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Scale-up of a peroxide-based pig slurry additive for gaseous emission reduction and downstream value retention

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ABSTRACT

Pig slurry is an agricultural residue with potential for utilisation as organic fertiliser and biomethane feedstock. That potential value is typically diminished via greenhouse and ammonia gaseous losses during temporary storage, an issue further exacerbated by the global warming, pollutant and malodorous nature of those compounds. Existing methods of reducing emissions from pig slurry may require significant capital outlay and/or may prove difficult to retrofit. A promising reactive oxygen-based additive (GasAbate®) was thus scaled-up to 1 m^3 tanks filled with 750 L weaner slurry. Several experiments were carried out in three distinct phases, namely i. ambient temperature scale-up; ii. heated 1 m^3 trials to determine optimal application method; iii. heated 1 m^3 trials to compare results in static and dynamic chamber scenarios, with each iteration aiming to garner understanding of treatment efficacy under various conditions. The results demonstrate the scalability of this additive, its efficacy in reducing total volume of gaseous emissions (63–90% reduction), ammonia emissions (22–58% reduction) and malodorous compound evolution (22–83% reduction for a range of compounds) during temporary storage and the resulting retention of energy and nutrient value in the slurry, with 34–57% higher biomethane potential. The use of this additive could be well suited to farms that require short-term slurry storage (ca. 30 days) before feeding the slurry to a biogas system.

1. Introduction

Meat production contributes more than half of all agricultural greenhouse gas (GHG) emissions and is continually rising due to population growth and increased meat consumption per capita (OECD/FAO, 2021). Pig meat constitutes 34% of the global meat trade, and despite being non-ruminants, pigs contribute approximately 668 million tonnes CO_2-equivalent GHG emissions each year, or 9% of total livestock emissions, principally from their excreta (McAuliffe et al., 2017). In addition to GHG, piggeries are also major sources of ammonia (NH_3) and hydrogen sulphide (H_2S). NH_3 is an atmospheric pollutant with negative impacts on terrestrial ecosystems (Krupa, 2003) and human health (Balasubramanian et al., 2021). Agriculture contributes over 81% of global ammonia emissions (Van Damme et al., 2021), of which 15% emanates from pig production (Philippe et al., 2011). H_2S also impacts health and can be lethal at concentrations above 500 ppm, where swine manure handling activities can expose both humans and animals to levels above recommended limits (Brglez, 2021). As well as being highly noxious, H_2S is also a nuisance gas in terms of odour, alongside dimethylsulfides and other sulphur containing gases (Blanes-Vidal et al., 2009). These can significantly affect the quality of life of residents near swine production facilities and as such their levels are under strict control and may be the limiting factor preventing expansion (Webb et al., 2014).

In addition to the negative climatic and social implications of emissions from animal manures, they also represent nutrient losses, and thus prevent closing of nutrient loops (Marques-dos-Santos et al., 2023). Pig slurry is a potential feedstock for anaerobic digestion (AD), however gaseous emissions during storage lower its calorific value, necessitating additional purchase of energy crops which increases operational costs (Schievano et al., 2009). EU policy movement toward increasing production of biomethane (target of 35 billion cubic metres under RePower EU), in particular from agricultural residues including slurry, requires strategies that prevent storage-associated methane losses in order to maximise capture of energy potential. Additionally, losses of nitrogen and sulphur in the form of NH_3 and H_2S, reduce nutrient value of slurry necessitating supplementation with costly inorganic fertilisers (Kavanagh et al., 2021).

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Effective mitigation solutions that address a range of gaseous products from manure management are therefore required if the desired emissions reductions (COP26) are to be achieved without impacting productivity. The extent of emissions from pig slurry, and resulting options for their mitigation vary according to several factors including, climatic conditions, pig diet, type of housing and how the slurry is managed, as reviewed by (Philippe et al., 2014). Each of these factors typically has a relevant recommended 'Best Available Techniques' (BAT) for reducing emissions from intensive pig production (Santonja et al., 2017). Following direction from EU Commission Notice on the Guidance to Member States for the update of the 2021–2030 national energy and climate plans (EU, 2022/C 495/02, 2022), covering of stored slurry will become mandatory by 2027. Covering will reduce ammonia emissions by 50–90%, but has inconsistent effects on methane emissions (Kupper et al., 2020).

BATs are based on farm/animal management practices such as slurry cooling, dietary interventions, acidification and slurry management techniques such as regular removal (Santonja et al., 2017), but each has their own drawbacks and limitations. For example, slurry cooling is not practical for large volumes of slurry or in hot climates (Blázquez et al., 2021); dietary interventions for reducing NH_3 do not reduce CH_4 (de la Fuente Oliver et al., 2018; Hansen et al., 2014; Külling et al., 2001); solutions requiring retrofitted infrastructural changes can be cost-prohibitive and regular cleaning of pits is not always practical (Petersen, 2018). In short, many mitigation solutions might be effective in addressing some but not all gaseous emissions (Maurer et al., 2017a) and they are situational – therefore a solution is needed that can be used in various farm setups, without large capital outlay in order to alter existing infrastructure.

Slurry additives represent a means of reducing gaseous emissions from manure, potentially without the need for expensive retrofitting and can also tackle multiple nuisance gasses at once e.g. GHG, ammonia and malodourous and/or noxious gases. Their application is also feasible in most slurry management systems, including slatted tanks, pits and external slurry stores.

Acidification is currently the only additive-based method included in the BAT recommendations and can reduce ammonia emissions by 10–80% depending on the extent of acidification (Kai et al., 2008; Petersen et al., 2014; Kupper et al., 2020) and reduces methane emissions by up to 80% (Wang et al., 2014; Kupper et al., 2020). However, the pH dependent equilibrium of H_2S-HS^--S^{2-} speciation must also be considered, which increases the proportion of sulphide present as dissolved H_2S from 50% at pH 7 to close to 100% at pH 5 (Yongsiri et al., 2004), which could increase H_2S emissions (Frost et al., 1990; Wang et al., 2014), particularly when sulphuric acid is used (Chmielowiec-Korzeniowska et al., 2022). The measured effect of acidification (increase or decrease), appears to alter seasonally (Petersen et al., 2016a) and depending on slurry age (Petersen et al., 2014), although when properly implemented at farm scale, these effects appear minimal (Overmeyer et al., 2023). Fangueiro et al. (2015) note that the impact of acidification impact on other gaseous emissions is not as clearly understood, while it has been found to increase non-methane volatile organic compounds and odour significantly (Pedersen et al., 2022). Furthermore, acidification entails significant capital outlay to the farmer and represents a notable health and safety hazard associated with handling of strong acids (Kavanagh et al., 2019). Relative to non-acidified slurries, land application of acidified slurry improves the fertiliser replacement value (Kai et al., 2008) and the uptake of N and P by plants (Fangueiro et al., 2018). However, while single applications of acidified slurry do not appear to affect soil pH (Schreiber et al., 2023), the impact of repeated land applications could be more detrimental, for example Frost et al. (1990) saw a reduction of 0.42 pH units after 3 applications while Fangueiro et al. (2018) saw a drop of 1.4 pH units after 6 consecutive applications of acidified slurry. As such, there exists the need for a slurry additive appropriate for reducing emissions in addition to odour, especially for manures such a pig slurry where this is an especially relevant issue.

Hydrogen peroxide has been used as a slurry additive to reduce H_2S emissions (reviewed in McCrory and Hobbs, 2001) and through its surface application, Xue and Chen (1999) reduced both odour and ammonia from dairy slurry. A peroxide-based slurry additive (GasAbate®) significantly reduced GHG emissions from cattle manure during laboratory-scale storage experiments (Thorn et al., 2022), and was the basis for this work. However, in an effort to mitigate ammonia emissions, instead of using urea-H_2O_2 as in Thorn et al. (2022), liquid H_2O_2 was employed (Connolly et al., 2023) to test for its efficacy in reducing GHG, ammonia and odour related emissions from stored pig slurry. As the additive is a strong oxidising agent it forms reactive oxygen species, generating conditions unfavourable for obligate anaerobic methanogenic archaea (Ambrose et al., 2023), by increasing the dissolved oxygen concentration and thereby altering the oxidation-reduction potential (ORP) of the slurry (Hjorth et al., 2012; Connolly et al., 2023).

