Journal of Cleaner Production 504 (2025) 145450

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Abatement of greenhouse gases and ammonia from cattle slurry during storage and land spreading: A pilot scale study

S. Connolly [a,b,*], V. O'Flaherty [a,c], C.E. Thorn [c], D.J. Krol [b]

[a] Microbiology, School of Biological and Chemical Sciences, University of Galway, Ireland
[b] Teagasc, Environment, Soils and Land Use Department, Johnstown Castle, Wexford, Ireland
[c] GlasPort Bio Limited, Business Innovation Centre, University of Galway, Ireland

ARTICLE INFO

Handling Editor: Liu Yu

Keywords:
Methane inhibition
Manure
Ammonia volatilization
Hydrogen peroxide
Calcium chloride
Total greenhouse gas emissions profile

ABSTRACT

The storage and spreading of cattle slurry are significant contributors to greenhouse gas (GHG) and ammonia (NH_3) emissions in agriculture, driven by the decomposition of organic matter and volatilization of nitrogen compounds. This study evaluates the impact of hydrogen peroxide and potassium iodide (HK) and its combination with calcium chloride ($CaCl_2$) (HKC) on mitigating GHG and NH_3 emissions during the manure management chain. Storage trials were conducted at multiple scales (660 L and 20 kg), alongside field trials assessing the effect of treated slurries on emissions during land spreading. Emissions of methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and NH_3 were monitored over both the storage and land spreading trials.

Results demonstrated that HK and HKC treatments inhibited CH_4 (HK - 651.41 g m^{-2}; HKC – 621.44 g m^{-2}; Control – 768.74 g m^{-2}) and N_2O (HK – 2.88 g m^{-2}; HKC – 1.01 g m^{-2}; Control – 7.43 g m^{-2}) production compared to control during storage but increased CO_2 (HK – 5140.83 g m^{-2}; HKC – 5609.22 g m^{-2}; Control – 2474.27 g m^{-2}) emissions due to foaming and agitation effects. NH_3 emissions were significantly influenced by the treatments, with HK (168.91 g m^{-2}) increasing emissions by 111 % and HKC (102.71 g m^{-2}) by 28 %, relative to the control (80.03 g m^{-2}). Application of a $CaCl_2$ spray reduced NH_3 emissions by 49 % in the first 48 h of treatment through surface pH modulation, though this effect was transient. Temperature significantly influenced CH_4 emissions; emissions under high-temperature (HT; 19 °C) (0.085 kg CH_4 kg^{-1} VS Day^{-1}) conditions were six times higher than under low-temperature (LT; 9 °C) (0.013 kg CH_4 kg^{-1} VS Day^{-1}) conditions. CH_4 inhibition was more effective at LT (86 % reduction, $p < 0.05$), highlighting the temperature sensitivity of methanogenic communities. However, no significant differences in cumulative GHG or NH_3 emissions were observed between treatments and controls during land spreading. When storage and spreading results were combined, treatments showed no significant cumulative reduction in GHG emissions compared to controls, highlighting the need for optimization of treatment protocols.

The results indicate that the oxidative treatments (HK & HKC) can suppress methane (CH_4) and nitrous oxide (N_2O) emissions during storage, offering a potential strategy for reducing emissions from livestock waste. Furthermore, the application of $CaCl_2$ as a surface treatment reduced ammonia volatilization, improving nitrogen retention in slurry, which can enhance its fertilization potential. These findings suggest that oxidative treatments and $CaCl_2$ spray have potential for reducing emissions during manure storage, particularly under cooler conditions typical of Irish winters. However, the efficacy of these treatments under warmer conditions may require adjustments in application frequency and concentration. Future research should focus on optimizing treatment protocols and assessing the agronomic benefits of treated slurries.

1. Introduction

The storage of animal manures on farms is almost ubiquitous and occurs in most countries with animal husbandry. Storage of manure, which is typically rich in many plant-available nutrients, is also a large point source of greenhouse gases (GHGs) including methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), as well as environmental pollutants, such as ammonia (NH_3) (Amon et al., 2006; Misselbrook

---

* Corresponding author. Microbiology, School of Biological and Chemical Sciences, University of Galway, Ireland.
E-mail address: Shaun.connolly@teagasc.ie (S. Connolly).

https://doi.org/10.1016/j.jclepro.2025.145450
Received 1 November 2024; Received in revised form 11 March 2025; Accepted 4 April 2025

et al., 2016; Petersen et al., 2012). Subsequent spreading of manure post storage is also a large source of emissions, at this stage mostly in the form of N_2O and NH_3 (Rivera and Chará, 2021; Nyameasem et al., 2022).

Methane, which has a 100-year global warming potential (GWP) 28 times that of CO_2, is produced as an end-product of anaerobic biodegradation of the organic material within slurry by archaea, known as methanogens (IPCC et al., 2023; Habtewold et al., 2018a). Methanogens produce CH_4 synergistically from the products of bacterial fermentation, such as volatile fatty acids, hydrogen and CO_2 (Bajpai, 2017). Methanogens are obligate anaerobes and are therefore highly sensitive to oxygen (Kiener and Leisinger, 1983; Lyu and Lu, 2018). In addition to oxygen, methanogenesis is sensitive to pH, redox potential and temperature, all of which must be within appropriate ranges for CH_4 to be produced (Visser et al., 1993; Kiener and Leisinger, 1983; Misselbrook et al., 2016). Significant amounts of CH_4 are produced annually from manure management, primarily during storage. Opio et al. (2013) estimated that 109 million tonnes of this GHG are emitted each year from the ruminant manure management chain, exacerbating the effects of climate change. CH_4 originating from manure management accounted for 11.8 % of the EU-27's agricultural emissions in 2021 (European Environmental Agency, 2023).

Ammonia is a pollutant that is volatilized from slurry stores due to the high mineral nitrogen (N) content of cattle slurry (Petersen et al., 2012). NH_3 is not a GHG but can serve as an indirect source of N_2O via N deposition to soils. This increased N input may alter plant speciation and have wider impacts on local sensitive ecosystems (Bobbink and Roelofs, n.d.). N deposition also causes soil acidification, increasing liming requirements for farmers, and thus increasing CO_2 emissions. In the atmosphere, NH_3 can react with other pollutants such as sulphuric acid to produce particulate matter 2.5, which has been shown to cause respiratory issues in people who are frequently exposed to it (Sigurdarson et al., 2018). Air pollution has been credited with many deaths across the European Union and the United States of America (Khomenko et al., 2021; Domingo et al. 2021).

Irish agriculture is responsible for 99 % and 38 % of the national NH_3 and GHG emissions, respectively (Buckley et al., 2020; Duffy et al., 2022). Actions to reduce both will aid in meeting national and European targets such as Ireland's Climate Action and Development (Amendment) Act 2021 and the National Emission Reduction Commitments Directive, as well as creating a more sustainable environment and agricultural industry.

Treatments, such as slurry acidification using concentrated sulphuric acid during storage, in which the pH of the slurry is brought to 5.5 or below, is considered a very effective technology to mitigate emissions and is becoming more popular in countries such as Denmark. Lowering slurry pH causes labile NH_3 to be protonated to the more stable NH_4^+. Since NH_4^+ is less volatile than NH_3, this reduces N loss from the slurry and offers a higher fertilization value (Sommer et al., 2013; Wagner et al., 2021). For example, Overmeyer et al. (2023) demonstrated a 39 % reduction in in-barn NH_3 emissions, while Misselbrook et al. (2016) achieved a 75 % reduction in NH_3 emissions across three slurry storage periods. Slurry acidification also reduces the amount of CH_4 produced, as methanogens are sensitive to pH (Visser et al., 1993; Staley et al., 2011; Habtewold et al., 2018b). However, this method does have disadvantages such as increased sulphur concentrations in the slurry once acidified. If the acidified slurry was intended for use in downstream anaerobic digestion (AD), it would require significant mixing with un-acidified slurry (Eriksen et al., 2012; Moset et al., 2012). The increased sulphur concentrations may lead to process instability and to increased wear and tear of the equipment due to the production of hydrogen sulphide during digestion. Therefore, slurry treatment alternatives to acidification, that are compatible with the AD process, are required.

Anaerobic digestion is increasing in popularity within the EU as a way to generate renewable energy and manage agricultural and/or other wastes (Grando et al., 2017). Therefore, management and treatment of the resultant digestate to minimise the potential negative impacts on the environment, such as gaseous emissions, is another important consideration. As AD technology is adopted, spreading of digestate onto farmland is becoming more common.

This work evaluated an alternative slurry additive that is compatible with downstream AD. This additive is a mix of hydrogen peroxide (H_2O_2) and potassium iodide (KI). The mode of action by which this method reduces CH_4 emissions is the same to that is reported by Thorn et al. (2022). In their study, oxygen was introduced into the slurry using a stabilised peroxide (urea hydrogen peroxide), resulting in an approximately 94 % reduction in CH_4 emissions over 65 days with multiple applications (Control - 1.7 L CH_4; Treated Slurries – 0.095 L). The addition of H_2O_2 has the effect of inhibiting methanogens for several days, the effects of which are temporary, as once oxidative conditions subside, methanogenesis resumes, and the treatment can therefore reduce CH_4 losses during slurry storage, without impacting CH_4 yield during AD.

As with slurry acidification, addition of peroxides to slurry induces foaming, potentially acting as a source of increased NH_3 emissions during storage. Thus the use of calcium chloride ($CaCl_2$) was assessed during storage in order to reduce the hypothesised increase in NH_3 emissions. $CaCl_2$ has previously been incorporated into soil and chicken slurry. Witter (1991) found that the addition of $CaCl_2$ to poultry litter decreased peak NH_3 volatilization rates by 71 %, while Husted et al. (1991) also described NH_3 abatement by which $CaCl_2$ acted as an acidifier in slurry. Recent studies have explored the effects of $CaCl_2$ in soil, particularly its role in altering soil microbial structure of nitrifying and denitrifying communities and acting as a nitrification inhibitor. Abbasi et al. (2011) demonstrated that $CaCl_2$ slows the conversion of NH_4^+ to nitrate, ultimately reducing NH_4^+concentrations by 30 %, enhancing plant N utilisation (Macêdo et al., 2019). $CaCl_2$, unlike other acidifiers, is compatible with downstream AD and may even increase biogas potential due the ability of the Ca^{2+} ion to reduce the toxicity of long chain fatty acids (Kumar et al., 2015). The reduction in long chain fatty acid inhibition during AD is attributed to their precipitation as calcium salts, which lowers their concentration and minimises their inhibitory effects on methanogenic activity.

Therefore, despite progress in manure management research, key gaps remain. Slurry acidification effectively reduces NH_3 and CH_4 emissions but is incompatible with anaerobic digestion due to increased sulphur levels. Alternative treatments that mitigate emissions while supporting AD are underexplored. Oxygen-based treatments can suppress CH_4 during storage, but their temporary effects and potential NH_3 increases require further study. While $CaCl_2$ has shown NH_3 reduction potential in other contexts, its role in cattle slurry management, particularly alongside oxidising treatments, remains unclear. Additionally, the influence of temperature on treatment efficacy is poorly understood, despite its importance in emission dynamics. Addressing these gaps is crucial for developing sustainable manure management strategies.

The aim of this study was to: (i) evaluate the effects of this oxidising treatment (mixture of H_2O_2 and KI) with and without surface addition of $CaCl_2$ on CH_4, CO_2, N_2O and NH_3 emissions during storage, (ii) to anaerobically digest treated and untreated slurry and assess the gaseous emissions of slurries and digestates following spreading to grassland, and (iii) assess the effect of temperature on the efficacy of the slurry amendment on CH_4 inhibition.

