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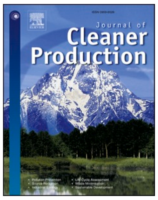

Inhibition of methane production in cattle slurry using an oxygen-based amendment

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ABSTRACT

Cattle slurry storage is a major point source for methane (CH_4) and ammonia (NH_3) emissions globally. Efficacy of an oxygen-based amendment in reducing these emissions was investigated. Two 1.6 kg cattle slurry incubations, each lasting for 40-days, were carried out in a climate-controlled chamber with CH_4 and NH_3 emissions measured. Multiple peroxide sources acting as a source of oxygen were tested to examine how compatible they were for addition to cattle slurry. An amendment comprising of hydrogen peroxide (HP) and potassium iodide (KI) has been highlighted as method to reduce CH_4 emissions from this source. While urea hydrogen peroxide and sodium percarbonate reduced CH_4 emissions, they increased the slurry pH and subsequently NH_3 emissions by 209 and 42%, respectively. Hydrogen peroxide did not infer any pH increase upon the slurry and therefore no increase in NH_3 emissions was observed. Hydrogen peroxide and KI were able to reduce CH_4 emissions by 63% during slurry storage. The use of this treatment on a larger scale system should be considered in the future considering the large reductions achieved.

1. Introduction

Methane (CH_4) is a major greenhouse gas (GHG) with a 20-year global warming potential (GWP) of 72 times that of carbon dioxide (CO_2) and a 100-year GWP of 25 times that of CO_2 (IPCC et al., 2022). The concentration of CH_4 in the atmosphere has risen sharply over the industrial age, from 720 ppb to 1850 ppb today (Prather and Holmes, 2017). Many countries have in the recent past approved legislation to reduce carbon emissions under the Paris Climate Agreement and the EU 2030 Climate and Energy Framework, Ireland in particular pledging a reduction of 51% in GHG emissions by 2030 (Government of Ireland, 2021). Therefore, new mitigation strategies in all sectors and especially agriculture are welcomed.

Ammonia (NH_3) while not a greenhouse gas, contributes indirectly to GHG emissions. NH_3 is quickly absorbed or chemically modified upon volatilization and its effects are typically localised to the areas in which it is released (Kelleghan et al., 2021). Increased NH_3 emissions can lead to acidification of soils through nitrification and may lead to exceeding critical loads of nitrogen deposition on grasslands or more sensitive areas such as peatland (Henry and Aherne, 2013). NH_3 emissions can also lead to particulate matter 2.5 formation within the atmosphere which can lead to increased rates of morbidity and alter cloud formation and lifetimes by acting as cloud condensation nuclei (Sigurdarson et al., 2018). Ireland is required to reduce its NH_3 emissions by 5% to comply with the National Emissions Ceilings Directive (European Environmental Agency).

Agriculture is a major source of both CH_4 and NH_3 emissions, producing approx. 24% of total global anthropogenic CH_4 emissions (IEA, Sources of methane emissions, 2020) and 80–90% of total global anthropogenic NH_3 emissions (Xu et al., 2019). Irish agriculture contributes a larger national proportion of each of these gases with CH_4 responsible for approx. 93% of Ireland's CH_4 emissions (Duffy et al., 2021) and over 99% of NH_3 lost to the atmosphere (Duffy et al., 2021). Therefore, mitigation is hugely important for Irish CH_4 and NH_3 emissions in order to meet our emission reduction targets. According to Buckley et al. (2020), even in a "low activity scenario", Ireland will miss this target if NH_3 mitigation techniques are not implemented.

Manure management leads to significant amounts of both CH_4 and NH_3 being released to the atmosphere during storage in tanks or lagoons and during land application. Manure management in 2021 accounted for 10% of the total GHG footprint within the EU (European Environment Agency). Ireland, for example, is a temperate pasture-based

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system, where cattle are usually only held in slatted sheds over the winter period. Slurry is then held for a period of months in which time CH_4 and NH_3 can be volatilized, increasing GHG emissions and reducing the fertilization value of the slurry. Manure management in this way accounts for 10 and 49% of national agricultural CH_4 and NH_3 emissions respectively (Duffy et al., 2021; FAO, 2020).

This has resulted in the adaptation of practices such as covering slurry with straw, acidification using high purity sulphuric acid and cooling, which have all shown a propensity to reduce both CH_4 and NH_3 emissions becoming increasingly popular (Hansen et al., 2009; Petersen et al., 2012; Webb et al., 2010). These strategies are difficult to implement however, especially in slatted sheds in which accessibility is low.

The reasons therefore to mitigate polluting gases from agricultural sources is two-fold, the first is to inhibit the emission of GHGs which are contributing to climate change and the second is to maintain high levels of nutrients within the slurry that would otherwise be lost to the atmosphere.

Lowering the pH of cattle slurry to 5.5 has been shown to be very effective in reducing CH_4 and NH_3 emissions by 61 and 75%, respectively during storage (Misselbrook et al., 2016). It was also shown that multiple acids such as sulphuric acid, acetic acid and ferric chloride mitigated NH_3 emissions from slurry storage effectively (Kavanagh et al., 2019). However, the use of acid, especially sulphuric acid on large scale on farms highlights safety issues for farmers as well as compatibility issues with other possible GHG mitigating and energy producing technologies such as anaerobic digestion (AD) (Moset et al., 2012). Therefore, a treatment for slurry during its storage that is capable of reducing CH_4 emissions and increasing its compatibility with AD may aid in reducing GHG emissions even further.

Thorn et al. (2022), investigated such a treatment primarily based on the interaction between urea hydrogen peroxide (UHP) and potassium iodide (KI) when mixed into slurry and used it to reduce CH_4 emissions. This combination may utilize multiple strategies, the first of which is a possible iodophor effect gained from the release of free iodine, which can penetrate bacterial and archaeal cell walls and disrupt vital cellular processes (Mckeen, 2012). The second is the decomposition of hydrogen peroxide (HP) which is aided by the use of KI, this can produce a variety of oxidative free radicals in the presence of metal ions (Phaniendra et al., 2015) or simply decomposing to water and oxygen likely providing an increase in the redox potential and dissolved oxygen content (Hjorth et al., 2012).

