

Low-Dose Acidification as a Methane Mitigation Strategy for Manure Management

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ABSTRACT: Excreta from housed animals are typically stored before land application, and storage is an important point source of CH₄, N gases, and odor. This study explored acidification as a strategy for greenhouse gas (GHG) mitigation, specifically the potential to reduce the acid dose to improve cost-effectiveness and minimize environmental impacts. Pig slurry was stored with five doses of concentrated sulfuric acid [1.2–6.0 kg (m³ of slurry)⁻¹] for 63 days. Emissions of CH₄ and NH₃ were reduced by 46–96% and 33–78%, respectively, with an increase in the acid dose. Odorant emissions, dominated by 4-methylphenol and H₂S, were strongly suppressed by acidification. Below pH 6, methanogen inhibition was most likely due to undissociated VFAs, and above pH 6, the inhibition could involve competition from sulfate reducers and inhibition by undissociated H₂S. If 1, 3, or 10 acidification treatments were needed, the annual costs for GHG mitigation across the five acid doses were 28–47, 44–57, and 93–134 € (ton of CO₂ equivalents)⁻¹, respectively. With 1 or 3 treatments, the most cost-effective acid dose was 2.1 kg m⁻³, or 3.2 kg m⁻³ with 10 treatments. This study strongly suggests that low-dose acidification is a viable strategy for GHG mitigation.

KEYWORDS: pig slurry, pilot-scale storage, acidification, methane, ammonia, odor, cost-effectiveness

INTRODUCTION

Agriculture is responsible for 32% of global anthropogenic methane (CH₄) emissions, and CH₄ mitigation within agriculture can contribute to meeting the goals of the Paris agreement.¹ Although mitigation of CH₄ with a short atmospheric life span is not a substitute for net-zero CO₂ emissions,² it may extend the period available to achieve this goal.³

Urine and feces excreted by housed animals are typically collected as a slurry and stored outside in large tanks or lagoons. During storage, anaerobic conditions predominate, which leads to the production of CH₄ and its release to the atmosphere. As a consequence, stored slurry is the main source of methane emissions from pig production⁴ and a significant source of methane from dairy production (20–50%) depending on climate.⁵ Cost-effective strategies for mitigating CH₄ emissions from manure storage are therefore critically needed to reduce the climate impact of livestock production.

It is well-known that acidification of a slurry with concentrated sulfuric acid (H₂SO₄), a strategy developed for ammonia (NH₃) mitigation, will also dramatically reduce CH₄ emissions.⁶ Reductions of 65–95% during storage for three months have been observed with both cattle slurry^{7,8} and pig slurry.⁹ Commercial technologies for acidification of slurry have targeted slurry in pits below housed animals, but acidification of slurry in storage tanks prior to field application is also practiced and less costly. Procedures have been developed for the safe handling of concentrated H₂SO₄, but current applications of the method involve high running costs because often >5 kg/ton of slurry is needed to achieve the target pH.¹⁰ The resulting S content greatly exceeds the requirement of most crops, and hence, the possibility that

sulfate will leach from agricultural land and contribute to eutrophication through P mobilization is a concern.¹¹

Interestingly, addition of sulfate or the S-containing amino acid methionine, without manipulation of the pH, has also reduced CH₄ emissions by >50%,⁷ indicating that the inhibition of methanogenesis is at least partly linked to S transformations and not simply a function of pH reduction. Therefore, a reduced dose of H₂SO₄ could potentially also achieve a substantial reduction of emissions.

Slurry storage is a well-known source of odorants, in particular S-containing compounds such as H₂S and methanethiol, but also 4-methylphenol, indole, 3-methyl-1H-indole, trimethylamine, and, in some cases, carboxylic acids.^{12–14} Apart from being an odorant, H₂S also contributes to the atmospheric burden of sulfur and contributes to the formation of secondary particles.¹⁵ In untreated slurry, H₂S is produced mostly from sulfate reduction,¹⁶ but slurry acidification with H₂SO₄¹⁷ and hydrochloric acid¹⁸ has been found to inhibit sulfate reduction. Although laboratory studies indicate that H₂SO₄ has only minor effects on total odor emissions,^{19,20} the effects of slurry acidification on the odor profile should be documented to avoid pollution swapping.

In this study, we investigated the effects of reducing the rate of H₂SO₄ addition below the recommended rate on emissions of CH₄, NH₃, and odorants in a pilot-scale storage experiment.