2. Materials and methods

2.1. Slurry storage: experimental setup

Nine 1 m^3 (0.8 m × 0.8 m x 1.5 m) slurry tanks were filled with 660 L of cattle slurry from a beef farm in county Wexford, Ireland. The storage tank from which the slurry was taken was approximately 115 m^3. Cattle were fed a diet of silage and 16 % concentrate. The slurry tanks were filled three weeks before the start of the experiment to allow for out-gassing following mixing and transport, which may inadvertently affect emissions. The tanks were covered with concrete slats similar to those used on commercial farms in order to simulate realistic airflow conditions over the surface of the slurry during the storage period. These slats were also in place during GHG and NH_3 measurements.

2.2. *Addition of treatment*

The storage experiment was carried out for 90 days. Treatment was applied every two weeks (7 treatment periods), apart from treatment period 3 and 6, where tanks were treated after 8 and 11 days respectively (see Fig. 1: A which includes treatment periods as bars above graph). 1.32 L of 30 % H_2O_2 (w/w) (0.67 g H_2O_2 L^{-1} slurry) and 1 L of 1.06 M KI (0.27 g KI L^{-1} slurry), were pumped into the bottom of the tanks separately, but simultaneously via two 2-m-long half-inch pipes (this treatment will now be known as HK). H_2O_2 was pumped into the tank at a rate of 0.5 L min^{-1} while KI was pumped in at a rate of 0.363 L min^{-1}. The HK treatment was used again, except 1 L of 0.75 M $CaCl_2$ solution (520.22 g $CaCl_2$ m^{-2}) was sprayed on top of the slurry after the addition of the oxidising treatment. This solution was sprayed using a backpack pressure sprayer to ensure appropriate coverage of the slurry surface (this treatment will now be known as HKC). The concentrations of H_2O_2 and KI were selected based on previous research by Connolly et al. (2023), which explored concentration gradients. A gradient was not applied in this study due to logistical constraints and concerns regarding comparability at this larger scale. Control slurry was left in the tanks undisturbed for 90 days apart from days in which multiparameter readings were taken. All treatments including HK, HKC and control were replicated n = 3.

2.3. *Sample collection*

Total solids (TS) and volatile solids (VS) samples were taken one day

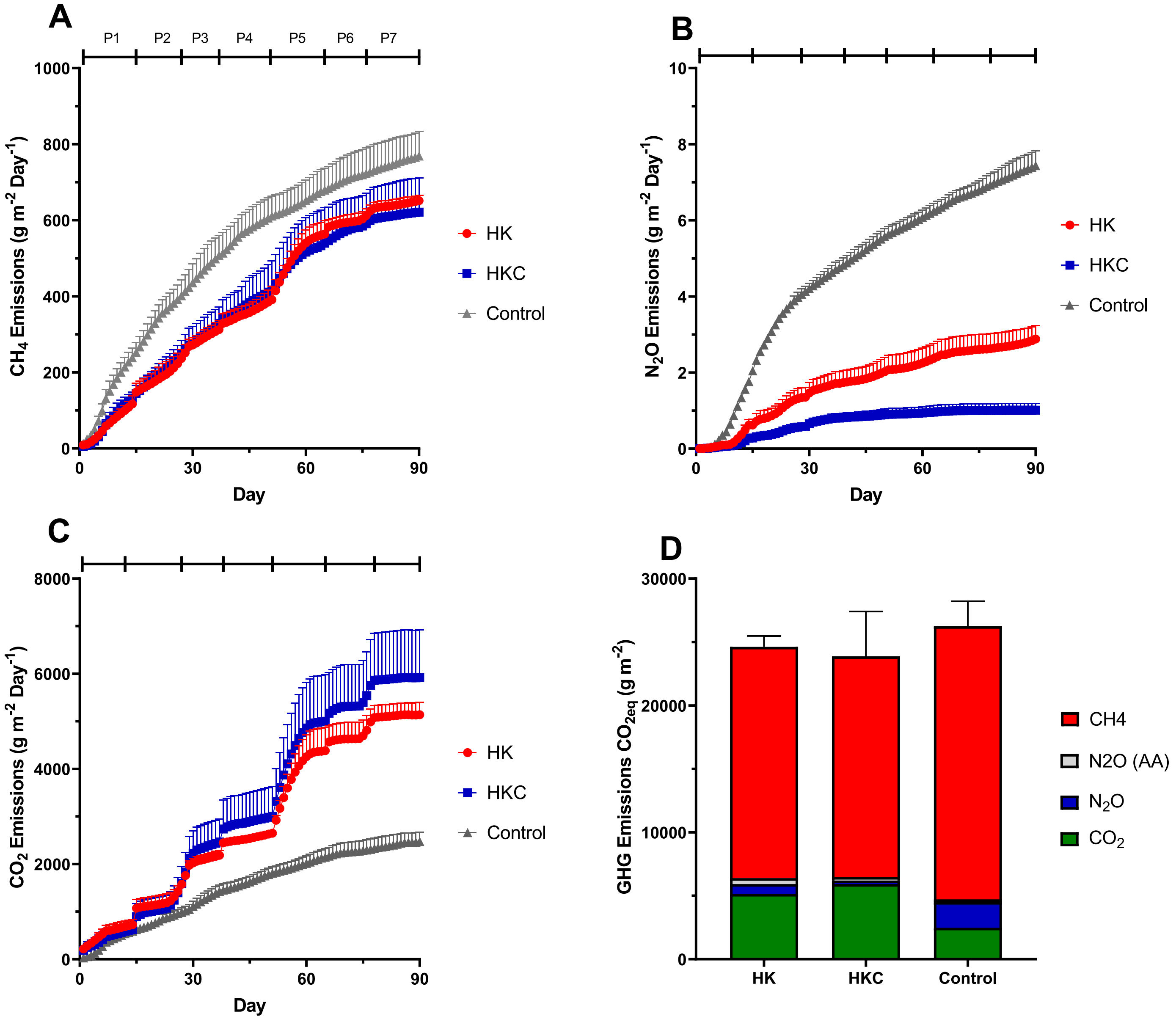

Fig. 1. A/B/C/D: A: Running cumulative CH_4; B: N_2O; C: CO_2 emissions during 90-day slurry storage experiment with error bars representing standard deviation to the mean. HK (hydrogen peroxide and potassium iodide), HKC (hydrogen peroxide, potassium iodide and calcium chloride) and control displayed. Horizontal bars displayed above graphs indicate treatment periods. D: Total GHG profile of 90-day slurry storage including CH_4, N_2O, CO_2 and N_2O (AA) in CO_{2eq}. Error bars representing standard deviation of cumulative emissions.

before the start of the experiment, after the slurry was agitated. The samples were analysed gravimetrically, fresh samples were dried at 105 °C for 24 h for TS, after which the samples were placed in a furnace at 550 °C for 2 h for VS determination, in accordance with standard methods (APHA, 2005). Samples were taken at the beginning and end of the experiment.

CH_4, CO_2 and N_2O gasses were measured using the static chamber technique in which a 250 L cover was placed over each tank creating an airtight seal (De Klein and Harvey, 2015). Gas samples were taken at 0, 30 and 60 min after cover placement using a 100 ml polypropylene syringe and were placed into pre-evacuated 7 ml glass vials. These gas samples were then analysed on a Bruker gas chromatograph model 456-GC which used helium as a carrier gas. Gas fluxes were taken 4 times in the first week and 4 times in the second week of the experiment. From then onwards, fluxes were taken 3 times per week in weeks in which treatments were added and 2 times per week when treatments were not. Individual fluxes were calculated using Equation (1) which is modified from (Kelliher et al., 2012):

$$F(daily) = (\Delta C/\Delta t)*((M*P)/(R*T))*(V/A) \qquad \text{(Equation 1)}$$

where F(daily) is the daily flux (g m^{-2} Day^{-1}), ΔC is the change in concentration of the target gas (ppm), Δt is the change in time (Day), M is the molar mass of the target gas, P is the atmospheric pressure (Pa), R is the ideal gas constant, T is the temperature (K), V is the volume (m^3) and A is the area (m^2).

Each individual flux was considered representative of the measurement day. Gap filling between measurement days was performed using trapezoidal integration between two points similar to Rahman and Forrestal (2021) to calculate cumulative emissions.

NH_3 measurements were carried out using the dynamic chamber technique by placing a 250 L cover on top of the slurry tank while an in-system fan was used to induce airflow within the chamber (Burchill et al., 2016; Kang et al., 2020; Misselbrook et al., 2016). The airflow over the slurry was variable due to wind but was always above 10.5 m $^{-1}$. Airflow was measured and recorded using a TSI airflow rotating vane (LCA501). Average observed airflow speeds were 11.28 m s^{-1}. The estimated air exchange rate within the chamber was 48 exchanges per minute. Similar airflow speeds are unlikely to occur in real underground slatted tanks but was done in order to obtain accurate comparisons between treatments. Samples were taken from air originating at the inlet of the chamber (unladen air) and air circulated through the chamber (laden air). Samples were taken at a rate of 2 L min^{-1} ± 0.2 and were drawn through two 0.05 M orthophosphoric acid bubblers. The airlines carrying the samples were made of PTFE. NH_3 sampling took place as often as GHG flux measurements and lasted for 1 h. Post measurement, the orthophosphoric acid was analysed using an Aquakem 600 discrete analyser. NH_3 emissions were calculated using equation (2) which was used by Kavanagh et al., (2019); Dinuccio et al., (2008):

$$Fj = Q*(Cex.j - Cin.j)/A \qquad \text{(Equation 2)}$$

where Fj is the gas flux (mg m^{-2} hr^{-1}), Cex.j is concentration of the outlet NH_3 (mg m^{-3}), Cin.j is the concentration of inlet NH_3 (mg mg^{-3}), Q is the airflow rate through the chamber (m3 hr^{-1}) and A is the surface area of the emission source (m^2).

Calculation of CO_2 equivalencies was carried out using 100-year GWPs recommended by Working Group I to the IPCC 6th assessment report, 2022 (IPCC et al., 2023). The potentials used were; CO_2 – 1, CH_4 – 28, N_2O – 273. Emitted NH_3 was presumed to have formed N_2O at a rate of 1 % and is included in CO_2 equivalency calculations as ammonia associated N_2O (N_2O (AA)) (IPCC2006- Intergovernmental Panel on Climate Change et al., 2006).

Temperature, dissolved oxygen (DO), oxidative redox potential (ORP) and pH were measured using a Hanna H91628 multiparameter probe, which was lowered into the slurry at four depths, 4 cm, 24 cm, 54 cm and 83 cm below the slurry surface three times per week. pH, DO and temperature were calibrated according to manufacturer's specifications. No measurements were taken during the night.

Total ammoniacal nitrogen (TAN) samples were taken 1 day before the start of the storage experiment and the end of the experiment (day 90). Slurry samples were taken and diluted (1:20), then shaken with 0.1 M hydrochloric acid and filtered through 100 μm Whatmann paper. Filtered samples were refrigerated and analysed using an Aquakem 600 discrete analyser.

2.4. *Storage temperature experiments*

Two 20 kg slurry storage experiments were carried out at Teagasc, Johnstown Castle. The first experiment took place during the summer, from July 6, 2020 until the September 3, 2020, hereon referred to as high temperature (HT) conditions. The second experiment took place in early spring from the February 15, 2021 until the March 30, 2021, hereon referred to as low temperature (LT) conditions.

Slurry was sourced from the same farm previously described. Slurry was collected three days prior to the beginning of each experiment. The slurry was dispensed into 30 L containers (H - 41 cm, r- 15.25 cm), where each container received equal amounts of slurry. HT containers received 20 kg of slurry while LT containers received 15 kg of slurry each. The differing weights during each experiment were due to restrictions in acquiring suitable slurry at that time. The containers were stored in a large polytunnel in which airflow was unrestricted. Neither experiment was temperature controlled but large differences in temperature occurred naturally, relating to the time of year (Fig. 4: A).