In order to scale up from previously reported laboratory scale tests (Thorn et al., 2022), a series of trials were performed in three distinct phases, with the following objectives; i) understand the scalability of treatment efficacy on swine manure, through 25 L containers to 1 m^3 experiments ii) determine efficacy of the additive at weaner housing temperatures whilst refining treatment application method iii) compare treatment performance in static and dynamic chambers, both in terms of gaseous emission reduction and value retention in the slurry, using nutrient and biomethane potential (BMP) analysis to assess retention of resource value in pig slurry.

The experiments were therefore carried out in three distinct phases (Fig. 1), namely Phase 1 – Ambient temperature scaleup, through 25 L to 1 m^3 intermediate bulk containers (IBCs); Phase 2 – Heated IBCs, testing injected vs mixed treatment application; Phase 3 – Heated IBCs, testing static vs dynamic chambers in a containerised testing facility.

2. Materials and methods

2.1. Slurry

For all trials, slurry was obtained from a weaner house of a large-scale (>3000 sow) pig farm on the day that each trial started. The pig slurry was analysed for total solids (TS) and volatile solids (VS) within 24 h. TS was calculated by drying for 24 h at 105 °C (ISO 11465) while VS was determined by loss on ignition at 550 °C for 2 h (EN 15935:2012). When required, samples were stored at −20 °C for elemental analysis (total C; total Kjeldahl and ammoniacal nitrogen; and total sulphur) which was performed by an accredited analytical laboratory (Cawood, UK). Briefly, analysis included total organic carbon (by combustion); total Kjeldahl nitrogen; ammonia nitrogen (using a Kjeltec analyser) and total sulphur (sample digestion followed by ICP optical emission spectrometry). Mean starting total solids of weaner slurry used throughout the trials was 4.1 ± 0.73% and mean volatile solids concentration was 2.9 ± 0.53%. When 25L drums were used, these were filled with 18L of slurry, while 1 m^3 IBCs were filled with 750 L of fresh slurry.

2.2. Treatment

The additive was tested at a dose of 0.87 g of H_2O_2 per kg fresh weight of slurry to match the peroxide content of treatments used by Thorn et al. (2022) on a fresh weight basis. Additive formulations in the initial trials (Phases 1 and 2) also included 0.266 g of potassium iodide (KI) per kg fresh weight of slurry, per Thorn et al. (2022), with a view to increasing efficacy via release of free iodine (McKeen, 2012). Following results of temperature-related persistence and slurry dry matter (DM) tests (data not shown) it was determined that KI only improved efficacy at higher DM concentration (>14%) and temperature (>25 °C) conditions untypical of full-scale pig farms. Furthermore, improved H_2O_2-only efficacy was observed via injection into the base of the slurry

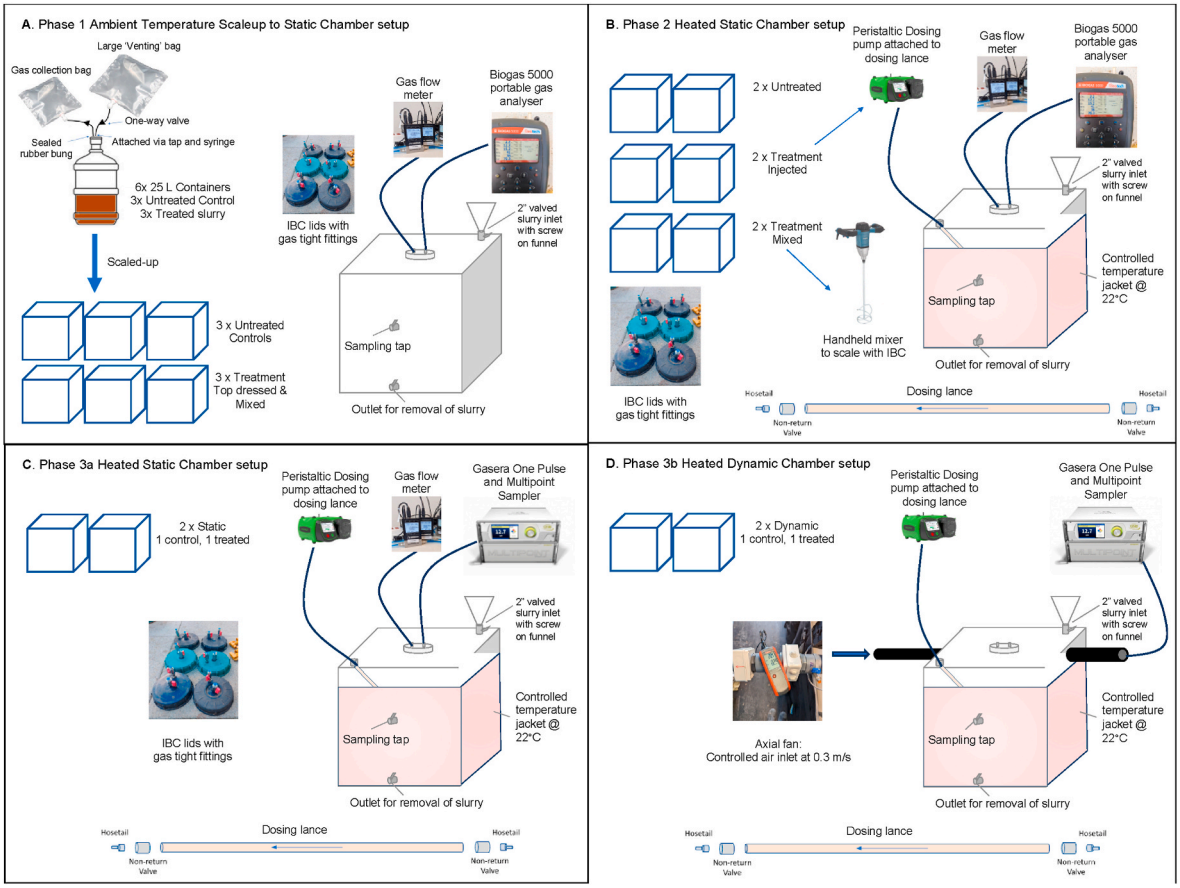

Fig. 1. Setup of IBCs used in a) Phase 1 trial; closed tanks stored at ambient temperature, b) Phase 2 trial; closed tanks at 22 °C and c) Phase 3 trial; closed vs dynamic IBC setup, dynamic IBCs fitted with axial fan to generate airflow over the surface, with photoacoustic analyser for constant gas monitoring. All tanks were 1 m^3 IBCs, had flow meters attached and contained 750 L of slurry.

during Phase 2 trials, and hence, given potential risks of excess environmental iodine (Luo et al., 2014), as well as the expense and added complexity of KI application, treatments in Phase 3 did not include added KI. IBCs either received H_2O_2 at standard dose or were left as untreated controls, to which the equivalent volume of water was added.

2.3. Phase 1 – Ambient temperature trials, 25 L and 1 m^3 scale up

An initial assessment of the scalability of the additive from laboratory tests was carried out in 25 L scale ambient temperature mesocosms, stored in a naturally ventilated outdoor shed with an average temperature of 15 °C (range of 4 °C–25 °C) over the trial period. The trial was started to coincide with the start of the winter storage period (October), as slurry is typically landspread in the preceding months, thereby maintaining lower storage volumes. Mesocosms consisted of 25 L drums (3 treated, 3 untreated) sealed with a rubber bung (Fig. 1a). A gas collection bag and a "venting" bag (Tedlar) containing ambient air from which air could be drawn if negative pressure arose in the sealed container were connected, using a non-return valve to prevent gaseous emissions entering (Fig. 1a). Gaseous emissions accumulated in the collection gas bag and total volume of emissions was measured by transferring the accumulated gas from the gas collection bag to a secondary gas bag from using a 100 ml syringe. The constitution of collected biogas was then analysed using a newly calibrated portable biogas analyser (GeoTech Biogas 5000), fitted with detectors for NH_3 (0–1000 ppm), H_2S (0–5000 ppm), CH_4, CO_2 and O_2 (all 0–100%), requiring ~250 mL per sample.

