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Evaluation of Hydrogen Sulfide Monitoring Devices and a Spray Method to Reduce Worker Exposure

Bernardo Predicala, Ph.D., Research Scientist - Engineering

Prairie Swine Centre Inc., Saskatoon, Saskatchewan, [bernardo.predicala@usask.ca]

Erin Cortus, Ph.D. Candidate, University of Saskatchewan

Prairie Swine Centre Inc., Saskatoon, Saskatchewan

Robert Fengler, Engineering Research Technician

Prairie Swine Centre Inc., Saskatoon, Saskatchewan

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Abstract A gas chromatograph-based analytical method was established to serve as reference method for verification of performance of commercial hydrogen sulfide (H₂S) monitoring devices and for evaluation of a spray treatment method to reduce worker exposure to H₂S. Preliminary results showed that the H₂S monitors yielded readings that were in close agreement with those from the reference method. Additionally, trials completed so far indicated that spraying with water was effective in reducing the levels of H₂S released from agitated manure, although an initial increase in H₂S levels was observed at the start of spray application. A spray additive derived from oilseed processing did not yield consistent results; additional tests are on-going to complete the evaluation of this spray treatment method.

BACKGROUND

Hydrogen sulfide is a potentially hazardous gas produced by anaerobic degradation of liquid manure. A large proportion of H₂S gas produced by anaerobic bacteria in manure pits remains dissolved in the liquid slurry as long as the manure is not agitated. Results from a research study by Chénard et al., (2003) strongly suggest that workers are at risk of H₂S exposure while performing manure management tasks in the barn, such as pulling pit plugs when clearing out manure pits in the barn. Out of 138 plug pulling events monitored in the study, 83% generated H₂S concentrations higher than the short term exposure limit (STEL) value of 15 ppm stipulated by the Saskatchewan Occupational Health and Safety. Economical and practical preventative measures need to be implemented to help ensure that H₂S levels do not reach hazardous concentrations in swine barns in order to protect the health and safety of both workers and swine.

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Various engineering control methods have been investigated at the Prairie Swine Centre Inc., (PSCI); one approach investigated was the spraying of water-based liquid on the manure surface during agitation (Christianson et al., 2004). Because H₂S is water soluble, the rationale for this method was to try to put back into solution the H₂S gas released during agitation, thereby reducing the airborne H₂S concentration. A commercially-available H₂S monitoring instrument was used in the preliminary studies on liquid spray effectiveness, but the performance of this monitor was not consistent when subjected to various conditions during spray application. Across the industry, barn workers rely on similar types of H₂S monitors with electrochemical sensors to warn them against high concentrations of H₂S, thus it is imperative that these instruments provide reliable readings under conditions that might be encountered in swine barns to safeguard worker safety.

Recently, a by-product from the extraction of fatty acids from oilseeds has been found to have properties that were suitable for spraying on roadways to control road dust, thus the potential of this material for controlling dust and gases in swine barns was raised. In previous studies, various chemicals have been added to swine manure to control the release of manure gases, thus it was suggested that the potential of this oilseed-extraction by-product as a chemical additive to the water-based liquid spray to enhance the treatment's effectiveness be investigated in this study.

OBJECTIVES

The overall goal of this research project was to assess H₂S monitoring and control methods used in swine barns in order to reduce exposure of workers to potentially hazardous levels of H₂S, and to prevent its subsequent release to the environment. The specific aims of this project were to:

1. develop an instrumentation set-up and protocol for evaluating the performance of H₂S monitors, and
2. investigate the effectiveness of using water-based liquid spray with added oilseed processing by-product to prevent the occurrence of elevated H₂S levels during manure handling.

METHODOLOGY

The project was conducted at the research facility of PSCI and at an analytical laboratory at the University of Saskatchewan (UofS). A laboratory set-up at PSCI developed in a previous related study was restored and modified accordingly, while a gas chromatograph system at UofS was retrofitted to enable H₂S measurements that will serve as a reference.

Laboratory set-up

The laboratory set-up consisted of an enclosed system in which H₂S was released from agitation of swine manure and the spray treatment was applied (Fig. 1). The impact of spray treatment on H₂S levels was monitored by drawing air samples from the system during and after the spraying process. The H₂S levels in the sampled air was determined using H₂S monitors (Draeger PacIII and PhD-Lite from Levitt Safety), as well as the GC system at UofS which served as the reference method.