GHG emissions were sampled 4–5 times in the first week and 2–3 times thereafter. Emissions were sampled in the same manner as previously described using a modified container lid with a rubber septum to seal the chamber. GHG fluxes were inferred using the increase in emissions over the time periods using equations from Kavanagh et al. (2019) and Kelliher et al. (2012). Calculated emissions were first determined in g m^{-2} $day^{-1}$and were then converted to kg CH_4 kg^{-1} volatile solids (VS).

2.5. *Treatment*

The slurry received a mix of H_2O_2 and KI in the same concentrations and manner as previously described. This will be known as peroxide treatment (PT). Two controls were used in this experiment, the first (Control 1) consisted of untreated slurry that was stored for the entire experimental period with no mixing/agitation or water addition apart from some crust destruction in order to acquire pH measurements. The second control (Control 2) was stored under the same conditions but received the same amount of water and mixing as PT (water added to mimic the effect of dilution by PT). All treatments were replicated ($n = 3$).

2.6. *Slurry characteristics*

Slurry pH was measured using a JENWAY 1510 pH meter and a JENWAY 924-050 pH electrode. Measurements were taken 2–3 times per week using 200 ml slurry samples which were subsequently returned to the containers from which they were taken. Total ammoniacal nitrogen (TAN) as well as TS and VS were measured at the start and end of both experimental periods. TAN was extracted using similar methods to Connolly et al. (2023). Slurry temperature was measured everyday during both experiments using a JENWAY temperature probe. Met Eireann data was used to tabulate the average temperature values for each day. Average slurry temperature over the HT time period was 19 °C, while during the LT time period it was 9 °C.

2.6.1. *Anaerobic digestion*

Seventeen litres of slurry was sampled from each HK and control tank during the storage experiment on days 29 and 67. The slurry was immediately transported to the University of Galway, where the slurry was anaerobically digested. This process was a mono-digestion that took place over two 5-week periods at 37 °C, in which anaerobic granules (inoculum), previously used to treat dairy waste, were mixed with the slurry to facilitate efficient breakdown of organic matter. The inoculum was held at 37 °C for 72 h prior to mixing with the feedstock. The inoculum was mixed with the feedstock at a fixed chemical oxygen demand ratio of 1:2 (Trego et al., 2020; Lim and Fox, 2013). The digestate originating from the control (untreated digestate) and HK (HK digestate) treatments were land spread.

2.6.2. Slurry and digestate land spreading experiment

Two land spreading experiments were carried out on grassland plots on September 6, 2021 and October 12, 2021 using material from the 660 L storage experiment and subsequent anaerobic digestion. Samples were taken 2 days prior to spreading and stored at 4 °C up to the day in which it was spread. The trial followed a fully randomised block design with 7 treatments ($n = 3$). Each plot measured 6 m*1.5 m, a treatment area of 9 m^2. 17 L of cattle slurry from each tank HK, HKC and control in the storage experiment were sampled and spread on the experimental plots along with 17 L of HK digestate and untreated digestate. Average N application rates of the slurries and digestates during the first spreading event was 9.37 kg N ha^{-1} while in the second spreading it was 24.55 kg N ha^{-1}. Calcium ammonium nitrate (CAN) was spread at a rate of 40 kg N ha^{-1} as a fertilizer control, no nitrogen was added to land control plots.

CH_4, CO_2 and N_2O were sampled using the static chamber method similar to Gebremichael et al. (2021). Gas samples were taken at 0, 20 and 40 min. GHG samples were taken directly after spreading and 6 h after spreading. Sampling was then carried out on a 5/4/3/2/1 basis in which sampling took place 5 times per week in the first week, 4 times in the second week, 3 times in the third week etc. GHG sampling periods were as follows: All GHG fluxes returned to background concentrations prior to the end of sampling. Analysis of fluxes was carried out in the same manner as described before and cumulative GHGs from storage and spreading were summed. Control emissions were subtracted and then statistically analysed so as to separate background soil emissions from the effect of slurry application.

NH_3 emissions from land spreading were estimated using the ALFAM2 model, in which average rainfall, wind speed and air temperature over the modeling period was used (Hafner et al., 2018). Weather data was provided by Met Eireann weather station located 700 m away. Slurry application at 18.89 t ha^{-1} and duration of emission at 168 h were consistent variables, other input variables such as TAN concentration, slurry dry matter and pH were variable.

The grass was cut to a height of 5 cm before the start of each land spreading trial. Soil cores were taken 1 week prior to the first spreading trial to assess bulk density and allow calculation of water filled pore space (WFPS). Calculations were carried out as described by Žurovec et al. (2021). Soil bulk density was on average 0.9 g cm^{-3}. Soil moisture readings were taken at least once per week and up to 3 times per week using a Thetaprobe (Delta T, Cambridge, UK).

2.6.3. Statistical analysis

All data analysis was carried out using GraphPad Prism (v8.01). All data was tested for normality ($p < 0.05$) using the Shapiro Wilks test. If normality failed, data was rendered normal via log transformation prior to further analysis. Cumulative GHG (CH_4, N_2O, N2O (AA) and CO_2) and NH_3 during both storage and land spreading were assessed using one-way ANOVA. A Tukey post-hoc test was performed to determine significant differences between treatments. A two-way ANOVA was also carried out on the CH_4 treatment periods in which a Tukey-post hoc test was performed to examine statistical differences. All tests were performed assuming a statistical probability of $p \leq 0.05$ was significant.

3. Results and discussion

3.1. Storage experiment: methane

Cumulative CH_4 emissions over the 90-day storage period from control slurry equalled 768.74 g m^{-2} (Fig. 1: A & D). Both HK (651.41 g m^{-2}) and HKC (621.44 g m^{-2}) reduced CH_4 emissions from cattle slurry by 15 and 19 % respectively ($p < 0.05$). P1 was the only treatment period in which either HK or HKC produced significant inhibition of CH_4, reducing emissions by 51 and 45 % respectively ($p < 0.05$). Maximum inhibition during periods 2, 3 and 4 varied from 26, 35 and 24 % respectively, which were not significant. During periods 5 and 6, CH_4 inhibition was negative (i.e. the treatment did not inhibit CH_4), increasing emissions by 153 and 17 % respectively (The rate of increase in emissions in Fig. 1: A for HK is larger than for Control). In treatment period 7, maximum CH_4 inhibition was 33 %, which was not significant. The lack of consistent CH_4 inhibition throughout the storage trial makes interpretation difficult. During P1, similar inhibition to Connolly et al. (2023) was observed before becoming weaker in the next 3 treatment phases. An increase in CH_4 emissions during periods 5 and 6 from treated slurry may be as a result of increased volatile fatty acid (VFA) concentrations during storage and their subsequent utilisation by methanogenic communities. Increased CO_2 emissions during periods 5 and 6 also confirm that a higher rate of microbial activity was present (Fig. 1: C). Emissions from HK and HKC were not significantly different, indicating that the addition of the $CaCl_2$ spray did not affect CH_4 production during the storage period. This aligns with previous research, which suggests that CH_4 is primarily produced near the bottom of the slurry pit where most of the VS settle (Ndegwa et al., 2002). Since the spray was applied as a top dressing, it is unlikely that it could have any meaningful impact on CH_4 emissions. The reduced level of CH_4 inhibition in this experiment, compared to Thorn et al. (2022) and Connolly et al. (2023), may be due to a high average slurry storage temperature which was 17.2 °C (Max-19.1 °C, Min-16.0 °C) (Fig. 2: D). Amon et al. (2006) also stored slurry at average temperatures of 17 °C and observed untreated methane emissions that were 94.9 % higher from untreated slurry than this study (1498.15 g CH_4 m^{-2}). This difference in emissions was most likely due to the high dry matter slurry used (9.24 %) versus the low dry matter slurry tested in this trial (3.0 %). Kavanagh et al. (2019) reported a similar trend, finding that CH_4 emissions were **88.24 % higher** in slurry with **7 % dry matter** compared to **4 % dry matter**. The high temperature was as a result of the time of year in which the experiment took place. It is well known that, with increasing temperature, the rate of methanogenesis also increases, which the oxidising treatment was unable to inhibit (Husted, 1994; Cárdenas et al., 2021). If slurry temperatures were similar to those more representative of Irish or northern/central European slurry during winter, CH_4 inhibition would likely have been much higher (Petersen et al., 2016).

The abatement of CH_4 emissions throughout the majority of the experiment can be explained by the presence of dissolved oxygen through the addition and catalytic decomposition of H_2O_2 (Fig. 2: C), and the subsequent rise in ORP (Fig. 2: A). This change in the environmental conditions of the slurry from an anaerobic (−400 mv) to aerobic (+100 mv) one, are conditions in which methanogens cannot produce CH_4 (Hungate, 1960). This approach of controlling redox potential to modify gaseous emissions from slurry was previously investigated by Hjorth et al. (2010), who found that ozone application reduced hydrogen sulphide emissions by **99.5 %** and lincreased redox potential to at least **-80 mV**. Similarly, Connolly et al. (2025) observed an **81 % reduction in hydrogen sulphide emissions** using the same treatment applied in this study, further demonstrating the effectiveness of redox manipulation in mitigating emissions. Methanogenesis is widely known to be highly sensitive to oxygen (Deppenmeier, 2002) and a similar H_2O_2 based amendment has also been shown to operate well by Thorn et al. (2022) in cattle slurry, albeit at a greater frequency of addition. There was on average 14 days in between each treatment in this study and it is