The objective of this study therefore was to demonstrate the effectiveness of this treatment in mitigating CH_4 emissions without increasing NH_3 emissions as a result. In doing so, this treatment should lead to simultaneously increasing the fertilization value of the slurry and decreasing a significant point source of polluting gases from agriculture.

2. Materials and methods

2.1. Experimental set-up and slurry collection

Two separate experiments took place within a climate-controlled growth-chamber located in Johnstown Castle, Teagasc, Ireland, that were held at 10 °C and 60% humidity in order to simulate typical weather conditions in Ireland during winter slurry storage. Both experiments were incubations of treated and untreated slurry and were carried out using 2-L urine containers (SARSTEDT) (10.6 cm*10.6 cm* 24 cm with a 7 cm diameter opening) filled with 1.6 kg of slurry in order to maintain appropriate headspace for accurate gas measurement. The containers were closed with perforated screw cap lids using ten 1 cm holes to simulate the conditions of a slatted shed.

Both incubation one and two lasted 40 days in total, testing multiple variations of the treatment. All containers were held in a randomised block design. All treatments in both incubations were replicated in triplicate.

Slurry for this work was collected during October 2019 (incubation one) and January 2020 (incubation two) from an underground storage tank with a slatted shed housed above it. The tank was 20 m^3 and was located on a commercial dairy farm. Cattle from this farm were on a diet of predominantly grass silage. Before collection, slurry in the storage tank was thoroughly mixed using a mechanical agitator and immediately after collection was sieved through a 9.5 mm mesh to remove large debris (clumps, rocks and some straw) to ensure homogeneity. The slurry was then held at 4 °C for a maximum of 4 days before being weighed into separate containers.

2.1.1. Incubation one

This experiment investigated the effects of treatment form, concentration and frequency of addition on gaseous emissions and slurry characteristics. A stabilized and solid form of peroxide, UHP was used for incubation one. Varying concentrations of UHP were placed into 30 ml of H_2O along with the KI (Table 1). This mixture was immediately mixed into the slurry to ensure a homogenous combination of slurry and treatment.

The moniker 1X was used to describe 0.43 g of HP and 0.13 g of KI per kilogram of slurry. The effect of higher concentrations was also tested in which the treatments 2X and 3X were used representing double and triple the dose of both compounds per kilogram of slurry (Table 1).

Effect of frequency of treatment was conducted at a single concentration, 2X. F1, F2 and F3 are used to represent treatment application frequencies in descending order. F1 was treated once every week, F2 treated every 2 weeks and F3 treated once during the experimental period.

Two controls were used for the experiment, Control 1 had no agitation or addition of water while Control 2 had both agitation and addition of water as frequently as F1.

2.1.2. Incubation two

The protocol was modified for incubation two, in which the effect of the peroxide source was tested. Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) (SPC), UHP and 33% HP were examined during this incubation. KI was used in conjunction with each peroxide source. The 2X concentration (the same as in incubation one) was used throughout incubation two. All treatments were added every two weeks (Table 2).

Two controls were used for the incubation, Control 1 had no agitation or addition of water, while Control 2 had both agitation and addition of water.

2.2. Sample collection- NH_3/CH_4

NH_3 and CH_4 measurements were taken 4–5 times per week for the first two weeks of each experiment respectively and 2–3 times per week thereafter. NH_3 emissions were measured using a dynamic chamber system that coupled an INNOVA 1412 field gas monitor with a GASMUX multiplexer GM3000. Air entering and leaving the chambers was measured for 16 min per container. Airflow was consistently held at 8 L/min. Air entering the dynamic chamber was stripped of NH_3 and moisture by passing it through glass wool soaked in 0.05 M oxalic acid. Daily

Table 1
List of incubation one treatments alongside amount of UHP (urea hydrogen peroxide), KI (potassium iodide) added per 1.6 kg container. Peroxide added per dose and number of applications that occurred during 40-day incubation also displayed.

Treatment	UHP Added (g)	KI Added (g)	Peroxide per Dose (g)	Number of Applications
1X	1.92	0.214	0.694	3
2X	3.84	0.427	1.389	3
3X	5.76	0.641	2.082	3
F1	3.84	0.427	1.389	6
F2	3.84	0.427	1.389	3
F3	3.84	0.427	1.389	1

Table 2

Incubation two treatments including UHP + KI (urea hydrogen peroxide + potassium iodide), HP + KI (hydrogen peroxide + potassium iodide) and SPC + KI (sodium percarbonate + potassium iodide) added per 1.6 kg container. Peroxide used per dose and number of applications during 40-day incubation also displayed.

Treatments	Peroxide Source Added (g) (*ml for HP)	KI Added (g)	Peroxide added per dose (g)	Number of Applications
UHP + KI	3.84	0.427	1.389	3
HP + KI	3.79	0.427	1.389	3
SPC + KI	4.27	0.427	1.389	3

NH_3 fluxes were calculated following equations derived from Dinuccio et al. (2012) and Kavanagh et al. (2019). Cumulative emissions were calculated by linear interpolation between measurement days.

CH_4 emissions were measured using a static chamber technique using lids with a rubber septum gas sampling port. CH_4 was sampled from the containers using a needle and syringe with time intervals of 0, 5 and 10 min. The 10 ml sample at each time interval was injected into pre-evacuated 7 ml screw cap vials. The samples were analysed using a Bruker gas chromatograph model 456-GC using helium as a carrier gas. Increase in CH_4 concentrations over the measurement time were used to infer daily fluxes using the equation described in (Kavanagh et al., 2019).

2.3. Slurry characteristics

Slurry pH was measured 2–3 times per week through the two incubation experiments using a JENWAY 1510 pH meter and a JENWAY 924-050 pH electrode. Total ammoniacal nitrogen (TAN) and total solids (TS) were measured at the start and end of both incubations. TAN was extracted by HCl extractions at a 1:20 ratio which was then filtered through Whatmann filter paper No. 2 and measured using an Aquakem 600 discrete analyser (Kavanagh et al., 2019). Total solids was measured gravimetrically using standard methods (APHA, 2005). Headspace within the containers and weight of the containers were measured 2–3 times per week.