Testing was then scaled up to six 1 m^3 intermediate bulk containers (IBCs) stored at ambient temperate winter and spring temperatures (central Ireland) averaging 9–13 °C; (Fig. 1a). The IBCs were sealed with lids modified to include outlets for gas flow meters (Omega FMA-1617A), allowing continuous monitoring of the total volume of gases emitted during slurry storage (Fig. 1a). Data from these flowmeters was recorded using a 6-channel chart recorder (ABB SM500F). The headspace gas was measured periodically using the GeoTech Biogas 5000 portable biogas analyser detailed above. The headspace volume was 250L and approximately 250 mL of gas was required for analysis, hence impact on the overall gas dynamics was minimally impacted. An additional sampling port was installed on the side of the IBC to facilitate substrate sampling during the trial. Six IBC tanks were employed, providing replicated untreated (n = 3) and treated tanks (n = 3).

For Phase l trials, the additive was applied via top-dressing followed by gentle manual mixing. Tanks were then left open for 3 h to allow for any potential pressure generated by the treatment interaction with slurry to subside, and time zero was counted as when the tanks were sealed.

2.4. Phase 2 – Heated IBC trials, testing injected vs mixed treatment application

While Phase 1 experiments were performed at ambient temperature, to replicate the temperature of slurry stored in weaner sheds (~22 °C), IBCs were fitted with heating jackets (Kuhlmann Electro-Heat 230V 2 × 1000 W), equipped with temperature controllers (Kuhlmann DigiTherm) and a temperature logger (Lascar EB-USB-TC-LCD) (Fig. 1b).

For treatment addition, the effect of two application methods was assessed, namely: i) by injection using a dosing lance made of 10 mm tubing connected to a dispersal head (Supplementary Fig. 1) designed to

promote interaction of the two treatment components within the slurry while maximising the depth at which the reagent could be delivered within the slurry, aiding dispersal of the treatment or ii) via top dressing with mechanical agitation using a handheld mixer to ensure adequate mixing. A total of 6 IBC tanks were used, therefore each delivery method, and untreated controls, were duplicated. Once all treatments had been applied (~1 h) IBC lids were then closed, and flow meters attached. Headspace gas constituents were again assessed with the Biogas 5000 analyser (5 times/week). On day 7, additional gas samples were taken in foil gas bags for odour analysis using a GC-MS thermal desorption system at a certified odour laboratory (Odour Monitoring Ireland). Concentrations (ppm) of detected odour compounds were then integrated with the emissions rates (from flow meters) to give odour emission rates (mg/hr).

2.5. Phase 3 – Heated IBC trials, testing static vs dynamic chambers

Four IBC tanks were used during this phase; two of which had constant airflow over the surface (dynamic chambers), and two of which had only an exhaust gas outlet, and no air forced over the surface (static chambers, Fig. 1c). For dynamic tanks (Fig. 1d), these were fitted with inlet and outlet pipes, utilising an axial fan (San Ace 60) and fan speed controller (set at 0.3 m/s) to draw fresh air through the inlet pipe from outside the sample room to generate air flow over the slurry surface. The outlet pipes from static and dynamic tanks led to a multipoint sampler (GASERA Ltd., Finland) connected to a newly calibrated photoacoustic multi-gas monitor (Gasera One Pulse; GASERA Ltd., Finland) with sensors for CO_2, CH_4, NH_3 and N_2O (ppb range). Peroxide additive was applied using the optimised injection system from Phase 2, in the absence of KI, where one of each set up remained untreated while the other was treated, making a total of 4 conditions (n = 1). As an injection line was fitted into the tanks, they did not need to be open for additive delivery so recording of emissions readings began from the moment of treatment addition.

2.6. Biomethane potential assays

Biomethane potential (BMP) assays were carried out after each phase to assess biomethane potential of treated versus untreated slurry. Briefly, fresh inoculum was collected from a full-scale agricultural anaerobic digestion plant and degassed for 3 days at 37 °C. BMPs were set up using a 2:1 inoculum to slurry ratio on a VS basis in triplicate 500 mL HDPE bottles with 400 mL working volume, sealed with rubber bungs. BMPs were incubated in a shaking Innova incubator at 80 rpm and 37 °C. Biogas was collected in 500 mL Tedlar gas bags via a needle, which pierced through the bungs and was measured using water displacement method. Methane content of the biogas was analysed on days 3, 7, 14 and 21 using a gas chromatograph (GC) equipped with a flame ionisation detector. The carrier gas was nitrogen and the flow rate was 25 mL min^{-1}. Results were interpreted as volume of methane produced per gram of VS fed.

2.7. Data analysis

Data were analysed in R (R Team, 2017) and plotted with ggplot2 (Wickham, 2016), where plotted data from Phase 1 and 2 are presented as the mean of replicate determinations and error bars represent the standard deviation from the mean. Repeated measures data were analysed by fitting a linear mixed effect model (NLME package; Pinheiro et al., 2023) using the restricted maximum likelihood (REML). The lme model was constructed with treatment and day as fixed effects and experimental unit as a random effect. The resulting model was analysed with an ANOVA and if a treatment effect was seen ($p < 0.05$) then pairwise comparisons were performed using estimated marginal means (emmeans; Lenth et al., 2022). For cumulative data, statistically significant differences in mean on the final day of the experiment were tested for using Kruskal Wallis test and Dunn post hoc tests.

3. Results and discussion

3.1. Phase 1 – Ambient temperature trials

Preliminary scaleup trials at 25 L demonstrated a treatment efficacy that persisted for 210 days (Fig. 2) at ambient temperate oceanic winter through to summer temperatures (west of Ireland), averaging 15 °C. Table 1 summarises gaseous emissions mitigation from all three trial Phases. Concentrations of CH_4, NH_3 and H_2S in the treated container headspace began to increase after 80 days, but the volume of gas being produced remained low (Fig. 2). Hence, during the effective dose period (210 days), the volume of gaseous emissions was 90% lower in treated slurry, with reductions of 96%, 43% and 60% for CH_4, NH_3 and H_2S respectively (Fig. 2). While CH_4 (percent and volume) and total gas volumes from treated drums were significantly different for the duration of the trial ($p < 0.05$), emissions of NH_3 and H_2S were only significantly lower ($p < 0.05$) for the first 120 days of the trial. There was no impact on CO_2 concentrations in the headspace gas in treated compared with untreated slurry ($p > 0.05$).

In terms of the lengthy CH_4 suppression, we hypothesise that the low ambient winter temperatures contributed to this in two ways. Firstly, if any methanogens were affected as a result of the additive, their growth, which is already slow (between 1 and 7 days at 37 °C depending on the species; Khelaifia et al., 2013) would be even slower given that even most methanogens isolated from cold environments have an optimal temperature above 23 °C (Mickol et al., 2018), and temperature is thus a key factor in CH_4 emissions from stored slurry (Qu and Zhang, 2021). Secondly, as enzyme activities are temperature dependent (Lee et al., 2007), those such as catalase which detoxify peroxides would do so more slowly at low temperatures, extended the presence of reactive oxygen species. As ambient temperatures increased (~ day 150), the treatment effect began to wear off. Concentrations of H_2S and NH_3 were also reduced, virtually ceasing for the initial 60 days of the experiment (Fig. 2). As the additive contains reactive oxygen species, it should alter the oxidation-reduction potential (ORP) of the slurry. Indeed, we hypothesise this is one of the modes of methane suppression as ORPs above −300mV are inhibitory to methanogens (Alvarado et al., 2014). Likewise, sulphate reducing bacteria (SRB) are inhibited by ORP values above −150mV (Postgate, 1984; Zhang et al., 2022) which perhaps accounts for the lower levels of H_2S, although ORP was not measured in this study. Indeed, micro-aeration has been used as a strategy to reduce H_2S from AD (Nghiem et al., 2014) and wastewater (Gutierrez et al., 2008). As CH_4 production is reduced, ebullition of gas through the slurry would be significantly less which could lower ammonia emissions by reducing mass flow (Huisman et al., 1990). While this could have significant impacts in closed storage systems such as this, full scale effects of ebullition rates on ammonia emissions may be minimal (Weaver et al., 2022).

Gaseous emissions from the ambient temperature 1 m^3 IBC trials averaged approximately 4.64 L per day of biogas from untreated tanks over the 50 day trial (0.2 L per kg VS per day). Over the course of the 50-day trial, 232 L of gas was emitted from untreated tanks while 93L was released from treated tanks (Fig. 3). This represents a 60% reduction in total gaseous emissions, following a single application of the additive. IBCs were initially dosed via top-dressing with mild manual mixing, and it is likely that inadequate dispersal of the additive reduced its efficacy, as later injection trials indicate (Fig. 4). When assessed on a daily basis (linear mixed model considering effect of treatment as a repeated measure over time), total emissions tended ($p = 0.07$) to be lower in additive treated samples. Differences in final cumulative gas produced by day 50 were significantly lower in treated tanks ($p < 0.05$).

