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Mitigating ammonia and greenhouse gas emissions from stored cattle slurry using agricultural waste, commercially available products and a chemical acidifier

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ABSTRACT

The production of bovine slurry and its subsequent storage are significant sources of ammonia (NH_3) and greenhouse gases (GHGs). Chemical acidification of manures has been shown to significantly reduce these emissions. Waste products, derived from food processing and on-farm practices, may be used as “natural” acidifiers. However, the efficacy of these products in reducing pH and any subsequent emissions are unknown. Commercial “slurry improvers” or “additives” may also be a viable mitigation option; however, their effectiveness is questionable. This study investigated the efficacy and cost of a range of waste and commercial amendments and a chemical acidifier, ferric chloride ($FeCl_3$), to identify the most effective amendment for NH_3 and GHG emissions reduction. Ammonia abatement potential was observed for 5% sugar beet molasses (67% reduction), 7% apple pulp (49% reduction), and 7% grass silage (38% reduction). Methane (CH_4) emissions were reduced only by spent brewers’ grain, sugarbeet molasses, and grass silage effluent at the higher inclusions (i.e. amounts added), with reductions ranging from 15% to 70%. Carbon dioxide (CO_2) emissions were significantly increased with the addition of waste amendments. Commercially available additives had little impact on emissions, with the exception of one treatment, which reduced CH_4 by approximately 10%. Ferric chloride reduced NH_3 emissions by 20%−68%, CH_4 by 6%−65%, and CO_2 by 6%−38%, depending on the inclusion. All waste amendments had low marginal abatement costs ranging from -€0.46 to €0.88 kg^{-1} NH_3 abated compared to $FeCl_3$ and commercial amendments (€1.80 to €231 kg^{-1} NH_3). This incubation experiment demonstrated that a range of on-farm and industry waste streams could be valorised to reduce NH_3 emissions. However, many of these may result in higher CH_4 and CO_2 emissions due to input of labile carbon sources. Therefore, based on the results of the current study, it is recommended that sugarbeet molasses and ferric chloride, at 5% and 1.1% inclusions respectively, be examined in field experiments.

1. Introduction

The production of greenhouse gases (GHGs) by agricultural manure management contributes up to 9% of global warming (Gerber et al., 2013; IPCC, 2019). Methane (CH_4) emissions are a direct result of organic matter decomposition under anaerobic conditions similar to those found in slurry storage. Nitrous oxide (N_2O) is a result of the denitrification of nitrate (NO_3^-) and the nitrification of ammonium (NH_4^+) from slurry solids during storage (Sommer et al., 2015, 2017). Ammonia (NH_3), although not a GHG gas, is a transboundary pollutant that represents a major loss pathway through volatilisation of ammonical nitrogen (N), with agriculture comprising over 90% of global NH_3 emissions (Galloway et al., 2008). Ammonia emissions have been shown to emanate from animal housing and subsequent slurry storage (Misselbrook et al., 2005; Amon et al., 2006). Once emitted, NH_3 can be redeposited and contribute to eutrophication of waterways and also contribute to the local N pool. Subsequently, this increase in N

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indirectly contributes to N_2O emissions through the nitrification and denitrification processes occurring during storage (Martikainen, 1985; Ni 1999).

Ireland and the UK are among the few countries that house their cattle during winter on slats above slurry storage pits. The historical design of these housing units means that gaseous emission reduction techniques used in other parts of the world, such as solid liquid separation (Kaparaju et al., 2011; Rico et al., 2007), physical covers (Balsari et al., 2013; Gioelli et al., 2020), or the addition of surface amendments to create barriers i.e. straw, Leca balls, or perlite (Hoeve et al., 2016; Scotto di Perta et al., 2020), are impractical due to the cost and continuous addition that would be required throughout the storage period. Slurry acidification during storage, with various chemicals, has been shown to significantly impact both NH_3 and GHG emissions (Kavanagh et al., 2019; Sokolov et al., 2020). The pH to which the slurry is reduced has a significant impact on the mitigation of these emissions, with a reduction in pH < 6 required to achieve an 86% (Li et al., 2008), 87% (Regueiro et al., 2016), and 96% and 98% (Kavanagh et al., 2019) reduction for NH_3 and CH_4, respectively, using sulphuric acid. Acidification of slurry can also be achieved by means of *in-situ* or *ex-situ* natural fermentation of carbohydrates or sugars. Bastami et al. (2016) achieved reductions in NH_3 emissions by introducing brewers' grain to pig slurry, which produced lactic acid and resulted in a lowering of the pH and a reduction in emissions of up to 42%. Prado et al. (2020) achieved 50–60% reductions for CH_4 using sugar and a whey by-product.

The aim of the "circular economy" concept is to gradually decouple growth from the consumption of finite resources and adopt a better utilisation of those resources (Scheel et al., 2020). Approximately one quarter of all global food production is lost or wasted globally (RedCorn et al., 2018; IPCC, 2019) and their upcycling could address the requirements for a circular economy (Toop et al., 2017; Antoniou et al., 2019). A major component of the circular economy is the environment and potential benefits gained from more efficient use of resources. Agricultural wastes such as dairy washings or brewers' grain, generated at production, post-harvest and processing stages, may have potential for use in the remediation of gaseous emissions. Waste streams within food production chains have the potential to reduce NH_3 and GHG (Gilhespy et al., 2009). To date, only a few studies have assessed GHG and NH_3 emissions from cattle slurry amended with agricultural waste. Bastami et al. (2016) concluded that a 7% inclusion of spent brewers' grain resulted in the reduction of pH and subsequent reduction in CH_4 of 70% compared to a study control, and also found that a 7.7% addition of milk resulted in an 31% reduction in CH_4 emissions. Clemens et al. (2002) found that the addition of sugar beet residues resulted in a lowering of pH and a reduction of NH_3 emissions by between 5% and 26% compared to a study control.

Another mitigation strategy that would be practical in an Irish context is the use of beneficial microorganisms and bacteria that may potentially reduce the emissions from slurry storage. Although relatively little experimental work has been completed to investigate their efficacy, McCrory and Hobbs (2001) reported some promising results with a reduction in CH_4 of 8% over a 24-hr period with commercially available additives, also known as "slurry enhancers/conditioners". Amon et al. (2005) found that the use of "effective" or "specific" microorganisms reduced emissions over the duration of a 120-d incubation study. Provolo et al. (2016) found that a commercially available additive resulted in the quicker stabilisation and crust formation of slurry over a 115-d period. Kuroda et al. (2017) identified specific nitrogen inhibiting microorganisms in a product identified as TaT105 and inoculated slurry to achieve a 20% reduction in NH_3 emissions over a 28-d period. Lavanya et al. (2020) achieved savings up to 98% using a microbial consortium in combination with seaweed over a 10-d period; however, this incubation was at 25 °C and it is unclear whether the microbial community would be as prevalent in more temperate conditions. McCory and Hobbs (2001) also identified bacterial additives as a potentially economically viable option for slatted housing units to reduce both NH_3 and GHG emissions, provided a critical size of microbial population can be established. However, knowledge gaps with regards to crust formation, ease of agitation, nutrient value of slurry, and emissions reduction still exist.