2.4. Analysis of results

GraphPad Prism (version 8.01) was used for all data analysis. Data was rendered normal prior to analysis. One-way ANOVA analysis using each treatment as an independent variable was carried out as well as a Shapiro-Wilk test to assess statistical differences of daily NH_3 and CH_4 emissions.$p < 0.05$ was considered statistically significant. One way ANOVA analysis was also carried out on pH and TAN measurements and Shapiro-wilk test carried out with statistically significant differences at $p < 0.05$.

3. Results

3.1. Incubation one: effect of concentration on pH

Both Control 1 and Control 2 in Fig. 1: A/B remained stable over the 40-day incubation period, ranging from 6.89 to 7.35. During the first treatment, all the concentrations appeared to have minimal impact on the pH of the slurry, shown in Fig. 1: A. During the second treatment period, all three concentrations diverged from the controls drastically and appeared to stabilise within a pH range that was dose dependent, with the highest pH associated with the highest concentration, 3X. This occurred again during the third treatment where the peak and gradual decline in pH was dose dependent.

3.2. Incubation one: effect of frequency on pH

A similar trend can be seen when investigating the effect of frequency of addition as shown in Fig. 1: B, in which the first treatment period appeared to have minimal impact on pH. However, after the second treatment, F1 increased dramatically which was followed by F2 after its second treatment. Each subsequent addition increased the pH further until F1 stabilized at pH 9.1. F3 remained stable at a slightly increased pH compared to both controls throughout the experiment.

3.3. Incubation one: effect of concentration on NH_3 volatilization

Fig. 2: A shows the NH_3 volatilized over the 40-day incubation by both controls were very similar. In contrast, 1X, 2X and 3X concentrations increased NH_3 emissions by 117, 238 and 391% respectively, p <

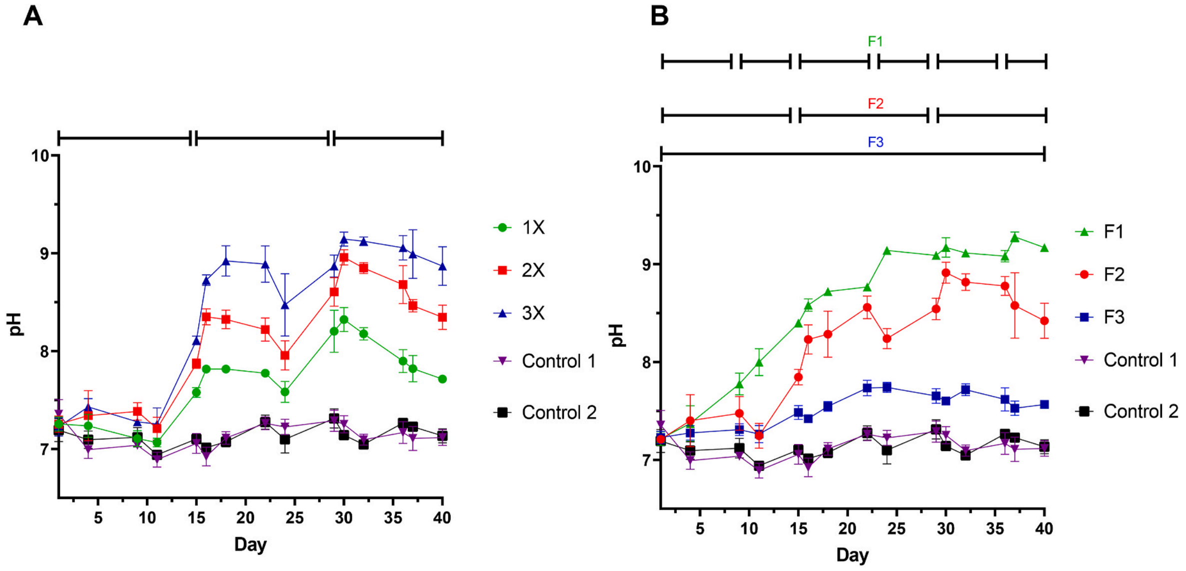

Fig. 1. Changes in pH as a result of concentration (A) and frequency of treatment (B). Horizontal bars displayed above each graph indicate the frequency of treatment i.e. period immediately post treatment and before next treatment, with F1 receiving the most treatments (6) followed by F2 (3) and F3 (1). Control 1 (received no water or agitation) and control 2 (received water and agitation) displayed. Standard error displayed for each day.