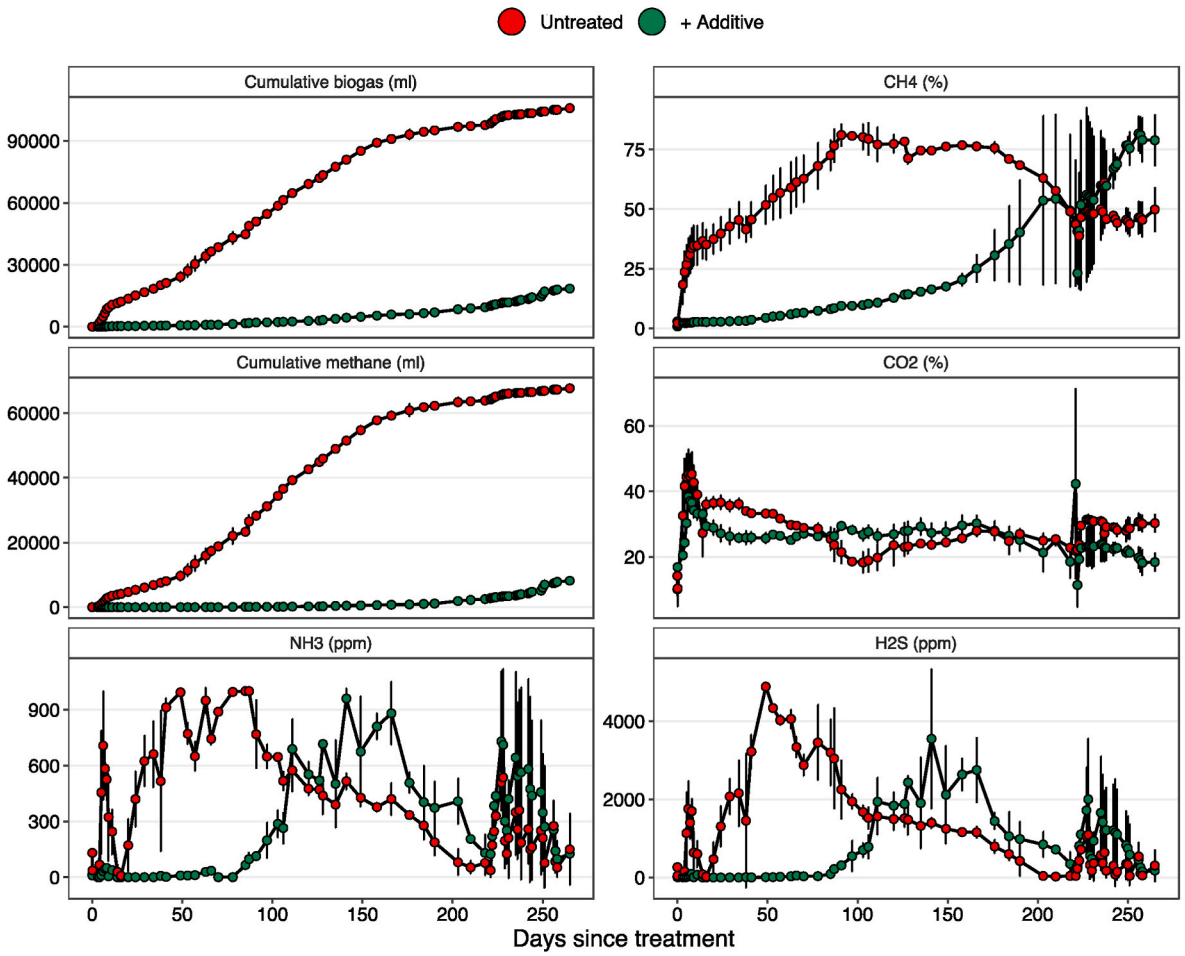

Fig. 2. Gaseous emission volumes and constituent concentrations from ambient temperature 25 L closed container trials.

Table 1
Summary of gaseous emission reduction data from all phases showing average treatment efficacy from Day 0 up to selected timepoints.

Trial	Trial Duration	Treatment Effect at	Gas Vol.	CH_4	CO_2	NH_3	H_2S
Phase 1: 25 L ambient	250 days	210 days	90%	96%	85%	43%	60%
Phase 1: 1 m^3 ambient	50 days	40 days	60%	85%	60%	46%	77%
Phase 2: 1 m^3 22 °C injected	28 days	14 days	78%	83%	68%	78%	76%
		28 days	65%	67%	54%	55%	58%
Phase 2: 1 m^3 22 °C mixed	28 days	14 days	59%	69%	44%	54%	45%
		28 days	26%	27%	6%	22%	12%
Phase 3: 1 m^3 22 °C static	31 days	21 days	71%	86%	81%	–	–
		28 days	71%	83%	62%		
Phase 3: 1 m^3 22 °C dynamic	31 days	7 days	N/A	76%	52%	−24%	–
Seven-day average reduction		14 days		78%	56%	56%	
		21 days		82%	65%	61%	
		28 days		68%	48%	58%	

3.2. *Phase 2 – Additive efficacy at 22 °C and optimal mode of application*

Total emissions from untreated tanks at 22 °C were two orders of magnitude greater than at ambient temperature (200 L vs 12000 L; Fig. 4) demonstrating the marked effect of temperature upon slurry emissions (Dalby et al., 2021; Petersen et al., 2016b; Qu and Zhang, 2021). Despite the temperature increase, significant reductions in total emissions were recorded following additive treatment, with the pumped injection method improving the efficacy of the additive. At two weeks post addition, a 78% reduction in total emissions (gas produced) was seen when using the pumped injection method, versus a 59% reduction following addition and mixing with both being significantly effective vs the untreated control ($p < 0.05$). Sokolov et al. (2021) reports successful methane reduction via acidification of dairy slurry (78% reduction) at 20 °C, but notably acidification efficacy was much lower at 23 °C (19% reduction). When assessing the full 30 day trial however, flow rates (total emissions) were significantly lower ($p = 0.02$) with the injected additive but not the mixed additive ($p = 0.18$), clearly demonstrating how the efficacy of the peroxide + KI additive was improved by injecting into the base of the slurry. Incorporating the content of gaseous emissions revealed reductions in CH_4, CO_2 and H_2S (Fig. 4; Table 1), where some variability was seen between replicates. In this closed system, reductions observed in specific greenhouse gas production were predominantly a function of overall reduction in the volume of gaseous emissions (Fig. 4).

