Full-scale implementation of a peroxide-based manure additive for methane mitigation, GasAbate, at an operational dairy farm

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1 Introduction

Livestock manures are valuable sources of crop nutrients which also serve to improve soil health (Tang et al., 2022) upon land-spreading. However, due to this nutrient content, many countries worldwide restrict the use of manures on soils during certain periods of the year in order to reduce the risk of contaminating waterways (etc; refs). During these storage periods, animal wastes begin to decompose due to microbial action, and this serves to release significant greenhouse gases (GHG), representing more than 10% of agricultural GHG emissions (Shukla et al., 2019). Physical conditions also lead to volatilisation of ammonia (NH_3) from the slurry surface, where manure accounts for the majority of agricultural NH_3 emissions. In addition to impacting the environment and human health (Wyer et al. 2022), these emissions represent losses of nitrogen and carbon, thereby lowering the nutrient value of slurry and precluding the closing of nutrient loops (Marques-dos-Santos et al., 2023).

Slurry additives represent a valuable means of mitigating such emissions, thereby potentially retaining their maximum fertiliser value and biogas potential. GasAbate is a peroxide-based slurry additive, which has successfully reduced GHG emissions in during laboratory scale dairy slurry trials (Thorn et al., 2021) and pig slurry trials up to 700L (Nolan et al., 2023). The next step with such an additive is to assess both its efficacy at full scale, in addition to the feasibility of applying the additive.

In order to encourage the uptake of GHG mitigating solutions, their installation and use should impede as little as possible on the day-to-day running of a farm. Retro-fitting a delivery represents minimum disturbance to an operational farm unit, and as such this was chosen as the system design. In addition, the system should also be relatively simple, as complexity has also been identified as a hurdle in update of new technologies (Lim et al., 2023). In addition to system design, another hurdle of assessing slurry additives at full scale is the measurement of GHG emissions from such large volumes of manure. Floating chambers are one method, and they serve to isolate a portion from the surface of a slurry pit and measure the changes in concentration within the chamber over a period. Conditions within the chamber vary from those outside, therefore emissions measured by the chamber method are not representative of the true emissions. However, this method is practical and provides valuable information when used to compare treatments.

The trial consisted of two phases the first of which was to scale up from previously performed laboratory scale research into prototype version of a GHG mitigating slurry additive (Thorn et al., 2021). To achieve this, replicated 1m^3 containers were filled with 700L of dairy slurry and emissions from GasAbate treated tanks were compared untreated. Once validating the efficacy as large scale, the second phase entailed retro-fitting a slurry-additive delivery system to an operational farm unit and performing this in a way that would maximise distribution of the additive with the tanks. To assess the efficacy of the delivered additive at

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full scale, floating chambers were employed to compare CH_4 and CO_2 emissions before and after additive delivery.

2 Materials and methods

2.1 1m^3 storage trial

2.1.1 Tank design and dosing

Replicated testing and validation of dose rate and schedule were performed in six 1 m^3 intermediate bulk containers (IBCs) stored at ambient temperate spring temperatures. Three tanks were fitted with dosing lances consisting of 10 mm tubing connected to a dispersal head sitting at the base of tank. IBCs were filled with 700L of dairy cattle slurry (8.95% solids) which was taken from the slatted tank used later in the trial for full scale testing.

The IBCs were sealed with lids containing outlets for gas flow meters (Omega FMA-1617A), for continuous monitoring of gas volumes emitted during storage, and data was recorded using a 6-channel chart recorder (ABB SM500F). A Geotech Biogas 5000 portable biogas analyser was used to measured headspace gas content weekly. This device was newly calibrated and fitted with detectors H2S (0–5000 ppm), CH4, CO2 and O2 (all 0–100%). The gas content data were integrated with the flow data on the day of sampling to infer volume of GHG produced. For treatment application, at the start of the trial, GasAbate was added at the same dose used in pig slurry (Nolan et al., 2023) to deliver 0.87 g of H_2O_2 per kg (fresh slurry). Thereafter, a maintenance dose of GasAbate was applied every 7 days thereafter which equated to 0.435 g of H_2O_2 per kg slurry. On treatment days all tanks (1-6) were opened (lids removed). Treatment of tanks 1,2 and 4 took place and all lids were put back on all tanks 30 minutes after treatment.

2.1.2 Biomethane potential

On day 56, the IBC tanks were agitated with a handheld mixer and a subsample from each tank was removed and stored at 4°C and shipped for biomethane potential (BMP) assay at Celignis Laboratories (Limerick).