Previous studies have shown that chemical amendments, such as ferric chloride ($FeCl_3$), are effective amendments that reduce pH with CH_4 and NH_3 reductions of up to 98% and 97%, respectively, once an initial pH of 5.5 is achieved (Kavanagh et al., 2019). Qasim et al. (2017) and Li et al. (2008) reduced NH_3 emissions by between 80% and 87%, as well as having potential benefits for reduction of phosphorus run-off once applied to land (Brennan et al., 2011). However, it is unclear whether effective reductions can be achieved at a higher pH, using a lower inclusion, as it was noted by Kavanagh et al. (2019) that despite an increase in pH throughout the inclusion period, the daily emission fluxes did not increase, meaning that the reduction of emissions could potentially be independent of pH. If so, this would subsequently reduce the initial inclusion cost, as well as reduce labour and agitation times.

This study investigates the efficacy in GHG and NH_3 reduction from dairy cattle slurry using waste products derived from agriculture and associated industry, commercially available bacterial additives, and $FeCl_3$, at different inclusions during storage in a temperate climate. The identification of effective, low-cost amendments capable of simultaneously reducing GHG and NH_3 emissions from slurry in storage has both practical and economic implications for the farmer in terms of costs to implement and the potential to add agronomic value, as the N content of slurry is retained and possibly improved during storage. Therefore, the objectives of this study were to (1) assess the efficacy of various wastes, commercial and chemical amendments to slurries in the reduction of GHGs and NH_3 and (2) evaluate the cost of using these amendments to achieve greatest reductions.

2. Materials and methods

2.1. Slurry collection

Slurry for the incubation experiments was collected from an underground storage tank, with a total capacity of 60 m^3, on a commercial beef and dairy farm in the south-east (52°23′8 N 6°22′ W) of Ireland. Prior to collection from the storage tank, the slurry was thoroughly mixed using a mechanical agitator. The dry matter (DM) of the slurry was measured using a slurry hydrometer (Moral et al., 2007; Suresh et al., 2009), and was found to be 8.4% prior to sampling. The slurry was immediately hand sieved through a 9.5 mm-sized mesh sieve to ensure homogeneity and to remove any foreign or undigested material. Sieving did not impact the DM or elemental characteristics of the slurry. A DM content of 7% was recorded after sieving using an oven dry technique as described by Gislon et al. (2020). This represents the average DM measured across most beef farms in Ireland (Hyde and Carton, 2005). Minimal foreign or undigested material was removed during the sieving process. Slurry used in the incubations originated from animals on a typical diet consisting predominantly of grass silage in the form of ensiled or bailed ryegrass, with supplemental protein and grain consisting of 54% barley, 8% soybean meal and 38% beet pulp.

2.2. Amendment selection

Three amendment types were investigated in this study

(Table 1): waste and four commercial products, and a chemical amendment ($FeCl_3$), which had previously been proven to be effective in NH_3 and GHG reductions from homogenised cattle slurry (Kavanagh et al., 2019). The four commercial products selected had the following active ingredients: sporomusa, flexibacter, cytophaga, bacteroides, clostridium, coccoides, botulinum, ferric chloride and calcium chloride. They are identified as A1, A2, A3 and A4 hereafter, due to commercial sensitivity. They were selected due to their popularity in the Irish market and relative availability. These amendments are recommended by the manufacturers to be incorporated in the slurry for at least three months.

2.3. Experimental setup and analyses

Three laboratory-scale incubation experiments were conducted in a temperature-controlled growth chamber (Temperature Applied Science Ltd., West Sussex, U.K.) over a period of up to 116 d (Table 1). These comprised experiments using waste agricultural materials (total duration, 70 d), commercial products (117 d) and $FeCl_3$ (117 d). Temperature (10 °C) and humidity (60%) were selected to replicate standard environmental conditions within storage tanks in Ireland during the winter period.

For each treatment, 1.6 L of slurry was first added to 2 L capacity containers, to which the amendments were then added. The experimental treatments were replicated at n = 3. The volume of amendment added per volume of slurry, referred to hereafter as “inclusions” (Table 2), were selected either to cover as wide a range as possible (7% and 15% for some of the wastes which had not previously been examined), or based on previous experimental results (i.e. sugar beet (*Beta vulgaris*); Bastami et al., 2016), or due to limited availability of the source material (dairy waste). The inclusions of commercial products were based on manufacturers’

Table 1

Chemical characteristics of amendments and control slurry at Day 0–70 and Day 0–116 for commercial and chemical amendments. ‘Start’ refers to the beginning of the experiment and ‘End’ refers to the final day of the experiment. % inclusion refers to amount added per 1.6 L of slurry.

Amendment	Treatment	% Inclusion[a]	Time	Slurry Characteristics		
				TN (g N kg^{-1})	TC (g C kg^{-1})	TAN (g N kg^{-1})
Waste	Apple pulp	7	Start	3.4	38.4	2.10
			End	3.0	39.2	1.11
	Apple pulp	15	Start	2.8	45.2	1.89
			End	3.3	38.9	1.37
	Brewers grain	7	Start	3.5	40.0	2.08
			End	3.0	38.0	1.29
	Brewers grain	15	Start	4.0	40.6	2.03
			End	3.3	38.0	1.35
	Dairy washings	7	Start	3.1	40.2	2.05
			End	3.0	39.3	1.40
	Dairy washings	15	Start	2.8	40.9	1.98
			End	3.1	36.8	1.18
	Dairy waste 1	10	Start	2.9	40.7	2.07
			End	3.0	39.5	1.15
	Grass silage	7	Start	3.2	41.0	2.46
			End	3.0	38.7	1.38
	Grass silage	15	Start	3.7	38.3	2.85
			End	3.3	38.0	1.71
	Maize silage	7	Start	3.4	38.7	2.33
			End	3.0	41.9	1.25
	Maize silage	15	Start	3.1	40.4	1.57
			End	3.3	38.7	1.39
	Sugarbeet molasses	3	Start	2.9	40.7	2.49
			End	3.3	38.2	1.32
	Sugarbeet molasses	5	Start	3.5	38.9	2.73
			End	3.0	39.6	1.59
	Sugarbeet molasses	7	Start	2.8	43.6	2.85
			End	3.1	38.4	1.70
	Control[b]	–	Start	3.1	38.4	2.24
			End	3.0	39.8	1.08
Commercial	A1	RA[c]	Start	2.8	35.9	1.79
			End	2.8	32.8	0.85
	A2	RA	Start	3.5	32.8	1.63
			End	3.1	33.9	0.80
	A3	RA	Start	3.0	28.7	1.74
			End	3.1	34.0	0.85
	A4	RA	Start	3.3	35.4	1.70
			End	3.3	28.2	1.21
Chemical	Ferric chloride	1.1	Start	2.9	33.3	1.73
			End	2.9	33.1	0.93
	Ferric chloride	0.9	Start	3.0	34.0	1.97
			End	2.9	33.2	1.03
	Ferric chloride	0.38	Start	3.2	35.4	1.70
			End	2.8	35.1	0.87
	Control	–	Start	3.3	39.4	1.65
			End	3.1	34.0	0.83