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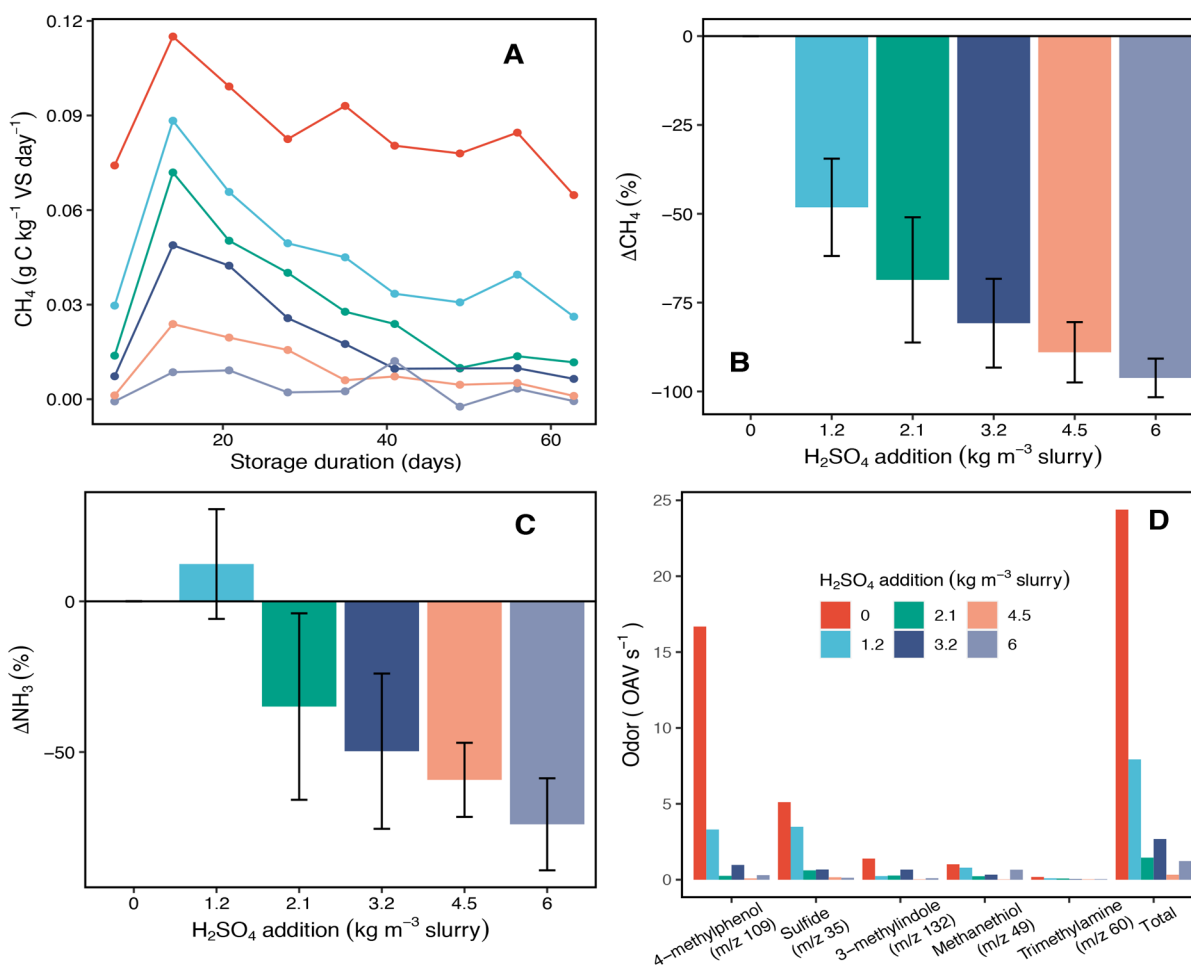


Figure 1. (A) Daily CH₄ emission rates. Percentage reductions in cumulative (B) CH₄ emissions and (C) NH₃ emissions. (D) Emissions of selected odorants at six levels of pig slurry acidification prior to storage as indicated. The color code shown in panel D applies to all subplots.

We hypothesized that both CH₄ and NH₃ emissions would be inversely related to the sulfuric acid application rate but that CH₄ emissions would be more sensitive to H₂SO₄ addition than NH₃ emissions, allowing for CH₄ mitigation with a lower dose. We further hypothesized that acidification would change the composition, if not level, of odor emitted from the slurry.

