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Hydrogen sulphide inhibition in cattle slurry by use of an oxygen based slurry amendment

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ABSTRACT

Hydrogen sulphide (H_2S) is a malodorous gas that is produced in anaerobic environments where sulphur containing matter is present. Globally, farms in which liquid manure/slurry is stored is a source of H_2S which can lead to many acute and chronic health problems and even death. Farming is one of the most dangerous professions globally and reducing the risk of sulphide poisoning on farms will help ensure a safer work environment. The inhibition of H_2S production from cattle slurry may also reduce air pollution. In this study, a series of slurry storage experiments were conducted. The first experiment treated 20 L of cattle slurry bi-monthly using a mix of hydrogen peroxide and potassium iodide as well as calcium chloride, while the second experiment treated 660 L in which the same treatments and schedule were used. A small-scale storage trial was carried out over 29 days in which slurry was treated as before and sulphate concentrations were measured repeatedly. A maximum inhibition of H_2S concentrations of 87 % and 81 % was recorded from the 20 L and the 660 L storage experiments, respectively. The treatment did not affect sulphate concentrations in slurry which are critical for plant growth.

1. Introduction

H_2S is a malodorous, colourless gas, significant amounts of which have been reported in America, China and Denmark from cattle, pig and chicken manure stores (Grant and Boehm, 2022; Feilberg et al., 2017; Grant et al., 2022; Shi et al., 2019; Park et al., 2020). Stored slurry is often used for the fertilization of farmland and has been shown to have many benefits when applied to soil including increasing organic matter concentration, microbial loading, mineralization rate, fertility etc. (Montes et al., 2013). Hydrogen sulphide is soluble in water and once slurry is agitated and the crust broken, H_2S gas is released to the air (Ni et al., 2001). This is a major health hazard for the farming community and poses an acute health and safety risk for farm workers handling animal manures (Malone Rubright et al., 2017). H_2S is part of a suite of gaseous compounds emitted from cattle slurry that is malodorous, causing many complaints when slurry land spread, with humans being particularly olfactorily acute, able to detect H_2S concentrations as low as 0.5 ppb (Eriksen et al., 2012; Hydrogen Sulfide, Medical Management Guidelines; Skrtic, 2006). As tanks are a useful and ubiquitous method of slurry storage in animal husbandry, there is substantial potential for both health and environmental effects associated with slurry management.

The effects of H_2S exposure on humans are varied and depend highly on the concentration of H_2S. In Ireland and Europe, short-term exposure limits and time-weighted averages are used to determine dangerous working conditions for employees. The time weighted average is 5 ppm over 8 hours, while the short-term exposure limit is 10 ppm for 15 minutes (Crook et al., 2017). At concentrations of 100 ppm, H_2S can cause eye and skin irritation, coughing, nausea, vomiting and headaches; above 150 ppm, it causes olfactory desensitisation, making H_2S particularly dangerous for rescuers of potential victims (Malone Rubright et al., 2017). At 700 ppm, H_2S may lead to coma, asphyxiation and/or death (Skrtic, 2006; Jiang et al., 2016; Hendrickson et al., 2004; Doujaiji and -Tawfiq Jaffar, 2010; Fuller and Suruda, 2000). In the airways of five victims of toxic gases from slurry tanks, concentrations of H_2S were above 100 ppm 24–36 hours post-mortem, while H_2S concentrations near the scene of another incident was over 2000 ppm (Oesterhelweg and Püschel, 2008).

The exact mode of action by which H_2S exposure leads to death has not been fully elucidated. However, H_2S is known to inhibit cytochrome c oxidase within the electron transport chain leading to inhibition of ATP and respiration (Jiang et al., 2016). The United States of America

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considers H_2S exposure a high priority chemical threat, as no treatment options are available for people suffering from poisoning (Malone Rubright et al., 2017). This is highlighted by the number of deaths in the USA where 77 people died from sulphide exposure between the years 1975 and 2004 (Rl and We, 2007). In Ireland between 2007 and 2019, nine people died from H_2S poisoning (Personal Communication; Central Statistics Office – Ireland).

