Evaluation of a Treatment Method to Control Hydrogen Sulphide Emission from Swine Manure

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SUMMARY

Based on results from previous work, further experiments were conducted to evaluate the use of metabolic inhibitors to control hydrogen sulphide (H_2S) emission from swine manure under room-scale conditions. Manure storage period impacted the extent of H_2S emission, with fresh manure generating the most H_2S gas in closed systems. Adding a metabolic inhibitor, molybdate, maintained low levels of H_2S over a 6-month monitoring period. In the semi-pilot scale open system and in room scale tests, the average concentration of H_2S measured just above the surface of agitated fresh manure slurry were 831 $\pm$ 26 ppm and 88.4 ppm, respectively; addition of molybdate at 0.1 to 1.0 mM levels reduced the emission of H_2S to about 18 and 2.5 ppm, respectively. A cost analysis for application of the molybdate treatment in the grow-finish stage of a 300-sow operation showed that total material and labour cost would amount to less than 1% of the overall production cost for each market hog.

INTRODUCTION

Effectiveness of manure amendment with nitrite or molybdate as a means to control the emission of H_2S from swine manure has been investigated in our previous work (Prairie Swine Centre Annual Report 2007, pp 14-15). This treatment approach has been developed originally in the oil industry to mitigate the souring of oil reservoirs. However, our previous proof-of-concept study was conducted in closed systems in which H_2S levels in the headspace were significantly higher than those expected in an open system. In this present work, molybdate mediated control of H_2S emission was investigated in semi-pilot scale open system, and in room-scale tests simulating an actual swine barn.

EXPERIMENTAL PROCEDURE

The effect of manure age on the extent of H_2S emission and the levels of nitrite and molybdate required to control these emissions were investigated using fresh, 1, 3, and 6-month old manures. Laboratory tests were conducted in closed systems with 125 ml serum bottles containing 30 ml of manure, capped with a rubber septum. Different concentrations of sodium nitrite ranging from 2 to 120 millimole (mM) and sodium molybdate (from 0.5 to 3 mM) were tested. The analysis of H_2S concentration in the gas samples was carried out with a Varian CP-3800 gas chromatograph (GC).

Because results from the closed system tests could potentially lead to overestimation of the required level of the treatment reagents, a number of experiments were conducted in semi-pilot scale with open top containers in order to simulate practical conditions. These tests were conducted with 6 open top cylindrical containers, each filled with approximately 250 L of manure collected from the manure pit of a grow-finish room. The desired amount of molybdate solution was sprayed on the surface of the manure using a conventional hand pump sprayer. Sampling for H_2S emissions was done on days 10, 20, and 30 following the addition of molybdate.

Room scale tests were conducted in a setup similar to a commercial grow-finish pig production facility. Two identical and fully controlled environmental chambers located at the PSCI facility were configured to house a pen for 8 pigs in each chamber. Trials were conducted with one chamber used as the control and the other with treatment applied. The first 18 days of the trial served as manure accumulation period. On day 18, a solution of molybdate was sprayed on the manure slurry in the collection tub under the floor slats of one of the chambers (Treatment) to achieve a final concentration of 0.1 mM. The levels of H_2S emitted from the manure collection tubs and the spatial H_2S distribution at the animal and human occupied zones within the chamber were determined on days 28, 38 and 48.

"Adding the metabolic inhibitor molybdate to swine manure maintained low levels of H_2S over a 6-month monitoring period"

RESULTS AND DISCUSSION

Laboratory tests with closed systems

Figure 1 (presents the H_2S concentration profiles in the headspace gas of sealed serum bottles containing fresh, 1-month and 3-month old manures treated with various levels of molybdate ranging from 1.0 to 2.0 mM (applied on Day 1), as well as those for the control systems (no treatment added). The H_2S concentration profiles observed in the control bottles indicated that the level of emitted H_2S decreased as the manure age increased, with the average H_2S concentration in the bottles containing fresh, 1-month and 3-month old manures at 4856 $\pm$ 460, 3431 $\pm$ 208 and 1037 $\pm$ 98 ppm, respectively. With 6-month old manure, H_2S concentration in the headspace gas in the control bottles was below the detection limit (<0.4 ppm), even after 2 weeks of monitoring.

For all treatment levels and regardless of manure age, addition of molybdate caused an immediate decrease in the concentration of H_2S, which was maintained or decreased further during the 30-day monitoring period.