MATERIALS AND METHODS

The experiment (August 17 to October 19, 2021, 63 days) was conducted in a pilot-scale storage facility.²¹ Six storage tanks were amended with 3.2–3.9 m³ (0.91–1.13 m depth) of slurry from finishing pigs obtained from an experimental pig farm (average age of ~1 month). Acidification levels of 0, 1.2, 2.1, 3.2, 4.5, and 6.0 kg (m³ of sulfuric acid)⁻¹ (industrial grade 96% H₂SO₄; Brenntag Nordic A/S, Ballerup, Denmark) were randomized among the six tanks. The acid was added slowly through a funnel with a long tube extending to below the surface of the slurry while vigorous stirring was performed with a slurry channel agitator. Personal protective equipment was worn during this process, which is automated in commercial equipment for full-scale tank acidification. The storage tanks were immediately covered with an airtight lid, and forced ventilation was applied at a rate (logged every 15 min) that varied between 74 and 101 m³ h⁻¹. Each unit had eight air-inlets in the tank wall and one central outlet through the cover, connected via a main duct to a radial fan.²¹

Sampling. GHG and NH₃ emissions during storage were quantified as described in ref 21. In short, a 15 mL min⁻¹ subsample of the ventilation air from each tank and background air from an

open-air position between two of the storage tanks were drawn through 1/4 in. Teflon tubing with a peristaltic pump placed in a nearby office container. The gas samples were first passed through a gas washing bottle with 80 mL of 20 mM H₃PO₄ close to the point of sampling, for trapping of NH₃, and then carried via an insulated sheath with a heating cable to avoid condensation. Downstream from the pump was an array of solenoid valves where time-averaged weekly samples were collected in 3 L alu-foil gas sampling bags (SKC, Eighty Four, PA). This was done by collecting gas for 1 min during every 1 h period, giving a pooled sample for analysis of 2.52 L during a week.

Odor activity was monitored between September 15 and October 7, 2021. A separate subsample of the ventilation air from each storage tank was taken through 30 m heated and insulated Teflon tubes to a 10-way Vici PEEK valve. A PTFE diaphragm vacuum pump (Charles Austen, Surrey, England) was used to continuously sample air from the valve at a rate of 1.9 L min⁻¹ to a proton-transfer-reaction mass spectrometer (PTR-MS) (PTR-TOF4000, Ionicon Analytik, Innsbruck, Austria). Data from each storage tank, as well as the instrumental background (charcoal-filtered air), were collected for 30 min, equivalent to a cycle time of 3.5 h. To avoid odorant carryover, only the last 10 min of data from the 30 min collection period was used in the data analysis step.

The slurry pH and temperature were measured weekly at depths of 5 and 30 cm below the surface using a 704 pH meter with a 50 cm glass electrode (Metrohm). Samples of mixed slurry (500 mL) for analysis were collected from each tank immediately before acidification treatments, and by the end of the storage period, again after thorough mixing. Samples were kept frozen until further analysis.

Analytical Methods. Slurry dry matter (DM) and volatile solids (VS) were determined as described in ref 21. Total and ammoniacal N were determined by Kjeldahl digestion (Kjeltec; Foss, Hillerød, Denmark). Sulfate was determined photometrically with a NOVA Spectroquant 60 instrument and a sulfate cell test 114564 kit (Merck KGaA, Darmstadt, Germany). Concentrations of CH₄ and N₂O were determined by gas chromatography.²³ Ammonia trapped in H₃PO₄ was determined colorimetrically.²⁴ The gas concentrations in time-averaged (CH₄ and N₂O) or cumulative (NH₃) samples were used, together with ventilation rates, to calculate average emission rates in each of nine weeks, and cumulative emissions during the entire monitoring period. Ventilation rates were monitored using a flow restrictor on the outlet ventilation tube from each tank, which was connected to a differential pressure transmitter that was logged every 15 min. No emission of N₂O was detected during the experiment.

Concentrations of odorants in the ventilation air, including NH₃, were determined with PTR-MS. The PTR-MS drift tube temperature, drift tube pressure, and drift tube voltage were 60 °C, 3.3 mbar, and 930 V, respectively [equivalent to an electric field to density ratio (*E/N*) of 139 Townsend]. Odor activity values (OAVs) were calculated as the odorant concentration divided by the odor threshold value (OTV) using the procedure described in ref 11 and applying OTVs from ref 13. PTR-MS calibration was done as described previously.^{12,25,26} Odor emission was expressed as the product of OAV and ventilation rate.