A 170-L barrel was used as the enclosed chamber for the set-up, thus, various treatment levels were readily replicated by preparing appropriate number of barrels for the tests. All the components necessary for applying the spray treatment and collecting gas samples to monitor H₂S levels were installed on one barrel lid, which was transferred from barrel to barrel. Each 170-L barrel was filled with manure collected from the manure pit of a grower-finisher swine room at PSCI. A sewage pump lowered into the manure pit of the room was used to fill a large tub. The manure in the large tub was mixed further prior to transferring the manure to the 170-L barrels (Fig. 2). After thorough mixing, each barrel was filled with manure up to 20-cm depth; all

barrels needed for one set of trials were filled from one large tub load to eliminate batch effect. Clean tap water was added to each barrel to increase the depth to 60 cm, then a lid was fitted on each barrel. The sealed barrels were stored for 2 weeks at ambient conditions in one of the rooms at PSCI before conducting any trial.

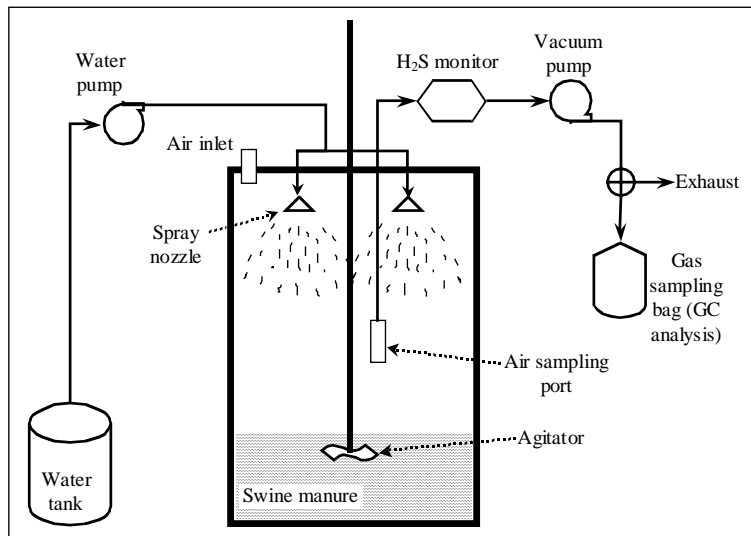


Figure 1. Schematic diagram of the laboratory set-up at PSCI.



Figure 2. Mixing the manure sample in the large tub prior to filling the barrels.

To enable access into the enclosed chamber during a test, one metal lid for the barrel was modified and fitted with ports for the agitator shaft and spray nozzles, as well as for entry of air and collection of air samples (Fig. 3). The agitator shaft drilled through the lid allowed mixing of the manure in the barrel using a power drill to release H_2S during the tests. The water-based liquid spray was introduced into the tank through two spray nozzles. A water pump was used to draw the water-based liquid solution from a tank and to disperse the spray in the enclosed chamber through the spray nozzles at specified operating pressure. Using a vacuum pump, air samples were drawn out from the headspace of the barrel through the sampling port. The sample airstream was passed through a container with the H_2S monitor in place, and then either exhausted to the outdoor environment through the room fan or collected in Tedlar sampling bags for analysis using the GC. The same basic procedure and operational settings used by Christianson et al (2004) in the previous study was implemented.



Figure 3. Modified barrel lid to allow agitation and spray, and sampling of headspace gases.

Gas chromatograph system

A gas chromatograph (5890 Series II Gas Chromatograph, Hewlett Packard) with flame photometric detector (GC-FPD) at UofS was retrofitted for use as the reference measurement method for determining H₂S levels in gas samples collected in this study (Fig. 4). The GC system was configured according to specifications of the U.S. EPA Method 15 for determination of hydrogen sulfide, carbonyl sulfide and carbon disulfide emissions from stationary sources (EPA, 2004). The system has a capillary column (GS-GasPro 113-4312, Agilent Technologies). GC components such as rotary valve, sample line, and other tubing and joints that were in contact with the sample gas were made from non-absorbent material (silcosteel). The sample gas was introduced into the GC/FPD system using a 10-port rotary gas valve, which allowed consistent injection of a 1-ml sample into the system. The sample line was flushed with at least 10 ml of sample gas before the 1-ml sample was injected into the analyzer. The GC was operated through a computer interface using the HPChem software (Agilent Technologies).