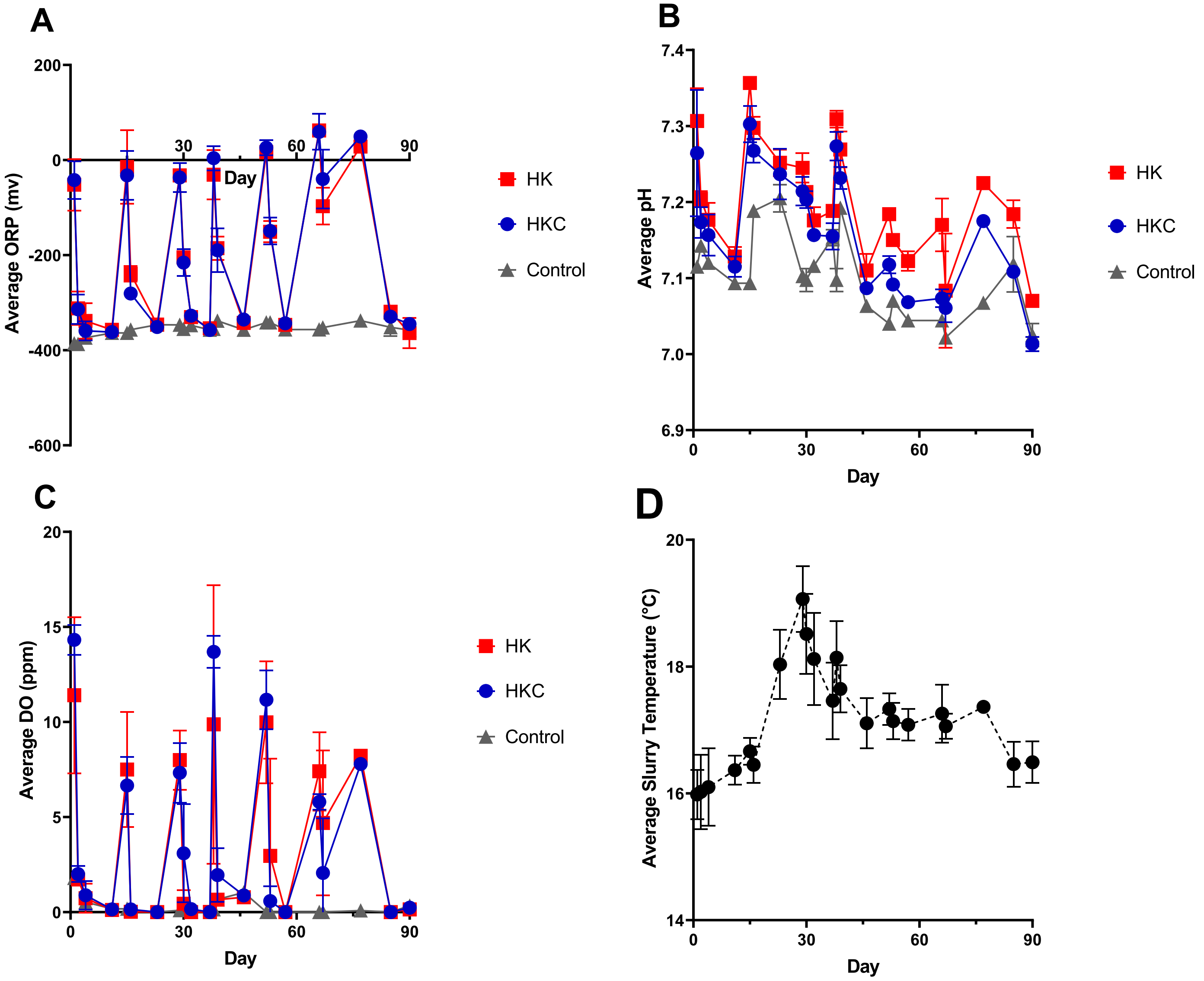

Fig. 2. A/B/C/D: A; average ORP (mv) B; pH C; dissolved oxygen of slurry during 90-day storage period, with error bars representing standard deviation displayed. D; Average temperature of slurry during experimental trial (does not include diurnal variations). HK (H_2O_2 + KI), HKC (H_2O_2 + KI + $CaCl_2$) and control shown in the figure. Depth of measurements were averaged between depths of 83, 54, 24 cm and 4 cm below slurry surface.

probable that a more frequent treatment regime, similar to Thorn et al. (2022) is required to reduce the CH_4 production further. The total and volatile solids content of the slurry (Table 1) were also very low which may have affected the treatment efficacy. Note that the TS and VS of all the slurries increased after 90 days of storage period, this is most likely due to the large amount of evaporation that took place during the experiment. However, it is unclear why HKC evaporated significantly more than HK.

Table 1
Total solids (g k^{-11} slurry), volatile solids (g kg^{-1} slurry) and total ammoniacal nitrogen (mg kg^{-1} slurry) pre and post storage. HK (H_2O_2 + KI), HKC (H_2O_2 + KI + $CaCl_2$) and control displayed. Pre-storage was measured 24 h before the beginning of the storage experiment. Letters indicate significance of given measurements within columns.

Treatment	TS (g kg^{-1} slurry)	VS (g kg^{-1} slurry)	TAN (mg kg^{-1} slurry)
Pre-Storage	29.9 ± 1.2^{a}	21.3 ± 1.4 ^{a}	871.35 ± 16.42^{a}
Control	32.2 ± 1.1^{b}	22.5 ± 1.1 ^{b}	784.42 ± 7.99^{b}
HK	33.4 ± 1.0 ^{c}	22.5 ± 1.2 ^{b}	716.88 ± 14.08^{b}
HKC	36.2 ± 2.3 ^{d}	24.0 ± 1.1 ^{c}	763.03 ± 5.79^{b}

Aeration is the process of pumping air into slurry storage units and is typically carried out multiple times per day in order to maintain high DO and ORP levels. It has been shown previously to reduce CH_4 emissions from slurry storage by approx. 43 % compared to control (Amon et al., 2006). Calvet et al. (2017) also studied low frequency aeration in pig slurry and found CH_4 emissions were reduced by 40 % compared to control. The treatment in this study uses a very similar process to aeration, i.e. the introduction of oxygen to an anaerobic slurry store, but is applied much less frequently than the studies outlined above. Introducing oxygen to the slurry store in a concentrated form such as H_2O_2 may prove a more effective method of raising the ORP as ambient air is composed of approx. 21 % oxygen. This difference in additives may influence the microbial environment in a way not previously observed via a release of more reactive oxygen species. The constant maintenance of aerobicity during aeration, although effective in reducing CH_4 emissions, will negatively impact the concentration of VFAs within the slurry. Paul and Beauchamp (1989) found total VFA concentrations were reduced by 22 % and 84 % when slurry was aerated for 1 and 4 days respectively. Although VFA concentrations were not measured during this study, it is speculated that since ORP levels were held in aerobic conditions for approx. 48 h (Fig. 2: A), that VFA concentrations may be negatively affected but not to the same extent as the more frequent aeration process. This may be similar to Ahn et al. (2014) who, although observed that aeration prior to anaerobic digestion increased the biogas yield of sewage sludge, the trend only held for 24 h of pre-aeration. After longer periods of pre-aeration (48 & 96 h), Ahn et al. (2014) observed reduced VS concentrations and biogas yields, giving more credence to the notion that intermittent, as opposed to continuous, aerobicity may enhance biogas potential.

3.2. Storage experiment: carbon dioxide & nitrous oxide

Total CO_2 emissions (Fig. 1: C & D) were increased as a result of both treatments HK (5140.83 g m^{-2}) and HKC (5609.22 g m^{-2}) compared to control (2474.27 g m^{-2}), a 108 and 139 % increase, respectively, ($p < 0.05$). These increases are a direct result of the additive foam formation, as after each treatment CO_2 emissions increased rapidly before returning to average baseline daily emissions of approx. 42 g m^{-2} day^{-1} within 24 h. The addition of $CaCl_2$ appeared to have some effect on the release of CO_2 from cattle slurry, increasing its emission by 15 % compared to HK, however this effect was not significant ($p > 0.05$).

Both HK (2.88 g m^{-2}) and HKC (1.01 g m^{-2}) reduced total N_2O emissions by 61 and 86 %, respectively, compared to control (7.43 g m^{-2}) over the 90-day storage period (Fig. 1: B & D) ($p < 0.05$). The N_2O emissions from untreated slurry are similar to those reported by Amon et al. (2006), who observed 0.05 g N_2O m^{-2} day^{-1} while control slurry reported in this study produced 0.083 g N_2O m^{-2} day^{-1}. Differences in emissions between studies are most likely due to differences in DM, TAN content and/or measurement techniques employed. Amon et al. (2006) also found that aerating slurry increases the emission of N_2O during storage by approx. 126 % as aerobic communities can develop (43 % of total GHG emissions abated during aeration due to a reduction in CH_4 emissions). The opposite effect was seen in this study, most likely as a result of the difference in oxygen supplies tested. In this study, oxygen was introduced into the slurry on average every 2 weeks, however, in Amon et al. (2006), slurry was aerated everyday with between 1 & 3 m^3 air m^{-3} slurry day^{-1}. The infrequency with which slurry was treated in this study most likely did not allow for aerobic communities to develop in the same way.

Control tanks produced a crust which started to form after approx. 1 week of storage and appeared dry on the surface. Dry crusts which form on slurry surfaces can produce N_2O emissions due to a combination of anaerobic and aerobic micro-sites (Philippe and Nicks, 2013). Approximately 47 % of control N_2O emissions occurred within the first 23 days of storage, even though the average temperature of the slurry during this time was lower than the rest of the experiment. This indicates that in dry, naturally occurring slurry crusts, the initial period of formation is the period in which most of the N_2O emissions are produced. This is in contrast to Wood et al. (2012) in which the highest N_2O fluxes occurred around day 40 and 120. This difference in observations may be due to the temperature differences between the studies.

HKC inhibited a large amount of N_2O, abating an extra 2.13 g m^{-2} over the 90-day storage compared to HK, $p < 0.05$. This is most likely due to nitrification inhibition caused by $CaCl_2$, although this effect has mostly been reported in soils (Abbasi et al., 2011; Macêdo et al., 2019). However, Witter (1991) did observe increased NH_4^+ (Control – 1.7 mg N g^{-1} slurry; Control – 2.2 mg N g^{-1} slurry) and reduced nitrate (Control – 3.0 mg N g^{-1} slurry; Control – 1.7 mg N g^{-1} slurry) concentrations 9 days post spreading in soil spread with chicken manure when it was amended with $CaCl_2$, also indicating possible nitrification inhibition. The combination of increased oxygen and $CaCl_2$ concentrations used by HKC appeared to operate in tandem to inhibit the denitrification and nitrification processes taking place at the slurry surface and crust.

Taking into consideration total CH_4, N_2O and CO_2 emissions, although HK (24,628 g m^{-2}) and HKC (23,877 g m^{-2}) reduced total GHG emissions by 7 and 9 %, respectively, compared to control (26,247 g m^{-2}), this was not statistically significant (Fig. 1: D) ($p > 0.05$). This simple gas balance is not taking into consideration the energy required in order to produce, transport and mix the chemicals required for the treatment. In this study Control CH_4 represented 82 % of the total GHG emissions (CO_{2eq}) during storage, while in the HK and HKC treatments, this contribution was reduced to 74 and 73 %, respectively. If the CH_4 inhibition exhibited higher efficacy and for a more consistent period of time, such as in Thorn et al. (2022) or Connolly et al. (2023), then GHG abatement may have been achieved.

3.3. Storage experiment: ammonia

Total NH_3 emissions emitted by control slurry was 80.03 g m^{-2}, while HK (168.91 g m^{-2}) and HKC (102.71 g m^{-2}) increased emissions by 111 % ($p < 0.05$) and 28 % ($p > 0.05$), respectively (Fig. 3). $CaCl_2$ treatment affected both cumulative and temporal NH_3 emissions compared to HK, $p < 0.05$. The $CaCl_2$ spray was most effective in the first 48 h of each treatment phase, in which it abated on average 49 % of NH_3 emissions compared to control. This is in contrast with HK, which in the same 48 h increased NH_3 emissions by 78 % compared to the control. The mechanism behind the fleeting nature of the $CaCl_2$ efficacy is explained by Husted et al. (1991) and Vandré and Clemens (1996) as a possible reduction in pH at the slurry surface caused by precipitation of $CaCO_3$ which is an incomplete removal of alkalinity. This reduced the pH of the slurry surface and thus reduced NH_3 volatilization. As CO_2 volatilized from the slurry surface, the $CaCO_3$ provided carbonates and therefore alkalinity, which restored the pH of the slurry surface to its original value, at which point the TAN-rich material and increased surface area of the foam increased NH_3 volatilization to above control levels.