The storage of slurry allows for microbial production of H_2S, as well as GHGs (such as methane and carbon dioxide) (Montes et al., 2013; Aguerre et al., 2012; Sommer et al., 2017; Eriksen et al., 2012). The production of H_2S takes place within the anaerobic environment of cattle slurry, carried out by sulphate (SO_4^{2-}) reducing bacteria (SRB) (McArthur, 2006; Habeeb et al., 2017). SRB use SO_4^{2-} as an electron acceptor in order to produce energy and grow. It has been shown by Hjorth et al. (2012), Chang et al. (2007) and Thorn et al. (2022) that that the addition of ozone and/or oxygen can decrease H_2S concentrations by up 99.5 % from animal slurry and within sewer systems. Both SRB and the H_2S that they produce are extremely sensitive to oxygen, the introduction of which can increase the oxidative reduction potential (ORP) of their environment, inhibiting H_2S production while also oxidising any dissolved sulphide present (Bianchi, 2007; Muyzer and Stams, 2008). However, it is still uncertain if treating cattle stores on a less regular basis than Hjorth et al. (2012) or Thorn et al. (2022) (treating constantly and multiple times per week) will still reduce H_2S concentrations from slurry.

In this study, the addition of hydrogen peroxide (30 %) (H_2O_2) and potassium iodide (KI) (acting as a catalytic decomposer of H_2O_2) to beef cattle slurry was examined to assess if such amendments effect H_2S mitigation. It is hypothesised that similar to Hjorth et al. (2012), H_2S oxidation will take place, leading to increased SO_4^{2-} concentrations and the rapid rise in measured ORP will cause repression of sulphate reduction over a sustained period of time. In this study, the effect of the oxidising treatment on H_2S concentrations during agitation was carried out at small scale (20 kg) and at mesoscale (660 L). An additional laboratory experiment measuring the effect of the oxidising treatment on SO_4^{2-} concentrations over 29 days was carried out to further explain the possible fate of potentially oxidised H_2S from slurry.

2. Materials and methods

2.1. Small scale storage: experimental set-up

This experiment was carried out in Teagasc, Johnstown Castle, Wexford, Ireland in February 2021. 240 kg of cattle slurry was taken from an agitated slurry tank on a beef farm in county Wexford, Ireland and weighed into twelve 30 L containers, each holding 20 kg of cattle slurry. The cattle were fed on silage (approx. 30 kg $head^{-1}$ day^{-1}) and concentrate feed (5 kg $head^{-1}$ day^{-1}).

The slurry was held in the buckets for a total of 40 days and four treatments were tested. In the first treatment, 28 ml of 30 % H_2O_2 (0.67 g H_2O_2 kg^{-1} slurry) and 23 ml of a 1.06 M KI solution (0.27 g KI kg^{-1} slurry) were combined and then added to the bottom of the slurry via peristaltic pump and mixed (HK-20), with repeated addition every 2 weeks. In the second treatment, the HK-20 regiment was repeated, however, $CaCl_2$ powder was added to the slurry post mixing (HKC-20) (436 g $CaCl_2$ m^{-2} slurry). Control 1 slurry was held in the containers unagitated for 40 days. Control 2 slurry was held for 40 days but had water added to the bottom of the bucket via peristaltic pump (compensating for water addition of HK-20 and HKC-20). All treatments were replicated n=3.

2.1.1. Small scale storage: H_2S measurements

After the 40-day storage period, the slurry was agitated using a modified lid with a mechanical agitator fitted and 2 septa used for sample analysis and re-circulation of sample gas. The lid and agitation time of 15 seconds were similar to Crook et al. (2017). A GeoTech Biogas 3000 analyser was then used to measure the H_2S concentrations from the slurry. The analyser had a range of 1–5000 ppm H_2S and used an electrochemical cell. The analyser was factory calibrated 2 months prior to measurements. Typical stated accuracy was ± 2 % when concentrations were below 1000 ppm. The primary cross sensitivity gases for the analyser were SO_2 and NO_2, however these gases were not expected to be present upon agitation of the slurry. Gas samples were analysed for 240 seconds (quoted response time of analyser) until a steady state was reached. Concentrations were then recorded.

2.1.2. Small scale storage: slurry sulphur content

Slurry was sampled for total sulphur content prior to the incubation and post agitation. It was then freeze dried, ball-milled and sieved using a 0.5 μm sieve. This sample was then analysed using a LECO elemental analyser.

2.2. Mesoscale storage: experimental set-up

This experiment was carried out in Teagasc, Johnstown castle, Wexford in July, August and September 2021. Nine 1 m^3 (0.8 m x 0.8 m x 1.5 m) underground concrete slurry tanks were filled with 660 L of cattle slurry each from a nearby beef farm. The cattle were fed on silage (approx. 30 kg $head^{-1}$ day^{-1}) and concentrate (5 kg $head^{-1}$ day^{-1}).

