{-1} NH_3—N) and greenhouse gas (€ t^{-1} CO_2e) were observed to vary across both amendment type and also with %DM (Table 5). The ranking of amendments in terms of cost-benefit for both ammonia and GHG were, from lowest to highest, sulphuric acid, acetic acid, ferric chloride and alum. The ranking was driven by the cost per m^3 slurry treated, which varied from €2.64 for alum to €0.38 for sulphuric acid (a variance of 695%) while the level of abatement only varied between ferric chloride and alum by 23% and 30% for ammonia and GHG respectively. There was also considerable variation in the GHG marginal abatement cost due to %DM that was driven by the extent of methane abatement. As detailed earlier, the % abatement relative to the control was much higher, most likely due to higher levels of microbial inoculum being present. This impacted greatly on the marginal costs, which at a carbon floor price of €27 t^{-1} CO_2e, resulted in all for amendments being cost neutral at 7% DM as well as sulphuric acid amendment at 4% DM (Table 5).

These abatement options in terms of ammonia abatement were relatively favorable compared to other technical options (eg. slurry spreading techniques, inhibitors, covering slurry stores, etc.). Previous ammonia marginal abatement cost curve (MACC) analyses have shown that mean abatement costs were between €2.1 kg^{-1}N and €4 kg^{-1}N (Reis et al., 2015; Lanigan and Donnellan, 2015). Amendments were also attractive in the context of overall GHG mitigation options. Previous MACC analyses for the UK and Ireland have shown mean abatement costs to be £37 and €75 per tonne CO_2e respectively (Eory et al., 2015; Lanigan and Donnellan, 2018).

This analysis considers only the cost of the amendments and shipping. Other costs and implications would have to be taken in to account for a full cost analysis. These considerations may include specialized amendment storage facilities, manpower and energy costs, or the cost of agitation. In order to fully realize the value of chemically amending slurry in storage, the full manure management chain must be taken into consideration with subsequent effects on land spreading. For example, higher N retention could lead to higher NH_3 emissions if low emission techniques are not utilized (e.g. trailing shoe) (Lalor & Lanigan, 2010). Other cost returns could be gained in terms of lower water quality losses due to amendments in runoff, which in turn have been shown not to negatively affect plant available P for crop growth (Brennan et al., 2015). Alternative waste streams should be evaluated to bring cost ratios between abatement and implementation downwards.

4. Conclusions

Emissions of GHG and NH_3 from cattle and cow slurry storage can be minimised by acidification with chemical amendments. Additives ranked from best to worst performing were ferric chloride, sulphuric acid, alum and acetic acid. However, when a holistic cost benefit analysis was considered, sulphuric acid was observed to be more cost-efficient, with chemical amendment of dairy cattle slurry in general only cost neutral for GHG at a price of €27 per

Table 5
Cost-benefit analysis of treatment of dairy cattle slurry with chemical amendments in storage.

DM %	Amendment	Stoichiometric addition rate %	€/tonne of amendment [a]	€/m^{3}slurry treated	€/tonne CO_2e. [b]	€/kg of N [c]
4	Alum	0.4	300	2.64	195	4.67
	Ferric chloride	0.36	229	1.50	91.2	1.79
	Acetic acid	0.18	140	0.82	42.4	0.53
	Sulphuric acid	0.09	200	0.38	26.0	0.05
7	Alum	1.14	300	4.40	18.1	5.79
	Ferric chloride	1.16	229	2.60	9.64	2.76
	Acetic acid	0.65	140	0.90	3.28	0.43
	Sulphuric acid	0.31	200	0.60	2.27	0.01

****Total costs are based on the savings achieved, minus the cost to treat 1 m3 of slurry.

[a] Costs only account for the direct price and transport of listed amendments.

[b] CO_2e represents methane & assuming that 1% of deposited ammonia is re-emitted as nitrous oxide. There were no significant differences between the treatments and control for carbon dioxide and nitrous oxide.

[c] N savings based on a replacement value of €300 per tonne, using CAN.

tonne CO_2e at best and therefore would require subsidies to enable implementation. In keeping with the principles of a circular economy, future research should focus on alternatives to chemical amendments such as lower cost alternatives e.g. on-farm or off-farm waste products.

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