TN: total nitrogen, TC: total carbon, TAN: total ammonical nitrogen.

[a] Same control was used for both commercial and chemical products.

[b] Inclusion % indicates the amount of amendment added per 1.6 L of slurry.

[c] RA, recommended amount as per product instructions.

Table 2
Amendment characteristics, addition rates and current use.

Amendment	Treatment	Amendment characteristics	Stoichiometric addition	Addition rate	Source/variety	Current end use	Handling and processing	Days of incubation
		DM %	g/kg	g amendment/g slurry DM				
	Control slurry	7	0				Sieving[a]	70/116
Waste	Apple pulp	26	70	1.32	*Malus domestica*	Compost	Sieving[a]	70
	Apple pulp	26	150	1.32				70
	Brewers grain	50	70	1.98	Olympus and Propino	Animal feed	Sieving[a]	70
	Brewers grain	50	150	1.98				70
	Dairy washings	4	70	1.1	On farm	Waste water	No	70
	Dairy washings	4	150	1.1				70
	Dairy waste 1	6	100	1.9	Creamery	Disposed of	No	70
	Grass Silage	9	70	0.8	On farm	Waste water	No	70
	Grass Silage	9	150	0.8			No	70
	Maize silage	10	70	0.87	On farm	Waste water	No	70
	Maize silage	10	150	0.87			No	70
	Sugarbeet molasses	76.8	30	1.33	Co-op	Feed additive	No	70
	Sugarbeet molasses	76.8	50	1.33			No	70
	Sugarbeet molasses	76.8	70	1.33			No	70
Commercial	A1	98	0.5	1.6	Commercial	Slurry additive	No	70
	A2	94	0.4	0.3	Commercial	Cubical disinfectant	No	116
	A3	–	8	0.12	Commercial	Slurry additive	Dilution[b]	116
	A4	–	0.2	0.12	Commercial	Slurry additive	Dilution[b]	116
Chemical	Ferric chloride	91	6.6	4.42	Commercial	Water treatment	No	116
	Ferric chloride	91	9.8	4.42	Commercial	Water treatment	No	116
	Ferric chloride	91	18.4	4.42	Commercial	Water treatment	No	116

[a] 10mm sieve was used for the more fibrous material.
[b] Dilutions were conducted as per manufacturers specification. One inoculation on day zero.

instructions and recommendations. The inclusions for $FeCl_3$ were based on previous work by Kavanagh et al. (2019).

To replicate *in situ* housing/storage conditions, each container was covered with a lid between sampling periods, which was perforated with twelve 2 mm-diameter holes. These holes simulated air flow in large-scale slatted storage tanks used on commercial livestock farms having the same ratio of air space. To ensure that the airflow across all containers was similar, they were placed in the centre of the growth chamber underneath the circulation fans, and divided into a randomised block design. The weight of each pot was measured weekly and the results indicated that the same level of evaporation occurred across all containers and blocks.

The slurry was characterised at the beginning and end of the experiment for total ammoniacal nitrogen (TAN), total nitrogen (TN) and DM. The TAN 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 subsample was dried in an oven at 105 °C for 24 h. For the waste amendments, measurements of NH_3 and GHG emissions were conducted every 2 d for the first two weeks of the experiment, followed by measurements once-a-week until the end of the experiment (d 70). For the commercial and chemical amendments, measurements of NH_3 and GHG emissions were conducted every 7 d throughout the duration of the experiment (d 116). Measurements of pH using the waste products were conducted every 4 d, whereas for the commercial and chemical amendments pH readings were taken every 7 d. All pH measurements were performed using a pH meter (JENWAY 1510, Straffordshire, UK). The weight of the containers and slurry volume were measured every 7 d and DM was measured at the start and end of the incubations.

2.4. Analytical methods and calculations

Ammonia emissions for all treatments were monitored using a dynamic chamber system, previously described in Kavanagh et al. (2019). Headspace samples were drawn by a Gasmux multiplexer GM3000 (IMT Vohenstrauss, Germany) and concentrations analysed with a photoacoustic INNOVA 1412 field gas-monitor (LumaSense Technologies, Denmark). Ammonia measurement time was a period of 15 min per sampling. Glass wool soaked with oxalic acid (0.05 M) was used to strip moisture from the background air entering the photoacoustic monitor. Ammonia fluxes (F_j in mg m^{-2} h^{-1}) were calculated using Eq. (1) in Kavanagh et al. (2019):

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

where Q is the airflow rate through the chamber (m^3 h^{-1}), $Cex.j$ is the NH_3 concentration of air exiting the chamber (mg m^{-3}), $Cin.j$ is the NH_3 concentration of air coming into the chamber (mg m^{-3}), and A is the emitting surface area (m^2).

Greenhouse gas emissions were measured using a retro-fitted static chamber technique, as described in Kavanagh et al. (2019). The containers were sealed and the solid lid modified with a rubber septum (Becton Dickinson, Oxford, U.K.). Gas samples (10 ml) were taken at 0, 5 and 10 min after the container was closed using a polypropylene syringe (BD Plastipak, Oxford, UK). The resulting gas samples were analysed for CH_4, CO_2 and N_2O 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 concentrations in the containers over time was used to determine the gas flux (adapted from Kelliher et al., 2013):

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

where ∂C is the change in gas concentration in the chamber headspace during the enclosure period in ppbv or $\mu l l^{-1}$, ∂T is the enclosure period expressed in days, M the molar mass of the gas element, P is the atmospheric pressure in Pa, R is the gas constant, and T is the temperature in Kelvin, V the headspace volume of the closed chamber in m^3, and A the area covered by the collar of the gas chamber (m^2).