2.2 Farm set up

A 220 cow dairy farm based in County Cork, Ireland was used to perform the research where no ethical approval was required. The animals were housed in a slatted shed, with a roof and open sides (Figure 1a). A slurry scraper ran length ways through the centre of the shed distributing slurry into a beneath-housing tank that arranged in a U shape around the scraper. The tank consisted of two longer sides connected by shorter deeper section of tank. The tank was served by a number of manholes to allow for slurry agitation and removal at the end of the closed period. These were used as sampling points during the trial, as labelled P1, P2 and P3 (Figure 1a).

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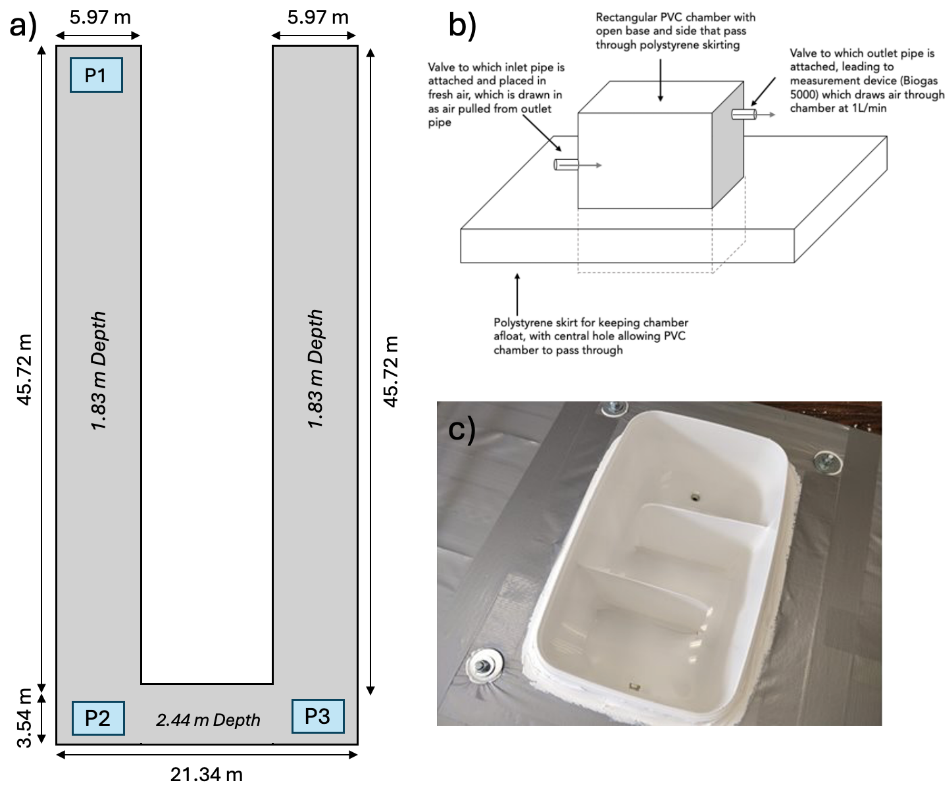

Figure 1. a) Dimensions of slurry tank including maximum slurry depth. Chambers were lowered though agitation point manholes as denoted by P1, P2 and P3. B) Schematic of floating dynamic chamber for emissions assessment c) interior baffles for air mixing.

2.3 Additive delivery system

For full scale implementation of the GasAbate slurry treatment, liquid additive was applied through a series of stainless-steel delivery tubes which fitted between the slats of the existing shed flooring and were designed to sit near the base of the slurry tank. Delivery tubes were serviced by pumping additive from 1m^3 bulk containers (placed on bunds) through a manifold, to ensure equal distribution. Pump control was based on slurry depth and achieved using a programmable logic controller (Figure 2).

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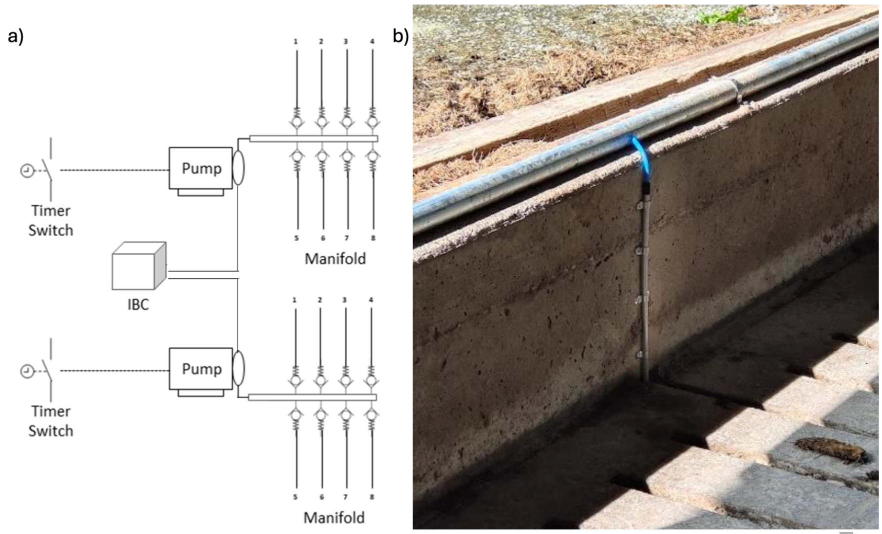