The loss of NH_3 is confirmed by the loss of TAN from the slurry over the 90-day storage period, in which HK (716.88 mg TAN L^{-1}) and HKC (763.03 mg TAN L^{-1}) lost 9 % and 2 % of their TAN, respectively, compared to control (784.42 mg TAN L^{-1}), although this decrease was not statistically significant ($p > 0.05$). Control slurry which lost approx. 10 % of its original TAN content had elevated NH_3 emissions compared to both HK and HKC in the first 7 days, however, once a natural crust formed, the rate of NH_3 volatilization decreased. The $CaCl_2$ spray retained 46.15 mg TAN L^{-1} slurry when compared to the HK, which is

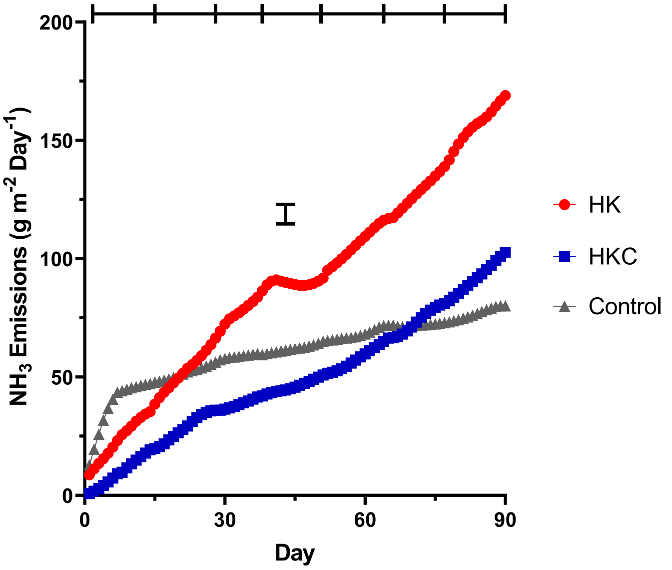

Fig. 3. NH_3 emissions over the 90-day storage period. The effect of $CaCl_2$ addition can be seen in the first 60 days of storage. Pooled standard error of the mean displayed in graph. HK (H_2O_2 + KI), HKC (H_2O_2 + KI + $CaCl_2$) and control displayed. Horizontal bars displayed above the graph indicate treatment periods.

approx. 5 % of the original TAN content. More frequent treatment with $CaCl_2$ may have increased the amount of TAN retained and reduced the NH_3 emissions associated with cattle slurry storage.

There was a slight downward trend in pH in all slurries, decreasing by approximately 0.2 units over the course of the experiment (Fig. 2: B). Upon addition of the treatments, there was an increase of approx. 0.2 units before returning to original levels over the next 7 days. This is most likely as a result of mixing and release of dissolved CO_2. This increase in pH may have increased the likelihood of NH_3 volatilization on the day of treatment. Calvet et al. (2017) also reported a pH increase when aeration was applied to pig slurry, observing a 0.7 unit rise following aeration.

3.4. *Effect of foaming on gaseous emissions*

Rapid decomposition of H_2O_2 and the subsequent release of oxygen caused a significant amount of foaming upon addition of the treatment. This foaming is similar to what is experienced when slurry is acidified and likely caused dissolved CH_4 release that mimicked what occurs during agitation (Kaharabata et al., 1998). This same mechanism also likely caused dissolved CO_2 to come out of solution, causing peaks in emissions on treatment days (Fig. 1: C) (Ni et al., 2001). Foaming also affected N_2O emissions, as it caused residue to settle on top of the slurry surface, destroying the dry crust that had formed. This likely reduced N_2O emissions compared to control tanks as nitrifying bacteria were no longer present along with denitrifying bacteria. Finally, NH_3 was likely the gas most affected by foaming as the exposed TAN-rich slurry that rose to the surface was liable to increased rates of emission. This foam also had an increased surface area due to the large air pockets that dried post treatment, which was in stark contrast to the flat dry mat that formed on top of the control tanks.

3.4.1. *Temperature experiment*

Due to the differences in CH_4 inhibition observed during the 660 L storage trial and Connolly et al., 2023, it was imperative to understand the role of temperature on the efficacy of the treatment. Temperature over the HT (High Temperature) and LT (Low Temperature) storage periods varied by a large amount (Fig. 4: A). The average temperature during the HT period was 19 °C (max – 26 °C, min – 15 °C), while during the LT period the average temperature was 9 °C (max – 11 °C, min – 6 °C). This large range between storage seasons should therefore be a good indicator of how the oxidative treatment operates in different climatic conditions.

Methane emissions increased substantially with temperature (Fig. 5: A & B), as demonstrated by the 6-fold difference in CH_4 emissions from the untreated Control 1 (0.085 kg CH_4 kg^{-1} VS Day^{-1}) at HT versus Control 1 at LT (0.013 kg CH_4 kg^{-1} VS Day^{-1}). Emissions from PT over these storage periods also differed significantly, with HT emissions of 0.152 kg CH_4 kg^{-1} VS and LT emissions of 0.005 kg CH_4 kg^{-1} VS. This represents a 35-fold difference between the seasons, demonstrating the difference in efficacy of the tested dose of the slurry treatment between the seasons.

Under LT conditions, PT emissions were reduced significantly ($p < 0.05$) by 86 % compared to control 2, but not relative to unmixed control 1. Meanwhile, during the HT period, PT produced more cumulative CH_4 than both control 1 and 2, however this was not statistically significant ($p > 0.05$). The emissions observed in this study are similar to values given by Cárdenas et al. (2021), who obtained values of 0.148 kg CH_4 kg^{-1} VS during the summer and 0.0011 kg CH_4 kg^{-1} VS during winter. Emissions also resemble Husted (1994) who stored slurry at 11.1 °C and observed emissions of 0.008 kg CH_4 kg^{-1} VS.

Elsgaard et al. (2016) found that a temperature increase of 20 °C increased CH_4 production by as much as 81 %, while Im et al. (2020) also recorded similar findings where a 20 °C difference in temperature (15–35 °C) increased CH_4 emissions by 94 %. As methanogens are highly temperature sensitive, methanogenic communities may also shift depending on temperature. This temperature driven community adaptation leads to increased abundances of psychrophilic methanogens when the temperature is low and mesophilic methanogens when the temperature increases to 35 °C respectively (Im et al., 2020). Dalby et al. (2021) has shown through simulated models that sub 10 °C is associated with low growth archaea such as *Methanolobus psychrophilus*, while above 10 °C, methanogen biomass increases consistently. PT, therefore, may operate more effectively at lower temperatures due to the reported low methanogenic efficiency of psychrophilic methanogens.

There were no differences in TAN, TS or VS contents of LT slurry between treatments or post storage (Table 2), this was most likely due to the low temperature of the slurry, slowing microbial degradation. Differences between treatments were exacerbated during the HT period in which concentrations of TAN, VS and TS in PT slurry increased significantly compared to pre-storage ($p < 0.05$).

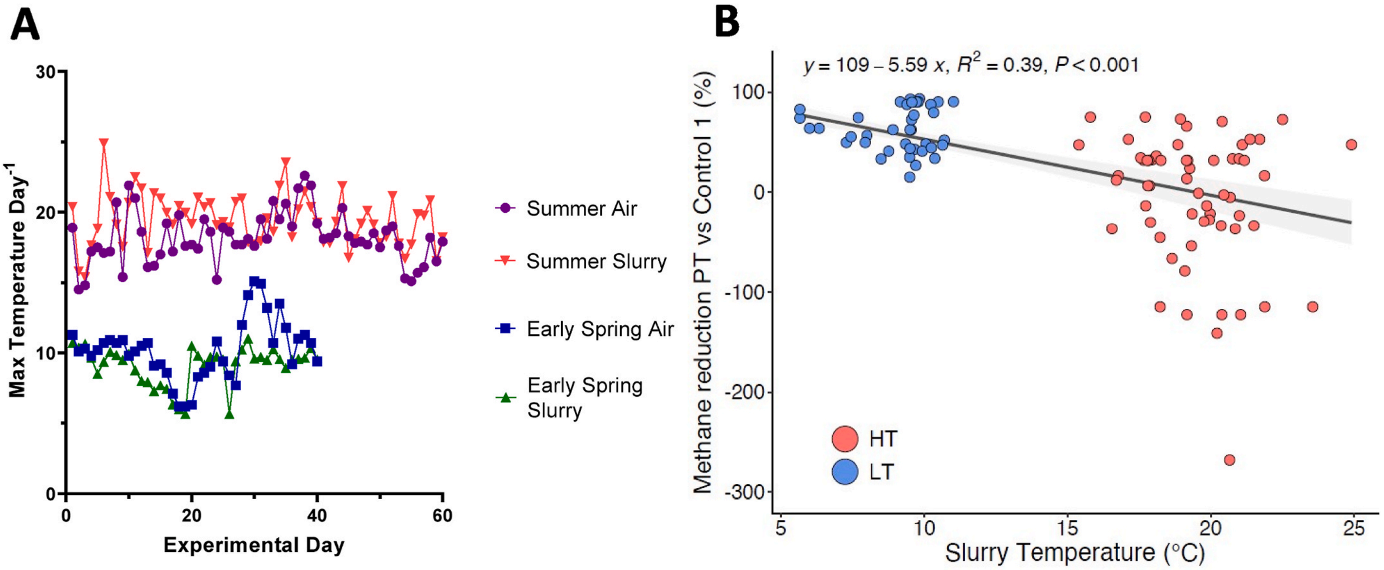

Fig. 4. A/B: A; Summer and early spring maximum air and average slurry temperatures per experimental day. B; CH_4 (kg CH_4 kg^{-1} VS) reduction (%) using the treatment PT during HT and LT time periods in which control 1 was used for comparison.

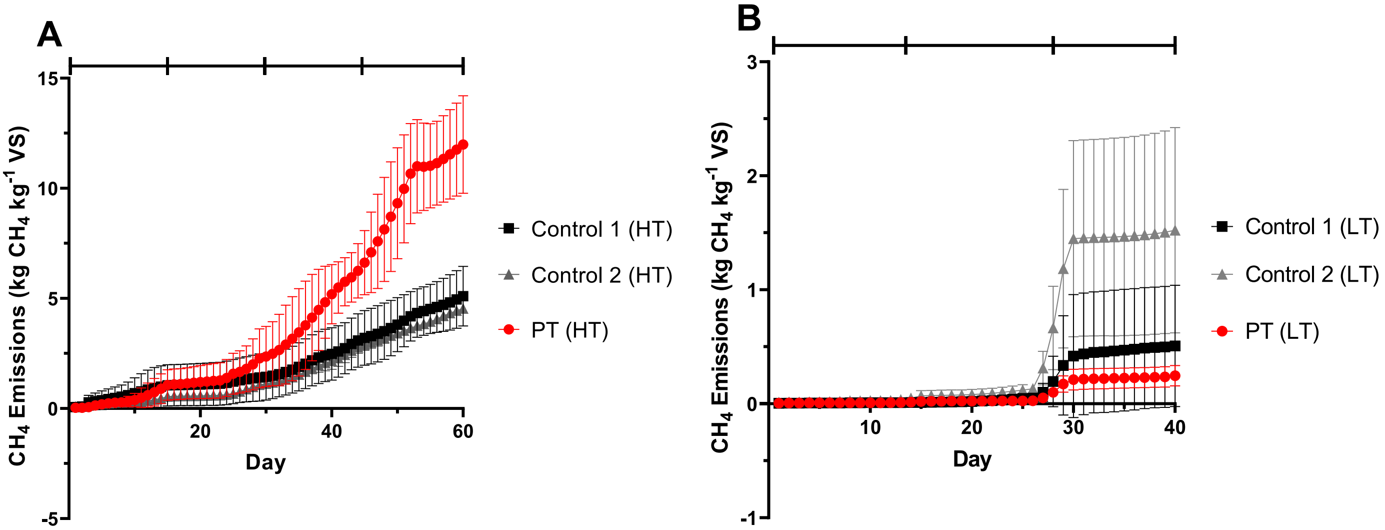

Fig. 5. A/B: Cumulative CH_4 emissions (kg CH_4 kg^{-1} VS) from high (A) and low (B) temperature slurry storage experiments. Horizontal bars displayed above each graph indicate the 2-week treatment period. PT = Peroxide treatment (PT); Control 1 = untreated (no agitation) Control 2 = untreated (with agitation and water). Points represent the mean of biological replicates and error bars show standard deviation (n = 3).

Table 2
Total ammoniacal nitrogen (TAN) (g), total solids (TS) and volatile solids (VS) pre and post storage during high and low temperature experiments. Peroxide treatment (PT) shown alongside control 1 and 2. Letters indicate significance of given measurements within columns.