2.5. Cost-benefit analysis of amendments

Each of incubation experiments had an associated cost in terms of the amendment price, handling and delivery. The marginal abatement cost of these amendments was calculated based on the method used in Kavanagh et al. (2019). Briefly, it was projected that slurry was treated at the following stoichiometric rates: alum 1.11:1 (Al:TP); aluminium chloride ($AlCl_3$) or PAC 0.93:1 (Al:TP); $FeCl_3$ 2:1 (Fe:TP). The annual cost of each amendment, including spreading and labour costs, were estimated for each amendment, minus fertilizer savings achieved. Each of the amendments was compared to the cost of one tonne of calcium ammonium nitrate (CAN) at €0.81 per kg N (CSO, 2020). The price of CAN has fluctuated in recent times, so this price is the average for 2018 and 2019. The waste products had no direct purchase costs; however, secondary costs such as transport and agitation were added. Transport for apple pulp, brewer and dairy industry by-products were calculated based on a mean transport distance of 75 km for a double-axle truck with a fuel consumption of 0.36 L per km, a fuel price of at €1.35 per litre and a load capacity of 18 tonnes. No transport cost was assumed for grass silage effluent or dairy washings as these are sourced directly on farm, and a 37 km transport distance was assumed for maize silage as the majority of maize is bought in as feed. A standard cost of agitation of € 0.07 h^{-1} m^{-3} was assumed based on a € 30 hr^{-1} cost for a 398 m^3 tank. Once this was achieved, the total cost of each amendment was subtracted from the savings achieved and the net cost/saving was divided by the emissions reduction (per kg NH_3 and per kg CO_2 equivalent).

2.6. Statistical analysis

Statistical analyses were carried out using SAS 9.4 (2002–2010) (SAS Institute Inc., USA). Slurry NH_4^+, NO_3^- and pH were analysed by ANOVA with measurement day included as a repeated measure in the model. 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 was the independent variable and replicate was a random term). 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 waste amendments and commercial products on slurry pH over time

The effect of waste products on pH may be divided into two response curves, immediate acidification and delayed acidification (Fig. 1). Immediate and significant ($p > 0.05$) reduction in pH was noted for grass silage effluent and maize silage effluent (both at 15% inclusions). These waste products are acidic by nature, as they are the result of bacterial sugar fermentation (Kung and Ranjit, 2001). A delayed acidification curve was noted for apple pulp (at 15% inclusion), reducing to pH 5.1 between d 8 and 42 and sugar beet molasses (at 3%, 5% and 7% inclusions) reducing to pH of 5.9, 5.3 and 4.6, respectively, during the same time period. Sorensen et al. (2012) reported that the reduction of pH using sugar beet molasses required an inclusion of a minimum of 3% to supersede the buffering capacity of the slurry. Bastami et al. (2016) inoculated cattle slurry with apple pulp and concluded that the lag phase was a result of the lack of microbial build-up, and the resistance of the slurry to acidify was due to buffering capacity, such that a critical mass has to be reached whereby the production of lactic acid secreted by the bacteria outweighs the buffering capacity of the slurry. Brewers' grain, dairy washings, dairy waste and grass silage effluent (at 7% inclusion) were ineffective at reducing pH to the minimum target pH of 6.

Commercial products were ineffective at reducing pH (Fig. 1) below the initial control pH of 7.0 on d 0. While commercial products A1, A2, A3 and A4 had initial pH values of 6.8, 6.9, 7.1 and 7.2, respectively, treatments were comparable with the control pH throughout the experiment, except for A4 which maintained a slight reduction at pH 6.6 for 18 d. This was statistically insignificant over the course of the incubation. This result was expected as microbial additives do not alter the pH of slurry *per se*, with the exception of A4, which contained a small amount of $FeCl_3$, accounting for the initial pH reduction. This was in agreement with the work of Amon et al. (2005, 2006), who also reported no reduction in pH post treatment using bacterial additives. All inoculations of $FeCl_3$ resulted in immediate reductions of pH on d 0 (Fig. 1). However, the buffering capacity of the slurry had an immediate effect in raising pH from d 3 onwards for the lower addition of 0.38. The 1.1% inclusion maintained a pH below 6 for 18 d, similar to the results of Kavanagh et al. (2019).

3.2. NH_3 emissions during storage

Of the waste products examined, sugarbeet molasses (at 5% inclusion) was most effective at reducing the NH_3 emissions, achieving a 67% reduction (49.59 g NH_3 m^{-2}) compared to the control (151.45 g NH_3 m^{-2}) ($p < 0.05$) (Fig. S1 in the Supplementary Information). However, sugarbeet molasses at a higher inclusion (7%) increased cumulative NH_3 emissions relative to the study control. This may be a result of the vigorous fermentation experienced during the storage period, as foaming was observed from d 20 until d 60. Clemens et al. (2002) also noted foaming during incubation, using sugar beet molasses at a 9% inclusion, resulting in higher NH_3 emissions than the control. The daily cumulative flux of sugar beet molasses at 1.1% inclusion was lowest on d 0, but gradually increased over the course of the incubation (Fig. 2), notably from d 20, and was correlated ($r = 0.7$) with the rapid decrease experienced in pH over the same time period (Fig. 1). However, when the effect of the brewers' grain amendment is compared with the results of Bastami et al. (2016), a much lower reduction in NH_3 was achieved in the current study. This effect can be explained by comparing the relative change in pH below 5.5 in

