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Novel slurry additive reduces gaseous emissions during storage thereby improving renewable energy and fertiliser potential

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ABSTRACT

Gaseous emissions from stored livestock manures and slurries are a significant source of greenhouse gases (GHG) and ammonia, accounting for more than 10% of all agricultural emissions in the US and EU. Nitrogen and carbon losses from these emissions reduce the utility of slurry as a fertiliser and as a feedstock for renewable energy generation. Slurry treatment technologies in the form of slurry additives represent an under-utilised means of reducing gaseous emissions and preserving the nutrient content of stored manures. A novel, reactive oxygen halide-based, temporal methanogenic inhibitor was tested on stored cattle slurry. Laboratory storage models were employed to replicate on-farm manure practices in a covered setting. Total gaseous emissions from slurry were reduced by up to 90% during storage. Different sources of reactive oxygen could be used to create a similar inhibition, where the breakdown products are not harmful to the environment or detrimental to the onward use of the slurry. Indeed, additive-treated slurry made a richer feedstock when anaerobically co-digested, increasing methane output by 17%. This proof of concept should now be assessed at farm-scale.

1. Introduction

The agricultural sector is under unrelenting pressure to increase production to provide for a projected 25% growth in population by 2050 (U.N., 2019), while concomitantly improving its sustainability in line with the aims of the Paris Agreement (UNFCCC, 2015). Furthermore, in the European Union (EU) the Green Deal has set an overall objective of achieving net zero emissions by 2050 (European Commission, 2019). Agriculture is a significant source of greenhouse gas emissions (GHG), namely carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), where the sector contributes 11% of total EU GHG emissions (Shukla et al., 2019), 8% of Chinese emissions (UNFCCC, 2012) and 11% of USA emissions (US EPA, 2020). When considering CH_4 emissions alone, agriculture can contribute significantly more, up to 40% in some cases (Shukla et al., 2019). Ammonia (NH_3) is also a significant atmospheric pollutant and while not a GHG, its detrimental impacts upon air quality and terrestrial ecosystems (Krupa, 2003) mean reduction of NH_3 emissions to the atmosphere is also imperative. Globally, agriculture is the largest source of anthropogenic NH_3 to the atmosphere, contributing more than 90% (EEA, 2015).

While improved farming practices in member countries of the Organisation for Economic Co-operation and Development (OECD) have helped to reduce NH_3 emissions, GHG emissions continue to rise (OECD, 2019b). Thus further reductions are required to meet targets set out in the (amended) Gothenburg protocol. This is particularly relevant for countries where agriculture contributes larger fractions of emissions, for example in Ireland and New Zealand where farming accounts for 32% and 48% of total GHG emissions respectively (OECD, 2019a). Further pressure has been created following the UN Climate Change Conference in Glasgow 2021), and the announcement of the Global Methane Pledge (EU Commission, 2021). In addition, technological advances are needed that will allow the developing world to meet growing food production demands while minimising environmental impacts, including emissions (Lybbert and Sumner, 2012).

Manure management contributes a significant proportion of these emissions, up to 58% of NH_3 (Eurostat, 2015) and 7% of GHG emissions (FAOSTAT, 2019). In intensively farmed regions, livestock manures are primarily in liquid form with solids of less than 15% often mixed with urine and bedding material (referred to as slurry). During their storage in pits or lagoons, a crust develops under which anaerobic conditions develop. Gaseous emissions then result from microbial activity within the manure breaking down organic matter into simpler molecules, often

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through bacterial fermentation in the anoxic lower layers, followed by CH_4 production by methanogenic archaea (Dalby et al., 2021). The efficient use of manures is a means of reducing the resulting gaseous emissions, through their capture and downstream use, for example as feedstocks for anaerobic digestion (AD) (Monteny et al., 2006). However, slurries are typically stored for extended periods of time before onward use, including during prohibited spreading periods, which in Europe can be up to 22 weeks long under the Nitrates Directive (91/676/EEC). During this time, not only do slurries contribute to agricultural GHG and NH_3 emissions, but the gaseous losses serve to lower the value of the slurry for onward uses. For example, CH_4 losses reduce the calorific value of slurry as an AD feedstock meaning it has to be co-digested, often with energy crops such as maize silage, which can represent significant additional costs (Schievano et al., 2009). Additionally, nitrogen losses *via* NH_3 volatilisation lower the fertiliser value and reduce the amount of plant-available N within the slurry, creating increased need for costly mineral fertilisers (Wang et al., 2017). This can represent a significant outlay, with synthetic nitrogenous fertilisers costing EU farmers €17 billion in 2017, or between €1000–8000 per farm, while also producing significant GHG during production (EU Commission, 2019). These estimates seem conservative when considering the recent increase in fertiliser prices, where the current (2021) price of diammonium phosphate (USD 643/mt) is double that in 2017 (326 USD/mt; Baffes and Koh, 2021).

Current approaches aimed at reducing emissions from stored slurries include slurry covers; temperature control (refrigeration) of tanks; acidification and lagoon aeration (Monteny et al., 2006), all of which typically involve a large capital outlay. Non-solid slurry covers are less cost inhibitive (for example straw, perlite or clay aggregate) and while effective for NH_3, they have typically proven ineffective in reducing CH_4 emissions and, in the case of straw, can even increase them (Berg et al., 2006; Rodhe et al., 2012). Similarly, Misselbrook et al. (2016) demonstrated that while large reductions in NH_3 (77%) were achieved with clay aggregate floating covers, they had no effect on CH_4 emissions from pig slurry. Solid covers are more effective, for example wooden covers can reduce CH_4 emissions from cattle slurry by 15% (Amon et al., 2006), while Rodhe et al. (2012) achieved more than a 40% CH_4 reduction from pig slurry with plastic covers. However, while covers might prevent CH_4 ebullition, they do not typically prevent CH_4 production, so that when covers are removed, trapped CH_4 will be released (Rodhe et al., 2012). Aside from their lack of effectiveness in terms of CH_4 mitigation, the drawback of solid covers is their cost, for example to cover a 3000 m^3 tank can cost between €19,000 and €30,000 (Kindbom et al., 2018) for installation alone. Furthermore, covers cannot solve GHG and NH_3 losses from slatted tanks beneath animal housing. The solution for such systems typically involves using a slurry additive.

A number of slurry additives exist that seek to achieve GHG and/or NH_3 mitigation and these can typically be divided into either microbial inoculants or chemical additives, where microbial inoculants aim to increase the abundance of certain microorganisms or enzymes, while chemical additives can include acidifying compounds, adsorbents, enzyme (e.g. urease) inhibitors and oxidising agents (McCrory and Hobbs, 2001). Acidification is the current gold standard of slurry additive, and has been demonstrated to achieve significant reductions in NH_3, of around 50% (Kai et al., 2008) and up to 95% (Petersen et al., 2012). The method has also shown significant effects on methanogenesis, where reductions of 67%–87% have been seen (Petersen et al., 2012). However, the most effective alterations in pH are achieved using strong acids (Kavanagh et al., 2019; Ndegwa et al., 2011), which, by their nature, are highly hazardous and also require on-farm infrastructural changes, meaning in a best-case scenario they are cost-neutral (Kavanagh et al., 2019). Furthermore, acidified slurry has been demonstrated to inhibit anaerobic digestion when co-fed at proportions greater than 10% of the feed (Moset et al., 2012). The long term effects of applying acidified slurry to soils is also uncertain, but short term research has demonstrated that its application can decrease soil pH (Park et al., 2018).