	High Temperature			Low Temperature		
	TAN (mg kg^{-1} Slurry)	TS (g kg^{-1} Slurry)	VS (g kg^{-1} Slurry)	TAN (mg kg^{-1} Slurry)	TS (g kg^{-1} Slurry)	VS (g kg^{-1} Slurry)
Pre-Storage	588.46 ± 6.64^{a}	106.82 ± 8.43^{a}	70.27 ± 2.50^{a}	622.82 ± 19.70^{a}	83.69 ± 6.15^{a}	62.96 ± 2.00^{a}
Control 1	689.62 ± 79.20^{ab}	98.45 ± 7.11^{a}	65.37 ± 4.27^{a}	619.65 ± 38.81^{a}	94.67 ± 3.28^{a}	66.02 ± 2.89^{a}
Control 2	724.52 ± 103.51^{ab}	101.98 ± 4.11^{a}	65.21 ± 2.02^{a}	562.78 ± 35.17^{a}	89.66 ± 4.54^{a}	66.40 ± 3.33^{a}
PT	813.22 ± 49.82^{cb}	126.59 ± 3.85^{b}	78.00 ± 0.04^{b}	533.33 ± 36.37^{a}	91.74 ± 7.19^{a}	68.75 ± 6.85^{a}

3.5. Temperature experiment – effect of temperature on CH_4 inhibition

CH_4 inhibition during HT and LT periods are shown in Fig. 4: B. The data exhibits less variation during the LT period than the HT period, which displayed periods of inhibition, but was nevertheless overshadowed by longer periods of increased CH_4 evolution. There was a significant difference between the inhibitory effects of the treatment during the LT and HT period, $p < 0.05$. Therefore, the concentration and frequency of the treatment, which was designed and optimized to operate in winter conditions, was less effective in the unforeseen temperature conditions experienced during the 660 L storage experiment. From the extrapolation of data collected, a 53 % inhibition of CH_4 is expected at 10 °C while a 14 % CH_4 inhibition is expected at 17 °C. These estimates are broadly in line with inhibitions observed by Connolly et al., 2023) and the 660 L storage trial and demonstrate the need for precise amendment concentrations and frequencies of addition depending on the specific conditions of the slurry. In order to increase inhibition at higher temperatures, a higher concentration or more frequent rate of addition would be needed to more effectively inhibit methanogenesis. This difference in the efficacy of slurry amendments due to temperature was also observed by Misselbrook et al. (2016), who treated cattle slurry with sulphuric acid and observed an 82 % reduction in CH_4 emissions (g CH_4 kg^{-1} VS) during cool conditions (8 °C) and a 60 % reduction in warm conditions (17 °C).

If winter temperatures were present during the 660 L storage period and a subsequent 53 % CH_4 inhibition was observed, then significant differences would likely have been observed between control (26430 g m^{-2}) and all other treatments, except untreated digestate post storage and spreading (HK; 15116 g m^{-2}, HKC; 14742 g m^{-2}, HK Digestate; 15317 g m^{-2}).

Countries such as Ireland have an agricultural system in which slurry tanks are filled over the winter, when average temperatures are below 10 °C (Met Eireann: Historical Data, 2023) and are emptied prior to and during summer months. In agricultural systems such as these, the treatment described can be effective in reducing CH_4 emissions from cattle slurry storage. However, if higher temperatures are encountered, a higher frequency of treatment may be needed to counteract the increased efficiency of methanogenesis.

3.5.1. Slurry and digestate land spreading: GHG and NH_3 emissions

During both the first and second land spreading trials WFPS increased with time (Fig. 6) in congruence with increased precipitation. Soil temperature also declined in these periods. The increased precipitation along with the decreased soil temperature and sunlight (owing to time of year) meant that the second harvesting period was less optimal for grass growth as compared to the first.

The primary GHG observed during spreading was CO_2, contributing 92 % of total emissions measured. Emissions presented and discussed have background emissions removed i.e. land control (0 N) (758.58 g CO_{2eq} m^{-2}), of which 99 % of emissions were CO_2-based. This was carried out for a more precise examination of treatment emission profiles of slurry and digestate applications.

All spreading associated with organic manures increased total GHG emissions (Fig. 7) compared to CAN fertilizer (37.88 g m^{-2}), however no significant differences were found between treatments. Some variance was observed in the WFPS between treatment blocks (data not shown), which may explain why significant results were not observed, especially considering N_2O emissions. Emissions from CAN fertilizer mostly consisted of N_2O emissions which aligns well with previous literature (Harty et al., 2016; Gebremichael et al., 2021).

Predicted NH_3 emitted over the 168-h period modelled by ALFAM2 are shown in Table 3. Average emission rates for digestates were slightly

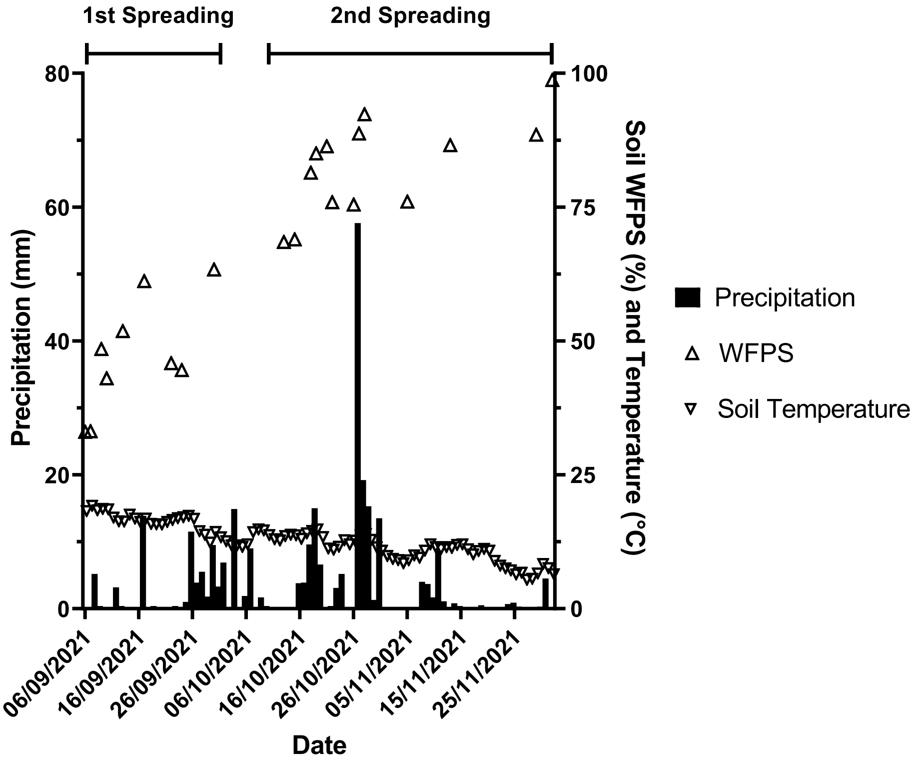

Fig. 6. Precipitation (left y-axis) and soil water-filled pore space and temperature (right y-axis) during the first (starting September 06, 2021) and second (starting October 12, 2021) spreading periods.

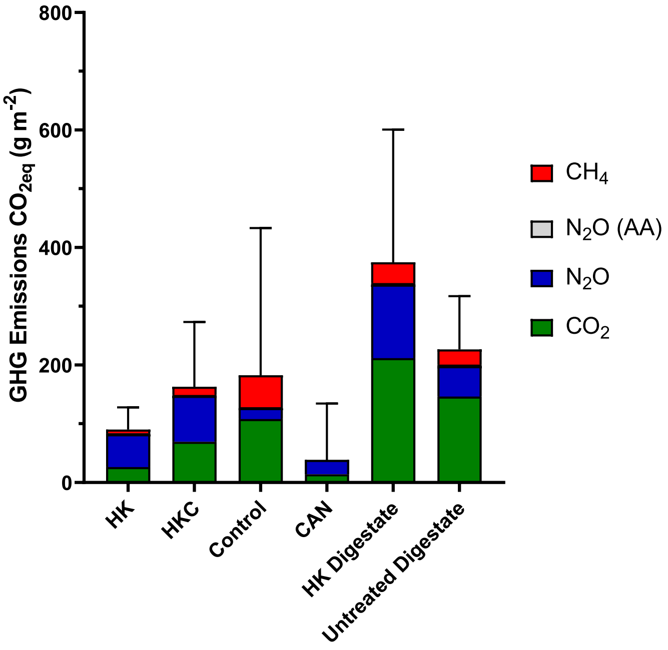

Fig. 7. Total greenhouse gas emissions from two spreading experiments. Error bars displayed represent standard deviation. HK (H_2O_2 + KI), HKC (H_2O_2 + KI + $CaCl_2$), control slurry, HK digestate (digestate originating from HK slurry tanks) and untreated digestate (digestate originating from control slurry tanks) shown in graph.

higher at 16.8 % (of applied TAN) compared to the average emission for slurries at 16.4 % (of applied TAN). This result is expected as digestate typically contains higher TAN concentrations as a result of the AD process and subsequently a higher pH. This comparison aligns with findings from Sun et al. (2014), Koirala et., (2013) and Zilio et al. (2020) who reported that digestate tended to volatilize NH_3 at significantly higher rates, 81 %, 61 % and 230 % respectively compared to undigested slurries.

Table 3

Estimated cumulative (sum of first and second spreading events) NH_3 emissions from field applied slurry and digestate counterparts using the ALFAM2 model.

Treatment	Applied TAN (g m^{-2})	Cumulative NH_3 Emissions (g m^{-2}) (168 h)
HK	2.82	0.46
HKC	3.02	0.51
Control	3.09	0.49
HK Digestate	4.96	0.85
Untreated Digestate	4.98	0.82

3.5.2. *Greenhouse gas emissions - combined storage and spreading*

Storage and spreading of slurries are the two manure management practices in which GHGs are released, however, combining the results and analysing the efficacy of treatments in both areas is rarely undertaken. Cumulatively, there were no significant differences between the various treatments and untreated control (Fig. 8). During storage, HK and HKC inhibited CH_4 production compared to control, but high temperatures as well as agitation and foaming released more CH_4 and CO_2 than expected (Fig. 1: A, C & D). The quantity of GHG emissions released during the spreading trials was very small in comparison to the storage experiment with no significant differences between treatments.

3.5.3. *Implications and limitations of this study*

This study demonstrates that oxidative treatments (HK and HKC) can effectively reduce CH_4 and N_2O emissions during slurry storage, particularly under cooler conditions. The temperature-dependent nature of CH_4 suppression suggests that treatment protocols should be tailored to seasonal and regional climates. In cooler conditions, these treatments

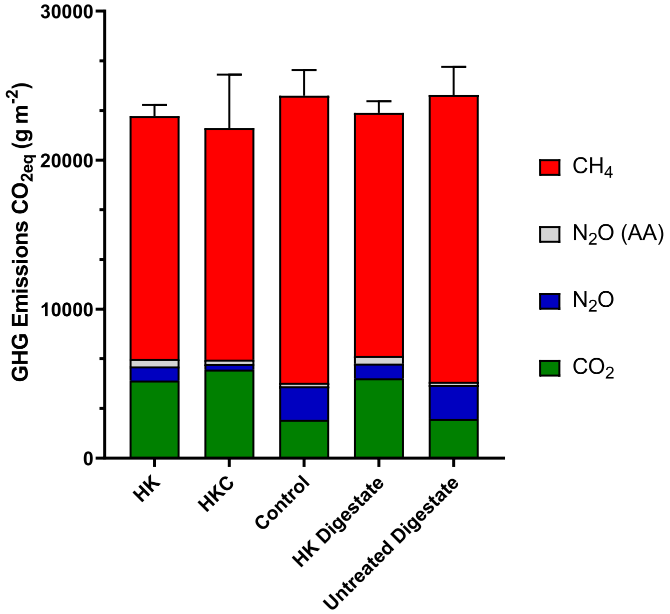

Fig. 8. Total GHG profile (CH$_4$, CO$_2$, N$_2$O & N$_2$O (AA)) of storage and spreading for slurries and digestates. Error bars displayed represent standard deviation for cumulative emissions. HK (H$_2$O$_2$ + KI), HKC (H$_2$O$_2$ + KI + CaCl$_2$), control slurry, HK digestate (digestate originating from HK slurry tanks) and Untreated digestate (digestate originating from control slurry tanks) shown in graph.

could contribute significantly to national and international climate targets, such as Ireland's Climate Action Plan and the EU's Green Deal (Climate Action Plan, 2023; A European Green Deal, 2021).