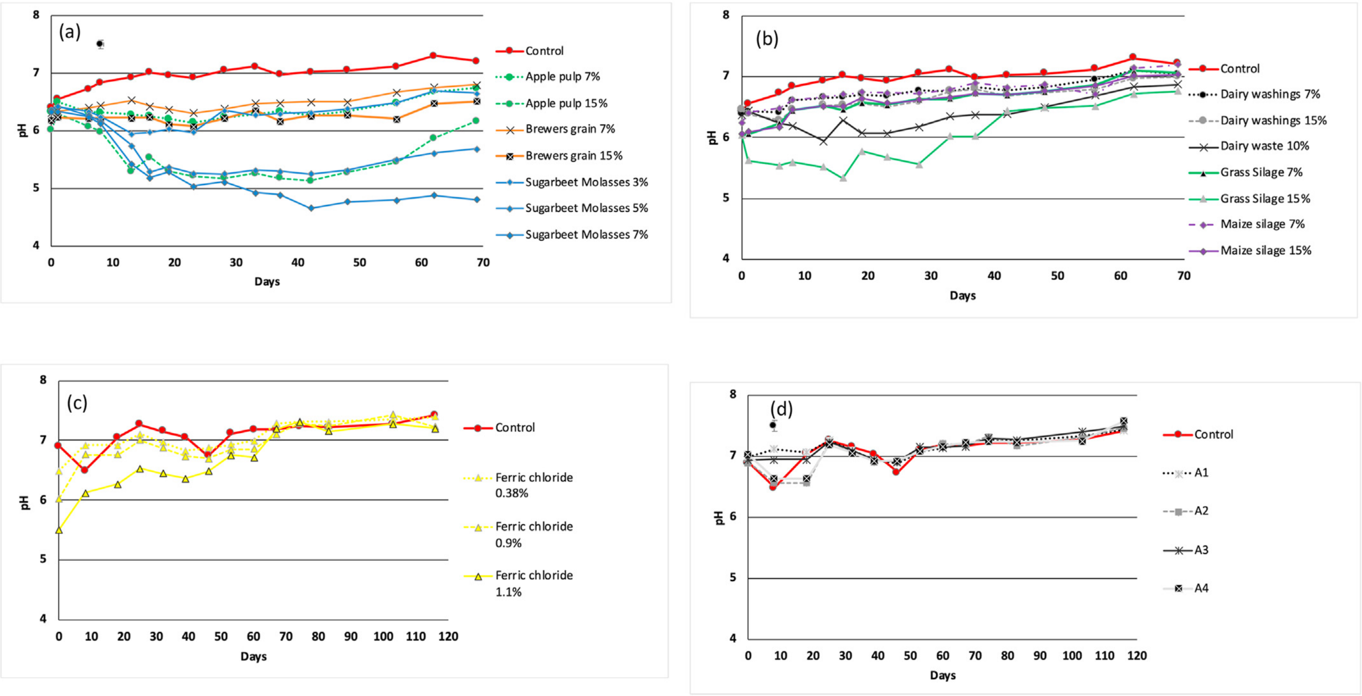

Fig. 1. Changes in pH over time for (a and b) waste products over 70 days, (c) chemical products over 117 days, and (d) commercial products over 117 days. Error bars indicate pooled standard error of the mean.

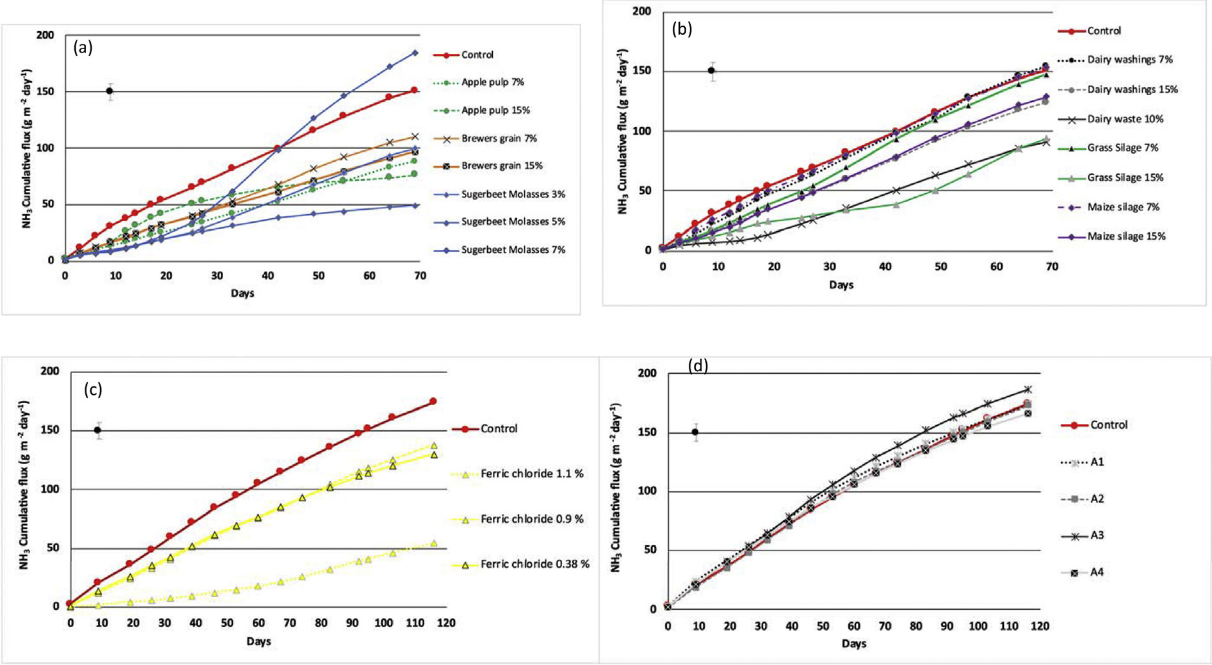

Fig. 2. NH_3 cumulative daily fluxes over time for (a and b) waste products over 70 days, (c) chemical products over 117 days, and (d) commercial products over 117 days. Daily flux error bars indicate pooled standard error of the mean.

Bastami et al. (2016) compared to the lowest value of 6 experienced in the current study. None of the brewers' grain inoculation used in this study significantly reduced slurry pH. The reason for the large difference between these two studies is due to the differing characteristics of the grain sugar content. Where Bastami et al. (2016) recorded a sugar value of 56 g/100 g, the brewers' grain used in the current study had a value of <0.2 g/100 g (Table 3). Fresh brewers' grain has a corresponding sugar content of approximately half its dry weight (Stojceska and Ainsworth, 2008; Mussatto, 2014). However, the grain used in this study was ensiled and it is hypothesised that the fermentation process consumed the majority of the available sugars, resulting in a reduced microbial fermentation once added to the slurry. The length of time the grain was ensiled for could have enhanced the difference in its characteristics

Table 3
Analysis of waste amendments for sugar content.

Amendment	Sugar content (as sucrose) (g/100 g)
Sugarbeet molasses	45.2
Apple pulp	4.9
Brewers grain	<0.2

between the two studies (three months compared to less than one week). Amendments with high sugar content, such as apple pulp 15% and sugarbeet molasses 3% and 5%, had similar fluxes to the control at d 0 until d 14 (Fig. 2), when fluxes started to decrease in line with pH decreases. As the buffering capacity of the slurry began to increase the pH, the daily fluxes increased. This is similar to the trends observed by Amon et al. (2005) and Misselbrook et al. (2016) using a range of acidifiers.