Independent odour analysis of closed tanks was carried out 10 days

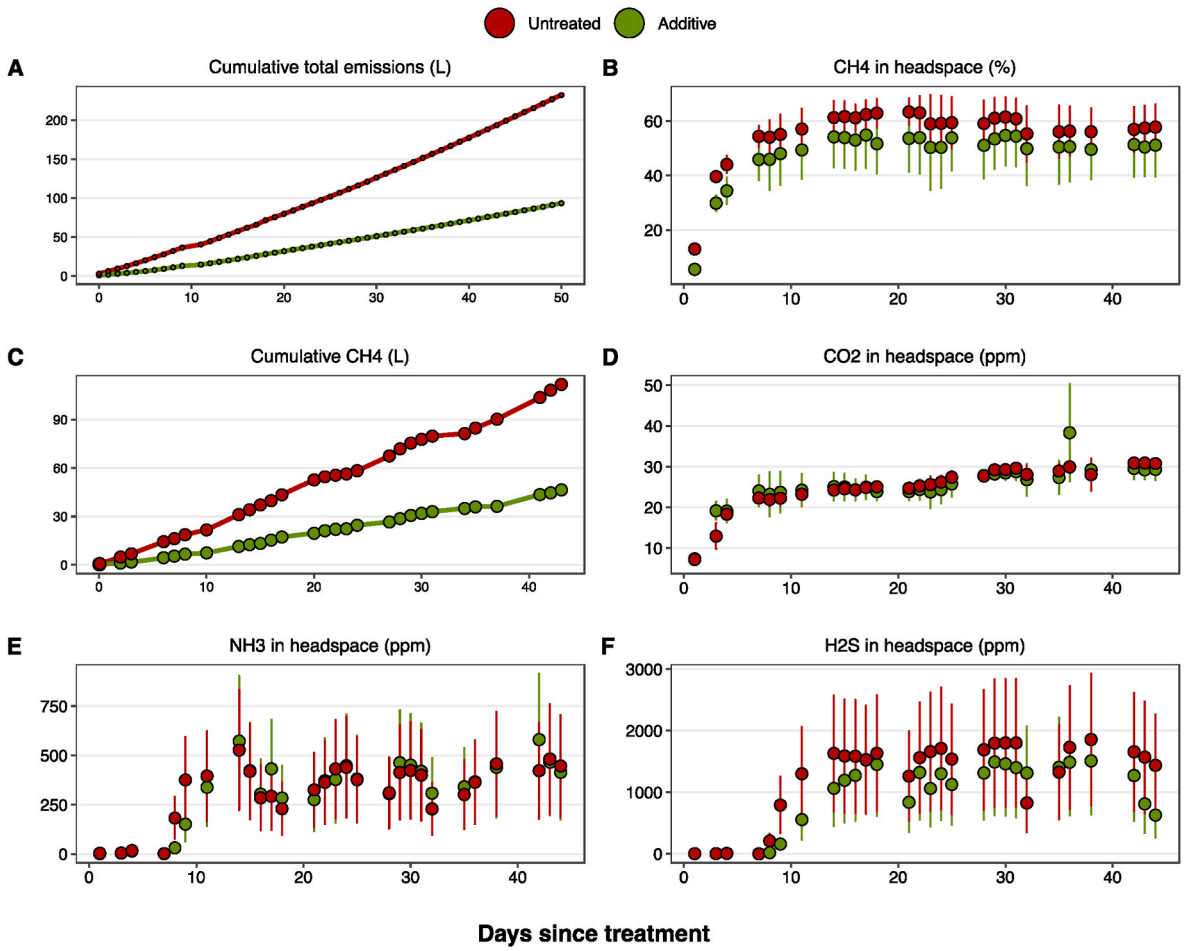

Fig. 3. Cumulative total gaseous and methane emissions from ambient temperature IBCs with or without top-dressed additive treatment (3A, 3C); CH_4, CO_2, NH_3 and H_2S concentrations in the headspace gas produced (3B, 3D, 3E, 3F) (n = 3).

after treatment and no differences were seen as a function of headspace gas concentration at the time of sampling. However, when integrating the total emissions rates, there was again a lower overall evolution rate of compounds normally associated with malodour (Table 2). Methanethiol, ethanethiol and 1-propanethiol evolution rates (mg/hr) were reduced by 77%, 22% and 83%, respectively. As well as being a significant contributor to odour issues arising at large-scale pig facilities, methyl mercaptan (methanethiol) is a toxic compound which may have an impact on swine facility workers (Chmielowiec-Korzeniowska et al., 2018). Hydrogen sulphide was the most abundant odour compound and its evolution rate was reduced by 76% following injection of the additive. These mitigative effects upon odour are in line with a number of studies involving the successful use of oxidising agents to manage livestock manure odour, as summarised in the review of McCrory and Hobbs (2001). Peroxidase enzymes, such as those found in horseradish root waste, have also been added with peroxide sources to enhance this inhibitory effect on odour (Govere et al., 2005; Parker et al., 2012; Yan et al., 2016).

Samples taken at the end of the trial were characterised prior to being used as a feedstock for BMP tests. The soluble chemical oxygen demand (sCOD) was between 25% and 35% higher in treated samples, versus untreated controls (Table 3), while the percent VS was between 9 and 25% higher in treated samples. The solids were slightly lower than average in this run, due to extra washing in the pig units, hence lower numbers. This higher sCOD correlated with the increase in methane production seen from treated samples when assessed as a feedstock using BMPs (Fig. 5).

These BMPs were used to assess the retention of biomethane potential and consequent value as an AD feedstock achieved by significantly reducing gaseous emissions during storage. The 9–25% higher VS in treated slurry, combined with 20% and 23% increases in methane per gram VS for "mixed" and "injected" treated slurry respectively, resulted in a ~40% increase in biomethane per gram fresh weight of treated pig slurry compared to untreated samples. These results indicate that the additive used in the present study may be more appropriate than acidification for reducing emissions from stored slurry which is to be used for anaerobic digestion, as acidification is known to reduce biogas yields if the slurry is used directly, without pH neutralisation or separation (Fangueiro et al., 2015).

3.3. *Phase 3 – Heated IBC trials, testing static vs dynamic, with BMP and elemental analysis*

While slurry is often stored in covered external tanks with little airflow, slatted tanks beneath housing and uncovered lagoons and pools are exposed to surface airflow which can alter gaseous emission rates, particularly of NH_3 (Kupper et al., 2020; VanderZaag et al., 2015). Thus, in addition to static chambers, dynamic tanks were run in parallel over a 31-day period. The profile of gaseous emissions from the static chambers (Fig. 6) relates well to the previously observed emissions profiles in Phase 1 and 2 (Figs. 3 and 4), with overall gaseous emissions reduction of 71% over a four-week storage period, and a corresponding 83% reduction in methane emissions, Wheeler et al. (2010) reported increased CH_4 emissions from dairy slurry (12% TS) following amendment with 30% H_2O_2, but the dose used in those trials ("153 mL of 30% H_2O_2 to 2 kg manure slurry") equates in g peroxide terms to 22.1 g per

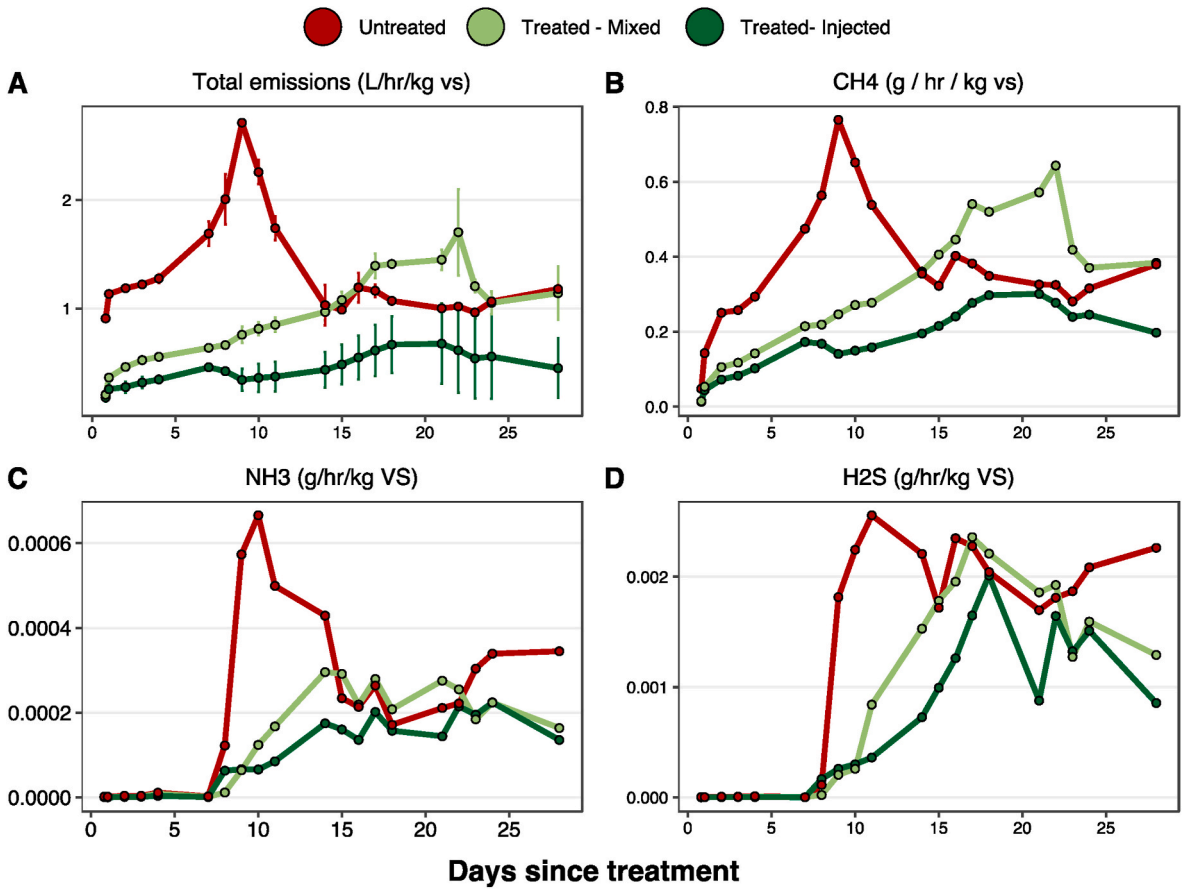

Fig. 4. Total gaseous emissions and CH_4, NH_3 and H_2S fluxes at 22 °C after delivery by pumped injection or top dressing then mixing versus untreated controls.