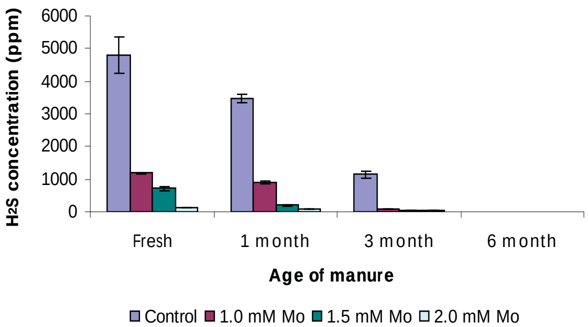


Figure 1. Average concentration of H_2S at the end of 30-day monitoring period in the control and treated (1.0 to 2.0 molybdate (Mo)) serum bottles containing swine manure of different ages.

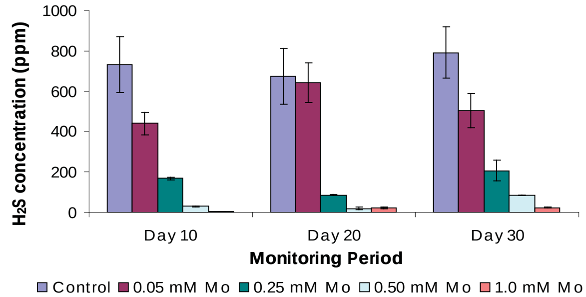


Figure 2. Concentrations of H2S from open-top containers containing fresh manure treated with various amounts of molybdate.

Higher levels of molybdate and increase in manure age both led to lower levels of H_2S. The final concentrations of H_2S at 30 days following the treatment with 2.0 mM molybdate were 142 ± 22, 105 ± 19, and 42 ± 5 ppm, for fresh, 1-month and 3-month old manure, respectively. In all tested cases, final H_2S concentration was lower than the level observed in the corresponding control system. Subsequent measurements over a period of six months confirmed the persistence of the molybdate treatment (data not shown in the graphs).

Semi-pilot scale tests in open top containers

Figure 2 shows concentrations of H_2S from the semi-pilot open top container treated with various amount of molybdate, as well as the untreated container (control). The average H_2S concentration from three sampling events ranged from 734 ± 59 and 831 ± 26 ppm for the Control container. The corresponding H_2S concentrations in the gas samples collected from the container treated with various amounts of molybdate were significantly lower than that of the control system ($P<0.05$). Furthermore, increasing the amount of molybdate added led to lower H_2S concentrations. The final H_2S concentration (day 30) in the gas samples collected from the containers treated with 0.05, 0.25, 0.5 and 1.0 mM Mo were 529.7, 153.1, 44.7 and 17.7 ppm, respectively.

Room scale experiments

Figure 3 shows H_2S concentrations from the control chamber (with untreated manure) and in the chamber in which manure was amended with 0.1 mM molybdate measured at different locations within the chamber on day 10 and 30 after application of the treatment. During gas sampling, manure was agitated for five minutes to simulate pit pulling event in actual pig production rooms, and gas samples were collected at various intervals over a period of 15 minutes. As expected, the highest H_2S concentration was observed at the pit level and during the first two minutes after start of agitation. The addition of molybdate led to much lower H_2S concentrations in all sampling locations. At 10 days after treatment application, H_2S concentration taken after two minutes of agitation at the pit, animal, and human levels in the control room were 88.4, 18.8 and 1.5 ppm, respectively, while respective concentrations in the treated chamber were 18.8, 0.6 and below the detection limit. Over the 15-minute sampling period, a decrease in H_2S concentration with time was observed mainly because manure agitation was stopped after five minutes and the ventilation system for both chambers was running continuously. Continuous monitoring of ammonia (NH_3) and carbon dioxide (CO_2) concentrations in the air exhausted from both chambers indicated that addition of molybdate did not impact the emission of these gases, although temporary spikes in NH_3 concentration were observed during manure agitation.

Based on the results of the present work and prior experiences in control of H_2S production in oil reservoirs, it is hypothesized that addition of molybdate contributed to control of H_2S emission from manure through two mechanisms which include catalysis of the chemical oxidation of sulphide resulting in an immediate sharp decrease in H_2S concentration, followed by the known inhibitory effect of molybdate on the activity of sulphate reducing bacteria (SRB) and biogenic production of sulphide.

A cost study for application of molybdate in a typical 300-sow operation showed that the main cost components included the costs of material (molybdate), labour, and the required application equipment. Calculations based on actual amounts used and the number of hours to prepare and apply the treatment in this study showed that applying the treatment in the finishing rooms of the operation will cost around CAN$1.00 per market pig, about 70% of which is labour and equipment.