Commercial amendments had no significant impact on cumulative NH_3 emissions compared to the control (Fig. S1), with similar TAN losses for the incubation period (Table 4). However, these amendments are recommended by the manufacturer to be incorporated into the slurry for a minimum of two to three months before any NH_3 reduction may be observed. Although there was a reduction in daily fluxes over time, this was in line with the reduction seen in the daily NH_3 flux of the control, and was likely due to the depletion of the available NH_4^+ pool. These results are similar to those reported by Amon et al. (2006), who also found no correlation between microorganisms and NH_3 reductions, and Provolo et al. (2016), who found that there was no impact on NH_3 emissions in a 155-d incubation using bacterial additives. Ferric chloride had a significant impact on cumulative NH_3 emissions compared to the control, with the 1.1% inclusion resulting in a 70% reduction compared to the control (Fig. S1). This is a similar result to Kavanagh et al. (2019).

3.3. CH_4 emissions during storage

Grass silage effluent (at a 15% inclusion) was the only amendment to significantly ($p < 0.05$) reduce cumulative CH_4 emissions over the 70-d incubation (Fig. S2), with the majority of the reduction occurring up to d 40. This was concurrent with an increase in pH to above 6 after d 40 (Fig. 1). For the remaining amendments, the fermentation and breakdown of this organic material resulted in the majority of the emissions occurring between d 10 and 40 of the experiment (Fig. 3). The amendments not only contained readily available sugar in the form of fructose, glucose and sucrose (MacLeod et al., 1953), but also increased the carbon pool in the slurry (Rico et al., 2012; Malakhova et al., 2015), which is important as the proportion of carbon to N ratio determines the quantity of the microbial community present (Das et al., 2017). The daily temporal fluxes show that the lower amendments for sugarbeet molasses, brewers' grain, apple pulp and silage effluent resulted in the highest cumulative readings. The higher inclusions followed the same increasing pattern of CH_4 emissions for the first 10 d until a plateau occurred, which was when the pH reduced. Clemens et al. (2002) hypothesised that once the bacteria have reached critical mass after around d 21, the subsequent population decrease results in the drop off in daily fluxes. The range of CH_4 fluxes in this study were similar to those found by Bastami et al. (2016).

Commercial amendments produced no decrease in cumulative CH_4 emissions over the incubation period (Fig. S2). Daily fluxes were unaffected compared to the control for the duration of the experiment and followed a similar cumulative flux to the control. The only slight increase in the flux occurred on d 110, which was caused by the destruction of the crust to determine the pH of the slurry.

Ferric chloride inclusions of 1.1% significantly ($p < 0.05$) decreased cumulative CH_4 to 94.9 gm^2 emissions relative to the control 273.6 gm^2 (Fig S2). This was equal to a ~65% reduction and was similar to the results reported by Kavanagh et al. (2019). It confirms the study hypothesis that a specific and high enough inclusion is needed to decrease CH_4 emissions significantly. The results also indicate that once this dosage is achieved, emissions are relatively unaffected by the pH increases over time. Ferric chloride at a 0.9% inclusion resulted in no impact on emissions; however, the lowest dosage of 0.3% resulted in a significant increase ($p < 0.05$) in CH_4 production from d 0 onwards. This would indicate that the methanogen microbial community interacted positively with the

Table 4
Percentage of total ammonical nitrogen (TAN) lost as ammonia (NH_3).

Amendment	Treatment	Cumulative NH_3 g m^{-2}	Average NH_3 g m^{-2} hr^{-1}	% NH_3 loss/TAN*
Waste products	Control	151.4	6.3	42.2
	Apple pulp 7%	76.4	3.1	22.7
	Apple pulp 15%	88.2	3.6	29.2
	Brewers grain 7%	110.3	4.5	33.3
	Brewers grain 15%	96.8	4.0	29.8
	Dairy washings 7%	154.4	6.4	47.2
	Dairy washings 15%	124.6	5.1	39.5
	Dairy waste 10%	90.7	3.7	27.4
	Grass Silage 15%	93.8	3.9	23.9
	Grass Silage 7%	147.4	6.1	32.4
	Maize silage 15%	129	5.3	34.6
	Maize silage 7%	153.6	6.4	61.3
	Sugarbeet Molasses 3%	99.8	4.1	25.1
	Sugarbeet Molasses 5%	49.5	2.0	11.3
	Sugarbeet Molasses 7%	184.8	7.7	40.5
Commercial	Control	174.0	7.2	66.1
	A1	173.7	7.2	60.7
	A2	172.8	7.2	66.2
	A3	186.6	7.7	67.0
	A4	166.2	6.9	61.2
Chemical	Ferric chloride 0.39	130.2	5.4	47.2
	Ferric chloride 0.9	138.0	5.7	43.9
	Ferric chloride 1.1	54.8	2.2	20.2

% NH_3 loss: amount of N lost per day.

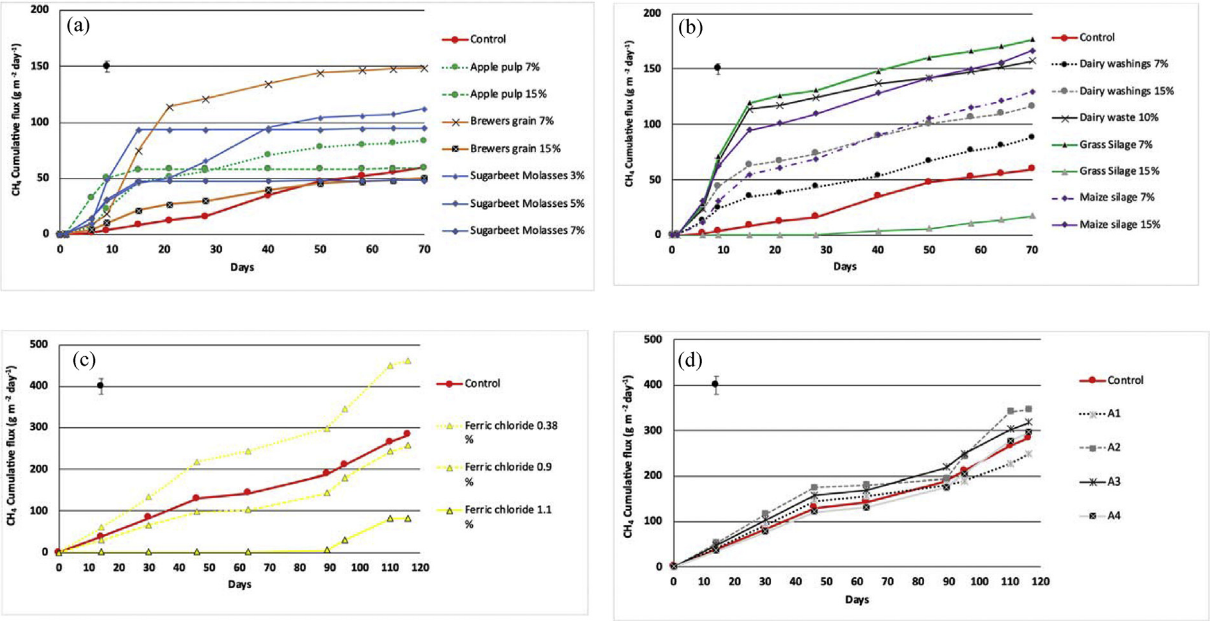

Fig. 3. CH_4 cumulative daily fluxes over time for (a and b) waste products over 70 days, (c) chemical products over 117 days, and (d) commercial products over 117 days. Daily flux error bars indicate pooled standard error of the mean.