Figure 4. GC system used as reference method for determining H₂S levels in gas samples.

Calibration was performed with standard 10, 25, 100 and 500-ppm H₂S gases (Praxair and Ackland-Grainger, Saskatoon, SK). Subsequent samples were analyzed using the same procedures and settings (i.e., level of split) as the calibration standards. The level of split was increased only when samples were too concentrated for the analyzer. Each sample was analyzed at least four times to account for variation in gas composition.

Experimental approach

The general experimental approach was to apply the spray treatment in the manure barrels while simultaneously collecting data using the H₂S monitors and gas samples for analysis using the GC system. The performance of the H₂S monitors were verified by comparing the readings from the monitor with the reference values obtained from the GC analysis of the gas samples taken during the tests. The effectiveness of the spray treatment was evaluated by comparing the H₂S levels in the enclosed chamber during tests without spray (Control) and with the application

of spray (Treatment). Treatment tests were conducted using water only, and with the oilseed-processing by-product added to the water at varying dilution levels. Preliminary tests were conducted to determine the operational parameters that will be used for the main set of tests for spray additive testing.

Preliminary tests

A set of 10 barrels was prepared to test various spray durations and additive dilution levels. For these tests, three barrels were used as Control (no spray), while the treatment barrels were sprayed at varying durations (1, 5, 10 min). Six barrels were sprayed with water only at varying durations; the remaining barrels were then sprayed with varying dilutions of the spray additive. Based on these tests, the spray duration that will be used in subsequent tests was determined, as well as the range of dilution levels for the spray additive that will pass through the spray nozzle system of the set-up.

H₂S monitor verification

To verify the performance of the H₂S monitors, the H₂S levels during the tests were measured continuously using the H₂S monitors while gas samples were collected simultaneously in sample bags. Each barrel was agitated for 1 min; the start of agitation was designated as the start of the test ($t = 0$). For each test, four gas samples were collected, one each at $t = 1, 3, 7,$ and 12 min after the start of the test. Each gas sample bag was filled in a 1-min duration. For treatment barrels, the spray commenced at $t = 2$ (after collecting the first bag) and lasted for 10 min. The H₂S levels in the sample bags were analyzed using the GC and compared with the corresponding H₂S monitor readings. The H₂S monitor was also installed on the sample line of the GC, so that H₂S monitor readings were taken as the gas sample from the bag was injected into the GC.

Spray additive testing

Evaluation of the effectiveness of the water-based spray treatment was conducted by running tests with spraying of water only, and with water and additive, using the same testing and sampling procedure used in the previous section. The H₂S levels in the headspace of the barrel, determined using the H₂S monitors and from GC analysis of bagged gas samples, were compared with that from tests without spray treatment. The spray duration and additive dilution levels used were determined from preliminary tests.

Data analysis

The performance of the H₂S monitors was verified by comparing the monitor readings with the corresponding values determined from the GC analysis of the bag samples. To examine the effectiveness of the spray treatment method, the average reduction in H₂S concentration of the exhaust air at varying intervals during the spray application, as measured by the GC, were compared between treatments.

Because the initial H₂S concentration varied from barrel to barrel, the H₂S concentration measured in each barrel at $t = 1$ min was used as initial value for calculating the percent reduction in H₂S levels at subsequent sampling time. The average percent reduction in H₂S levels for barrels with the same treatment was computed, and then compared with the corresponding values for other treatments.

RESULTS

Preliminary tests

Results from preliminary tests showed that average H₂S levels in the Control barrels (no spray) was gradually reduced to about 57% of initial values at $t = 5$ min and down to about 28% at $t =$

10 min. This drastic reduction was attributed to continuous aspiration of the barrel headspace as the gas stream was extracted from the barrel to pass through the H₂S monitors and to fill the sample bags. Water spray durations of 1 and 5 min did not show significant reduction in H₂S levels compared to the Control barrels. A 10-min spray showed consistent reduction to 49% and 13% (at t = 5 and 10 min, respectively), thus this spray duration was used in subsequent tests.

Use of pure (100%) oil-seed additive did not pass through the spray nozzles because of its high viscosity. The solution was diluted progressively until a consistent spray pattern was attained (65%). This level was used as the maximum concentration of the spray additive in subsequent tests; a lower dilution level (25%) was also tested to determine if the additive would still be effective in reducing H₂S levels when used at a lower concentration.