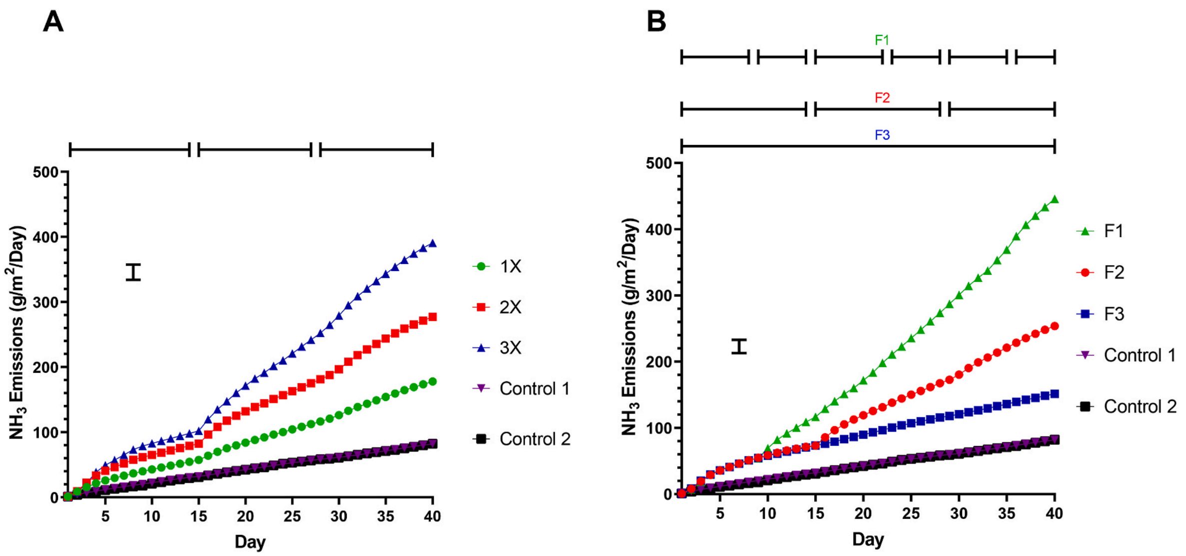

Fig. 2. Changes in NH_3 volatilization as a result of concentration (A) and frequency of treatment (B). Horizontal bars displayed above each graph indicate the frequency of treatment i.e. period immediately post treatment and before next treatment, with F1 receiving the most treatments (6) followed by F2 (3) and F3 (1). Control 1 (received no water or agitation) and control 2 (received water and agitation) displayed. Pooled standard error of the mean displayed in each graph (left).

0.05. The effect of the treatment on NH_3 volatilization was almost immediate, as all concentrations began to diverge from day five onwards (Fig. 2: A). As with the increase in pH, the amount of NH_3 volatilized was dose dependent.

3.4. Incubation one: effect of frequency on NH_3 volatilization

The effect of frequency of addition displayed a similar trend to that observed for the concentration, where F1, F2 and F3 increased NH_3 emissions by 444, 210 and 85% respectively over 40 days, $p < 0.05$. These sets of results effectively show that greater amounts or greater frequencies of addition of the treatment UHP + KI increase NH_3 emissions in a proportional manner.

3.5. Incubation one: effect of concentration on CH_4 mitigation

Treatments at 1X, 2X and 3X concentrations mitigated cumulative CH_4 emissions compared to Control 1 by 49, 34, and 32% which were not significant over the 40-day incubation period, shown in Fig. 3: A. However, compared to Control 2, which had water addition and agitation as frequently as F1, the treatments 1X, 2X and 3X reduced CH_4 emissions by 74, 67 and 66% which was significant, $p < 0.05$.

3.6. Incubation one: effect of frequency on CH_4 mitigation

F1, F2 and F3 mitigated cumulative CH_4 emissions by 16, 54 and 29% ($p < 0.05$) respectively when compared to control 1, shown in Fig. 3; B. Control 1 and 2 also produced dramatically contrasting cumulative CH_4 results, differing by approx. 52 g CH_4/m^2 ($p < 0.05$).

3.7. Incubation one: effect of concentration and frequency of addition on slurry characteristics

Table 3 shows the total solids content and TAN of the slurry pre and

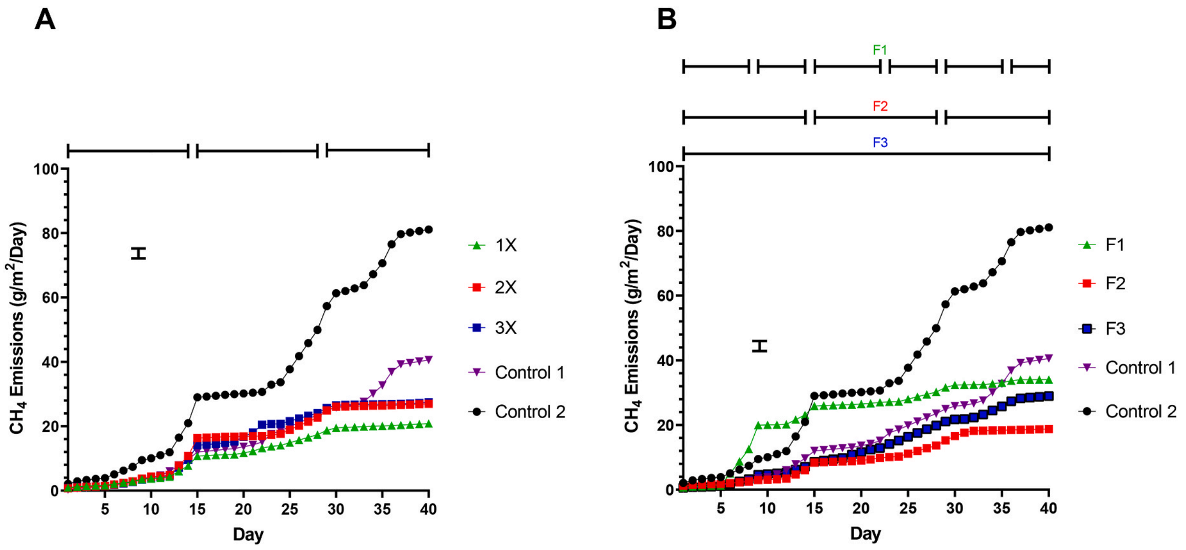

Fig. 3. Changes in CH_4 emission due to concentration (A) and frequency of treatment (B). Horizontal bars displayed above each graph indicate the frequency of treatment i.e. period immediately post treatment and before next treatment, with F1 receiving the most treatments (6) followed by F2 (3) and F3 (1). Control 1 (received no water or agitation) and control 2 (received water and agitation) displayed. Pooled standard error of the mean displayed in each graph (left).

Table 3
Slurry characteristics including total solids content (%) and total ammoniacal nitrogen (g TAN/kg slurry) pre and post incubation one with standard deviations shown. Concentrations of treatment (urea hydrogen peroxide and potassium iodide) represented by 1X, 2X and 3X. Frequency of addition of treatment with F1 representing 6 treatments, F2, 3 treatments and F3, 1 treatment shown. Control 1 and 2 are also displayed.