Figure 2. Additive delivery system showing a) depiction of manifold system and b) the injection lines fitting between floor slats.

2.4 Floating chamber design and operation

The design and implementation of the floating chamber was based on that described by Robin et al. (2013).). The chamber was designed to be of adequate size to fit through the agitation point cover, where three chambers were used and lowered onto locations P1, P2 and P3 (Figure 1a). Each chamber consisted of an open-bottomed plastic box with dimensions 0.35 m (L) × 0.215 m (W) × 0.205 m (H). The box was fitted with a polystyrene skirt for buoyancy, where the edge of the plastic box protruded beneath the skirt to create a closed seal once on the slurry surface (Figure 1b). Two holes were drilled at either end of the box, and silicone tubing was attached to create inlet and outlet valves to allow withdrawal of the accumulated gas through one end and pulling in of fresh air to the other end. The chamber contained two dividing walls two thirds the width of the chamber (Figure 1c) to encourage air turbulence therefore improving mixing and accuracy (Robin et al., 2013).

On sample days, each chamber was lowered down through the agitation point of the slatted tank, with protective slat rods in place to prevent falls into the tank. At minutes = 0 a Biogas analyser 5000 (Geotech) was connected to the outlet port and pulled air through the chamber at 1L/minute. This was repeated at 30, 60, 90 and 120 minutes to assess the accumulation of of CH_4 and CO_2. To determine baseline emissions, prior to additive addition,

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2.5 Data analysis

Data were analysed in R (V; cite) and visualised using ggplot (V; Wickham, 2016). For CH_4 and CO_2 content from the floating chambers, background (time zero) readings were subtracted from all readings and the average volume of gas produced between each time point was used to determine the emission flux of polluting gas expressed in mg h^{-1}, based on the area of slurry covered by the chamber. To determine if the treatment effects were statistically significant, data were analysed by fitting a linear mixed effect model (NLME Vx; Pinheiro et al., 2023) using the restricted maximum likelihood (REML). Treatment and day were included as fixed effects and experimental unit (either IBC tank or floating chamber number) as a random effect. After checking residuals for normality, the model was analysed with an ANOVA and if a treatment effect was seen ($p < 0.05$) pairwise comparisons were performed using estimated marginal means (emmeans Vx; Lenth et al., 2022).

3 Results and discussion

3.1 Emissions from replicated, static chambers

Flow meters were used to quantify the volume of gaseous emissions emitted from static storage tanks. Over the course of the 56-day trial, untreated tanks produced 27.5 (± 9.26) L per day amounting to a total of 1538 (± 171.7) L of gaseous emissions (Figure 3). GasAbate treated tanks meanwhile produced on average 27.5 (± 9.26) L per day resulting in a cumulative total of 418 (± 94.2) L emissions, which was a reduction of 73 % (p = 0.006).