Monitor verification

Summarized in Table 1 are the H₂S readings obtained from the bagged samples using the GC system and the H₂S monitor. In the preliminary tests, the H₂S monitor readings were taken by manually pressing the bags to force the gas sample over the sensing part of the monitor. In trials 1 and 2, an alternative system was devised to extract the gas sample from the bags using a vacuum pump for a more consistent manner of sampling. Results showed that the H₂S monitors recorded readings that were close to the values indicated by the GC. The corresponding mean values differed by an average of about 15%; the largest deviation was observed in Trial 1 during the initial testing of the vacuum pump system for sampling the bags. In Trial 2, paired t-test comparison of the H₂S readings showed no significant difference (P>0.05) between the GC values and the H₂S monitor readings. Additional data are being collected and further analysis of the data will be done to confirm this observation.

Table 1. Summary of H₂S values determined using the GC system and H₂S monitor.

		H ₂ S concentration values, ppm		
		GC readings	H ₂ S monitor	
			Manual measurement	Vacuum pump
Preliminary	Mean	178.4	173.9 *	--
	SD	134.9	131.4	--
	Min	13.5	11.0	--
	Max	546.5	555.0	--
	n	29	29	--
Trial1	Mean	292.7	327.4	364.8 *
	SD	192.4	176.0	252.3
	Min	10.6	100.0	13.0
	Max	807.3	805.0	870.0
	n	43	37	22
Trial 2	Mean	295.1	--	292.2
	SD	197.2	--	192.7
	Min	0.0	--	0.0
	Max	747.6	--	750.0
	n	48	--	48

*indicates significant (P<0.05) difference with corresponding GC mean value.

Spray and additive effectiveness

Two trials were completed so far to determine the effectiveness of the spray method for reducing the release of H₂S from agitated manure. Preliminary analysis of the data showed that spraying with water only caused an initial increase in H₂S levels (at t = 3), followed by subsequent significant reduction in H₂S toward the end of the test (Table 2). The water spray treatment was consistently effective in both trials, reducing the H₂S levels to very low levels in Trial 2. A similar

initial increase in H₂S levels was observed for spray treatments with oilseed by-product added at both dilution levels (65% and 25%); the cause for this spike is not yet clear at this time. However, the spray with additive treatment did not result in consistent subsequent reduction in H₂S levels at the latter part of the test. Additional tests are being conducted to fully evaluate this spray treatment method.

Table 2. Summary of H₂S concentrations in barrels subjected to different treatments, and the corresponding percent reduction (with respect to initial t = 1 level) at subsequent intervals.

Trial	Treatment	Average H ₂ S concentration*, ppm				% Decrease wrt t = 1 level		
		t = 1 min	t = 3	t = 7	t = 12	t = 3	t = 7	t = 12
1	Control	338.0	268.8	215.7	118.9	-20.5%	-35.5%	-64.2%
	Water only	343.1	437.7	185.7	69.5	31.2%	-41.1%	-80.1%
	65% Additive	219.4	278.4	167.6	50.5	23.1%	-22.0%	-76.8%
	25% Additive	450.6	640.4	445.1	266.3	38.6%	-1.0%	-40.2%
2	Control	590.8	604.2	385.9	218.0	2.2%	-34.8%	-63.1%
	Water only	184.7	203.5	32.3	1.3	30.7%	-78.3%	-99.1%
	65% Additive	323.4	357.3	243.3	167.4	10.8%	-28.1%	-53.5%
	25% Additive	434.7	568.2	385.0	247.9	31.7%	-7.2%	-39.4%

*average of at least 3 replicates for each treatment, measured using the GC.

CONCLUSIONS

The following preliminary conclusions can be drawn based on the data collected so far at this stage of the study:

1. the H₂S monitors showed values that were consistent with those indicated by the GC system, which was considered as the reference method in this study. However, further data collection and analysis will be done to confirm this observation.
2. initial assessment of the data on spray treatment method showed that a 10-min water spray was effective in reducing the H₂S levels in gas samples extracted from the headspace of the enclosed chamber. However, the spray application caused a spike in H₂S levels at the start of the spray treatment, followed by a drastic reduction in H₂S levels as the treatment progressed.
3. the spray additive tested in this study caused a significant spike in H₂S levels when the spray was applied; the subsequent reduction in H₂S levels was not as significant nor as consistent as the water spray treatment. Additional tests are being conducted to complete the evaluation of this spray treatment method.

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