0.3% inclusion. It is hypothesised that the instant formation of a crust on d 0 created anaerobic or hypoxic conditions, without an impact on pH reduction, allowing for the microbial population to exponentially grow and increase CH_4 formation.

3.4. CO_2 emissions during storage

As no microbial analysis was undertaken, CO_2 production can be used as in indicator to ascertain the strength and activity of the methanogens and other microorganisms present over the duration of the experiment. Grass silage, at a 15% inclusion, was the only waste amendment to have no impact on CO_2 emissions (Fig. S3). The remaining amendments increased emissions, which is a result of the microbial communities as they break down the substrates and reproduce (Geyer et al., 2016). The temporal emission pattern indicated an upward trend from d 10 across all waste amendments (Fig. 4), which was similar to results reported in Bastami et al. (2016).

Slurry amended with the commercial amendments showed no significant difference ($p > 0.05$) in CO_2 fluxes compared to the control over the 116 d (Fig. S3). This indicates that these bacterial additives did not increase the population density of the slurry, resulting in similar emissions to the control.

Ferric chloride, at the lower inclusions of 0.38% and 1%, resulted in CO_2 fluxes not significantly different to the control ($p > 0.05$). However, $FeCl_3$ at a 1.1% inclusion did have a significant impact on emissions when compared to the control. Carbon dioxide production was not impacted as greatly as CH_4, with CO_2 daily fluxes remaining relatively low for the duration of the study. This finding suggests that $FeCl_3$ is specifically affecting methanogens; however, it is not completely depleting the other microbial communities present.

3.5. Crust observation

Of the waste products examined, silage effluent, maize silage effluent, dairy washings and dairy waste led to only minimal crust formation, similar to that of the control. In all these cases, the inclusions of 15% produced slightly thinner crusts of 0.5–1 cm compared to the lower inclusions. Sugarbeet molasses had no measurable impact on crust formation, irrespective of dose when compared to the control. Brewers' grain was observed to form a 2–3 cm crust almost immediately due to the higher DM of the amendment. However, this reduced throughout the sampling period. Apple pulp resulted in differing crusting formations depending on the inclusion: the 7% inclusion formed a crust almost immediately, but reduced over the study duration, whereas the 15% inclusion gradually produced a 3 cm crust over the study duration. These observations of crust formation and the quicker formation of crusts by slurries of higher DM was also observed by Misselbrook et al. (2005) and Li et al. (2008), who observed a direct correlation between slurry DM and crust formation. In the current study, the slurry was disturbed on an almost weekly basis to carry out pH analysis. Although this disturbance was minimal and located to a small section of the pot to facilitate accurate pH readings, it may have reduced the effectiveness of this natural barrier. Smith et al. (2007) also noted that a reduction of up to 60% NH_3 could be achieved despite regular disturbance in the form of agitation and transport, and that crusts were found on 80% of sampled farms.

There was no difference in crust thickness between the commercial additives and the control over the study duration. This is in contrast to Provolo et al. (2016), who noted an ease of agitation once the 155-d incubation had concluded, and Zhu et al. (1996), who made a similar observation after completing an 84-d incubation.

Ferric chloride resulted in the formation of an immediate crust for all treatments on d 0; however, the thickness for $FeCl_3$, at a 0.38% inclusion, was only 2 cm compared to the 3.5 cm and 4 cm achieved by $FeCl_3$ at a 0.9% inclusion and $FeCl_3$ at a 1.1% inclusion, respectively. This crust thickness was not affected over the duration of the experiment, which would indicate that even at the lowest rate the flocculation ability of $FeCl_3$ is sufficient to create an immediate crust and natural barrier which would make it applicable for lagoon and storage usage.