Statistical Analyses. To compare the effects of acidification on gaseous emissions, we used a repeated-measures mixed effect analysis of variance with acid dose as the fixed effect and sampling day as the random effect. The “lme4” package²⁷ in R was used to run the model. Posthoc Tukey tests of results from the mixed effects model were used to determine any differences (*P* < 0.05) between the acid doses by the “emmeans” package.²⁸ All statistical analyses were run using R (version 3.6.3).²⁹

RESULTS AND DISCUSSION

Characteristics of the Slurry. The slurry temperature was initially around 17 °C and decreased, with some fluctuations, to 11 °C during the monitoring period. The temperature was consistently higher at the 5 cm depth than at the 30 cm depth and peaked at 20 °C during the second week of storage (Figure S1). The slurry pH consistently increased in untreated slurry, from 6.7 to 7.3, while there were only sporadic peaks in other treatments (Figure S2); the average pH with 1.2, 2.1, 3.2, 4.5, and 6.0 kg of H₂SO₄ m⁻³ were 6.8, 6.5, 6.5, 6.2, and 6.1, respectively. Volatile solids (2.8–3.4%), total N (4.1–4.3 kg of N m⁻³), and ammoniacal N (2.6–3.0 kg of N m⁻³) did not consistently change during storage (untreated slurry) or between treatments (Table S1), and there was no indication of major changes in slurry volumes due to evaporation. Slurry SO₄²⁻ concentrations were aligned with levels of H₂SO₄ added, ranging from 0.14 g of SO₄²⁻ L⁻¹ in untreated slurry to 5.4 g of SO₄²⁻ L⁻¹ at 6.0 kg of H₂SO₄ m⁻³. A whitish crust had formed at the surface of treatments with acidified slurry by the end of storage (Figure S4).

CH₄ Emissions. The temporal dynamics of CH₄ emissions from pig slurry during storage (Figure 1A) were similar across treatments, peaking after two weeks, at which point the slurry temperature was also highest (Figure S1). The emission from untreated slurry was always higher than emissions from acidified treatments and varied from 0.065 to 0.12 g of CH₄-C (kg of VS)⁻¹ day⁻¹. The average CH₄ emission from untreated slurry during the storage period corresponded to 0.15 g of CH₄ m⁻³ h⁻¹, which is well below the average rate of 0.67 g of CH₄ m⁻³ h⁻¹ reported in a recent review.³⁰ A main reason is probably the autumn storage temperatures, because average CH₄ emissions from pig slurry during summer and

winter storage corresponding to 1.8 and 0.02 g of CH₄ m⁻³ h⁻¹, respectively, have previously been reported at this site.²²

The reduction of CH₄ emissions increased with acid dose, from 46% at 1.2 kg of H₂SO₄ m⁻³ to 96% at 6 kg of H₂SO₄ m⁻³ (Figure 1B). The nearly complete inhibition observed with conventional acidification, represented in this study by the 6 kg m⁻³ dose, confirms earlier observations.³¹ Sokolov et al.³² reported equivalent effects of increasing acid dose for liquid dairy manure when taking into account that manure in that study was diluted with lake water.

NH₃ Emissions. Ammonia emissions were observed throughout the monitoring period. Sulfuric acid doses of 2.1–6 kg m⁻³ reduced emissions from 33 to 78% with an increase in dose (Figure 1C). In contrast, the 1.2 kg of H₂SO₄ m⁻³ dose did not change the NH₃ emission significantly relative to the control (*P* > 0.05, posthoc Tukey). The effects of treatment on NH₃ emissions were in general agreement with the differences in slurry pH, which increased steadily from 6.7 to 7.3 in untreated slurry but was more variable in acidified slurry (Figure S2); toward the end of the study, the decreasing temperature dampened treatment effects.

Odor Emissions. The odor profile of untreated slurry was dominated by 4-methylphenol and, to a lesser extent, H₂S (Figure 1D). The predominance of 4-methylphenol suggests that excess tyrosine was present in pig excreta.³³ Emissions of 3-methylindole, methanethiol, and trimethylamine were less significant, but their relative impact on total odor increased with H₂SO₄ dose. Total odor emission, which averaged ~24.4 OAV s⁻¹ during the measurement period, was reduced by 67% at 1.2 kg of H₂SO₄ m⁻³ and by >95% at 4.5–6 kg of H₂SO₄ m⁻³. Odor from 4-methylphenol was reduced by 74–99% regardless of H₂SO₄ dose, whereas at 1.2 kg of H₂SO₄ m⁻³, the emission of H₂S was reduced by only 18% and that of methanethiol was slightly higher. Carboxylic acid gaseous concentrations were in general low, which is not unexpected due to their low air–water partitioning and aqueous phase dissociation (Figure S3).

Sulfide oxidation (chemical or biological) at the air–liquid interface has been presented as a mechanism that suppresses H₂S emissions from manure.³⁴ Eriksen et al.³⁵ observed the oxidation of sulfide to sulfate in untreated pig slurry during storage, though not when the slurry was acidified. A whitish crust was observed in the acidified slurry (Figure S4), which may have offered a niche for aerobic sulfide-oxidizing bacteria in microsites protected from the acidified slurry. Regeneration of sulfate by sulfide oxidation, possibly via polysulfides,³⁶ could thus also have stabilized the potential for sulfate reduction and the effect of H₂S on methanogenesis.