Table 2
Odour compound concentrations and rates.

	Untreated	Mixed Treatment	Injected Treatment	Unit
Hydrogen Sulphide	851.5 ± 43.5 29.37 ± 1.50	954 ± 11.0 16.13 ± 0.19	874.5 ± 67.5 6.94 ± 0.54	ppm mg/hr
Methanthiol	0.115 ± 0.03 0.0056 ± 0.002	0.21 ± 0.08 0.0050 ± 0.002	0.12 ± 0.05 0.0013 ± 0.001	ppm mg/hr
Ethanethiol	0.05 ± 0.00 0.0032 ± 0.00	0.05 ± 0.00 0.0015 ± 0.00	0.17 ± 0.12 0.0025 ± 0.002	ppm mg/hr
1-Propanethiol	0.085 ± 0.005 0.0066 ± 0.0004	0.075 ± 0.025 0.0028 ± 0.0009	0.060 ± 0.03 0.0011 ± 0.0005	ppm mg/hr

Table 3
Phase 2 slurry analysis.

Timepoint	Treatment	tCOD (g/L)	Total Solids (%)	Volatile Solids (%)	VS/TS
Day 0	Untreated	57.3 ± 1.4	3.37 ± 0.132	2.36 ± 0.117	70.1
	Treated Mixed	67.4 ± 3.2	3.85 ± 0.191	2.79 ± 0.165	72.4
	Treated Injected	65.5 ± 3.0	3.55 ± 0.186	1.30 ± 0.167	71.4
Day 28	Untreated	34.4 ± 1.3	2.02 ± 0.06	1.19 ± 0.05	59.0
	Treated Mixed	46.5 ± 0.3	2.38 ± 0.003	1.48 ± 0.004	62.1
	Treated Injected	43.2 ± 0.2	2.15 ± 0.054	1.30 ± 0.042	60.5

kg slurry, substantially higher than the 0.87 g used in the present work. Similarly, CH_4 increases were recorded with surface application of soybean peroxidase and calcium peroxide, but again the minimum dose used was >2.5 times higher than the dose used herein, and ranged up to 45.7 g per kg slurry (Maurer et al., 2017b). The excessive foaming resulting from application of such high doses likely liberates substantial quantities of dissolved methane from the slurry matrix and may explain Wheeler's observations. The methane reductions recorded in Phase 3 of the present work were particularly pronounced in the first two weeks for static chambers (91%) while the effect on methane emissions had begun to wear off by Week 4 (83% reduction relative to untreated controls). These results compare favourably with the ~67% methane reduction reported by Overmeyer et al. (2023) applying acidification of pig slurry within barns.

The dynamic chamber setup is designed to mimic conditions present in a slatted tank within a pig barn, namely, less anaerobic (particularly at the surface) and more prone to ammonia losses (constant air flow over the surface), thereby allowing for more precise assessment of additive potential for reducing ammonia emissions from open and/or slatted tanks. Hence, as the CH_4 and CO_2 concentrations were consistently diluted with fresh air, the emissions profile differed from static chambers (Fig. 6 versus Fig. 7). Mean production rates of GHG and NH_3 from untreated pig slurry were 0.00583 g N_2O m^{-2} hr^{-1}, 0.268 g NH_3 m^{-2}

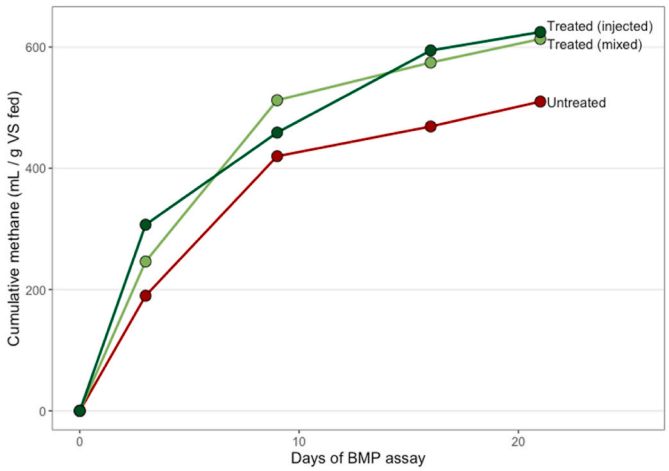

Fig. 5. Cumulative methane per gram VS of slurry fed into a biomethane potential assay, where slurry fed was taken from the final day of Phase 2.

hr^{-1}, 13.8 g CO_2 m^{-2} hr^{-1} and 8.32 g CH_4 m^{-3} hr^{-1}, which are in line with those reported in a review by Kupper et al. (2020), except for methane emissions which were somewhat higher than the baseline emissions of 3.5 g CH_4 m^{-3} hr^{-1} reported therein. Emission rates of all gases were notably reduced by the additive (Fig. 7).

By the end of the 31-day dynamic chamber trial, cumulative emissions for CH_4 and CO_2 were reduced by 68% and 48%, respectively in treated slurry relative to untreated controls. The difference in CH_4 reductions between static and dynamic chambers (83% vs 68%) may be attributed to the more anaerobic environment in the static chambers, which is more conducive to activity of obligate anaerobic methanogenic archaea, and may be indicative of the differences in treatment efficacy when applied to full scale covered or open slurry tanks. Although there was a persistent treatment effect on methane emissions for three weeks (82% reduction in week 3), the treatment effect rapidly wore off by Day 31 (Fig. 7), when the relative reduction figures achieved for CH_4 and CO_2 were 32% and 13%, respectively (Table 1). This indicates that a reapplication of treatment would be required after three weeks under these conditions to maintain treatment efficacy. Acidification of slurry similarly tends to lose impact within 20 days, with pH increasing over time due to formation of carbonate and ammonium and hence repeated or continuous acidification is required (Overmeyer et al., 2021).

Cumulative NH_3 emissions (g NH_3 m^{-2} slurry hr^{-1}) were 47% lower at the end of the 31 day trial. Despite the lower overall NH_3 emissions observed there was however, an initial increase in NH_3 from the treated dynamic trials, lasting ~5 days post-treatment and equating to a ~24% increased emission rate over the first week compared with untreated slurry (Table 1; Fig. 7c), before falling to an average of 57% lower for the remainder of the trial. As a result, the total reduction in NH_3 emissions in dynamic chambers equated to 43% over the course of the trial. A repeated trial running for 12 days for increased granularity on the period immediately following treatment demonstrated a similar GHG emission profile, but lower treatment-associated NH_3 effects in the first ten days (data not shown). Using data collated by Kupper et al. (2020), the overall NH_3 emissions reductions achieved in this study, were similar to those achieved via anaerobic digestion or covering pig slurry using a floating cover of plastic fabrics, maize stalks or wood chips (39–45% reduction) and more effective than solid-liquid separation (-1-18% reduction). In contrast, the treatment was not as effective as acidification or impermeable covers (64–88%) (Kupper et al., 2020). However, existing overground tanks are difficult (and expensive) to retrofit with impermeable covers due to structural integrity, while slatted slurry tanks cannot be covered. Furthermore, acidification with sulphuric acid