	TS	TAN		TS	TAN
	%	g TAN/kg Slurry		%	g TAN/kg Slurry
Pre 40-Day Incubation	8.07 ± 0.05	1.12 ± 0.003			
1X	8.42 ± 0.04	1.51 ± 0.05	F1	7.89 ± 0.08	3.66 ± 0.06
2X	8.25 ± 0.04	2.24 ± 0.06	F2	8.25 ± 0.12	2.24 ± 0.08
3X	8.47 ± 0.21	2.98 ± 0.03	F3	8.30 ± 0.11	1.38 ± 0.03
Control 1	8.14 ± 0.05	0.92 ± 0.01			
Control 2	7.95 ± 0.04	0.94 ± 0.005			

post the 40-day incubation period. The 1X, 2X and 3X concentrations all increased the TS contents significantly $p < 0.05$.

The frequency of addition had an atypical impact on the TS contents reducing F1 solids by 2.20% while increasing F2 and F3 by 2.23 and 2.85% respectively, $p < 0.05$.

The effect of the 1X, 2X and 3X concentrations on the TAN content was significant increasing it by 34, 100 and 164%, respectively $p < 0.05$. F1, F2 and F3 increased slurry TAN content by 226, 50 and 23%, respectively $p < 0.05$. Both responses to the concentration and frequency of addition indicate a proportional response to the addition of UHP + KI to the slurry. Increasing the concentration or frequency of treatment increased the TAN content of the slurry.

3.8. *Incubation two: mitigation of increased NH_3 volatilization*

It was determined experimentally (results not shown) that the addition of urea in the slurry treatment was the sole reason for the increased slurry pH (Fig. 1: A/B) and TAN concentrations (Table 3) and therefore NH_3 emissions during incubation one (Fig. 2: A/B). Thus, the stabilizing agent for HP, which previously was urea was modified in incubation two.

3.9. *Incubation two: effect of modifications on slurry pH*

There was no effect on slurry pH as a result of HP + KI, with both the maximum and average pH values extremely similar to both controls shown in Fig. 4: C and no significant increases in pH were observed. SPC + KI and UHP + KI however all impacted slurry pH. UHP + KI had a similar impact as incubation one, increasing pH throughout the experiment. The rate at which the pH dropped in slurry treated with SPC + KI

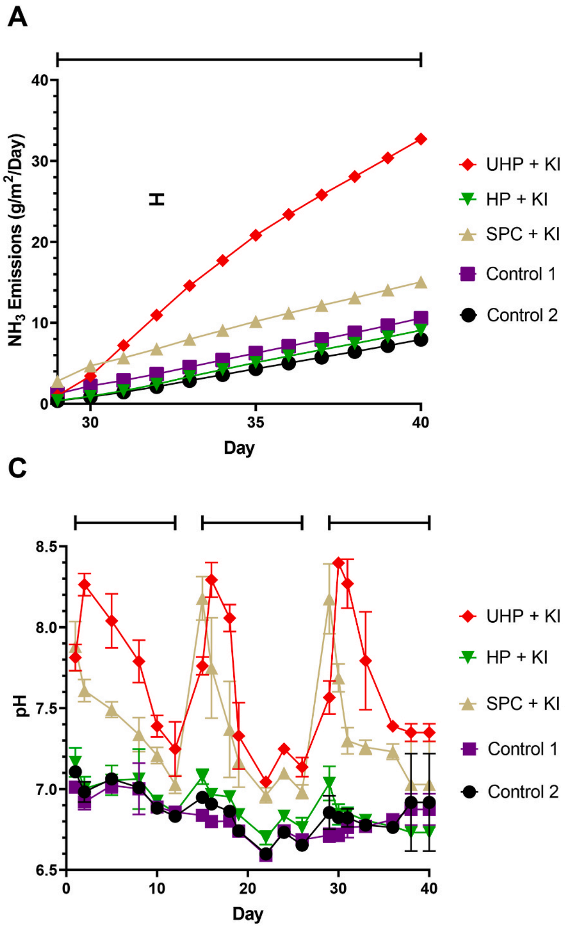

Fig. 4. Changes in NH_3 (A), CH_4 (B) and pH (C) as result of repeated and modified treatment options, urea hydrogen peroxide, hydrogen peroxide and sodium percarbonate. Control 1 (received no water or agitation) and control 2 (received agitation and water) are also displayed. Graph A and B displays the results in a running cumulative format, while graph C is a temporal graph. Pooled standard error of the mean is displayed in both graph A and B. Standard error for each point is displayed in graph C. Horizontal bars above each graph represent the frequency with which the treatments were used. Each treatment period last for two weeks. Only the final two weeks of NH_3 sampling was carried out, equating to one treatment period.

was much faster than UHP + KI, the reasons for which are related to the stabilizing agent used and discussed further in section 4.3.

3.10. Incubation two: effect of modifications on slurry NH_3 emissions

By effectively inhibiting the rise in pH, HP + KI performed adequately well, as shown in Fig. 4: A, in mitigating emissions slightly by 14%, but not significantly compared to Control 1. UHP + KI and SPC + KI increased NH_3 emissions by 209 and 42% respectively ($p < 0.05$), this result is surprising since the pH for both treatments appeared to shadow one another. Both control 1 & 2 appeared very similar throughout the 2-week measurement period.

3.11. Incubation two: effect of modifications on CH_4 production

HP + KI shown in Fig. 4: B mitigated 63% CH_4 emissions over the 40-day period compared to control 1 ($p < 0.05$). While SPC + KI and UHP + KI mitigated 44 and 39% respectively ($p < 0.05$). These results indicate that UHP + KI is the least effective treatment in terms of mitigating CH_4 under these conditions. Both control 1 and 2 produced similar amounts of CH_4 during this incubation which is contrary to the results obtained in incubation one.

3.12. Incubation two: effect of modifications on slurry characteristics

Control 1 appeared to increase total solids content during the 40 days of incubation, shown in Table 4, this was most likely due to evaporation. Control 2 however had water addition which countered the effect of evaporation and as such appears to be slightly contrasting, this difference was significant ($p < 0.05$). A similar dilution effect can also be seen in treatments UHP + KI and HP + KI ($p < 0.05$) but not in SPC + KI which increased total solids content to a similar degree as control 1. This increase in apparent TS may be due to the leftover sodium and total inorganic carbon deposited by the stabilizing agent.