This experiment consisted of three treatments. Control slurry was left undisturbed for 90 days apart from when the multiparameter readings were taken (Control-660). In the second treatment, 1.32 L of 30 % H_2O_2 (0.67 g H_2O_2 kg^{-1} slurry) and 1 L of 1.06 M KI (0.27 g KI kg^{-1} slurry) were pumped into the slurry tanks at the same time but separately through 2 m pipes connected to peristaltic pumps by plastic tubing. This plastic tubing was placed in separate containers of H_2O_2 and KI. The treatment was pumped into the bottom of the tank at a rate of 0.5 L min^{-1} for H_2O_2 and 0.363 L min^{-1} for KI (HK-660). The third treatment (HKC-660) consisted of the same practice as HK-660, except a 0.75 M $CaCl_2$ solution was sprayed onto the resulting slurry foam after treatment (520 g $CaCl_2$ m^{-2} slurry). All treatments and controls were replicated n=3.

The slurry was treated every 2 weeks up until day 77 in which treatments were halted. The treatment schedule deviated once after day 29 in which there was 1 week in between treatments. This was carried out due to unforeseen circumstances not connected to the experiment. The treatment schedule resumed every 2 weeks after this deviation. The slurry was stored in the tanks for 90 days in total, after which a specialized agitator with an airtight lid attached was lowered into the slurry. The slurry in each tank was agitated for 30 seconds in order to accommodate the large amount of slurry being mixed, similarly to Crook et al. (2017).

2.2.1. Mesoscale storage: H_2S measurements

Directly after agitation a GeoTech Biogas 3000 analyser was attached to a custom stainless-steel lid and gas samples analysed (Fig. 1). Gas samples were analysed for 240 seconds until a steady state was reached. Total slurry sulphur concentrations were measured post storage identically to the small-scale experiment. Agitation at both scales was carried out in an enclosure with adequate airflow and a CrownCon T4 Personal Multigas Detector for health and safety.

2.2.2. Mesoscale storage: multiparameter data

Oxidative-redox potential (ORP), dissolved oxygen (DO), temperature and pH were recorded using a Hanna H91628 multiparameter probe. This probe was lowered into the slurry at four different depths, 4 cm, 24 cm, 54 cm and 83 cm below the slurry surface. This was completed directly after each addition of the treatment as well as 2, 4 and 13 days after treatment with 7 treatment periods in total, therefore treatment days are indicative of the entire day. Calibration of the pH and dissolved oxygen sensors were carried out each day in which measurements were taken.

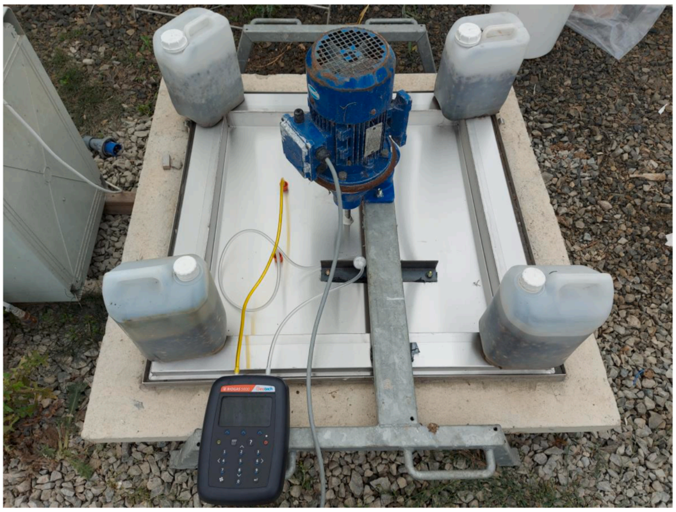

Fig. 1. Stainless-steel lid covering slurry storage prior to agitation during mesoscale incubation. Biogas analyser present in the bottom left. Agitator present in centre of image.

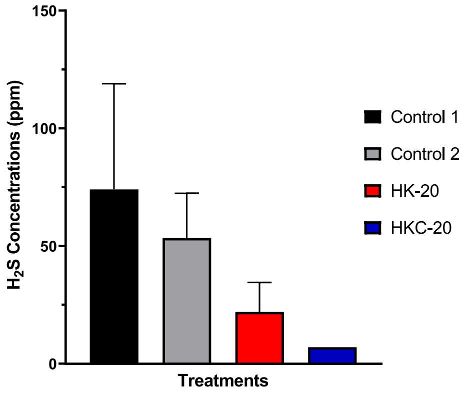

Fig. 2. H_2S concentrations post agitation of slurry following 40-day slurry incubation experiment at small scale. HK-20 (hydrogen peroxide and potassium iodide – 20 kg scale) and HKC-20 (hydrogen peroxide, potassium iodide and calcium chloride – 20 kg scale) displayed as well as control 1 and control 2. Standard deviation shown for each treatment (no bar shown for HKC-20 as all replicates were equal).