Thus, there exists a need for an effective, non-hazardous, cost-effective slurry additive that does not compromise the downstream use or recycling potential of the material. While a number of commercial slurry additives exist, peer-reviewed performance data is not available for the vast majority of these. The exceptions include SOP Lagoon (Peterson et al., 2020), which was able to reduce CH_4 emissions by 23% and NH_3 emissions by 46% from cattle slurry. In addition, Fabian et al. (2011) tested a number of additives and, of the 22 products tested, none were able to simultaneously reduce both CH_4 and NH_3 over both short (3 days) and long (30 days) storage periods.

In the past, chemical amendments, based on oxidising agents, have been demonstrated to reduce hydrogen sulphide (H_2S) emissions and odour from cattle slurry (reviewed by McCrory and Hobbs, 2001). In addition to H_2S reductions, Xue and Chen (1999) also noted a decrease in NH_3 emissions following surface application of oxidising agents hydrogen peroxide and potassium permanganate. However, we are not aware of peer-reviewed literature detailing the use of oxidising agents as a means of GHG mitigation. Thus, we aimed to test if an antimicrobial agent based on reactive oxygen species (ROS) would serve as a slurry additive capable of reducing both GHG and NH_3 emissions during storage. In particular, we hypothesised such an agent (hereon referred to as additive) would have noted effects on methanogenic archaea, due to their well-known oxygen sensitivity. A range of experiments were performed to address these aims, beginning with i) initial screening of the additive at a range of doses using small, methanogenic activity assays, followed by ii) testing of an effective dose of the agent, using two peroxide sources, in slurry storage mesocosms which were also used to test the efficacy of the additive iii) when regular additions of untreated slurry occur, as in a slatted tank, and iv) over repeated applications. Finally, slurry was tested to confirm the additive did not compromise the slurry's onward use as v) an AD feedstock or vi) an organic fertiliser. Indeed, we hypothesised that if it was possible to retain sufficient carbon and plant available nitrogen, a concomitant enhancement in the AD (carbon) and fertiliser (nitrogen) value would be seen.

2. Materials and methods

2.1. Additive preparation and delivery

Treatments were delivered to the mesocosms in liquid format, where both reagents were dissolved in water and reacted together immediately prior to treatment of the slurry. A treatment dose of 2.66 g/kg [2.4 g Urea Hydrogen Peroxide (UHP) + 0.244 g Potassium Iodide (KI)] was used and delivered in 200 mL of water. If alternate sources of peroxide were used, such as sodium percarbonate (SPC), then doses were normalised to deliver the same peroxide (H_2O_2) content as 2.4 g/kg UHP.

2.2. Methanogenic activity assays to assess dose effect of antimicrobial additive on rates of methanogenesis

To assess the impact of the additive on methanogenic activity from cattle slurry, an adaptation of the Specific Methanogenic Activity (SMA) assay of Coates et al. (1996) was used, whereby gas production rates are measured by changes in headspace pressure. Cattle slurry was mixed 1 : 2 (v/v) in anaerobic buffer (1.6 g/L trypticase, 12.5 mM ammonium bicarbonate, 104 mM sodium bicarbonate, 10 mM Na_2HPO_4, anhydrous, 10 mM KH_2PO_4 and 0.625 mM $MgCl_2 \cdot 6H_2O$), prepared as detailed in Goering and Van Soest (1970). The slurry mix was sieved at 200 μm (Biodesign™ CellMicroSieves) to remove large particulate matter but not larger microbial species (e.g. protozoa). The same anaerobic buffer (Goering and Van Soest, 1970) was used for the SMA assays, where 110 mL anaerobic vials were filled with 36 mL buffer and 9 mL of the sieved cattle slurry mix, and sealed with rubber bungs and aluminium crimp seals. A gas exchanger (GRInstruments; Anaerobe Gas Exchange System) was used to exchange and then over-pressurise vial headspace with H_2:

CO_2 gas (80%:20%) or N_2:CO_2 (80%:20%; ambient pressure) for unfed controls. Treatment stock solutions were prepared fresh on the day of the assay, at a concentration of 8 mg/L. The peroxide containing reagent (UHP) and KI were mixed immediately before addition to the vials, at a 3.5 : 1 ratio (peroxide: KI), and added to achieve final additive concentrations ranging from 0.68 to 1.27 mg/g slurry. Unfed controls and untreated controls both received no additive, and were included in all assays. Vials were incubated shaking (100 rpm) at 37 °C and headspace pressure regularly monitored using a pressure transducer modified to fit a Luer-lock needle, until no further changes in headspace pressure were recorded. Production of CH_4 was calculated by a decreased headspace pressure, as hydrogen is consumed to produce CH_4, where a conversion factor was used to transform millivolts to mL of CH_4. The steepest part of the curve was used to estimate SMA rate, using the following Equation (1) and lag time was calculated by time of inclination, where the second derivative of each curve was zero.

$$\textit{Maximum methane production rate} = \frac{Gr \times 24}{VS} \times STP \quad (1)$$

Where Gr = slope of the line at steepest part of the methane production curve.

VS = percentage of volatile solids in whole vial.

STP = correction factor for standard temperature and pressure.

2.3. Storage mesocosms for scaled up testing of additive dose, variants and efficacy over repeated cycles

Fresh cattle slurry was collected from a grass-fed dairy cattle farm in the west of Ireland and placed in 25 L plastic drums (High Density Polyethylene; HDPE), with 12 kg (fresh weight) of slurry in each. Slurry used for each experiment was characterised (Table 1). After collection, pH was measured (Jenway 3510) and sub-samples stored (−20 °C) or immediately analysed for inorganic nitrogen quantification and total solids (TS) and volatile solids (VS). TS was calculated by drying for 18 h at 100 °C (ISO 11465) while VS was estimated by loss on ignition at 550 °C for 2 h (EN 15935:2012). Ammoniacal N was quantified using the Merck Ammonium Spectroquant Test (0.010–3.00 mg/L; Sigma). The lids of the HDPE drums were modified to enable gas collection by boring a hole through each and inserting a rubber bung. Silicone piping and air-tight taps were connected to the bungs allowing the attachment of gas bags (Tedlar) for biogas collection from 25 L drums. As treatments induced some expansion of slurry material, 'venting' bags were attached to prevent negative pressure within the drums upon settling of the slurry. These 'venting' bags were filled with ambient air and attached to the drums via one way valves to avoid biogas accumulation in these bags. After treatment addition, a rod was used to briefly stir the treatment into the slurry. Untreated mesocosms received an equivalent volume of dH_2O, and were stirred to the same extent as the treated mesocosms. Drums were closed and biogas volumes were recorded regularly, with volumes in Tedlar bags measured via water displacement. Percentage CH_4 from biogas was determined by gas chromatography (GC) using flame ionised detection (FID; Varian) with N_2 as a carrier gas, performed on triplicate injections per sample, where CH_4 content was calculated against standards. A Biogas Analyser 5000 (GeoTech) fitted with detectors for NH_3 (0–1000 ppm), H_2S (0–1000 ppm), CH_4, CO_2 and O_2 (all 0–100%) was used for biogas characterisation.