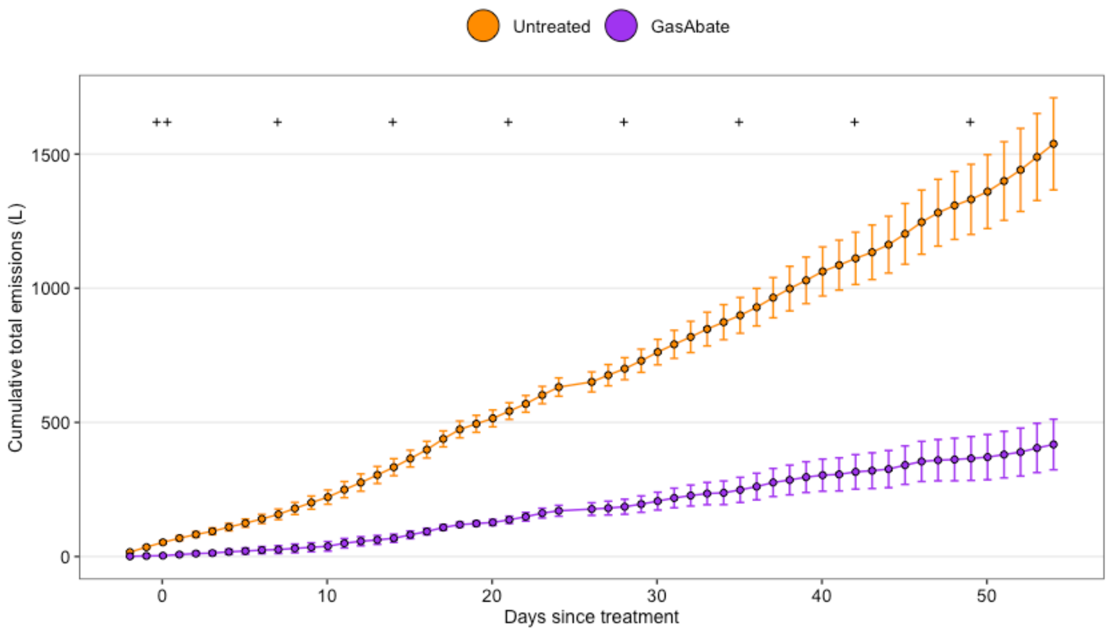

Figure 3. Cumulative total gaseous emissions from 700L dairy slurry stored at ambient temperature in static 1m^3 IBCs where points represent the mean of replicate tanks and error bars the standard deviation of the cumulative emissions (n=3). Additions of GasAbate are denoted by '+' symbols, where double dose was applied on day 0 and a maintenance dose (single dose) every 7 days thereafter.

Over the course of the trial, the content of the emissions was measured weekly, and on average untreated tanks produced 0.37 (± 0.175) g CH_4 hr^{-1} m^2 of slurry (Table 1). In contrast, GasAbate treated slurry produced 0.08 (± 0.042) g CH_4 hr^{-1} m^2. In terms of CO_2, 0.86 (± 0.372) g CO_2 hr^{-1} m^2 were emitted from untreated tanks while emissions were 0.30 (± 0.174) g CO_2 hr^{-1} m^2.

Table 1. Mean methane and carbon dioxide production of the gaseous emissions from 700L stored dairy slurry sampled on 8 separate days over the 56-day storage trial.

	Untreated	GasAbate treated
CH_4 (g hr^{-1} m^{-2})	0.37 ± 0.175	0.08 ± 0.042
CO_2 (g hr^{-1} m^{-2})	0.86 ± 0.372	0.30 ± 0.174

3.1.1 Biomethane potential

Slurry from the end of the storage trial in IBC containers underwent a 28 day assessment of biomethane potential (Figure 5). There was a 10% increase in cumulative biogas from GasAbate treated slurry after the 28 days. This suggests that the CH_4 that was retained during storage with GasAbate, was then released during the biomethane assay. This demonstrates that the additive treated slurry would make a richer feedstock for biomethane production.

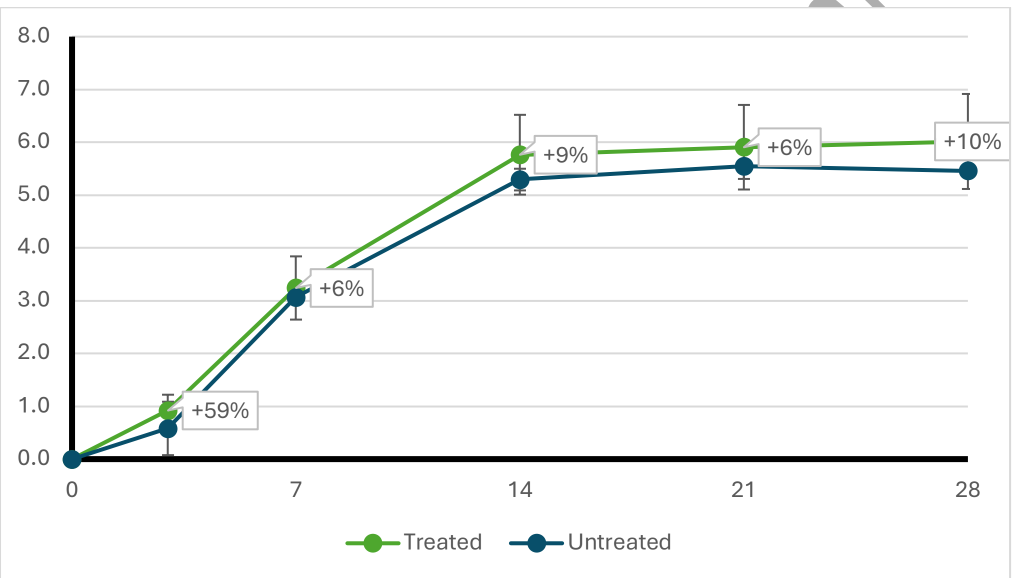

Figure 4. Biomethane potential of untreated and GasAbate treated slurry after storage period.