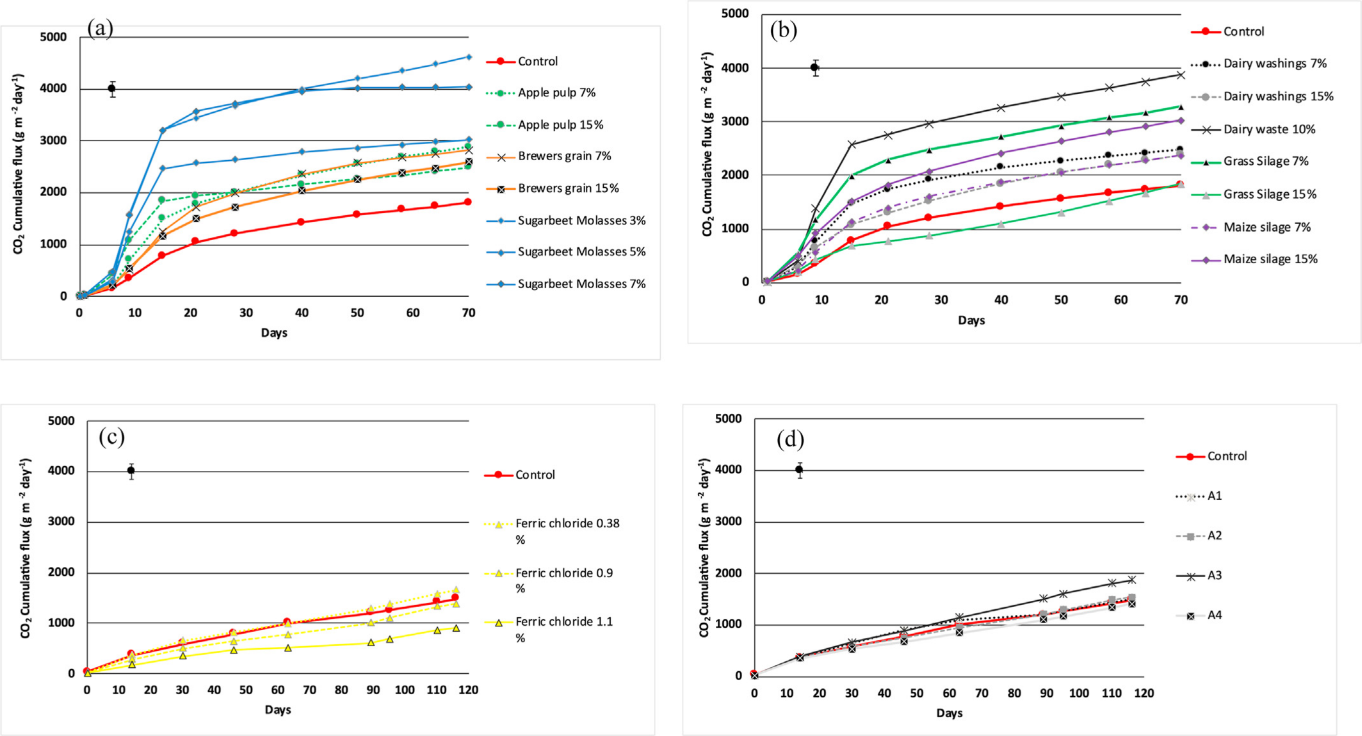

Fig. 4. Changes in carbon dioxide (CO_2) over time for (a and b) waste products over 70 days, (c) chemical products over 117 days, and (d) commercial products over 117 days. Error bars indicate pooled standard error of the mean.

Table 5
Marginal abatement costs (€ kg^{-1}N € kg^{-1}CO_2e) and associated with the mitigation of ammonia and GHG from slurry treated with amendments. In the case of enhanced emissions associated with amendments, marginal abatement was not applicable (na).

Amendment	Amendment Cost (€ t^{-1} slurry)	Inclusion rate (kg t^{-1} slurry)	Agitation cost (€ t^{-1} slurry)	Transport cost (€ t^{-1} slurry)	Amendment Rate (Kg t^{-1} slurry)	Gross Cost (€ t^{-1} slurry)	Mitigation cost (€ kg^{-1}NH_3)	Mitigation cost (€ kg^{-1}CO_2e)
Apple pulp	0	70	0.08	2.03	71.5	2.10	0.13	na
Apple pulp	0	150	0.08	2.03	153.2	2.10	0.51	na
Brewers grain	0	70	0.08	2.03	71.5	2.10	0.88	na
Brewers grain	0	150	0.08	2.03	153.2	2.10	0.52	na
Dairy washings	0	70	0.08	0.00	71.5	0.08	na	na
Dairy washings	0	150	0.08	0.00	153.2	0.08	−0.46	na
Dairy waste 1	0	100	0.08	2.03	102.1	2.10	0.38	na
Grass Silage	0	70	0.08	0.00	71.5	0.08	−0.28	na
Grass Silage	0	150	0.08	0.00	153.2	0.08	0.12	0.002
Maize silage	0	70	0.08	1.01	71.5	1.09	0.63	na
Maize silage	0	150	0.08	0.00	153.2	0.08	na	na
Sugarbeet Molasses	0	30	0.08	2.03	30.6	2.10	0.42	na
Sugarbeet Molasses	0	50	0.08	2.03	51.1	2.10	0.14	na
Sugarbeet Molasses	0	70	0.08	2.03	71.5	2.10	na	na
A1	300	0.5	0.08	2.03	0.5	2.25	na	0.14
A2	305	0.4	0.08	2.03	0.4	2.23	na	na
A3	315	8	0.08	2.03	8.2	4.67	na	na
A4	300	0.2	0.08	2.03	0.2	2.16	na	na
Ferric chloride	229	6.6	0.08	2.03	6.7	3.64	na	na
Ferric chloride	229	9.8	0.08	2.03	10.0	4.39	4.46	0.34
Ferric chloride	229	18.4	0.08	2.03	18.8	6.40	1.80	0.05

3.6. Cost-benefit analysis of amendments

The marginal cost of abatement associated with all amendments is shown in Table 5. In terms of NH_3 abatement, the gross cost per tonne of slurry ranged from €0.08 for dairy washings and silage effluent to €6.40 for $FeCl_3$ addition (for a target pH 5.5). When the cost saving in terms of N fertilizer were factored in and priced in terms of mitigation potential, the marginal costs ranged from a cost saving of €0.46 kg^{-1} NH_3 form dairy washings to a cost of €4.46 kg^{-1} NH_3 for $FeCl_3$. Most measures were > €2 kg^{-1} NH_3, which is low in terms of the range of abatement costs observed in other studies (Reis et al., 2015; Lanigan et al., 2015). EU-wide marginal abatement costs have generally been estimated at circa €4 kg^{-1} NH_3 (Reis et al., 2015), while Irish NH_3 abatement cost for individual measures has previously been estimated at €2.98 kg^{-1} NH_3 (Lanigan et al., 2015). In terms of GHG abatement, most of the amendments increased CO_2e (either in terms of CH_4, CO_2, or both). Hence, there was no associated marginal abatement cost. Only $FeCl_3$ (at the high rate), A1, and grass silage effluent (at the high rate) reduced CH_4 and/or CO_2. The marginal costs of all three measures were low, with previous studies calculating the mean cost of GHG abatement at circa €14 per t CO_2e for slurry and N-associated measures (Lanigan et al., 2018). It should be noted that if the environmental pollution associated with the enhanced GHG emissions from other amendments were factored in, the associated cost could increase by between €2 to €5 per kg CO_2e (assuming a base cost of €31 t^{-1} CO_2).

3.7. Conclusions

The use of waste amendments can mitigate NH_3 emissions, but have limited benefits in terms of GHG emissions. The largest NH_3 abatement potential was observed for 5% sugar beet molasses (67% reduction), 7% apple pulp (49% reduction), and 7% grass silage (38% reduction). Methane emissions either increased or were similar to the control, with only grass silage at 15% inclusion having a significant reduction on emissions. When all the factors were considered, sugarbeet molasses at a 5% inclusion has the best potential to be used in a larger scale experiment. The use of commercial amendments was only marginally effective at reducing NH_3 and CO_2 emissions, while only commercial amendment A1 substantially reduced methane (25% reduction). These results highlight the importance of investigating expensive commercial products sold on the market, but which have little empirical data to substantiate their claims. Ferric chloride, at a 1.1% inclusion, was found to reduce emissions significantly and is recommended for use at a larger scale. However, this experiment highlights the importance of establishing the correct inclusion, with lower inclusions having a negative impact on cumulative emissions. The importance of measuring multiple parameters when considering the use of an amendment in slurry is highlighted in this study, as the results indicate a potential for pollution swapping if amendments are not chosen correctly.

CRediT authorship contribution statement

I. Kavanagh: Writing - original draft, Writing - review & editing, Data curation, Formal analysis, Visualization. **O. Fenton:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **M.G. Healy:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **W. Burchill:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **G.J. Lanigan:** Conceptualization, Investigation, Methodology, Writing - original draft. **D.J. Krol:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2021.126251.

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