This experimental set-up was used to address a number of aims, including; testing an effective dose of the agent, using two peroxide sources and its individual components; the efficacy of the additive when regular influxes of untreated slurry occurred and when repeated treatments were performed. Slurry was collected fresh before the start of each experiment, and characterised (Table 1). Untreated controls, receiving water only, were included for all experiments and all treatments and controls were performed in triplicate.

2.3.1. Testing effective dose on CH_4 inhibition at scale, using two additive variants

The performance of UHP + KI and a second additive variant (SPC + KI) against hydrogenotrophic methanogenesis during a closed slurry storage trial was examined. Total biogas volume (i.e. total emissions) was quantified and its content characterised for CH_4, NH_3, H_2S, CH_4 and CO_2. At the end of the trial, ammoniacal N content of the slurry was determined. The individual components of UHP + KI (i.e. UHP; urea and peroxide alone) were each also assessed for any inhibitory effects where all quantities were matched to that delivered in the UHP + KI additive.

2.3.2. Efficacy of additive in the presence of fresh, untreated slurry inputs

UHP + KI was used to treat triplicate mesocosms containing 12 kg of cattle slurry on the initial day of the experiment. Thereafter, every 2–3 days an additional aliquot of 5% (weight basis) of fresh, untreated cattle slurry was added to the drums through a valve in the top of the drum and left to sit on top of the treated slurry, un-mixed. Biogas production, and CH_4 content therein, were compared to matched untreated controls, which received the same input of fresh cattle slurry.

2.3.3. Additive performance over repeated applications

Fresh slurry was treated with UHP + KI and monitored for biogas and CH_4 production. Once biogas production began to occur in UHP + KI treated samples, indicating recovery from the treatment, the UHP + KI was re-applied and the same process repeated. This was done for 4 treatment cycles in order to observe any alteration in the number of days required for recovery of biogas production from treated material. Ammoniacal N content of the slurry was determined as before, and 1 kg of slurry was removed from each mesocosms for plant yield trials which were performed immediately thus precluding cold storage of slurry. The remaining slurry (treated and untreated) was stored at 4 °C before their use as feedstocks for laboratory scale AD.

2.4. Laboratory scale anaerobic digestion operation

Triplicate 10 L bioreactors (continuously stirred tank reactors; CSTR) were co-fed cattle slurry and food production waste (2:1 wt/wt basis) at a 24–27 day retention time, where feeding was performed at 3 day intervals. Throughout the trial, an organic loading rate (OLR) of 2 g VS L^{-1} d^{-1} was used. The reactors were cycled between co-feeding with untreated slurry for at least 5 feed intervals, and then with additive treated slurry for at least 5 cycles. Biogas was collected in Tedlar gas bags and volumes measured using water displacement, while CH_4 percentage was determined by FID-GC using the pre-described conditions. NH_3 in the digestate was measured using AmVer High-Range Ammonia test (Hach), while total and soluble chemical oxygen demand (tCOD/sCOD) analysis were performed according to standard methods (SCA, 1987).

Table 1
Characterisation of dairy cattle slurry used for each of the described mesocosm experiments.

Purpose	Slurry characteristics			Additive variants tested	No. of treatments
	TS (%)	VS (%)	pH		
Testing two additive variants for CH_4/ biogas inhibition	14.1	7.7	6.72	UHP + KI SPC + KI	1
Efficacy of additive in the presence of fresh slurry additions	6.7	4.4	6.83	UHP + KI	2
Additive performance over repeated applications	14.1	7.0	7.08	UHP + KI	4

2.5. Plant trials

A randomised pot trial, with 10 replicate plots per treatment was set up in a greenhouse (mean temperature 20.1 °C ± 4.32). Pots of 1 L size were filled with 1 kg (fresh weight) of topsoil (fine loamy drift with stones removed) to achieve a bulk density of 1.12 g/cm^3. Soil moisture (gravimetric) was kept between 25 and 35% by watering every second day through roof installed sprinklers. Slurry was added to pots at a rate equivalent to 33 m^3/ha, and instead of surface applying, the slurry was mixed with topsoil prior to filling pots. Both untreated and additive-treated slurry was applied at the same rate. Finally, each pot was sown with 40 mg of perennial ryegrass seeds (*Lolium perenne*) and herbage harvests were taken every three weeks of the nine week trial, by cutting grass at 1 cm above the soil line (Paula et al., 2020). Grass was then dried at 55 °C for 72 h to determine dry matter yields per pot. Pots were re-randomised each week.

2.6. Data analysis and visualisation

Data was analysed in the statistical program R (R Team, 2017) and plotted with ggplot2 package (Wickham, 2016). Plotted data is presented as the mean of replicate determinations ($3 < n < 10$) and error bars represent standard deviation from the mean.

3. Results & discussion

3.1. Dose dependent inhibition on specific methanogenic activity

Using UHP as a peroxide source and KI as the iodine source, a range of concentrations of the additive (0.68 mg–1.27 mg/g slurry) were tested to determine effects upon hydrogenotrophic CH_4 production rates from slurry inoculum (Fig. 1). Initial doses were chosen to consider effectiveness, cost and end user applicability.

While the lowest tested dose of the additive (0.68 mg/g) had little effect, doses in excess of 0.80 mg/g slurry reduced the max rate of methanogenesis by between 20 and 32% (Table 2). Furthermore, the additive delayed the time at which maximum (exponential) CH_4 production began. At lower concentrations (0.68–1.00 mg/g) a delay in the onset of maximum CH_4 production of 4.4–5.9 h was seen, and once it did start, the rate of CH_4 production in these samples was not affected by prior additive treatment and was comparable to the untreated controls (Table 2). As the doubling time of methanogenic archaea is between four to 14 h (Łukaszewicz et al., 2015), it is unlikely that sufficient time had passed for the total replacement of a population killed by the additive. Therefore, it seems more plausible that at low doses, the additive is primarily inhibiting the resident microbiota, as opposed to having cidal effects. Marginally higher concentrations (1.12 and 1.27 mg/g), reduced methanogenesis rates by as much as 32%, however the most notable effect was on the duration of the lag phase until these maximum rates began (24 h at 1.27 mg/g *vs* 1.5 h in 0 mg/g controls). Again this points more to an inhibitory, rather than a biocidal, effect.

Table 2
Rates of specific methanogenic activity and time of onset of maximum methane production rates from cattle slurry, as a function of a range of additive doses.