A large increase in TAN, 93%, was measured when slurry was treated with UHP + KI as shown in Table 4 ($p < 0.05$). Both HP + KI and SPC + KI reduced TAN concentrations within the slurry by 10 and 15% respectively compared to control 1 over the 40-day incubation ($p < 0.05$). As did control 2 which reduced TAN concentrations by 7%.

3.13. Incubation two: foaming and crust formation

During all treatments in incubations 1 & 2 foaming was considerable in each container. Although not measured, the amount of foaming appeared to be proportional to the concentration of the treatment. The foam eventually receded but left a crust like residue on top of the slurry surface. This is different to both controls in each incubation as they both produced "skin-like" crusts after approx. 1 week and much thicker crusts by the end of both incubations.

Table 4
Slurry characteristics including total solids content (%) and total ammoniacal nitrogen (g TAN/kg slurry) pre and post incubation two, with standard deviations shown. UHP + KI (urea hydrogen peroxide + potassium iodide), HP + KI (hydrogen peroxide + potassium iodide) and SPC + KI (sodium percarbonate + potassium iodide) are displayed along with control 1 and 2.

	TS	TAN
	%	g TAN/kg Slurry
Pre-40-Day Incubation	10.19 ± 0.6	1.09 ± 0.001
UHP + KI	9.79 ± 1.2	2.76 ± 0.05
HP + KI	9.90 ± 0.9	1.29 ± 0.05
SPC + KI	10.43 ± 1.8	1.22 ± 0.05
Control 1	10.46 ± 2.0	1.43 ± 0.03
Control 2	10.17 ± 1.1	1.33 ± 0.02

4. Discussion

4.1. Treatment formulation

The aim of these studies was to develop an approach that could mitigate CH_4 emissions, without increasing NH_3 volatilization.

During incubation one it is apparent that NH_3 emissions increased even with a single treatment. Therefore, a new formulation for the treatment was needed. SPC and HP were chosen as reliable and relatively cheap sources of peroxide. It again became apparent in incubation two however that chemically stabilizing HP would inevitably lead to an increase in NH_3 emissions due to the release of basic compounds, urea (UHP) and sodium carbonate (SPC). The use of HP with no chemical stabilisation was invaluable therefore in determining how the treatment affected slurry without increasing pH which may also enhance methanogenic inhibition. HP + KI is therefore the most appropriate treatment for use in terms of reducing NH_3 volatilization.

4.2. Impact of amendments on CH_4 emissions

The 1X concentration in incubation one mitigated CH_4 most effectively, most likely due to the smaller amount of foaming compared to both 2X and 3X treatments which may have disturbed less dissolved CH_4 and reduced its subsequent release from the slurry. Dissolved CH_4 is most often reported in anaerobic reactors and resulting waste streams, such as McKeown et al. (2012) and Lettinga et al. (2001) in which lower psychrophilic temperatures, similar to cattle slurry temperatures during winter periods, increase the solubility of gases as described by Servio and Englezos (2002). However, both Hartley and Lant (2006) and McCarty et al. (2011) increased biogas CH_4 concentrations in their AD reactors by mixing or aerating with air and/or oxygen. Small increases in temperature of 1–2 °C (data not shown) were also measured during both incubations when the treatments were added (due to exothermic reaction of hydrogen peroxide and potassium iodide), this may have marginally increased the likelihood of dissolved methane release.

Interestingly, F1 which was treated most frequently produced the most CH_4 of all three frequencies, this is most likely related to the issue of dissolved CH_4 being released upon agitation and ebullition on a weekly basis (VanderZaag et al., 2019). F3 which was only treated once over the 40-day incubation period mitigated CH_4 emissions, but it is likely due to the formation of a natural crust post foaming, and that CH_4 production took place but was simply not released during the incubation, however a biochemical methane potential was not carried out to confirm this.

The various concentrations in incubation one acted consistently and produced a proportional amount of NH_3 to the urea added. This created a significant problem for further experimentation. The high pH measured during the treatment period may have caused the inhibition of CH_4 production as methanogens are highly sensitive to pH and environmental stresses (Kim et al., 2004; Visser et al., 1993; Habtewold et al., 2018a). Thus, the addition of urea along with HP + KI may have given a false positive as to what was causing CH_4 mitigation. However, the addition of HP + KI solely (Fig. 4: B & C) and the subsequent observed CH_4 mitigation, gives credence to the theory that HP + KI can be used as a treatment to mitigate CH_4 in cattle slurry.

The release of peroxide and the subsequent release of oxygen therefore appears to be the underlying factor in the inhibition of CH_4 from cattle slurry. The release of oxygen, although not measured, would have increased the dissolved oxygen concentration and redox potential of the slurry (Hjorth et al., 2012). Methanogenic activity is typically an obligate anaerobic process and the introduction of oxygen into the system will typically change the environment so that methanogenesis cannot take place (Deppenmeier, 2002; Shi et al., 2020, 2020van Dijk and Veeger, 1981). This may be dominant inhibitory factor within both incubations.

The inhibition of methanogenesis in this study is similar to that found in Thorn et al. (2022) in which both specific methanogenic assays and mesocosm (12 kg) closed system experiments were performed. The properties of the treatment UHP + KI were found to be inhibitory rather than biocidal owing to the need to re-treat numerous times during the storage period. The treatment used in the closed mesocosm experiment in Thorn et al. (2022) is identical to the 2X concentration described in this study. This concentration in both studies were found to reduce CH_4 by similar amounts, 55% in Thorn et al. (2022) and between 34 and 67% in this study. The CH_4 inhibition observed in this study and the one described in Thorn et al. (2022) is similar even with large differences in frequency of addition. Thorn et al. (2022) also found that the addition of SPC + KI reduced biogas production by approx. 34% and total CH_4 production by 20%. In the present study SPC + KI was found to be more inhibitory, reducing CH_4 emissions by 44%. However, since Thorn et al. (2022) used closed containers with no airflow this may have inadvertently reduced CH_4 emissions (Kupper et al., 2020), whereas the study presented in this paper is more accurate in discerning the effects of the treatment in a storage facility which is exposed to airflow. Both studies therefore appropriately replicate specific storage conditions by both limiting and allowing airflow. The effect of this closed system is more widely exacerbated when discussing NH_3 volatilization in section 4.3.