2.3. Lab-scale: sulphate concentration during storage

Six 400 g sub-samples were taken from an agitated mesoscale control slurry tank and were weighed into 600 ml containers. In 3 containers, 0.798 ml of 30 % H_2O_2 and 0.107 g KI were mixed into the slurry (HK-LS) each week for 4 weeks, while 3 separate containers had no added treatments (Control-LS). Both treatments were replicated n=3. 2 ml of slurry was sampled after being mixed thoroughly at the start and end of the experiment, as well as 8 separate times throughout the 4 week experiment. These samples were centrifuged @ 5000 relative centrifugal force for 10 mins and the supernatant taken. The supernatant was diluted 1:20, from which 5 ml was placed into a cuvette (HACH Sulphate cuvette test; 40–150 mg L^{-1} SO_4 -LCK153). Samples were measured using a HACH DR2800 spectrophotometer and normalised versus negative (0 mg $L^{-1}SO_4^{2-}$) and positive (50 mg $L^{-1}SO_4^{2-}$) controls. The 600 ml bottles were weighed at the start and end of the experimental period.

2.4. Statistical analysis

Statistical differences in cumulative H_2S concentrations and slurry sulphur concentrations were assessed using one-way ANOVA analysis using GraphPad Prism (v8.01). A Tukey post-hoc test was carried out to determine if differences between treatments and controls were significant. A statistical probability of $p \leq 0.05$ was considered significant.

3. Results and discussion

3.1. Small scale storage

Upon agitation, peak H_2S concentrations were measured (Fig. 2). The concentrations from Control 1 (un-agitated and no water added) and Control 2 (agitated similar to treatments with water addition), were 74 ppm and 52 ppm respectively (not significant). The primary difference between Control 1 and Control 2 was the addition of water and the subsequent mixing/agitation. Even though these differences are not significant, it appears that the agitation that occurred throughout the storage period released H_2S from Control 2 but was not detected, as formal agitation and H_2S measurements were only completed at the end of the storage period. HK-20 and HKC-20 produced 22 ppm and 7 ppm, respectively (Fig. 2), representing a 70 (not significant) and 91 % ($p < 0.05$) decrease in concentrations compared to Control 1. However, it can be assumed that a similar amount of H_2S was lost from HK-20 and HKC-20 via the same agitation experienced in Control 2. However, the reduction in H_2S concentrations from the treatments when compared to Control 2 were 58 (not significant) and 87 % ($p < 0.05$) respectively. Therefore, it can be assumed that oxygen played a pivotal role in reducing H_2S concentrations even further.

The control H_2S concentrations measured post agitation were similar to control slurry tested by Crook et al. (2017) while the slurry sulphur concentrations were similar to Andriamanohiarisoamanana et al. (2015). It is apparent that H_2S concentrations are not at such a level that may cause immediate death or loss of consciousness, however they would still be a cause for concern from a health and safety perspective. The low H_2S concentrations observed may be due to the small amount of slurry available, whereas at farm-scale in which thousands of litres of slurry is stored, total H_2S concentrations would increase considerably while the concentrations per unit of slurry may be similar.

The addition of $CaCl_2$ was done in order to reduce concentrations of another polluting gas, ammonia, however the effect of $CaCl_2$ on H_2S has not been described previously. The addition of $CaCl_2$, shown in Table 1 (HKC-20), had no effect on the S concentration of the slurry. Although HK-20 and Control 2 experienced reductions of 20 mg S kg^{-1} slurry, this was not significant. This shows that the oxidising treatment does not affect sulphur concentrations but impacts H_2S concentrations directly.

H_2S measurements were taken from un-agitated slurry during the first two weeks of storage, but the analyser did not detect any H_2S across any treatment on any day (data not shown). This result was similar to Crook et al., (2017) who found that H_2S concentrations from cattle slurry were nil before stirring. As a result, H_2S measurements were discontinued due to the absence of detectable concentrations. This was most likely related to the limited accuracy of the equipment and scale of the experiment as ambient H_2S is detectable outside of periods of

Table 1
Small Scale Storage; slurry sulphur concentrations post 40-day storage period. HK-20 (hydrogen peroxide and potassium iodide – 20 kg scale) and HKC-20 (hydrogen peroxide, potassium iodide and calcium chloride – 20 kg scale) displayed as well as control 1 and control 2. Differing letters beside figures indicate significance within columns.