Treatment (UHP + KI)	Max rate of methanogenesis (ml CH_4/g VS/hr)	Percent inhibition of max rate of methanogenesis [a]	Lag time [b]
0 mg/g	125.6	–	1.5 h
0.68 mg/g	132.8	−0.5%	4.4 h
0.80 mg/g	99.0	21%	5.9 h
1.00 mg/g	112.5	11%	11.2 h
1.12 mg/g	85.7	32%	20.4 h
1.27 mg/g	95.4	26%	23.9 h

[a] Percent inhibition of the maximum rate of methanogenic activity was used to estimate inhibitory concentrations.
[b] Lag time denotes time of inclination (i.e. onset of exponential phase of methanogenesis based on H_2:CO_2 consumption).

3.2. Inhibition of total emissions from slurry storage mesocosms

To determine the effects of the additive upon the production of methane and other gaseous products as a result of naturally occurring biodegradation of the organic matter in slurry, mesocosms containing 12 kg fresh slurry were employed. The treatment dose chosen was double the highest previously tested dose (Table 2), at 2.4 mg/g UHP + KI, in an effort to achieve stronger inhibition. Two additive variants, consisting of alternative sources of peroxide, were used to achieve the same reaction between peroxide and KI, thereby producing both reactive-oxygen and -halide species, where treatments were normalised to deliver the same hydrogen peroxide content.

Measurable volumes of biogas (i.e. total emissions) were produced from untreated slurry within two days, while there was a total absence of biogas production until 7 days and 10 days post-treatment for SPC + KI and UHP + KI respectively (Fig. 2). Over the course of the trial, untreated samples produced biogas at a rate of 9.1 mL/kg/day while slurry treated with SPC + KI produced biogas at a 34% lower rate (5.72 mL/

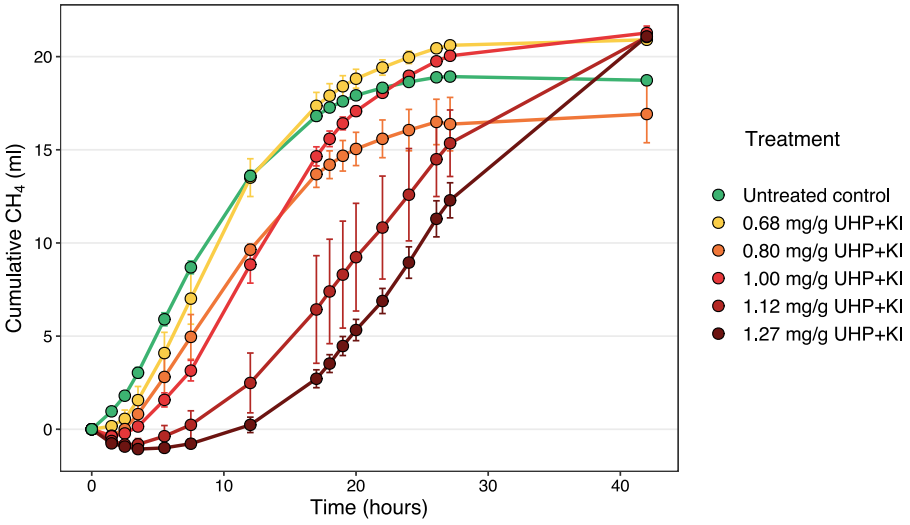

Fig. 1. Cumulative methane production from cattle slurry incubated with buffer and H_2:CO_2 gaseous substrate, incubated with a range of concentrations of the additive, where rates of specific methanogenic activity are denoted in Table 2.

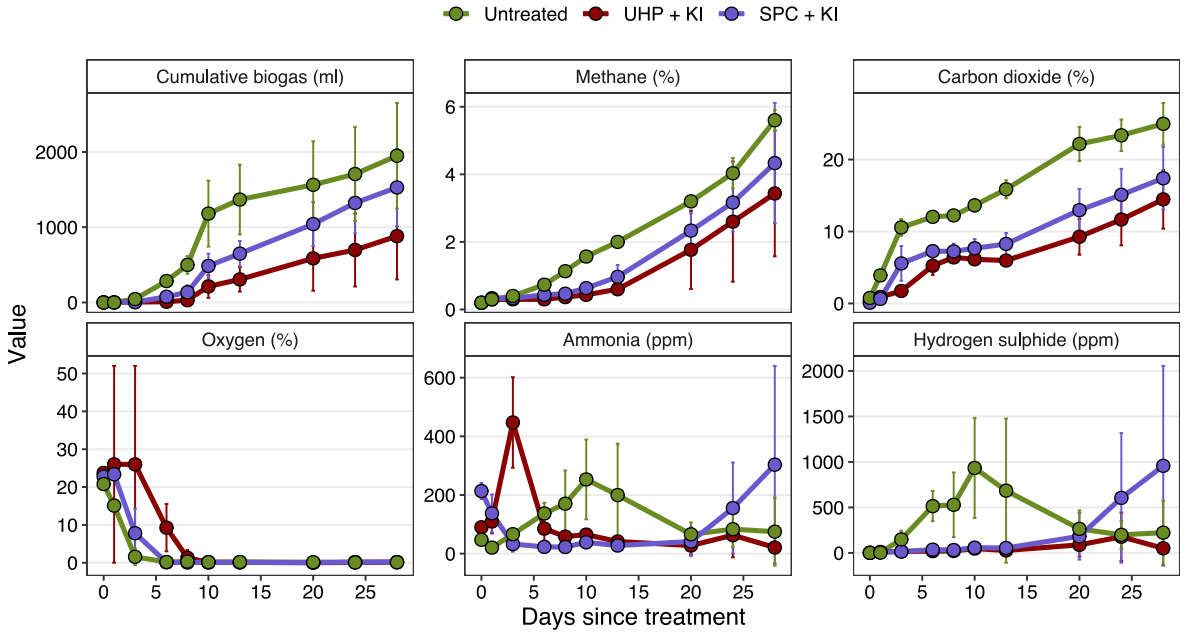

Fig. 2. Cumulative biogas and methane, carbon dioxide, oxygen, ammonia and hydrogen sulphide content of biogas at each sample point, following treatment of fresh cattle slurry with two variants of the additive namely UHP + KI (red) and sodium percarbonate (SPC) + KI (blue), as compared to an untreated control (green).

kg/day) and UHP + KI at a 66% lower rate (3.09 mL/kg/day). The individual components of the UHP + KI additive were each tested for any inhibitory effects, where some inhibition was seen with peroxide and UHP alone, however the largest effects were seen with UHP + KI (Supplementary Fig. 1A). In addition, the content of this biogas was significantly lower in CH_4, CO_2 and H_2S. CH_4 produced over the 28 days was 55% lower with UHP + KI treatment and 20% lower with SPC + KI treatment. Similarly, the CO_2 content of the biogas was significantly reduced, by more than 50%, following either additive application.