CONCLUSION

Building on the findings from our previous work which demonstrated the effectiveness of nitrite and molybdate application for controlling H_2S emission from swine manure in closed systems, the present study showed that the extent of H_2S emission from the manure depended on manure age. Furthermore, molybdate application at a rate of 0.1 to 0.25 mM, which was lower than previously estimated from closed system experiments (2 mM), was established as effective for control of H_2S emission under conditions close to an actual swine production room with open manure holding system. A cost study for a typical 300-sow operation that produces 7500 market hogs per year revealed that costs associated with control of H_2S emission through application of molybdate in the finishing stage amounted to less than 1% of the total costs conventionally associated with a complete growth cycle.

Additional tests are on-going to assess the impact of the treatment on nutrient properties of the treated manure, as well as the fate of the treatment agents in manure applied to crop lands. Based on these results appropriate recommendations in proper application of the treatment in the actual barn will be drawn up.

ACKNOWLEDGEMENTS

Strategic Program funding provided by Sask Pork, Alberta Pork, Manitoba Pork Council and Saskatchewan Agriculture and Food. Project funding provided by the Alberta Livestock Industry Development Fund (ALIDF), Saskatchewan Agriculture Development Fund (ADF), and the Alberta Agriculture and Food Council.

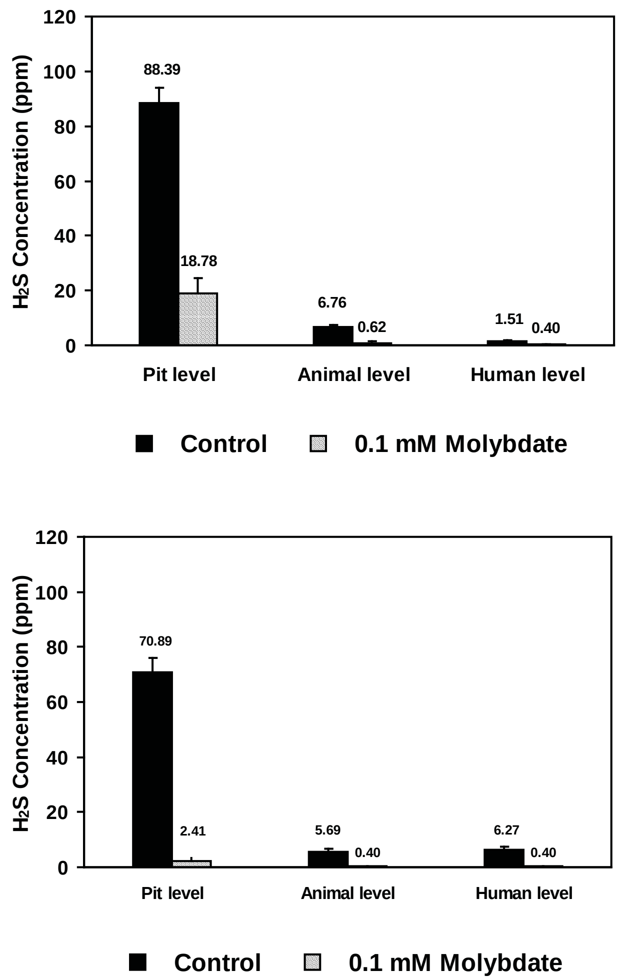
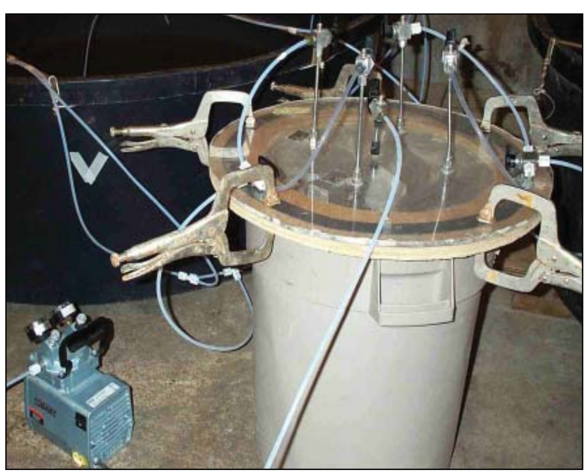


Figure 3. Concentration of H^{2}S at different sampling locations within the room-scale chambers, one with manure treated with 0.1 mM molybdate and the other untreated (Control). Gas samples were taken at two minutes after start of manure agitation to simulate pit pulling. Number on each bar represents the average concentration (Detection Limit: 0.40 ppm).



Sampling Apparatus