Possible Mechanisms behind Methane Mitigation. The effects of acidification on methanogenic communities were not investigated. It has been hypothesized that inhibition of methylotrophic methanogens could lead to increased VOCS (primarily methanethiol and dimethyl sulfide), which was not observed despite a significant reduction in CH₄ emissions, although it should be noted that concentrations of methanethiol and dimethyl sulfide were generally low. Habtewold et al.⁸ reported a selective reduction of *Methanosarcina*, as well as CH₄ reduction, in acidified dairy cattle slurry. *Methanosarcina* are metabolically versatile,³⁷ and acetotrophic methanogenesis may have dominated. Petersen et al.⁸ discussed the possible role of *Thermoplasmata* based on T-RFLP profiles of untreated and acidified pig slurry, but here *Thermoplasmata* clustered with *Methanosarcina*.

Inhibition of methanogenesis in pig slurry acidified to pH 5.5 has been reported in several studies.^{17,38} Ottosen and co-workers¹⁷ argued that at this pH free (undissociated) acetic acid (FAA) could interfere with membrane functions. This is also true for free H₂S,³⁹ and >90% of dissolved sulfide is undissociated at pH 6.⁴⁰ However, the levels of volatile fatty acids and sulfide in slurry from finishing pigs clearly indicate that FAA would be more inhibitory than H₂S at pH 5.5–6 (Table S3). At 2.1–6 kg of H₂SO₄ m⁻³, the emission of H₂S was suppressed (Figure 1D), indicating that dissolved H₂S was low (if not oxidized at the slurry–air interface as discussed above), and this would also support FAA as the main mechanism of inhibition at higher doses of H₂SO₄.

Notably, CH₄ emissions were also reduced by nearly 50% at 1.2 kg of H₂SO₄ (m³ of slurry)⁻¹, where the average pH (7.0 ± 0.2 in untreated slurry) never decreased below 6.5 [6.8 ± 0.3 (Figure S2)]. At this pH, the estimated FAA and H₂S levels, approximately 0.3 and 0.1 g L⁻¹, respectively, were both well below those expected to inhibit methanogenesis. The SO₄²⁻ concentration in the unamended control was 264 mg L⁻¹ before and 135 mg L⁻¹ after storage (Table S1), indicating the presence of active sulfate-reducing bacteria (SRB). Chen and co-workers³⁷ described the coexistence of a SRB (*Desulfovibrio vulgaris*) with the hydrogenotrophic/acetotrophic methanogen *Methanosarcina barkeri* in the absence of sulfate, whereas increasing the sulfate availability suppressed methanogenesis due to competition for H₂ as an electron donor. Hence, sulfate reduction may contribute to CH₄ mitigation at moderate doses of H₂SO₄.

The fact that different mechanisms potentially contribute to reduce CH₄ emissions from acidified slurry, across a wide range of H₂SO₄ doses, makes this a potentially robust greenhouse gas (GHG) mitigation option. Some odor emission persisted at moderate doses, but with a change in the composition of the odorants, whereas at higher doses of H₂SO₄, there was clear odor suppression.

Cost-Effectiveness of GHG Mitigation. In view of the results described above, low-dose acidification should be investigated as strategy for CH₄ mitigation under practical storage conditions. This section presents a preliminary cost analysis, with a complete account of assumptions included in Text S1 of the Supporting Information.

The relative reductions in CH₄ and NH₃ observed were assumed to represent practical storage. The average rate for untreated slurry, 2.7 g of C m⁻³ day⁻¹, was lower than the average annual rate currently estimated for management of pig slurry in Denmark, 4.9 g of C m⁻³ day⁻¹,⁴¹ but the latter value includes contributions from the barn as well as outside storage. Export of slurry from the barn to the storage tank typically occurs several times during the year, and it is unclear if a single acid dose at the beginning of storage would be sufficient to maintain the effects observed after repeated input of fresh slurry. For cost estimation, it was therefore assumed that acidification took place on either 1, 3, or 10 separate occasions. With 3 or 10 applications, the costs will increase due to the variable cost of transport, application, and mixing of acid in the storage tank.