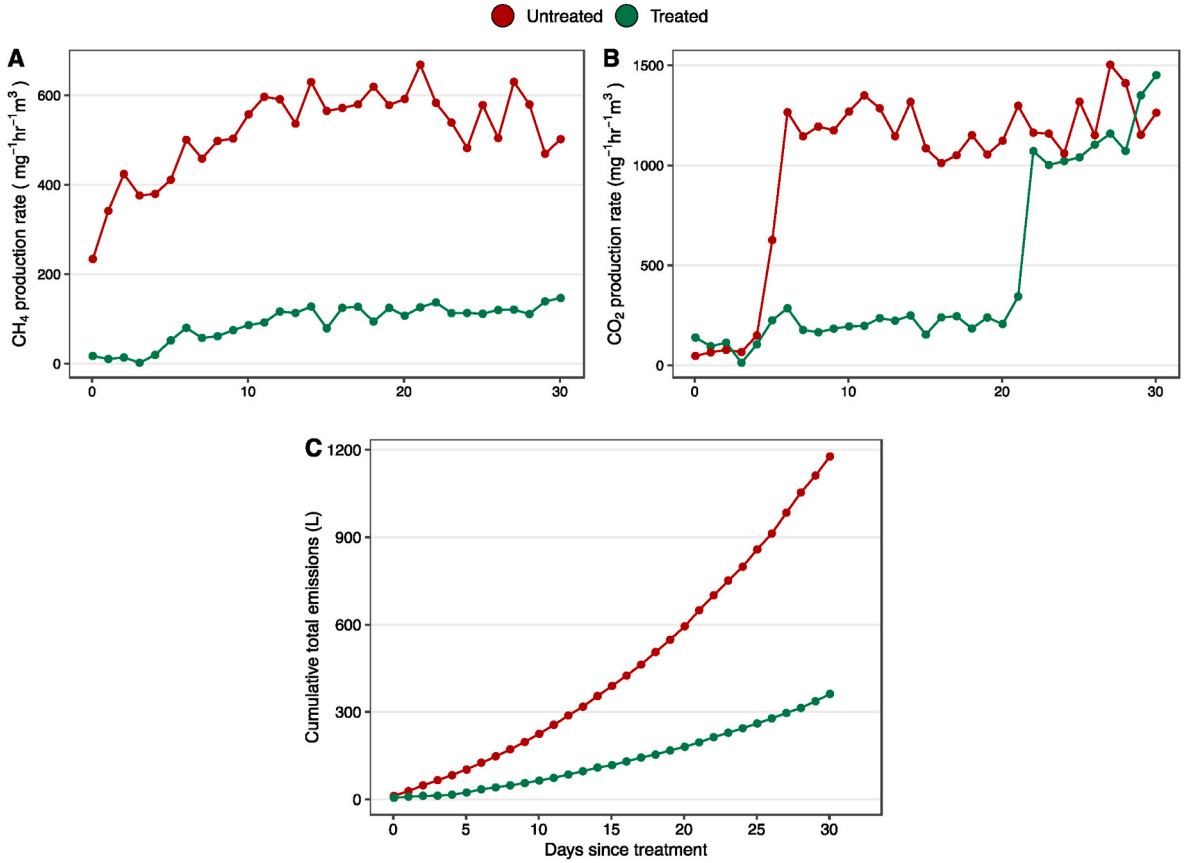

Fig. 6. CH_4 and CO_2 production and cumulative total gaseous emissions from pig slurry stored at 22 °C in static IBCs, following a single dose of additive.

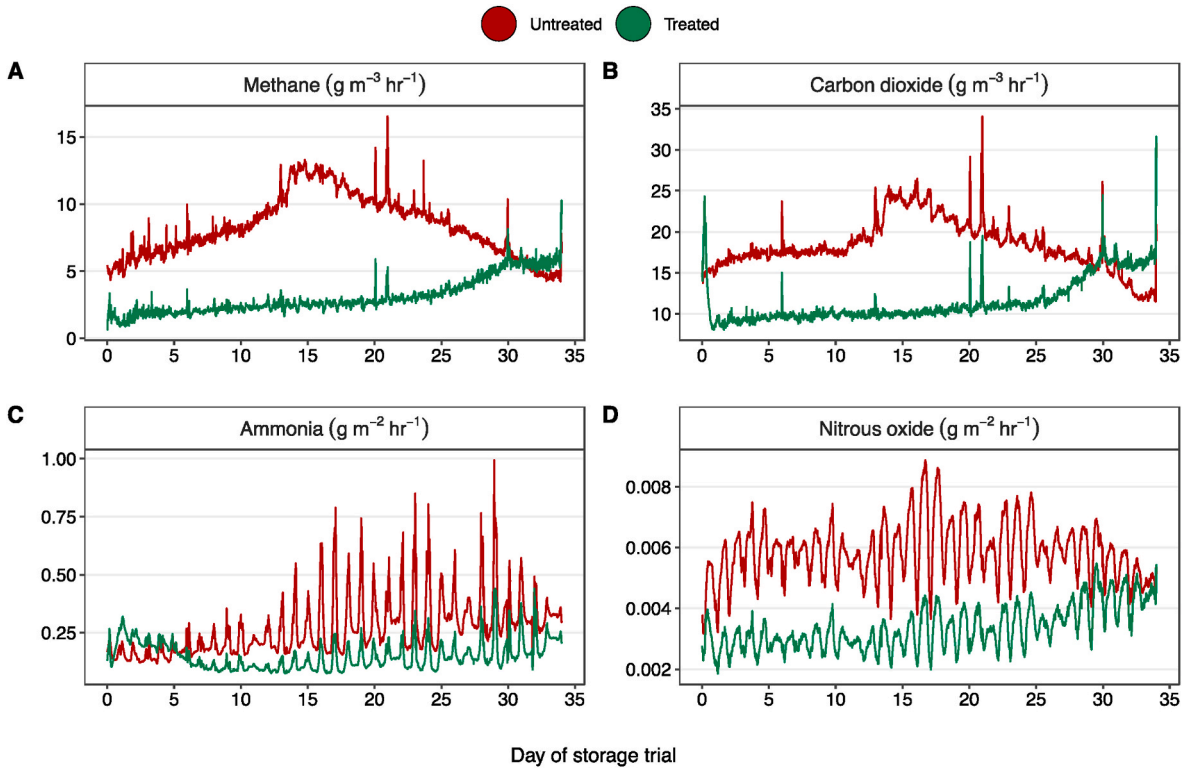

Fig. 7. GHG and NH_3 emissions from pig slurry stored at 22 °C in dynamic IBCs, following a single dose of additive.

renders the slurry unsuitable for downstream anaerobic digestion (Moset et al., 2012), limiting its utilisation in a circular bioeconomy, and requires specialised safety equipment and training which limits rapid and widespread adoption (Overmeyer et al., 2021).

As with CH_4 and CO_2, N_2O emissions were reduced (78%) for the first 21 days, but increased with time, in line with total gaseous emissions. Similar to the emissions figures reported by Kupper et al. (2020) for untreated pig slurry stored in tanks, concentrations of N_2O were three orders of magnitude lower than CO_2 emissions. However, as N_2O emissions are approximately 298 times more potent than CO_2 in terms of 100-year global warming potential (Vallero, 2019), the reductions observed in this trial are significant.

The capability for constant monitoring of the chambers allowed observation of fluctuating concentrations of N_2O and NH_3 in the outlet gas, which were consistent with day/night fluctuations in temperature despite the use of temperature controls on the IBCs. Although IBCs were temperature-controlled at 22 °C, inlet air temperature in the dynamic chambers likely fluctuated with time of day, influencing diffusion of N_2O and NH_3 via convection, which is a function of air movement over the surface and temperature (Kupper et al., 2020; VanderZaag et al., 2015). This is not seen in the data for static chambers as the flow meter took readings every 10 min which were used to calculate an average flow per day, and there is no "inlet" air in static chambers.

As with the preceding phases, samples taken from treated and untreated controls were assessed for residual biomethane potential (Fig. 8). Slurry from the static chambers produced more biomethane than that from dynamic chambers, and treated slurry exhibited more biomethane potential than untreated slurry in both static (34%) and dynamic (57%)

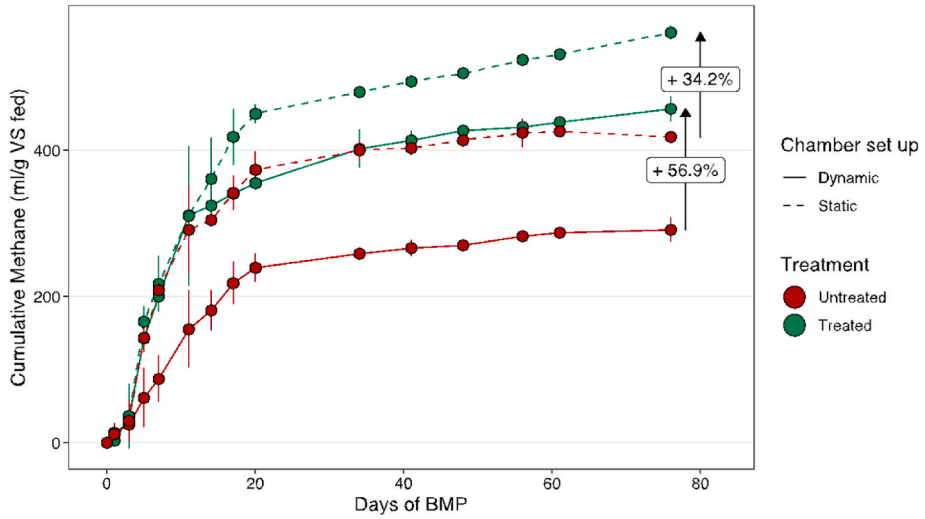

Fig. 8. Biomethane potential of treated and untreated slurry samples from the end of the 35 day storage trial, of both static and dynamic IBC chambers.

chambers. Previously reported biomethane yields for pig slurry range from 330 L CH_4/kg VS (Poulsen et al., 2011) to 568 L CH_4/kg VS (Santos et al., 2022), but it is worth noting that the lower limit of this range may be attributable to biomethane losses during storage.