The addition of CaCl$_2$ as a surface amendment successfully reduced NH$_3$ volatilization during storage, improving nitrogen retention in slurry. This has direct implications for agricultural productivity, as reducing NH$_3$ losses may enhance the fertilizer value of slurry. However, the NH$_3$ reduction effect was transient, lasting primarily within the first 48 h. Future research should explore whether more frequent applications or alternative CaCl$_2$ formulations could extend this effect over a longer duration.

Unlike acidification treatments, which can negatively impact anaerobic digestion (AD) due to low pH and high sulphate concentrations, the oxidative treatment tested in this study is compatible with AD. This means treated slurry could still be used for biogas production, making it a viable strategy for farms integrating AD into their waste management systems. This is directly in the line with Ireland's Biomethane Strategy (Biomethane Strategy, 2024).

A key limitation of this study is that it was conducted as a **batch experiment**, with no fresh slurry added throughout the storage period. In real on-farm slurry tanks, emissions may fluctuate due to continuous slurry additions, potentially altering emission patterns in terms of frequency and concentration. Future studies should consider **dynamic systems** that better reflect real-world slurry management.

Finally, despite significant reductions in CH$_4$ and N$_2$O during storage, no statistically significant differences were observed in cumulative GHG emissions after land spreading. This suggests that while storage-phase treatments are beneficial, additional measures may be needed to mitigate emissions at the spreading stage. Complementary strategies, such as calcium-based sprays or slurry incorporation should be explored to maximize overall emissions reductions.

4. Conclusion

The treatments HK (H$_2$O$_2$ + KI) and HKC (H$_2$O$_2$ + KI + CaCl$_2$) used during the storage of cattle slurry significantly inhibited both CH$_4$ (HK - 651.41 g m^{-2}; HKC – 621.44 g m^{-2}; Control – 768.74 g m^{-2}) and N$_2$O (HK – 2.88 g m^{-2}; HKC – 1.01 g m^{-2}; Control – 7.43 g m^{-2}) production but increased CO$_2$ (HK – 5140.83 g m^{-2}; HKC – 5609.22 g m^{-2}; Control – 2474.27 g m^{-2}) emissions as a result of the method of addition. As such, total GHG emissions during storage were not significantly reduced. GHG emissions from two spreading trials were not significantly different from control regardless of treatment. In this study, when combined, the treatments during storage and spreading showed no significant effect in mitigating cumulative GHG emissions. However, CH$_4$ emissions were significantly affected by temperature during the storage phase of the trial. Slurry stored at 9 °C as opposed to 19 °C was more susceptible to CH$_4$ inhibition. This was primarily due to the increased CH$_4$ production that occurs at higher temperatures. As temperature increases therefore, more frequent treatment may be needed in order to inhibit a more productive methanogenic community. This however, will require real-time CH$_4$ analysis and subsequent amending of slurry to fully elucidate.

The use of CaCl$_2$ as a method of reducing NH$_3$ and N$_2$O emissions and subsequently retaining available TAN during slurry storage is a viable method of slurry treatment especially in its current form of targeting the slurry surface in a spray. HKC reduced NH$_3$ and N$_2$O emissions by 66 g m^{-2} and 1.87 g m^{-2} compared to HK and was most effective in reducing NH$_3$ emissions the first 48 h post application.

Future research should focus on the optimization of the oxidising treatment, the frequency with which to treat the slurry and impact of the total solids content on the treatment formulation. The optimization of the CaCl$_2$ spray is also recommended considering its low cost and ease of implementation. Subsequent spreading trials should be carried out with treated slurry that aims to obtain a fertilizer replacement value for the slurries treated with this oxidising amendment.

CRediT authorship contribution statement

S. Connolly: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **V. O'Flaherty:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition. **C.E. Thorn:** Writing – review & editing, Visualization, Software, Methodology. **D.J. Krol:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

GlasPort Bio Ltd. has applied for patent protection of aspects of the slurry treatments described in this paper.

Acknowledgments

This research was conducted as part of the Teagasc Climate Centre.

The authors would like to thank the funding organisations who helped to support this research.

Sustainable Energy Authority of Ireland (RDD349).

Science Foundation Ireland (14/IA/2371).

Department of Agriculture, Food and the Marine (Ireland) (2021R550).

Data availability

Data will be made available on request.

References

A European Green Deal [WWW Document]. https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en, 2021–. (Accessed 15 April 2023).

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, twenty-first ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington DC.

Abbasi, M.K., Hina, M., Tahir, M.M., 2011. Effect of Azadirachta indica (neem), sodium thiosulphate and calcium chloride on changes in nitrogen transformations and inhibition of nitrification in soil incubated under laboratory conditions. Chemosphere 82, 1629–1635. https://doi.org/10.1016/j.chemosphere.2010.11.044.

Ahn, Y.-M., Wi, J., Park, J.-K., Higuchi, S., Lee, N.-H., 2014. Effects of pre-aeration on the anaerobic digestion of sewage sludge. Environ. Eng. Res. 19, 59–66. https://doi.org/10.4491/eer.2014.19.1.059.

Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. Mitigation of Greenhouse Gas Emissions from Livestock Production 112, 153–162. https://doi.org/10.1016/j.agee.2005.08.030.

Bajpai, P., 2017. Basics of anaerobic digestion process. In: Bajpai, P. (Ed.), Anaerobic Technology in Pulp and Paper Industry, SpringerBriefs in Applied Sciences and Technology. Springer, Singapore, pp. 7–12. https://doi.org/10.1007/978-981-10-4130-3_2.

Biomethane Strategy, 2024. Government of Ireland. Department of the Environment. Climate and Communications. https://www.gov.ie/en/consultation/9b170-consultation-on-the-draft-national-biomethane-strategy/. (Accessed 1 May 2024).

Bobbink, R. Roelofs, J.G.M. n.d. Nitrogen critical loads for natural and semi-natural ecosystems: the empirical approach. Acid Reign 4.

Buckley, C., Krol, D., Lanigan, G.J., Donnellan, T., Spink, J., Boland, A., Forrestal, P., Humphreys, J., Murphy, P., O'Brien, D., O'Dwyer, T., O'Mara, F., Richards, K., Shalloo, L., Wall, D., Waters, S., 2020. An Analysis of the Cost of the Abatement of Ammonia Emissions in Irish Agriculture to 2030.

Burchill, W., Lanigan, G.J., Forrestal, P.J., Reville, F., Misselbrook, T., Richards, K.G., 2016. A field-based comparison of ammonia emissions from six Irish soil types following urea fertiliser application. Ir. J. Agric. Food Res. 55, 152–158.

Cárdenas, A., Ammon, C., Schumacher, B., Stinner, W., Herrmann, C., Schneider, M., Weinrich, S., Fischer, P., Amon, T., Amon, B., 2021. Methane emissions from the storage of liquid dairy manure: influences of season, temperature and storage duration. Waste Manag. 121, 393–402. https://doi.org/10.1016/j.wasman.2020.12.026.

Calvet, S., Hunt, J., Misselbrook, T.H., 2017. Low frequency aeration of pig slurry affects slurry characteristics and emissions of greenhouse gases and ammonia. Biosyst. Eng. 159, 121–132. https://doi.org/10.1016/j.biosystemseng.2017.04.011.

Climate Action Plan, 2023 [WWW Document], 2022. https://www.gov.ie/en/publication/7bd8c-climate-action-plan-2023/. (Accessed 15 April 2023).

Connolly, S., Krol, D.J., Kelleghan, D., O'Flaherty, V., 2025. Hydrogen sulphide inhibition in cattle slurry by use of an oxygen based slurry amendment. Process Saf. Environ. Prot. 193, 125–131. https://doi.org/10.1016/j.psep.2024.11.022.

Connolly, S., O'Flaherty, V., Krol, D.J., 2023. Inhibition of methane production in cattle slurry using an oxygen-based amendment. J. Clean. Prod., 136272 https://doi.org/10.1016/j.jclepro.2023.136272.

De Klein, C., Harvey, M., 2015. Nitrous Oxide Chamber Methodology Guidelines.

Deppenmeier, U., 2002. The unique biochemistry of methanogenesis. Prog. Nucleic Acid Res. Mol. Biol. 71, 223–283. https://doi.org/10.1016/s0079-6603(02)71045-3.

Dinuccio, E., Berg, W., Balsari, P., 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmos. Environ. 42, 2448–2459. https://doi.org/10.1016/J.ATMOSENV.2007.12.022.

Domingo, N.G.G., Balasubramanian, S., Thakrar, S.K., Clark, M.A., Adams, P.J., Marshall, J.D., Muller, N.Z., Pandis, S.N., Polasky, S., Robinson, A.L., Tessum, C.W., Tilman, D., Tschofen, P., Hill, J.D., 2021. Air quality–related health damages of food. Proc. Natl. Acad. Sci. 118, e2013637118. https://doi.org/10.1073/pnas.2013637118.

Duffy, P., Black, K., Fahey, D., Hyde, B., Kehoe, A., Monaghan, S., Murphy, J., Ryan, A. M., Ponzi, J., 2022. IRELAND NATIONAL INVENTORY REPORT 2022.

Eriksen, J., Andersen, A.J., Poulsen, H.V., Adamsen, A.P.S., Petersen, S.O., 2012. Sulfur turnover and emissions during storage of cattle slurry: effects of acidification and sulfur addition. J. Environ. Qual. 41, 1633–1641. https://doi.org/10.2134/jeq2012.0012.

European Environmental Agency, 2023. National emissions reported to the UNFCCC and to the EU greenhouse gas monitoring mechanism, October 2023 [WWW Document]. https://www.eea.europa.eu/data-and-maps/data/external/national-emissions-reported-to-the-4. (Accessed 4 May 2024).

Gebremichael, A.W., Rahman, N., Krol, D.J., Forrestal, P.J., Lanigan, G.J., Richards, K.G., 2021. Ammonium-based compound fertilisers mitigate nitrous oxide emissions in temperate grassland. Agronomy 11, 1712. https://doi.org/10.3390/agronomy11091712.

Grando, L.R., de Souza Antune, A.M., da Fonseca, F.V., Sánchez, A., Barrena, R., Font, X., 2017. Technology overview of biogas production in anaerobic digestion plants: a European evaluation of research and development. Renew. Sustain. Energy Rev. 80, 44–53. https://doi.org/10.1016/j.rser.2017.05.079.

Habtewold, J., Gordon, R., Sokolov, V., VanderZaag, A., Wagner-Riddle, C., Dunfield, K., 2018a. Targeting bacteria and methanogens to understand the role of residual slurry as an inoculant in stored liquid dairy manure. Appl. Environ. Microbiol. 84, e02830. https://doi.org/10.1128/AEM.02830-17, 17.

Habtewold, J., Gordon, R., Sokolov, V., VanderZaag, A., Wagner-Riddle, C., Dunfield, K., 2018b. Reduction in methane emissions from acidified dairy slurry is related to inhibition of methanosarcina species. Front. Microbiol. 9.