As both additives are basic (~pH > 9), upon addition to slurry they increased pH by a factor of between 1 and 1.5 (Supplementary Fig. 2). By 3 days post application, the pH had returned to the same as the untreated control. This initial pH increase induced an efflux of NH_3 i) immediately after addition in the case of SPC + KI and ii) after 2–3 days in the case of UHP + KI. After this initial flux, NH_3 levels dropped to levels below that in untreated for both additives, until 20 days post-treatment. Thus, over 23 days of the trial, there was a net saving of NH_3 despite initial losses (Fig. 3A). Samples analysed for inorganic nitrogen content at the end of the trial (day 27) demonstrated that both SPC + KI and UHP + KI increased the ammoniacal N content of the slurry (Fig. 3B), this equated to a 12% increase after one treatment. While a notable portion of this was explained by the presence of urea within the UHP reagent, it did not account for the total increase. For instance, when comparing UHP + KI against its different components (UHP, urea or H_2O_2), more ammoniacal N species were detected in the UHP + KI treated slurry versus other treatments (Supplementary Fig. 1B). Additionally, the SPC + KI variant does not contain urea, yet ammoniacal N increased with this additive (Fig. 3B). We can therefore consider that these increases in ammoniacal N are not only a consequence of that added via the urea component of the UHP + KI additive

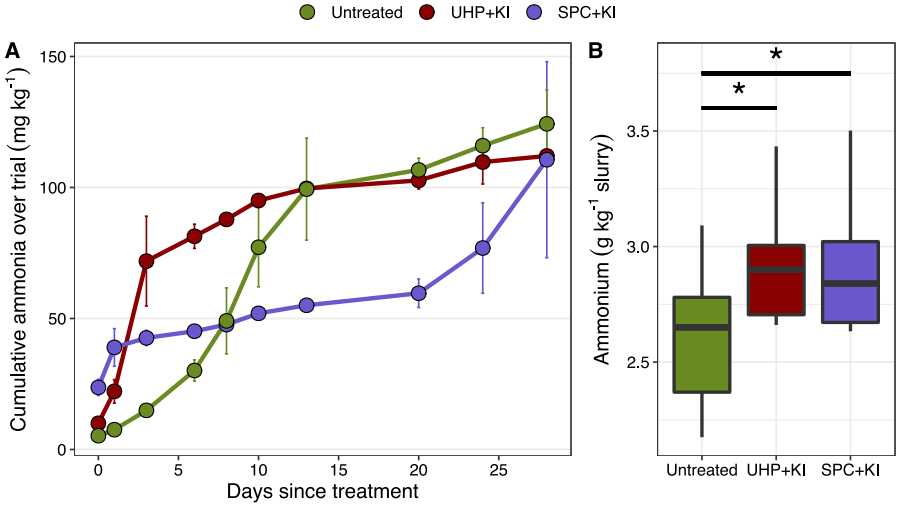

Fig. 3. A) Cumulative ammonia emissions following slurry treatment, where data shown represent cumulative values of those represented in the ammonia panel of Fig. 2. B) Ammonium content of untreated cattle slurry and slurry treated with two variants on the additive, as measured on day 27 of the trial, where statistically significant differences in mean are denoted by asterisks (*$p < 0.05$; **$p < 0.001$).

variant. We hypothesise the remaining fraction is likely a result of retention of the NH_3 typically emitted from untreated manure. Thus, when inhibition of emissions was more efficient (i.e. when using UHP + KI), a larger increase in ammoniacal N was observed (i.e. compared to UHP alone).

In total over the 28 day trial, approximately 300 mg of H_2S was released per kg of untreated slurry, while less than 34 mg was released per kg of either UHP + KI or SPC + KI treated slurries. The effects of the additive upon pH in the initial days could also explain some of the drop in H_2S, as it disassociates to HS^- when pH becomes more basic (Li and Lancaster, 2013), and H_2S probes fail to detect HS^- species. However, as the dampening effect upon H_2S is seen for many days after the slurry pH has returned to that of the untreated control, the cause is perhaps the oxygen species released by H_2O_2 upon decomposition. Chang et al. (2007) demonstrated that 0.1% H_2O_2 inhibited H_2S production from wastewater for four days, while 0.4% MgO_2 inhibited production for 40 days. They proposed two modes of action for this, the first being that the presence of oxygen allows abiotic oxidation of sulphide to sulphate and the second that this oxygen also reduced biotic conversion of sulphate to sulphide through inhibitory effects upon sulphate reducing bacteria (Chang et al., 2007).

3.3. Efficacy of additive in the presence of fresh material

Among the different ways to produce the reactive species, which act to inhibit biogas and CH_4 production, UHP + KI was taken forward for further analysis, the first of which was to test the additive in the presence of regular influxes of fresh untreated slurry, as would happen on a working farm. Over the course of the 26 days of this trial, two additive treatments were applied, on day 0 and day 13, at a dose of 2.66 g/kg dose to treat only the slurry already within the mesocosm. Despite the regular influxes of fresh, untreated slurry (2% every ~3 days), marked biogas inhibition was still observed in treated samples (Fig. 4), where an average of 420 mL was produced over 27 days, compared to 2560 mL from untreated mesocosms. This demonstrates the applicability of the additive in a farm setting where fresh animal manure would soon be added to any treated material.

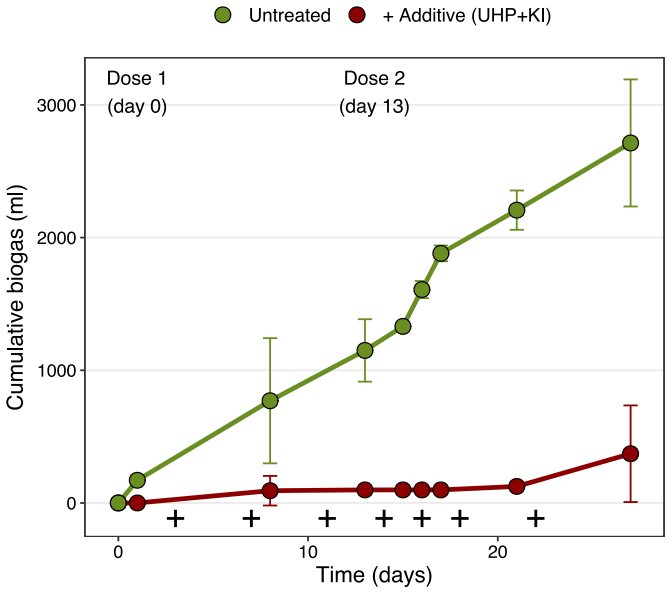

Fig. 4. Effectiveness of additive (UHP + KI) in the presence of regular influxes of fresh, untreated cattle slurry, where addition of 2% fresh slurry (untreated) is denoted by '+' symbols.

3.4. Additive performance over repeated applications

As cattle slurry can be stored in storage tanks for extended periods, multiple treatments may be required to dampen biogas inhibition for the duration of storage. To ensure that no acclimatisation to the treatment would occur, multiple treatment cycles were tested to mimic such situations. Each treatment phase ended when biogas production was first detected in treated samples, and the additive was then re-applied.