Treatments	Slurry Total Solids (g kg^{-1} Slurry)	Slurry S Concentration (mg S kg^{-1} Slurry)
Control 1	95 ± 3.0^a	460 ± 20.1^a
Control 2	90 ± 5.2^a	440 ± 10.1^a
HK−20	92 ± 7.4^a	440 ± 10.3^a
HKC−20	113 ± 4.0^b	460 ± 20.0^a

agitation at farm scale as demonstrated by Grant and Boehm, (2022). In typical Irish farming conditions, where most cattle are housed above slatted tanks, slurry agitation only occurs before land spreading via a mechanical tractor-powered agitator, after approx. 3–5 months, allowing for the build-up and subsequent release of dissolved H_2S. Therefore, it was essential for this and the following mesoscale experiment to simulate realistic conditions, which is why only a single agitation event was conducted. Although the dispersion of H_2S from these tanks was not directly studied, as done by Gyte and Kelsey (2024), it is reasonable to assume that any reduction in H_2S emissions during agitation would similarly decrease worker exposure. This reduction could potentially shorten the time required for an open-ventilated shed to become safe for re-entry, in line with the 30-minute period recommended by Gyte and Kelsey (2024).

3.2. *Mes×oscale storage*

Hydrogen sulphide concentrations from Control-660 were 78 ppm when agitated after 90 days of storage. However, both HK-660 and HKC-660 emitted 17 and 15 ppm, a 78 and 81 % reduction in H_2S concentrations from the cattle slurry, respectively ($p < 0.05$) (Fig. 3). This abatement of H_2S concentrations was not as effective as Hjorth et al. (2012) who found that 99.5 % of H_2S concentrations were abated. This difference may be due to how often the slurry was treated, when H_2S was measured, and the oxidising agents used. In Hjorth et al. (2012) the slurry was treated constantly while H_2S concentrations were continually measured. The use of ozone, a more powerful oxidiser than oxygen is likely more capable of oxidising H_2S. However, in the 660 L storage experiment presented here, there were 13 days in between the last treatment and agitation, meaning that there was a sustained SO_4^{2-} reduction repression within the treated slurry for that time. Although no ozone was detected by Hjorth et al. (2012) in the headspace above the slurry i.e. all of the ozone was reduced, ozone has been shown to reduce plant productivity and cause chronic health impacts in humans when concentrations increase in the atmosphere if it was mistakenly released (Ainsworth et al., 2012; McKee, 1993). Kupper et al., (2024) also observed maximum H_2S concentrations of 20.2 ppm from un-acidified pig slurry within slurry channels. Although this method slurry storage/removal was not tested, this may be an area of future interest if acidification remains unpopular in Ireland (Lanigan et al., 2023).

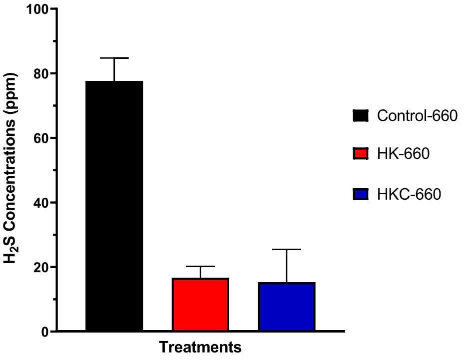

Fig. 3. H_2S concentrations post agitation of slurry following 90-day slurry storage experiment at mesosclae scale. HK-660 (hydrogen peroxide and potassium iodide – 660 L scale), HKC-660 (hydrogen peroxide, potassium iodide and calcium chloride – 660 L scale) and control-660 displayed. Standard deviation shown for each treatment.

Table 2
Mesoscale storage; slurry sulphur concentrations post 90-day storage and H_2S concentrations observed after week 8 and 12. HK-660 (hydrogen peroxide and potassium iodide – 660 L scale), HKC-660 (hydrogen peroxide, potassium iodide and calcium chloride – 660 L scale) and control-660 displayed. Differing letters beside figures indicate significance within columns.