The cost of GHG mitigation, expressed as euros per ton of CO₂ equivalents, were calculated as a function of acid dose and application strategy (Figure 2). For 1, 3, and 10 acid treatments, the costs were 28–47, 44–57, and 93–134 € (ton of CO₂ equivalents)⁻¹, respectively. With 1 or 3 acid treatments, the best cost-effectiveness was achieved with 2.1 kg

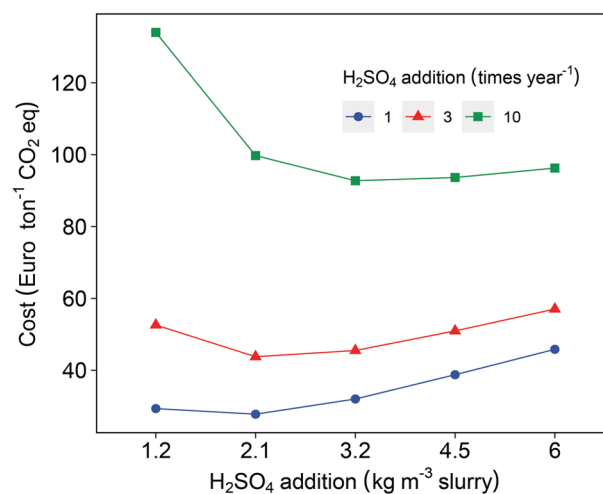


Figure 2. Cost of GHG mitigation by acidification 1, 3, or 10 times annually during storage of pig slurry. The costs include acidification and the value of N savings from NH₃ mitigation, while GHG effects include CH₄ mitigation and effects on indirect N₂O emissions derived from NH₃.

of H₂SO₄ m⁻³. With 10 individual mixing events, the cost was considerably higher, especially at the two lower acid dose levels, and 3.2 kg of H₂SO₄ m⁻³ gave the best economy. If the fertilizer value of S, and the cost for liming of soil receiving acidified slurry, had been included, this would reduce the overall cost by ~5 € (ton of CO₂ equivalents)⁻¹.

Current emissions trading system prices for carbon credits are ~50–80 € (ton of CO₂ equivalents)⁻¹,⁴² and hence, acidification of pig slurry in storage tanks 1–3 times per year could be a cost-effective GHG mitigation strategy for agriculture. Cost-effectiveness can be further improved by frequent export of slurry from barns to outside storage tanks, whereby acidification can affect a larger share of the total CH₄ emissions from manure management. Furthermore, because the bulk of CH₄ emissions occurs during summer and early autumn, the full acid dose corresponding to, e.g., 2.1 kg of H₂SO₄ m⁻³ in the final volume could be applied before summer, ensuring a mitigation potential corresponding to a higher acid dose during the warm period with high emissions, but avoiding excessive input of S to soils with field application of the slurry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsagscitech.2c00034>.