The performance of UHP + KI over the four treatment phases remained relatively consistent; during the first two phases, the additive was effective for approximately 11 days (Fig. 5). The third treatment phase corresponded to the longest period of inhibition, lasting 22 days, while the final treatment resulted in 19 days of biogas inhibition. Over the course of the 65 day storage trial, an average of 1.15 L of biogas was produced per kg of untreated slurry, versus 0.1 L biogas per kg of additive-treated slurry, representing a 90% reduction in biogas production. This equated to a total of 1.7 L of CH_4 from untreated samples, and 95 mL from slurries receiving the additive over the course of the trial. This suggests that under the ambient temperatures tested (15 °C average), a bi-to tri-weekly application of the additive would be sufficient to prevent the majority of biogas production and associated GHG and NH_3 losses from stored cattle slurry. Additionally, the extension of inhibition duration with repeated applications suggests it is unlikely that slurry microbiota would develop strategies for coping with the stress provided by these reactive oxygen and halide species.

3.5. Assessment of biogas potential of anaerobically digested, treated slurry

Anaerobic co-digestion of slurry sampled from day 65 of the repeated application experiment (Fig. 5) was used to assess alterations in biogas potential from the additive-treated slurry. The trial ran for 150 days, during which time 3 repeated runs of at least 5 consecutive feed cycles were completed for each untreated slurry and treated slurry, co-digested with fats, oils and grease (FOG; 2:1 w/w) (Fig. 6). Characterisation throughout the trial revealed no differences between feedstock (FS) containing untreated or treated slurry in terms of VS, while TS was slightly higher in treated (14.9%) than untreated (14.0%) material (Table 3; Supplementary Fig. 3), perhaps due to moisture losses associated with biogas production from the untreated material during the storage period. The pH of the feedstocks fluctuated between 6.36 and 8.10, with that containing additive treated slurry having a slightly higher mean pH (6.94) than that containing untreated slurry (6.68; $p < 0.01$) (Table 3; Supplementary Fig. 4). The lowest pH (on day 62) was associated with a change in FOG source, which also had a higher VS (Supplementary Fig. 3) and consequently induced a spike in biogas production on day 66 (Fig. 6). The pH within reactors was less variable (7.9 ± 0.08) and in contrast to the pH of FS, was significantly lower ($p < 0.01$) during days when treated material was used (6.86) compared to untreated material (6.92), despite the FS itself having a higher pH (Table 3). This could be a result of higher volatile fatty acids (VFA) content, for example due to inhibition of acetoclastic methanogenesis, or as a result of an overall increase in VFA production during this time, due to more available organic matter. The pH observed was well within the optimal AD pH range of 7–8 throughout, indicating that the process was stable.

The largest change in FS resulting from slurry source was the NH_3 concentration, which was significantly higher ($p < 0.001$) in FS containing treated slurry (1.1 g/L) compared to the untreated slurry (2.6 g/L). Once within the reactors however, the opposite trend was seen and slightly higher NH_3 content was seen on days when fed with untreated slurry FS ($p < 0.05$; Table 3); in addition there was a trend of increasing NH_3 with time, suggesting some accumulation in the system (Supplementary Fig. 5). Despite reaching in excess of 2000 mg/L, levels were not inhibitory to the system in terms of CH_4 production, which is cited as being especially sensitive to levels above this threshold (reviewed by

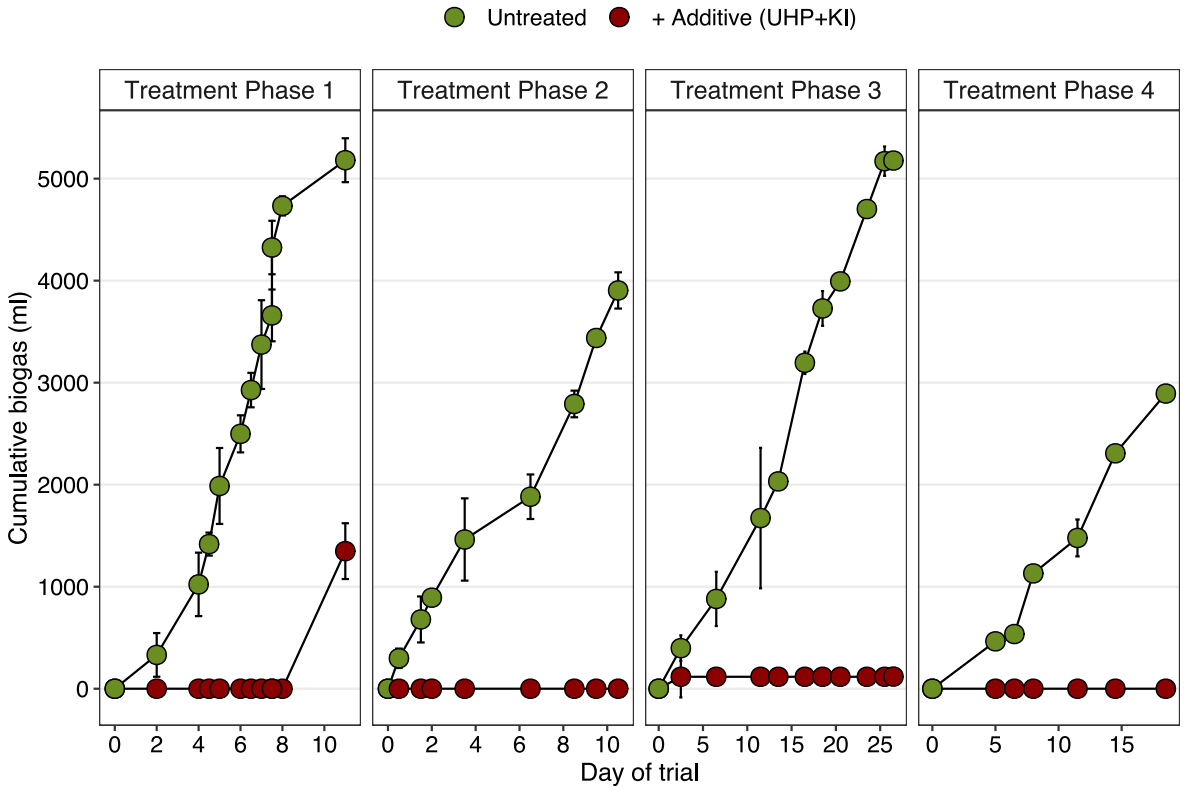

Fig. 5. Biogas and methane production rates from cattle slurry in the absence (untreated) and presence (treated) of the UHP + KI additive, where the treatment was reapplied when biogas recovery was seen, which equated to days 0, 12, 22 and 46.