Treatments	Slurry Total Solids (g kg^{-1} Slurry) (Week 8)	Slurry S Concentration (mg S kg^{-1}) (Week 8)	Slurry Total Solids (g kg^{-1} Slurry) (Week 12)	Slurry S Concentration (mg S kg^{-1}) (Week 12)
HK−660	15 ± 0.4^{a}	36 ± 1.0^{a}	33 ± 1.4^{ab}	79 ± 2.3^{a}
HKC−660	17 ± 2.3^{a}	42 ± 3.4^{b}	36 ± 2.2^{a}	87 ± 5.4^{a}
Control−660	14 ± 0.4^{a}	37 ± 2.1^{ab}	32 ± 0.6^{b}	76 ± 6.4^{a}

It is important to note that in Table 2, week 8 S concentrations were sub-sampled from un-agitated slurry which contributes to the lower S concentrations in slurries compared to week 12 which were agitated. The addition of $CaCl_2$ in HKC-660 increased slurry S concentrations in week 8 and 12, while HK-660 and control-660 remained similar throughout. This may be due to the $CaCl_2$ spray, however no previous research concerning the interaction between $CaCl_2$, and sulphur can explain this trend. The increased S concentrations post (week 12) compared to pre (week 8) agitation does however demonstrate the effectiveness of agitation in cattle slurry, in which nutrients that have fallen to the bottom of the tank, stratifying the slurry based on depth during storage (Ndegwa et al., 2002), are re-suspended in the slurry matrix. The slurry S concentrations were also similar to Andriamanohiarisoamanana et al. (2015) considering the total solids content of the slurry in this study were approx. 10 % lower.

Considering H_2S concentrations of approx. 700 ppm need to be present in order to cause fatalities, the lower H_2S concentrations from both the small and mesoscale experiments would indicate that slurry storage is not particularly dangerous, however we know this is not the case. Lower H_2S concentrations may be a result of the diet of the cattle. Andriamanohiarisoamanana et al. (2015) found that the amount of concentrate feed in the diet relates to the amount of H_2S produced during storage, arguing that doubling the concentrate feed led to a 36 % increase in S and a 400 % increase in SO_4^{2-}. Since no acidification took place in that study such as in Eriksen et al. (2008) which would inhibit sulphide reduction, H_2S emissions were increased as a result. Concentrate in the diet of cattle in both experiments in this study was approx. 16.6 % (w/w), approx. 5 % higher than the lowest feeding rate in Andriamanohiarisoamanana et al. (2015). However similar H_2S concentrations were observed from the slurry in the current work, this does not disprove the link between cattle feed and H_2S emissions, but points to other factors such as total solids, temperature and the time in which the slurry was stored, which all impact H_2S production. For instance, it would be expected from Andriamanohiarisoamanana et al. (2015) that mixing slurry with a low total solids content, such as in the mesoscale experiment compared to the small-scale experiment, would lead to reduced H_2S concentrations, but no such reduction took place, most likely as the slurry in the mesoscale experiment was stored for a longer period of time. Differences in slurry S concentrations are also explained by the large differences in the total solids content of the slurry between experiments, by which more concentrated slurries contain higher concentrations of nutrients.

During the small scale and mesoscale experiments with two volumes that differed by over 30 times, the method of treatment involved was effective for both. However, in the mesoscale storage experiment there was no agitated Control (i.e. Control 2 – Small Scale Storage). Therefore, if the same proportion of H_2S was lost from Control-660 as Control 2, an "agitated" Control-660 would equal 55 ppm. Theoretically, this means that HK-660 and HKC-660 would reduce H_2S concentrations by 69 % and 73 % compared to this agitated control, $p < 0.05$. However, if this experiment was to be repeated, an agitated control at this volume may offer differing amounts of out-gassing during the storage period.

The ORP of the slurry during the experimental period was very stable except for when the treatment was added. The ORP rose from approx. −350 mV to approx. +50 mV over the course of the experiment (Fig. 5). This difference in ORP on the day of treatment can be explained by the catalytic decomposition of H_2O_2 into oxygen which rose from the bottom of the tank and moved quickly upwards through the slurry becoming reduced. ORP readings quickly reduced to below −300 mV 24 hours post treatment.

When the oxidising treatment was added to the slurry, the treatment could reduce H_2S emissions in two ways. The first mechanism being oxygen, released by the reaction between H_2O_2 and KI and oxidising the vast majority of sulphide within the slurry to either elemental sulphur or perhaps thiosulphate as reasoned by Janssen et al. (1995). This is possible since sulphide is unstable in the presence of oxygen (Bianchi, 2007). The second mechanism being that the increased ORP within the slurry had a negative impact on the rate at which SRB could utilise SO_4^{2-} as an electron acceptor and produce H_2S. It is well known that SRB are obligate anaerobes, therefore exposure to high oxygen levels most likely resulted in some inhibition of H_2S generation (Hao et al., 1996; Hardy and Hamilton, 1981; Krekeler et al., 1998; Cypionka et al., 1985). This is also the case with other slurry treatments such as aeration systems (Skjelhaugen and Donantoni, 1998; Zwain et al., 2020). The inhibition of SRB under high oxygen loads was also shown to be effective by Chang et al. (2007) in sewer systems.