Harty, M.A., Forrestal, P.J., Watson, C.J., McGeough, K.L., Carolan, R., Elliot, C., Krol, D., Laughlin, R.J., Richards, K.G., Lanigan, G.J., 2016. Reducing nitrous oxide emissions by changing N fertiliser use from calcium ammonium nitrate (CAN) to urea based formulations. Sci. Total Environ. 563–564, 576–586. https://doi.org/10.1016/j.scitotenv.2016.04.120.

Husted, S., 1994. Seasonal variation in methane emission from stored slurry and solid manures. J. Environ. Qual. 23.

Husted, S., Jensen, L.S., Jørgensen, S.S., 1991. Reducing ammonia loss from cattle slurry by the use of acidifying additives: the role of the buffer system. J. Sci. Food Agric. 57, 335–349. https://doi.org/10.1002/jsfa.2740570305.

Hungate, R.E., 1960. I. Microbial ecology of the rumen. Bacteriol. Rev. 24, 353–364.

Hjorth, M., Christensen, K., Christensen, M., Sommer, S.G., 2010. Solid-liquid separation of animal slurry in theory and practice. A review. Agron. Sustain. Dev. 30, 153–180. https://doi.org/10.1051/agro/2009010.

IPCC, 2006- Intergovernmental Panel on Climate Change, 2006. In: Eggleston, H.S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.), IPCC Guidelines for National Greenhouse Gas Inventories: Prepared by the National Greenhouse Gas Inventories Programme. Institute for Global Environmental Strategies.

IPCC, 2023. Climate change 2023: synthesis report. In: Lee, H., Romero, J. (Eds.), Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team. IPCC, Geneva, Switzerland, pp. 35–115. https://doi.org/10.59327/IPCC/AR6-9789291691647.

Kaharabata, S.K., Schuepp, P.H., Desjardins, R.L., 1998. Methane emissions from above ground open manure slurry tanks. Glob. Biogeochem. Cycles 12 (3), 545–554.

Kang, S., Hong, Y., Im, M.S., Kim, S.-D., Jeon, E.-C., 2020. Key factors in measuring ammonia emissions with dynamic flux chamber in barns. Sustainability 12, 6276. https://doi.org/10.3390/su12156276.

Kavanagh, I., Burchill, W., Healy, M.G., Fenton, O., Krol, D.J., Lanigan, G.J., 2019. Mitigation of ammonia and greenhouse gas emissions from stored cattle slurry using acidifiers and chemical amendments. J. Clean. Prod. 237, 117822. https://doi.org/10.1016/j.jclepro.2019.117822.

Kelliher, F., Sherlock, R., Clough, T., Premaratne, M., Laughlin, R., McGeough, K., Harvey, M., Mcmillan, A., Reid, A., Saggar, S., 2012. Air sample collection, storage and analysis. In: Nitrous Oxide Chamber Methodology Guidelines, pp. 56–72.

Khomenko, S., Cirach, M., Pereira-Barboza, E., Mueller, N., Barrera-Gómez, J., Rojas-Rueda, D., de Hoogh, K., Hoek, G., Nieuwenhuijsen, M., 2021. Premature mortality due to air pollution in European cities: a health impact assessment. Lancet Planet. Health 5, e121–e134. https://doi.org/10.1016/S2542-5196(20)30272-2.

Kiener, A., Leisinger, T., 1983. Oxygen sensitivity of methanogenic bacteria. Syst. Appl. Microbiol. 4, 305–312. https://doi.org/10.1016/S0723-2020(83)80017-4.

Koirala, K., Ndegwa, P., Joo, H., Frear, C., Stockle, C., Harrison, J., 2013. Impact of anaerobic digestion of liquid dairy manure on ammonia volatilization process. Presented at the Transactions of the ASABE. https://doi.org/10.13031/aim.20131593184.

Kumar, S., Das, A., Srinivas, G., Dhar, H., Ojha, V., Wong, J., 2015. Effect of calcium chloride in abating inhibition due to volatile fatty acids during the Start-Up period in anaerobic digestion of municipal solid waste. Environ. Technol. 37, 1–25. https://doi.org/10.1080/09593330.2015.1119204.

Lim, S.J., Fox, P., 2013. Biochemical methane potential (BMP) test for thickened sludge using anaerobic granular sludge at different inoculum/substrate ratios. Biotechnol. Bioproc. Eng. 18, 306–312. https://doi.org/10.1007/s12257-012-0465-8.

Lyu, Z., Lu, Y., 2018. Metabolic shift at the class level sheds light on adaptation of methanogens to oxidative environments. ISME J. 12, 411–423. https://doi.org/10.1038/ismej.2017.173.

Macêdo, W.V., Sakamoto, I.K., Azevedo, E.B., Damianovic, M.H.R.Z., 2019. The effect of cations (na+, Mg2+, and Ca2+) on the activity and structure of nitrifying and denitrifying bacterial communities. Sci. Total Environ. 679, 279–287. https://doi.org/10.1016/j.scitotenv.2019.04.397.

Misselbrook, T., Hunt, J., Perazzolo, F., Provolo, G., 2016. Greenhouse gas and ammonia emissions from slurry storage: impacts of temperature and potential mitigation through covering (pig slurry) or acidification (cattle slurry). J. Environ. Qual. 45, 1520–1530. https://doi.org/10.2134/jeq2015.12.0618.

Moset, V., Cerisuelo, A., Sutaryo, S., Møller, H.B., 2012. Process performance of anaerobic co-digestion of raw and acidified pig slurry. Water Res. 46, 5019–5027. https://doi.org/10.1016/j.watres.2012.06.032.

Ni, J.-Q., Heber, A., Kelly, D., Sutton, A., 2001. Mechanism of gas release from liquid swine wastes. https://doi.org/10.13031/2013.15699.

Nyameasem, J.K., Zutz, M., Kluß, C., Huf, M.T., Essich, C., Buchen-Tschiskale, C., Ruser, R., Flessa, H., Olfs, H.-W., Taube, F., Reinsch, T., 2022. Impact of cattle slurry application methods on ammonia losses and grassland nitrogen use efficiency. Environ. Pollut. Barking Essex 1987 (315), 120302. https://doi.org/10.1016/j.envpol.2022.120302.

Opio, C., Gerber, P., Mottet, A., Falcucci, A., Tempio, G., MacLeod, M., et al., 2013. Greenhouse Gas Emissions from Ruminant Supply chains—A Global Life Cycle Assessment. Food and Agriculture Organization of the United Nations (FAO). FAO, Rome.

Overmeyer, V., Trimborn, M., Clemens, J., Hölscher, R., Büscher, W., 2023. Acidification of slurry to reduce ammonia and methane emissions: deployment of a retrofittable system in fattening pig barns. J. Environ. Manag. 331, 117263. https://doi.org/10.1016/j.jenvman.2023.117263.

Paul, J.W., Beauchamp, E.G., 1989. Relationship between volatile fatty acids, total ammonia, and pH in manure slurries. Biol. Waste 29, 313–318. https://doi.org/10.1016/0269-7483(89)90022-0.

Petersen, S.O., Andersen, A.J., Eriksen, J., 2012. Effects of cattle slurry acidification on ammonia and methane evolution during storage. J. Environ. Qual. 41, 88–94. https://doi.org/10.2134/jeq2011.0184.

Petersen, S.O., Olsen, A.B., Elsgaard, L., Triolo, J.M., Sommer, S.G., 2016. Estimation of methane emissions from slurry pits below pig and cattle confinements. PLoS One 11, e0160968. https://doi.org/10.1371/journal.pone.0160968.

Philippe, F.-X., Nicks, B., 2013. Emissions of Ammonia, Nitrous Oxide and Methane from Pig Houses: Influencing Factors and Mitigation Techniques.

Rahman, N., Forrestal, P.J., 2021. Ammonium fertilizer reduces nitrous oxide emission compared to nitrate fertilizer while yielding equally in a temperate grassland. Agriculture 11, 1141. https://doi.org/10.3390/agriculture11111141.

Rivera, J.E., Chará, J., 2021. CH_4 and N_2O emissions from cattle excreta: a review of main drivers and mitigation strategies in grazing systems. Front. Sustain. Food Syst. 5.

Sigurdarson, J.J., Svane, S., Karring, H., 2018. The molecular processes of urea hydrolysis in relation to ammonia emissions from agriculture. Rev. Environ. Sci. Biotechnol. 17, 241–258. https://doi.org/10.1007/s11157-018-9466-1.

Sommer, S.G., Christensen, M., Schmidt, T., Jensen, L., 2013. Animal manure recycling: treatment and management. https://doi.org/10.1002/9781118676677;jsessionid=44AC77B289944BB81266A638B92599A5.f03t04.

Staley, B.F., de los Reyes, F.L., Barlaz, M.A., 2011. Effect of spatial differences in microbial activity, pH, and substrate levels on methanogenesis initiation in refuse. Appl. Environ. Microbiol. 77, 2381–2391. https://doi.org/10.1128/AEM.02349-10.

Sun, F., Harrison, J.H., Ndegwa, P.M., Johnson, K., 2014. Effect of manure treatment on ammonia and greenhouse gases emissions following surface application. Water Air Soil Pollut. 225, 1923. https://doi.org/10.1007/s11270-014-1923-z.

Thorn, C.E., Nolan, S., Lee, C.S., Friel, R., O'Flaherty, V., 2022. Novel slurry additive reduces gaseous emissions during storage thereby improving renewable energy and fertiliser potential. J. Clean. Prod. 358, 132004. https://doi.org/10.1016/j.jclepro.2022.132004.

Trego, A.C. Galvin, Sweeney, E., Dunning, C., Murphy, S., Mills, C., Nzeteu, S., Quince, C., Connelly, C., Ijaz, S., Collins G, U.Z., 2020. Growth and Break-Up of methanogenic granules suggests mechanisms for biofilm and community development. Front. Microbiol. 11, 1126. https://doi.org/10.3389/fmicb.2020.01126.

Vandré, R., Clemens, J., 1996. Studies on the relationship between slurry pH, volatilization processes and the influence of acidifying additives. Nutrient Cycl. Agroecosyst. 47, 157–165.

Visser, A., Gao, Y., Lettinga, G., 1993. Effects of pH on methanogenesis and sulphate reduction in thermophilic (55°C) UASB reactors. Bioresour. Technol. 44, 113–121. https://doi.org/10.1016/0960-8524(93)90184-D.

Wagner, C., Nyord, T., Vestergaard, A.V., Hafner, S.D., Pacholski, A.S., 2021. Acidification effects on in situ ammonia emissions and cereal yields depending on slurry type and application method. Agriculture 11, 1053. https://doi.org/10.3390/agriculture11111053.

Witter, E., 1991. Use of CaCl2 to decrease ammonia volatilization after application of fresh and anaerobic chicken slurry to soil. J. Soil Sci. 42, 369–380. https://doi.org/10.1111/j.1365-2389.1991.tb00415.x.

Wood, J.D., Gordon, R.J., Wagner-Riddle, C., Dunfield, K.E., Madani, A., 2012. Relationships between dairy slurry total solids, gas emissions, and surface crusts. J. Environ. Qual. 41, 694–704. https://doi.org/10.2134/jeq2011.0333.

Zilio, M., Orzi, V., Chiodini, M.E., Riva, C., Acutis, M., Boccasile, G., Adani, F., 2020. Evaluation of ammonia and odour emissions from animal slurry and digestate storage in the Po valley (Italy). Waste Manag. 103, 296–304. https://doi.org/10.1016/j.wasman.2019.12.038.

Žurovec, O., Wall, D.P., Brennan, F.P., Krol, D.J., Forrestal, P.J., Richards, K.G., 2021. Increasing soil pH reduces fertiliser derived N_2O emissions in intensively managed temperate grassland. Agric. Ecosyst. Environ. 311, 107319. https://doi.org/10.1016/j.agee.2021.10731.