Details about cost calculation assumptions and odor activity value calculation; additional figures, including the dynamic profiles of slurry temperature, pH, and odor emission; additional tables of slurry characteristics and free acetic acid (FAA) or hydrogen sulfide levels in untreated slurry; and photographs of slurry surface crusts (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) United Nations. *Environment Programme and Climate and Clean Air Coalition Global methane assessment: benefits and costs of mitigating methane emissions*; United Nations Environment Programme: Nairobi, 2021.
- (2) Lynch, J.; Cain, M.; Pierrehumbert, R.; Allen, M. Demonstrating GWP*: a means of reporting warming-equivalent emissions that captures the contrasting impacts of short- and long-lived climate pollutants. *Environ. Res. Lett.* **2020**, *15* (4), 044023.
- (3) Collins, W. J.; Webber, C. P.; Cox, P. M.; Huntingford, C.; Lowe, J.; Sitch, S.; Chadburn, S. E.; Comyn-Platt, E.; Harper, A. B.; Hayman, G.; Powell, T. Increased importance of methane reduction for a 1.5 degree target. *Environ. Res. Lett.* **2018**, *13* (5), 054003.
- (4) Philippe, F.-X.; Nicks, B. Review on greenhouse gas emissions from pig houses: Production of carbon dioxide, methane and nitrous oxide by animals and manure. *Agric., Ecosyst. Environ.* **2015**, *199*, 10–25.
- (5) Owen, J. J.; Silver, W. L. Greenhouse gas emissions from dairy manure management: a review of field-based studies. *Global Change Biol.* **2015**, *21* (2), 550–565.
- (6) Hou, Y.; Velthof, G. L.; Lesschen, J. P.; Staritsky, I. G.; Oenema, O. Nutrient recovery and emissions of ammonia, nitrous oxide, and methane from animal manure in Europe: effects of manure treatment technologies. *Environ. Sci. Technol.* **2017**, *51* (1), 375–383.
- (7) Petersen, S. O.; Andersen, A. J.; Eriksen, J. Effects of cattle slurry acidification on ammonia and methane evolution during storage. *J. Environ. Qual.* **2012**, *41* (1), 88–94.
- (8) Habtewold, J.; Gordon, R.; Sokolov, V.; VanderZaag, A.; Wagner-Riddle, C.; Dunfield, K. Reduction in methane emissions from acidified dairy slurry is related to inhibition of methanosarcina species. *Front. Microbiol.* **2018**, *9*, 2806.
- (9) Petersen, S.; Højberg, O.; Poulsen, M.; Schwab, C.; Eriksen, J. Methane mitigation and methanogen community changes with acidification of pig slurry. *J. Appl. Microbiol.* **2014**, *117*, 160–172.
- (10) Frandsen, T. Q.; Schelde, K. M. *Farm test no. 41 (Buildings) Slurry acidification*; 2007.
- (11) Lamers, L. P. M.; Tomassen, H. B. M.; Roelofs, J. G. M. Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.* **1998**, *32* (2), 199–205.
- (12) Feilberg, A.; Liu, D.; Adamsen, A. P. S.; Hansen, M. J.; Jonassen, K. E. N. Odorant emissions from intensive pig production measured by online proton-transfer-reaction mass spectrometry. *Environ. Sci. Technol.* **2010**, *44* (15), 5894–5900.
- (13) Eriksen, J.; Andersen, A. J.; Poulsen, H. V.; Adamsen, A. P.; Petersen, S. O. Sulfur turnover and emissions during storage of cattle slurry: effects of acidification and sulfur addition. *J. Environ. Qual.* **2012**, *41* (5), 1633–41.
- (14) Hansen, M. J.; Kasper, P. L.; Adamsen, A. P. S.; Feilberg, A. Key odorants from pig production based on improved measurements of odor threshold values combining olfactometry and proton-transfer-reaction mass spectrometry (PTR-MS). *Sensors* **2018**, *18* (3), 788.
- (15) Feilberg, A.; Hansen, M. J.; Liu, D.; Nyord, T. Contribution of livestock H₂S to total sulfur emissions in a region with intensive animal production. *Nat. Commun.* **2017**, *8* (1), 1069.
- (16) Dalby, F. R.; Hansen, M. J.; Feilberg, A. Application of proton-transfer-reaction mass spectrometry (PTR-MS) and 33S isotope labeling for monitoring sulfur processes in livestock waste. *Environ. Sci. Technol.* **2018**, *52* (4), 2100–2107.
- (17) Ottosen, L. D.; Poulsen, H. V.; Nielsen, D. A.; Finster, K.; Nielsen, L. P.; Revsbech, N. P. Observations on microbial activity in acidified pig slurry. *Biosys. Eng.* **2009**, *102* (3), 291–297.
- (18) Dalby, F. R.; Nikolausz, M.; Hansen, M. J.; Feilberg, A. Effects of combined tannic acid/fluoride on sulfur transformations and methanogenic pathways in swine manure. *PLoS One* **2021**, *16* (9), e0257759.
- (19) Dalby, F. R.; Svane, S.; Sigurdarson, J. J.; Sorensen, M. K.; Hansen, M. J.; Karring, H.; Feilberg, A. Synergistic tannic acid-fluoride inhibition of ammonia emissions and simultaneous reduction of methane and odor emissions from livestock waste. *Environ. Sci. Technol.* **2020**, *54* (12), 7639–7650.
- (20) Fuchs, A.; Dalby, F. R.; Liu, D.; Kai, P.; Feilberg, A. Improved effect of manure acidification technology for gas emission mitigation by substituting sulfuric acid with acetic acid. *Clean. Eng. Technol.* **2021**, *4*, 100263.
- (21) Petersen, S. O.; Skov, M.; Droscher, P.; Adamsen, A. P. S. Pilot scale facility to determine gaseous emissions from livestock slurry during storage. *J. Environ. Qual.* **2009**, *38* (4), 1560–1568.
- (22) Petersen, S. O.; Dorno, N.; Lindholm, S.; Feilberg, A.; Eriksen, J. Emissions of CH₄, N₂O, NH₃ and odorants from pig slurry during winter and summer storage. *Nutr. Cycling Agroecosyst.* **2013**, *95* (1), 103–113.
- (23) Petersen, S. O.; Hoffmann, C. C.; Schäfer, C. M.; Blicher-Mathiesen, G.; Elsgaard, L.; Kristensen, K.; Larsen, S. E.; Torp, S. B.; Greve, M. H. Annual emissions of CH₄ and N₂O, and ecosystem respiration, from eight organic soils in Western Denmark managed by agriculture. *Biogeosciences* **2012**, *9* (1), 403–422.
- (24) Keeney, D.; Nelson, D. Nitrogen inorganic forms. In *Methods of soil analysis part II*; Page, A. L., Ed.; American Society of Agronomy, 1982; Vol. 643.
- (25) Hansen, M. J.; Liu, D. Z.; Guldborg, L. B.; Feilberg, A. Application of proton-transfer-reaction mass spectrometry to the assessment of odorant removal in a biological air cleaner for pig production. *J. Agric. Food Chem.* **2012**, *60* (10), 2599–2606.
- (26) Liu, D. Z.; Nyord, T.; Rong, L.; Feilberg, A. Real-time quantification of emissions of volatile organic compounds from land spreading of pig slurry measured by PTR-MS and wind tunnels. *Sci. Total Environ.* **2018**, *639*, 1079–1087.
- (27) Bates, D.; Mächler, M.; Bolker, B.; Walker, S. Fitting linear mixed-effects models using lme4. *Journal of Statistical Software* **2015**, *67*, 201–210.
- (28) Lenth, R.; Singmann, H.; Love, J.; Buerkner, P.; Herve, M. Emmeans: Estimated marginal means, aka least-squares means. R package, ver. 1.1; 2018. <https://CRAN.R-project.org/package=emmeans>.
- (29) R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, 2020.
- (30) Kupper, T.; Hani, C.; Neftel, A.; Kincaid, C.; Buhler, M.; Amon, B.; VanderZaag, A. Ammonia and greenhouse gas emissions from slurry storage - A review. *Agric., Ecosyst. Environ.* **2020**, *300*, 106963.