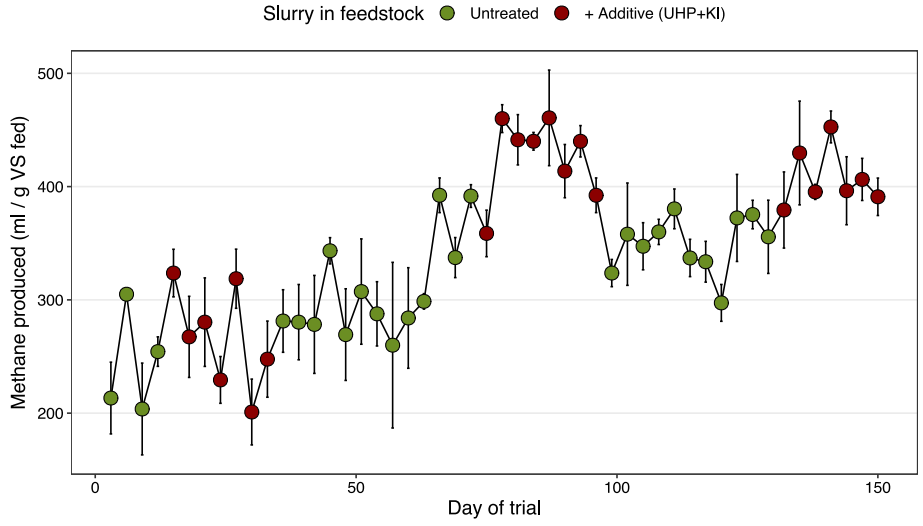

Fig. 6. Methane production from replicated, 10 L anaerobic digesters co-fed with untreated (green) or UHP + KI treated (red) slurry and food production waste, where slurry samples were taken from the end of the trial in Fig. 5. The mean of triplicate reactors is plotted, with error bars denoting standard deviation of the mean.

Table 3
Summary of physicochemical parameters of both the feedstock (FS) and replicate reactors, averaged for the period when FS included i) untreated and ii) additive treated cattle slurry. For each parameter, statistically significant differences in mean values between untreated vs additive ($p < 0.05$) are denoted by unmatched letters, where all p values were corrected for multiple comparisons (FDR).

	TS (%)		VS (%)		pH		Ammonia (g/L)		Total COD (g/L)		Soluble COD (g/L)	
	FS	Reactor	FS	Reactor	FS	Reactor	FS	Reactor	FS	Reactor	FS	Reactor
Untreated	14.9 [a]	6.67 [a]	7.17 [a]	3.87 [a]	6.68 [a]	7.92 [a]	1.090 [a]	2.021 [a]	173.1 [a]	60.4 [a]	27.1 [a]	14.3 [a]
+ Additive	14.0 [b]	6.78 [b]	7.35 [a]	3.92 [b]	6.94 [b]	7.86 [b]	2.598 [b]	1.836 [b]	160.1 [a]	53.1 [a]	31.9 [b]	14.8 [a]

Yenigün and Demirel, 2013). This is likely a consequence of historic use of the reactors, which for two years preceding this trial had been fed with a mix of FOG and cattle slurry, and were perhaps therefore acclimatised to the higher ammoniacal N content often associated with animal excreta used as AD feedstocks, as has been seen elsewhere (Melbinger et al., 1971). As AD systems using cattle slurry treated with the additive would be similarly acclimatised to higher NH_3 concentrations, the slightly elevated NH_3 levels observed in this trial are not a significant concern. Additionally, a mechanism for concentrating N represents another potential income stream where NH_3 can be precipitated out to form struvite, a potential fertiliser (Uludag-Demirer et al., 2005).

Over the 150 day trial, the daily CH_4 production from co-digested, untreated cattle slurry averaged 122 mL CH_4/g VS fed/day, while that from slurry receiving the UHP + KI additive, produced on average 143 mL CH_4/g VS fed/day equating to a 17% increase in CH_4 over the 150 day trial (Fig. 6). This was a result of a 10% increase in biogas volume produced from the treated material during AD, in combination with a higher CH_4 content of this biogas at 64.6% in treated cattle slurry versus 60.2% from untreated slurry (7% increase). This increase in CH_4 and biogas production could be attributed to an increase in sCOD seen in the feedstock when additive-treated slurry was used, as when CH_4 production was interpreted as a function of g sCOD in the feedstock, there were no differences in the CH_4 produced (Supplementary Fig. 7). Indeed, in the presence of the same source of FOG, the sCOD of feedstock containing treated slurry was 17% higher than that containing untreated slurry, at 31.9 g/L versus 27.1 g/L (Table 3; Supplementary Fig. 6). We propose this is due to accumulated intermediate compounds that were not lost as CH_4, CO_2 or NH_3 during storage of the slurry.

3.6. Assessment of fertiliser value of increased N content in treated slurry

The two-fold increase in NH_3 detected in the AD feedstock mirrors what was detected in the cattle slurry itself, where ammoniacal N was shown to increase step-wise with each treatment application (Fig. 7), partly as a consequence of the additive itself (urea content). On day 0 of the trial NH_4^+ was 1.5 g/kg (fresh weight), and after 11 days of storage it had increased in untreated samples to around 2.2 (±0.31) g/kg and in treated slurry to 3.4 (±0.58) g/kg fresh slurry. Thereafter, NH_4^+ remained relatively stable in untreated slurry for the remainder of the trial (at 2.3 g/kg), while in treated slurry, on average each treatment resulted in a further increase of 0.7 (±0.17) g/kg fresh slurry detected at the end of each phase.

To test if UHP + KI treated slurry contained more plant available N, and could therefore enhance the fertiliser value of the material, a yield assessment in a pot trial setting was undertaken. Both slurry sources, (untreated and additive treated), provided valuable fertiliser value and increased growth relative to unamended controls by more than 45% at the first harvest and more than 300% at the following harvests (Fig. 8). Additive treated slurry was able to support higher yields than untreated, where the largest increase in yield was at the first herbage harvest (week 3), where pots amended with treated slurry saw 12.8% higher dry matter than untreated. At harvest 2 and 3, yields were enhanced by a lesser extent, 4% and 3.8% respectively. In practice, slurry would be applied more than once in a growing season so additional yield improvements would be expected. The increased plant-availability of N sources within the additive treated slurry equates to a reduced need to purchase inorganic fertilisers, thereby increasing the fertiliser replacement value of the same volume of slurry, with associated environmental and economic benefits to the farm. Finally, in contrast to when acidification is used as a slurry treatment, any pH shifts resulting from the additive itself were transient and thus pose less risk to long term soil health.

4. Conclusions

By harnessing an antimicrobial for a novel use, we were able to identify a safe and effective means of reducing gaseous emissions from