CH_4 emissions were broadly similar to those reported by Kavanagh et al. (2019) considering the length of the incubations. However, the slurry during this experiment which was 8.07% dry matter pre-incubation emitted similar CH_4 emission to 4% dry matter slurry presented by Kavanagh. Both control 1 and control 2 act as a range for CH_4 emissions from untreated slurry, ranging from the least CH_4 released to the most. However, it is notable to add that even if control 1, which is attempting to mimic a slurry tank that would not be agitated over the 40-day period, did not release significantly more CH_4 than some treatments, it would do so upon agitation (VanderZaag et al., 2010, 2019). The CH_4 emissions from control 2 in incubation one & two show the extent of the CH_4 emissions possible if the slurry is agitated on a weekly or bi-monthly basis. Therefore, it would be reasonable to assume that a similar amount of CH_4 would be released from control 1 upon agitation as CH_4 could have been trapped underneath the crust, similar to full scale slurry tank systems. Therefore, any treatment that is within the range between control 1 and control 2 or below control 1, may be thought of as to mitigate CH_4 emissions from cattle slurry.

Thorn at el., 2022 found that slurry treated with UHP + KI increased CH_4 production during anaerobic digestion by 17% and increased biogas production by 10%. It is possible therefore that slurry treated with HP + KI similar to this study would have a similar affect on the AD process, however the reduced N concentration as a result of urea not being added may impact results positively or negatively due to an increase in the carbon: nitrogen ratio of the feedstock (Hills, 1979).

In a farm setting, the store of slurry is constantly being added to, however in this study fresh cattle slurry was not added to the container once the experiment started in order to eliminate this variable. The addition of fresh cattle slurry to the containers may have no impact on the treatment or a negative impact on the treatment depending on the when the slurry is added. In this study the ratio of peroxide to slurry was controlled, if however fresh slurry was added directly post treatment this may dilute the inhibitory effects of the treatment as the ratio of peroxide is decreased. However, if the fresh slurry was added days after the treatment period, then very little difference may be observed in the inhibitory effects of the treatment, as fresh slurry typically has less methanogenic activity than older stored slurry (Habtewold et al., 2018a). This effect was studied by Thorn et al. (2022) in which fresh excreta addition was carried out every 3 days. In the study, despite excreta addition, biogas production was still inhibited by 84% during storage.

4.3. Impact of amendments on NH_3 volatilization

During incubation one, CH_4 emissions were mitigated however, NH_3 emissions increased by as much as 444% as a result of F1. During this incubation, urea was added to the slurry through UHP and its subsequent breakdown into NH_3/NH_4^+ caused large shifts in pH as result of the increased TAN content. This rise in pH lead to increased NH_3 emissions due to the equilibrium shift from NH_4^+ to labile NH_3 (Park et al., 2018; du Plessis and Kroontje, 1964). It was determined that the rise in pH was responsible for 97.8% of the increased NH_3 emissions.

The rise in pH was always followed by sharp decline, which typically held just above the control pH before rising again due to additional treatment. This pattern can be explained by the increase in TAN concentrations post treatment, the volatilization of NH_3 and the subsequent decline in pH as a result. This explanation resembles closely the role of the buffer system in slurry as outlined by Husted et al. (1991) and Overmeyer et al. (2020).

The effect of even a single treatment using UHP + KI is notable as seen with treatment F3 in Fig. 1: B and Fig. 2: B, the increased pH and NH_3 levels continue throughout the entire 40-day period. TAN levels increased by 23% which explains the slight increase in pH for the entire experiment. F3, compared to F1 which volatilized the most amount of NH_3 over the 40-day period, shows the impact of adding urea to the slurry on a consistent basis. Increasing the TAN to 3.66 g TAN/kg slurry and raised the pH to such an extent that it was only limited by the buffering capacity of the slurry shown in Fig. 1: B (Husted et al., 1991).

NH_3 measurements in incubation two were hampered by the fact that only the last 2 weeks of NH_3 data could be compiled. However, a comparative analysis of the final 2 weeks can still take place. The NH_3 emissions for both controls measured during both incubation one were similar to control levels in Kavanagh et al. (2019) while incubation two produced lower NH_3 emissions per day that were similar to emission figures collated by Kupper et al. (2020) in which NH_3 emissions from cattle slurry at laboratory scale was 0.96 g NH_3/m^2/day, n = 19.

The NH_3 emissions from the treatment using HP + KI in incubation two appeared to hold continuously within control levels and volatilized slightly less NH_3 over the 40-day period compared to control 1. However, it was notable that there was a reduction of TAN (Table 4) in the slurry which may be explained by the foam produced from the treatment. Foaming would inevitably expose TAN-rich material to the air, which would volatilize NH_3 as a result. This increased NH_3 emission rate implied by the TAN concentrations indicates that peak NH_3 emissions directly after dosing were missed, leading to a disagreement in figures.

Airflow within the containers was relatively high to achieve a target headspace turnover per minute. This airflow would not be expected in farm-scale operations in which tanks are held under ground or in above ground stores which are covered. Since high airflow rates induce NH_3 volatilization (Ni et al., 2000), NH_3 emissions from this study or studies like it may have elevated NH_3 emissions compared to real-world scenarios.