Finally, results from samples taken weekly from the dynamic chambers and analysed for carbon (C), sulphur (S), pH (T_0: 7.8), and nitrogen (Kjedahl, T_0: 0.53% and 0.51%, and ammonia, T_0: 3648 and 3562 mg/kg for treated and untreated respectively) are presented in Fig. 9 below as a function of change in units from time zero. Additional analysis results are presented in Table 4, which clearly show the retention of volatile solids and COD in the treated slurry, resulting in higher value as a biomethane substrate.

Total organic carbon dropped steadily in the untreated control, starting at 2.2% and falling to 0.89% by week 4, representing a 50% loss of organic carbon (Fig. 9). This is similar to the 38% loss of total carbon seen by Popovic and Jensen (2012), after four weeks storage of pig slurry at 25 °C. Meanwhile in the treated tank, total carbon remained stable throughout the trial, which meant a steady increase in total carbon relative to untreated control was seen week on week, reaching 150% of the untreated control by week 4. Despite the reduction in ammonia emissions following treatment, ammoniacal N was not strongly influenced by the additive, indeed a slight reduction relative to untreated control was seen. Longer term storage studies indicate that a more significant drop in ammoniacal N concentrations in pig slurry can be observed after four months (Popovic and Jensen, 2012), indicating the potential for future studies of long-term treatment with repeated reapplication. Both tanks, starting at ~3600 mg/kg saw a slight increase in ammonia N, likely as organic N in the manure was mineralised. In terms of Kjeldahl Nitrogen, levels remained fairly stable until week 3 where it was 20% higher in treated tanks due to a drop in untreated tanks, from 0.51% on day zero to 0.45% by week 4 (Fig. 9). A similar trend was seen with total sulphur, which dropped off dramatically at week 3 in untreated tanks and at week 4 in treated tanks (Fig. 9). By the end of the experiment total sulphur was still 20% higher (281 mg/kg) in the treated tank than in the untreated tank (230 mg/kg), likely a function of reduced hydrogen sulphide emissions from the former, resulting in retention of these S containing compounds during storage. Higher S in slurry when used as fertiliser results in more efficient nitrogen assimilation and a positive impact on plant growth, facilitating increased activity of S oxidising microbes (Aspel et al., 2022; Chaudhary et al., 2023). Once the most effective phase of the additive passed (~3 weeks) the sulphur content rapidly fell, mirroring the rapid resumption of sulphate reduction typically seen when oxygen stressors are removed (Gutierrez et al., 2008).

Table 4
Slurry analysis from dynamic IBCs in Phase 3 trials (Time 0 samples taken before treatment).

Week	Treatment	TS (%)	VS (%)	% Difference VS Treated & Untreated	tCOD (g/L)	sCOD (g/L)	pH
0	Treated	5.10 ± 0.06	3.66 ± 0.15	14.1	75.9	35.65	7.63
0	Untreated	4.55 ± 0.16	3.21 ± 0.10		72.1	31,2	7.62
1	Treated	4.80 ± 0.09	3.55 ± 0.09	20.0	68.3	29.8	7.65
1	Untreated	4.08 ± 0.05	2.96 ± 0.08		68.7	21.6	7.79
2	Treated	4.61 ± 0.04	3.60 ± 0.41	31.0	60.7	31.8	7.72
2	Untreated	3.97 ± 0.06	2.74 ± 0.38		51.9	20.3	7.93
3	Treated	4.33 ± 0.44	3.33 ± 0.06	27.1	60.5	30.3	7.66
3	Untreated	3.60 ± 0.04	2.62 ± 0.01		45.7	19.2	7.82
4	Treated	4.34 ± 0.05	3.40 ± 0.02	34.6	72.8	26.1	7.74
4	Untreated	3.42 ± 0.15	2.53 ± 0.07		51.6	17.3	7.91

4. Conclusions

A novel chemical additive was used to treat fresh pig slurry at pilot-

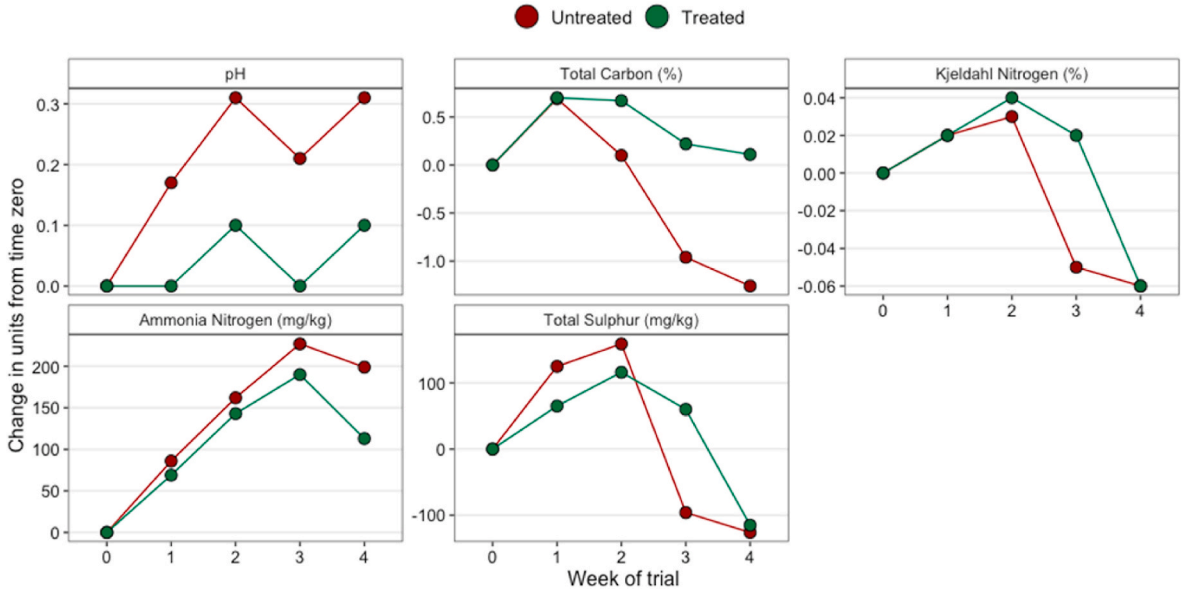

Fig. 9. Weekly elemental slurry analysis from dynamic IBC chambers.

scale, under ambient and warm temperature conditions, in closed and dynamic tanks, and was capable of reducing total gaseous emissions by up to 85%. This included reductions in the potent GHG methane, alongside reductions in carbon dioxide, ammonia, and odorous compounds, particularly the noxious gas H_2S. The additive dose used remained effective at warmer temperatures, but more frequent application would enhance emissions reductions. Indeed by reducing gaseous losses, pig slurry retains demonstrably higher downstream utilisation value.

CRediT authorship contribution statement

Stephen Nolan: Conceptualization, Investigation, Writing – original draft. **Dermot Hughes:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Camilla E. Thorn:** Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Ruairi Friel:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Vincent O'Flaherty:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ruairi Friel reports financial support was provided by Sustainable Energy Authority of Ireland. Vincent O'Flaherty reports financial support was provided by Science Foundation Ireland. Vincent O'Flaherty reports financial support was provided by Government of Ireland Department of Agriculture Food and the Marine. Camilla Thorn, Ruairi Friel, Vincent O'Flaherty has patent issued to GlasPort Bio. 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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