3.2 Delivery system installation

Prototype delivery systems were developed for dairy farm settings which enable slow, controlled delivery of the additive to prevent foaming. When scaled to multiple farms, this delivery system would be cost-effective to the farmer, particularly when considering the increased value of the treated manure.

3.3 Efficacy of GasAbate additive at full scale

Using floating chambers, recorded baseline CH_4 emissions were similar in tanks 2 and 3, at 0.99 and 0.92 g CH4 hr^{-1} m^{-2} and higher in tank 1 (1.62 g CH_4 hr^{-1} m^{-2}) due to two days where very high emissions were detected (Figure 3). When removing these high readings, baseline emissions from Tank 1 were 1.23 g CH4 hr^{-1} m^{-2} which is more in line with what was seen in other tanks. While manure CH_4 emissions are preferably reported per m^3 (Kupper et al. 2020), this is not possible using the floating chamber method where instead emissions are reported as a function of the surface area of slurry over which the chamber was sited indeed in other emissions studies (Kupper et al. 2020). After GasAbate addition, emissions fell to an average of 0.30, 0.32 and 0.20 g CH4 hr^{-1} m^{-2} in Tanks 1, 2 and 3 respectively over the 8 days (during a 23-day period) that chamber was used. In terms of percentage reduction, CH_4 emissions from Tank 1 were reduced by 81 % (or 75 % when excluding the two high baseline emissions days), and similar CH_4 reductions of 68 % and 78 % were seen from Tank 2 and Tank 3 respectively.

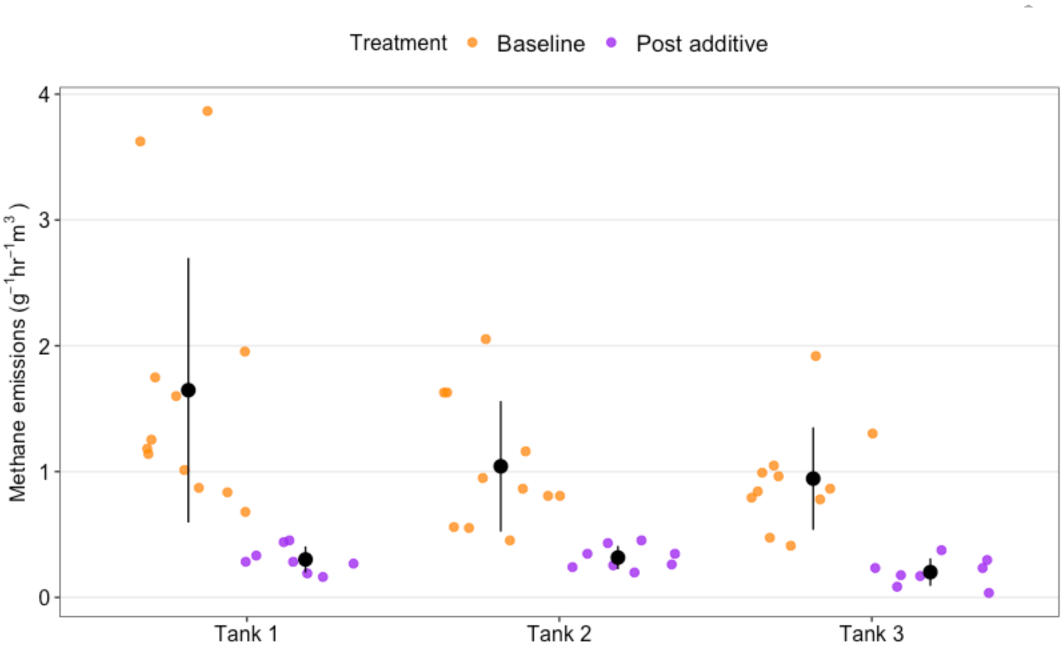

Figure 5. Methane emission from the three slurry tanks before and after addition of the GasAbate additive. Coloured points represent emissions from different sample days while black points represent the average of 13 days pre-treatment (baseline) and 8 days post additive, and error bars denote standard deviation.

4 Conclusions

Full-scale implementation began and was successfully achieved. Together this work demonstrates the progression from successful laboratory scale work (Thorn et al., 2021) to large experimental scale and full-scale use of GasAbate, a peroxide-based slurry additive.

5 Bibliography

(in progress)

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