The pH of the slurry was largely unaffected due to treatment (Fig. 4), however on days in which the treatment was added, the pH increased by between 0.1 and 0.2 units. This is most likely due to the mixing and/or the oxidising treatment possibly causing an increase in the use and subsequent reduction of volatile fatty acids due to the increased ORP concentration. However, in terms of H_2S concentrations these slight differences are not considered significant (Overmeyer et al., 2020).

3.3. Sulphate storage experiment

During the 29-day storage period, SO_4^{2-} was found to remain constant in both treated and control slurries and remained almost non-changing throughout the entire experimental period (Fig. 6). There are slight linear changes over time by which Control-LS loses approx. 10 % of its SO_4^{2-} content by the end of the experiment, however, no single day produced significantly different results between treatments. It was hypothesised that the addition of the treatment would increase SO_4^{2-} concentrations however, the oxidation of sulphide to elemental S may

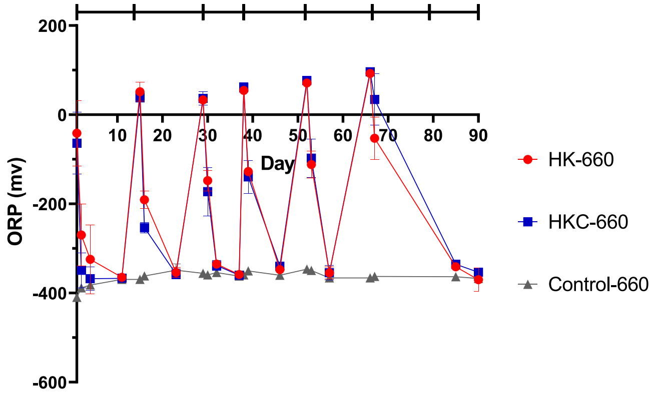

Fig. 5. Oxidative reduction potential of slurry. Control slurry (control-660) remained consistent over 90 days while the addition of the oxidising treatment (blue squares & red circles) caused increased ORP. HK-660 indicates treatment with hydrogen peroxide and potassium iodide at mesoscale while HKC-660 indicates treatment with hydrogen peroxide, potassium iodide and calcium chloride at a mesoscale. Horizontal bars above graph represent treatment periods, i.e. period between the day of treatment and immediately prior to next treatment.

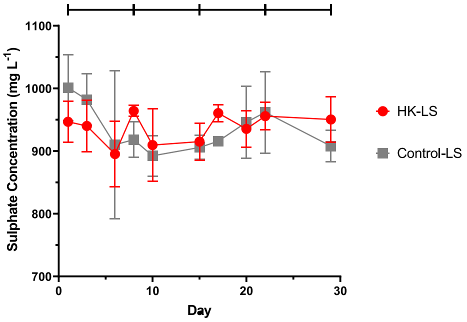

Fig. 6. Sulphate concentrations during small scale slurry storage experiment. HK-LS (hydrogen peroxide and potassium iodide – Lab Scale) and control-LS displayed. Standard deviation shown for each day. Horizontal bars above graph represent treatment periods, i.e. period between the day of treatment and immediately prior to next treatment.