Although the pH of SPC + KI did rise significantly over the 40-day period, there was a more rapid decline in the pH compared to UHP + KI until it stabilized just above control levels. This reduced the time the slurry experienced in "high" pH zones and subsequently decreased NH_3 emissions compared to UHP + KI. The lack of N input by SPC + KI also increased the likelihood of mitigating NH_3 emissions compared to UHP + KI since the sodium carbonate dissociates in water into sodium and carbonate ions. This is in contrast with UHP, in which the added urea is hydrolysed into two ammonium molecules Alexandrova and Jorgensen (2007). The increased concentrations of carbonate ions increased the pH of the slurry and NH_3 volatilization. However, effective concentrations of each base produced per dose by SPC and UHP were 1.63 g (carbonate) and 4.90 g (NH_3/NH_4^+) respectively. Therefore, although the pH of SPC + KI and UHP + KI were similar on treatment day (Fig. 4:C), the amount of weak base acting on the slurry treated with SPC + KI was much less than UHP + KI. It is expected however that due to this increased carbonate concentration that carbon dioxide emissions may also increase once the pH has returned to original levels. In this way the products of sodium carbonate interact less with the slurry buffering systems as compared to the products of UHP (Husted et al., 1991).

Thorn et al. (2022) found UHP + KI did not increase NH_3 emissions, unlike in this study in which an identical treatment increased NH_3 emissions by 238%. These differences are likely as a result of the differing experimental conditions. In this study open airflow was allowed which did not allow for saturation of the air above the slurry surface with NH_3. This hypothesis was shown to be true when, a 1.6 kg closed container system using the UHP + KI treatment was measured throughout incubation two (data not shown). During the storage period the treatment did not increase NH_3 emissions significantly similarly to Thorn et al. (2022). This is a similar method to covering slurry stores, which has been shown to be very effective in reducing NH_3 emissions (Misselbrook et al., 2016; Sommer et al., 1993). However, if this treatment UHP + KI was to be used in an uncovered slurry store, the increased air pollution as a result of NH_3 emissions would not be acceptable.

Foaming occurred as a result of the rapid breakdown of HP into oxygen, while proteins contained within the slurry most likely acted as surfactants. This foam did recede and fully disappeared after a period of time due to three processes, these being drainage, coarsening and collapse of bubbles (Young, 2011; Weaire and Hutzler, 2001; Garrett, 1992).

4.4. *Alternative treatment options*

Many other treatment options are available for cattle slurry storage that can reduce both NH_3 and CH_4 emissions. For instance, acidification using sulphuric acid is a very popular and effective technique in which NH_3 emissions may be reduced by between 84% and 95% and CH_4 emissions reduced by 84%–87% (Petersen et al., 2012; Habtewold et al., 2018b; Kavanagh et al., 2019). The reduction in CH_4 emissions as a result of acidification may be as result of a lower methanogenic population as observed by Habtewold et al. (2018b). Other acidifiers such as ferric chloride and sugar beet molasses may also reduce NH_3 emissions by 97% and 67% respectively and CH_4 emissions by 98% and 7% (not significant) respectively (Kavanagh et al., 2019, 2021).

Aeration which is very similar to the treatment studied in this paper, has been shown to increase NH_3 emissions by 345% and reduce CH_4 emissions by 56%, both the increase in NH_3 emission and reduction in CH_4 emissions are broadly similar to what was observed in this paper (Amon et al., 2006). As well as these similarities, the main cause of the reduction in CH_4 emissions appear to also be similar in that methanogenic exposure to oxygen decreases their ability to respire. Slurry covers of varying permeability have also been shown to be effective, with an impermeable lid (i.e. concrete/wood) reducing NH_3 emissions by 73% and CH_4 emissions by 3% and permeable lid (i.e. straw) by 71% and CH_4 emissions by 15% (Kupper et al., 2020).

Sulphuric acid addition and aeration during storage are not compatible with AD due to increased concentrations of sulphate in the first instance (Moset et al., 2012) and a lack volatile fatty acids in the second (Paul and Beauchamp, 1989). Alternative acidifiers such as sugar beet molasses may aid in two-phase AD as the lower pH aids in hydrolysis (Janesch et al., 2021). Slurry covers on the other hand are extremely difficult to place over slatted shed storages but are very effective in almost any other storage applications.

4.5. *Feasibility*

Based on the dosing used in this study approx. 1.8 L of 33% HP and 267 g of KI would be needed to treat 1 tonne of slurry. This would require investment in chemicals and infrastructure to treat frequently, accurately, and safely. This treatment may be compared to an abatement technique such as sulphuric acid addition, a popular slurry amendment which may use between 2.85 L Kavanagh et al. (2019) and 3.46 L Sørensen and Eriksen (2009) of sulphuric acid per tonne of slurry in order to reach the recommended pH 5.5 (rates vary). Sulphuric acid addition at farm scale typically relies on large external pumps and internal pH sensors to maintain a stable pH (Sørensen and Eriksen, 2009). A similar system may be required for the addition of this oxidising treatment which may rely on either dissolved oxygen or redox potential for optimization purposes. The external pump, similar to acid addition may reduce foam formation also.

The purpose of this paper was to examine at small scale, the effectiveness of multiple oxidising treatments on CH_4 and NH_3 emissions from cattle slurry. Therefore, in order to assess the treatments feasibility at pilot or farm scale, further experimentation is needed at larger scales.

5. Conclusions

HP + KI was the most favourable treatment in both reducing CH_4 emissions and negating any increase in measured NH_3 emissions as a result of the treatment process. UHP + KI as well as SPC + KI, although inhibited methanogenesis, increased NH_3 emissions due to the subsequent rise in slurry pH. In future, work focused on maintaining the CH_4 inhibition from slurry storage while abating NH_3 emissions using a peroxide-based treatment would be valuable. Future work should also be directed towards answering the question of how effective cattle slurry treated with the additive described above, performs during anaerobic digestion and how feasible it is to use this treatment at larger scales.

CRediT authorship contribution statement

S. Connolly: Undertook experimental work, data collection, Formal analysis, Visualization, Writing – original draft, Writing – review & editing, Conceptualization, All authors involved in conceptualization. **V. O'Flaherty:** Funding acquisition, Obtained funding, Writing – original draft, Writing – review & editing, Conceptualization, All authors involved in conceptualization. **D.J. Krol:** Funding acquisition, Obtained funding, Writing – original draft, Writing – review & editing, Conceptualization, All authors involved in conceptualization.

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.

Data availability

Data will be made available on request.

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