

FINAL REPORT

DryLet M2[®] H₂S/ODOR REDUCTION STUDY

to

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by

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Executive Summary

The objective of this study was to evaluate DryLet's M2[®] efficacy in reducing H₂S and odor from swine manure under controlled lab conditions.

This test evaluated the effect of three doses of DryLet M2[®] on gas and odor emissions from stored finisher pig manure. The 42-day laboratory study measured noxious gas release from six (6) simulated pits (reactors) containing swine manure from a local finishing building, which was analyzed prior to adding manure to the reactors and prior to emptying the reactors on the last day of the test. Gas samples taken six times from each reactor were analyzed for hydrogen sulfide, ammonia, methane, nitrous oxide, and carbon dioxide. In addition, a human panel was employed twice – at the midpoint and at the endpoint of the test period – to evaluate odor concentrations in each reactor.

The conclusions of the study were as follows:

1. The release of H₂S from swine manure that is handled and then subsequently stored without further additions will increase for about three weeks and then decrease to relatively low levels by day 42. Odor release from the manure appears to follow a similar pattern as H₂S.
2. DryLet M2[®] significantly ($P < 0.05$) reduced odor release by 43% on day 24 of the test and apparently ($P > 0.05$) reduced odor release by 27% on day 42.
3. DryLet M2[®] reduced the release of hydrogen sulfide by 27% based on the collective samples taken from all treated reactors on days 17, 24, 31 and 36.
4. DryLet M2[®] had no observable effect on manure fertilizer value.
5. The effectiveness of DryLet M2[®] on H₂S and odor release was not apparently influenced by the dosage level.
6. The best DryLet M2[®] performance was obtained with a medium dose, achieving a reduction of H₂S relative to the controls of about 50% after 24 days.
7. The results of this study indicate that ammonia, methane, carbon dioxide and nitrous oxide gas production are not significantly changed by the use of DryLet M2[®] relative to the controls.

The olfactometry with a trained sensory panel revealed that the perceived odor contained in these same samples is in line with analytical findings of the reduction of hydrogen sulfide gas. Odor reduction adds credibility to the analytical findings. Further tests would certainly require more frequent and more extensive data collection.

Based on the positive results with the small data set, further testing is warranted and recommended, with emphasis on more frequent odor samples, continuous gas sampling and analysis, and more experimental replicates to increase the statistical power of the test.

Introduction

Emissions of odor and gases from animal production have created ecological, environmental, safety, meat quality, and production efficiency concerns. Over the last many years, modern livestock production facilities became much larger with a greater concentration of animals in a given area and the trend continues today. Public scrutiny and state and local regulations of livestock operations are increasing. Most complaints associated with animal confinement operations are related to odor. It is thought by most people that reductions in odor emitted to the surroundings would increase the public acceptance of animal production operations (Bereznicki et al., 2012).

Workers at livestock production facilities in the U.S. spend most of their time exposed to hydrogen sulfide (H_2S), ammonia (NH_3), and other noxious gases which have negative effects on their health. The facilities also emit significant amounts of greenhouse gases including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). The combination of these and hundreds of volatile organic compounds (VOC) create offensive odor perceived downwind of the facilities.

Ammonia (NH_3) is released from livestock manure as it chemically and biologically breaks down (Groot-Koerkamp et al., 1998). Chronic exposure to NH_3 is the most common hazardous gas to which livestock workers are exposed and 20 Tg/yr are released from livestock production to the atmosphere (Mitloehner and Calvo, 2008). NIOSH recommends an average exposure threshold of 25 ppm (NIOSH, 2005). The highest ammonia concentrations near farms, feedlots, and manure applications have ranged from 0.28 to 88 ppm according to ATSDR (2004), which provided no references to support the claim.

Hydrogen sulfide, which is heavier than air, can accumulate to high levels in manure pits, is produced by anaerobic fermentation and is toxic to humans and deadly at high concentrations (Ni et al., 2002). Concentrations increase during any planned or unplanned disturbances of stored manure in deep pits (Chénard et al., 2003) and the levels can become fatal. Hydrogen sulfide adds significantly to the human perception of odor from these operations. Acute exposures to toxic or asphyxiating manure gases released may occur during planned and unplanned manure disturbances, especially in buildings with deep pits, which are commonplace in swine buildings throughout the Midwest.