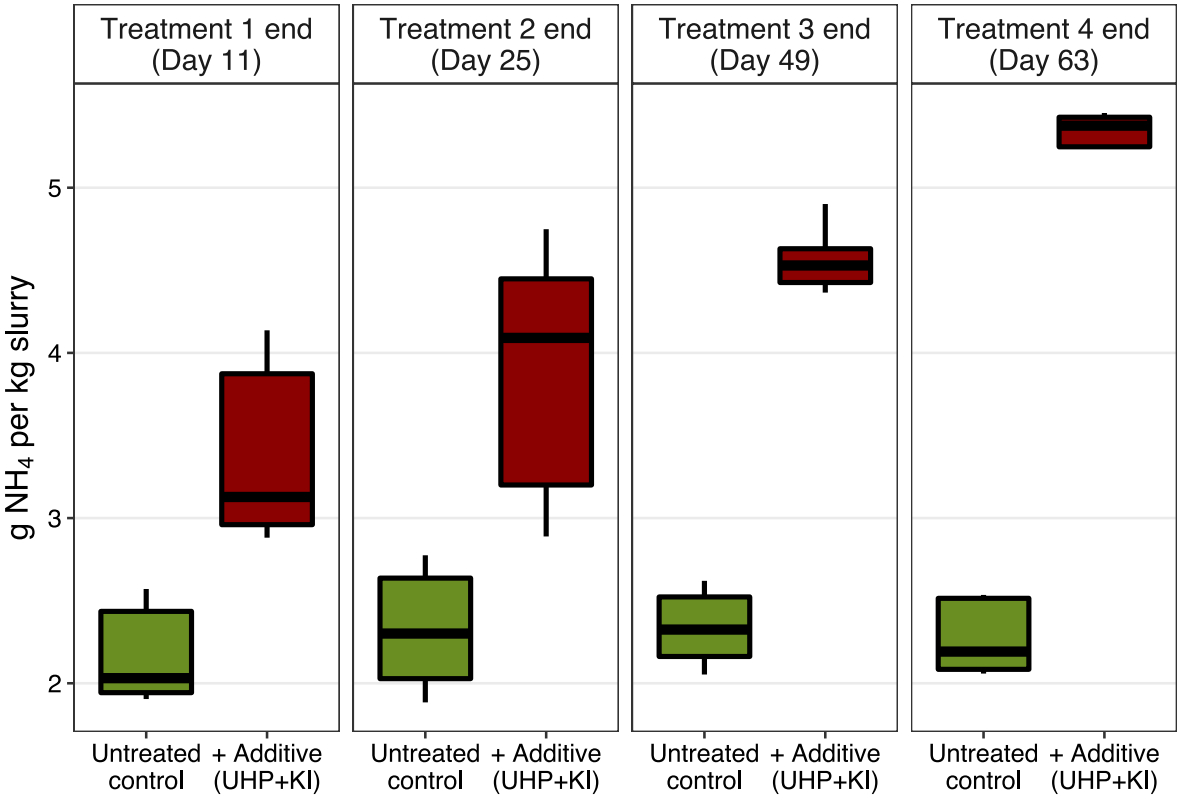

Fig. 7. Ammonium N content of untreated and treated slurry at the end of each treatment phase, as depicted in Fig. 5.

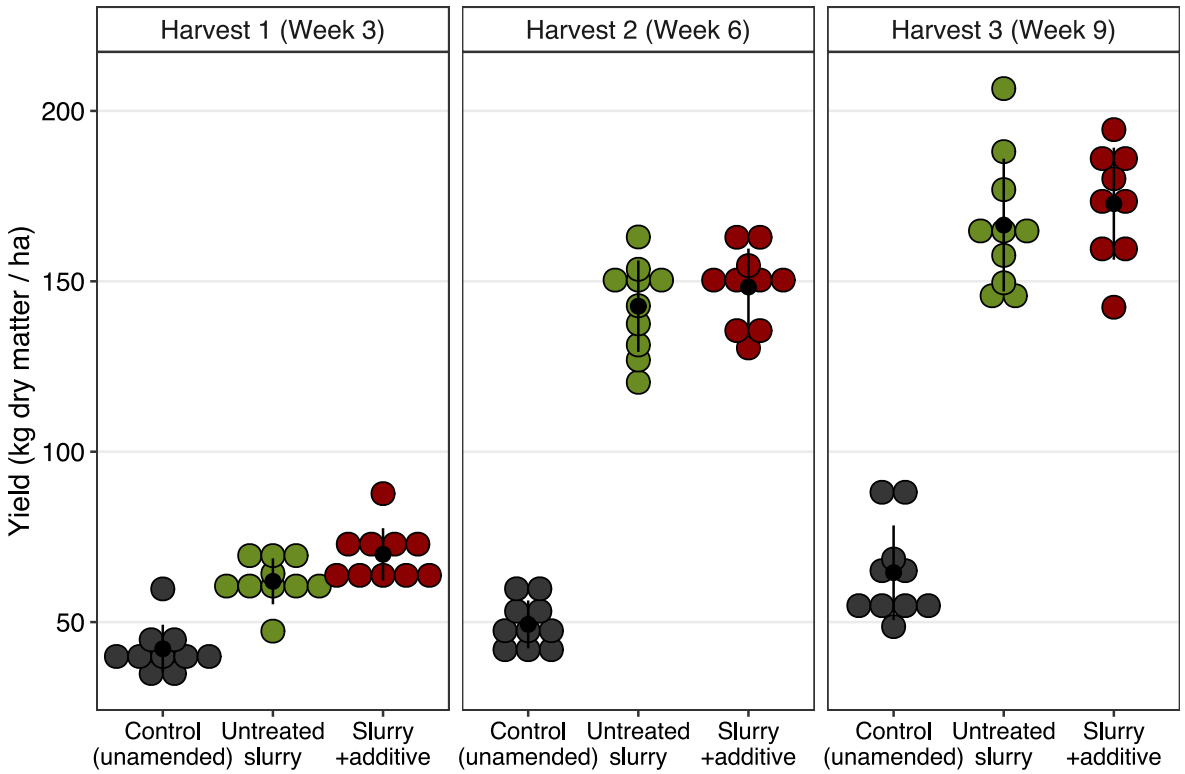

Fig. 8. Dry matter yields of ryegrass at three herbage harvests, from unamended control soils (grey); soils amended with untreated slurry (green) and UHP + KI treated slurry (red), where slurry was taken from the end of the third treatment phase from Fig. 5.

stored cattle slurry. As well as reducing CH_4, the additive was effective at significantly reducing CO_2, NH_3 and H_2S emissions. The reactive species could be produced using a range of reagents, including hydrogen peroxide solution, sodium percarbonate and urea hydrogen peroxide as peroxide sources. These reagents are cost effective in bulk and due to the transient nature of their activity and their innocuous breakdown products (principally H_2O), do not pose risks as environmental contaminants. Indeed, using hydrogen peroxide as the reactive oxygen component of the additive would be more suitable in terms of cost (no urea) and additionally this product is already used in bulk for various industrial treatments (such as waste water treatment). As well as reducing emissions, the treatment enhanced the value of the slurry for downstream uses including anaerobic digestion and use as a fertiliser. In terms of practicality, such an additive could be added to slurry tanks using a simple pump mechanism with outlet pipes submerged into the tank. While this would represent some capital outlay, it would be small in comparison to some slurry treatment technologies and relatively easily implemented. Additionally, as the treated slurry has enhanced resource value this would offset costs associated with using such an additive.

The target of producing more food on less land in a more sustainable manner can only be achieved by changing the status quo, including using cost-effective, technological advances to allow us to decouple production from emissions and to close nutrient loops. Recovery and reuse of valuable carbon and nutrient resources from stored manures and slurries could be enabled using the treatments we describe here. Further research to examine the efficacy of the treatments at farm-scale should now be undertaken.

CRediT authorship contribution statement

Camilla E. Thorn: obtained funding, undertook experimental work, data collection, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Stephen Nolan:** obtained funding, Writing – original draft, Writing – review & editing. **Chui Sang Lee:** Formal Analysis, obtained funding. **Ruairi Friel:** All authors were involved in, Conceptualization, Writing – original draft, Writing – review & editing. **Vincent O'Flaherty:** All authors were involved in, Conceptualization, Writing – original draft, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2022.132004.

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