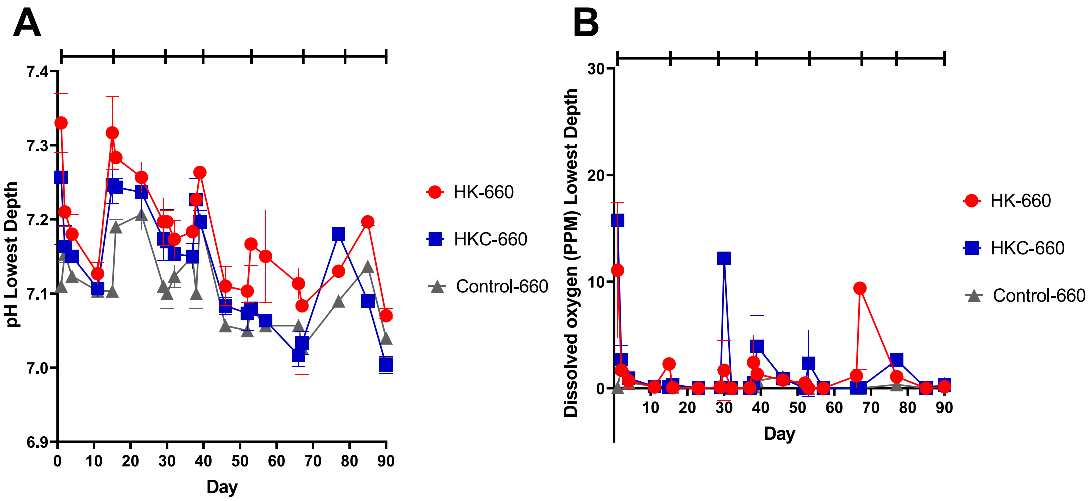

Fig. 4. A; pH of slurry taken at the lowest depth in tank (83 cm below the slurry surface). B; Dissolved oxygen (ppm) of slurry taken at lowest depth in tank (83 cm below the slurry surface). Standard error shown for days in all figures. HK-660 (hydrogen peroxide and potassium iodide – 660 L scale), HKC-660 (hydrogen peroxide, potassium iodide and calcium chloride – mesoscale) and control-660 displayed. Standard deviation displayed for each day. Horizontal bars above graph represent treatment periods, i.e. period between the day of treatment and immediately prior to next treatment.

not have had the ability to drastically affect SO_4^{2-} pools which was also a factor in both previous storage experiments. This stability of SO_4^{2-} pools in slurry was also shown clearly in work carried out by Eriksen et al. (2008) in which pig slurry was stored for 90 days.

Slurry amendments are often used to reduce emissions such as methane and ammonia, however, some amendments may lead to unforeseen hazards. For instance, the use of gypsum, a popular soil conditioner, may sometimes be used on farms as a replacement for straw or sawdust in cattle bedding. This however leads to increased H_2S generation if it falls into slurry pits due to the increased SO_4^{2-} concentration leading to reduction by SRB (Crook et al., 2017).

Sulphuric acid is also used to reduce the pH of slurry and subsequently reduce ammonia and methane emissions. This amendment does increase SO_4^{2-} concentrations within slurry throughout its storage period, while also keeping sulphide concentrations similar to control levels. In the early stages of acidification however, or if the pH of the slurry is let rise to its original pH, then sulphide concentrations can increase past control levels as described by Eriksen et al. (2008) and Eriksen et al. (2012).

The addition of solid-state peroxide to slurry has already been carried out in various studies in which H_2S emissions were reduced as a result. The use of 0.4 % magnesium oxide by Chang et al. (2007) to inhibit H_2S emissions for more than 40 days and urea hydrogen peroxide (H_2O_2) used by Thorn et al. (2022) reduced H_2S emissions by 89 %. The use of H_2O_2 was criticized by Chang et al. (2007) for not generating a long-lasting method of oxidation. Though the reasons for this are varied as seen in the current work, it is most likely due to the ORP dropping below −150 mv which allows SRB respiration and growth. However, despite the criticism, H_2O_2 has been shown to significantly reduce H_2S emissions in this study, albeit with multiple treatments. A product such as magnesium oxide may however be very beneficial for use in reducing H_2S emissions during slurry storage due to its method of slow-release oxygen, which may maintain a higher ORP for a longer period of time.

3.4. Future research

The treatment presented in this study has demonstrated its effectiveness as a proof of concept in reducing H_2S concentrations from cattle slurry storage across two storage scales, 20 kg and 660 L. Given these promising results, it is recommended that the treatment be tested at the farm scale in openly ventilated slatted cattle sheds during slurry agitation. Additionally, exposure limits at varying distances should be assessed to minimize the risk of farm-related fatalities. Future research should also explore the treatment's impact on H_2S emissions from slurry channels during flushing.

4. Conclusion

This research provides evidence that repeated addition of H_2O_2 and KI during cattle slurry storage reduced H_2S concentrations upon agitation. The rise in DO and subsequently ORP within the slurry both inhibits the production of this toxic gas and oxidises it so that it cannot be released upon agitation. However, the ORP in this work was not held within a range that consistently inhibits SRB, therefore H_2S production most likely took place in between treatment periods. It is recommended that more frequent treatment of slurry or a slow-release oxygen system be used which could inhibit SRB even more effectively. Inhibiting H_2S emission throughout storage did not increase total sulphur or sulphate concentrations within the slurry. Reducing H_2S concentrations may lead to reduced S pollution and improve health and safety for farmers by reducing severe injuries and possibly fatalities. Future research should focus on farm-scale validation of this treatment technology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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