(31) Petersen, S.; Højberg, O.; Poulsen, M.; Schwab, C.; Eriksen, J. Methanogenic community changes, and emissions of methane and other gases, during storage of acidified and untreated pig slurry. *J. Appl. Microbiol.* **2014**, *117* (1), 160–172.

(32) Sokolov, V.; Habtewold, J.; VanderZaag, A.; Dunfield, K.; Gregorich, E.; Wagner-Riddle, C.; Venkiteswaran, J. J.; Gordon, R. Response curves for ammonia and methane emissions from stored liquid manure receiving low rates of sulfuric acid. *Frontiers in Sustainable Food Systems* **2021**, *5* (224), 678992.

(33) Spoelstra, S. F. Degradation of tyrosine in anaerobically stored piggery wastes and in pig feces. *Appl. Environ. Microbiol.* **1978**, *36* (5), 631–638.

(34) Feilberg, A.; Bildsoe, P.; Adamsen, A. Influence of surface processes on gaseous emissions from manure slurry—Surface oxidation and pH gradient. In *RAMIRAN 2015 - 16th International Conference Rural-Urban Symbiosis: Proceedings Book*; Körner, I., Ed.; TuTech Innovation GmbH: Hamburg, Germany, 2015; pp 334–337.

(35) Eriksen, J.; Sørensen, P.; Elsgaard, L. The fate of sulfate in acidified pig slurry during storage and following application to cropped soil. *J. Environ. Qual.* **2008**, *37* (1), 280–286.

(36) Berg, J. S.; Schwedt, A.; Kreuzmann, A. C.; Kuypers, M. M. M.; Milucka, J. Polysulfides as intermediates in the oxidation of sulfide to sulfate by *Beggiatoa* spp. *Appl. Environ. Microbiol.* **2014**, *80* (2), 629–636.

(37) Chen, J.; Wade, M. J.; Dolfig, J.; Soyer, O. S. Increasing sulfate levels show a differential impact on synthetic communities comprising different methanogens and a sulfate reducer. *J. R. Soc., Interface* **2019**, *16* (154), 20190129.

(38) Petersen, S. O.; Andersen, A. J.; Eriksen, J. Effects of cattle slurry acidification on ammonia and methane evolution during storage. *J. Environ. Qual.* **2012**, *41* (1), 88–94.

(39) O'Flaherty, V.; Mahony, T.; O'Kennedy, R.; Colleran, E. Effect of pH on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria. *Process Biochem.* **1998**, *33* (5), 555–569.

(40) Rintala, J. A.; Puhakka, J. A. Anaerobic treatment in pulp and paper-mill waste management - a review. *Bioresour. Technol.* **1994**, *47* (1), 1–18.

(41) Petersen, S. O.; Gyldenkerne, S. *Redegørelse omkring forventede justeringer i beregning af metan-emission fra husdyrgødning - med bilag*; 2020.

(42) Ember Daily carbon prices. <https://ember-climate.org/data/carbon-price-viewer/> (accessed 2021-12-13).

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