DryLet M2 has produced a manure pit microbial additive and anecdotal evidence has indicated its effectiveness in reducing odor. However, a scientific laboratory test of DryLet MM had not yet been conducted to confirm the observed results in the field.

Objective

The objective of this study was to evaluate DryLet's efficacy in reducing H_2S and odor from swine manure under controlled lab conditions.

Materials and Methods

The evaluation of DryLet M2[®] for reducing gas and odor emission reduction was conducted using the same lab used in the NPPC's test of manure additives in 2000 (Heber et al., 2001).

Six manure reactors were set up to mimic the column of air above a deep (8 ft) manure pit under a swine finishing facility. Manure was added to the simulated pits on July 14, 2015. For the next 42 days, the headspace of each reactor was purged or ventilated continuously with fresh air that entrained and diluted the gases emitted from the manure in the bottom of the reactor.

Reactor exhaust air samples in 50-L bags were taken on days 7, 17, 24, 31, 36 and 41 from each of the six reactors and analyzed for concentrations of ammonia, carbon dioxide, methane, hydrogen sulfide, and nitrous oxide. The measured concentrations were directly proportional to the gas release from the reactors because the volumetric ventilation rate was held constant across reactors and the duration of the test. Reactor exhaust air samples in 10-L bags taken on days 24 and 42 were evaluated with a human panel of trained sniffers.

The reactor emission rates for each of the six sampling days was calculated from the ventilation airflow rate and the measurement concentrations. The cumulative masses (in mg or g) of gas emitted from the reactors for the last 30 days of the test were calculated.

Test Schedule

The test started on July 14, 2015 or day zero (0) when the reactors were loaded with swine manure to a depth of 12 inches. The test finished on August 25 2015 or day 42 (Table 1).

Test Configuration

The laboratory was located on the campus of Purdue University in the Department of Agricultural and Biological Engineering. Figure 1 illustrates the diagram of the test system. An air compressor provided fresh air to the manure reactors (Figure 1). A stainless steel air supply manifold (M_a) distributed air equally to all reactors using stainless steel precision orifices.

The exhaust air from each reactor flowed through a Teflon tube to a computer controlled 3-way, Teflon-lined solenoid in the gas sampling system, which allowed automatic sequential sampling of the exhaust air of the reactors (6 with manure plus 1 with water). The fresh air from the air supply manifold (M_a) was sampled along with the reactor exhausts. Teflon filter holders (with filter-support-meshes but no filters) impeded potential manure flies (none observed in this test). Sampled air flowed to a Teflon gas sampling manifold (M_s , Figure 1), the 0-10 L/min mass flow meter (Model 50S-10, McMillan, Georgetown, TX) and the analyzer manifold, M_d whereas inactive solenoids directed air to the fume hood. In this way, ventilation air was supplied to each reactor continuously.

Table 1. Test schedule.

Date	Time	Test day	Event
7/14	12:00	0	Sampled source manure and loaded reactors
7/14	16:00	0	Sealed reactors and started vent flows
7/20	16:20	6	Started bag sampling test 1
7/21	14:30	7	Stopped bag sampling test 1
7/31	12:25	17	Started bag sampling test 2
8/1	10:25	18	Stopped bag sampling test 2
8/5	16:20	22	Collected odor samples for 75 min per bag
8/6	13:00	23	Evaluated odor samples
8/6	16:08	23	Started bag sampling test 3
8/7	10:30	24	Stopped bag sampling test 3
8/13	10:40	30	Started bag sampling test 4
8/14	8:40	31	Stopped bag sampling test 4
8/18	17:00	35	Started bag sampling test 5
8/19	15:00	36	Stopped bag sampling test 5
8/23	19:20	40	Started bag sampling test 6
8/24	15:20	41	Stopped bag sampling test 6
8/25	10:10	42	Collected odor samples for 75 min per bag
8/25	13:30	42	Evaluated odor samples
8/25	20:00	42	Collected manure samples from each reactor

The air temperature around each reactor was monitored. Two pressure sensors monitored the test system. The first one (WIKA, Tronic Line) measured pressure inside the air distribution manifold. The second one (Setra System, Inc., Boxborough, MA) measured the vacuum pressure inside the sampling manifold (Figure 1).

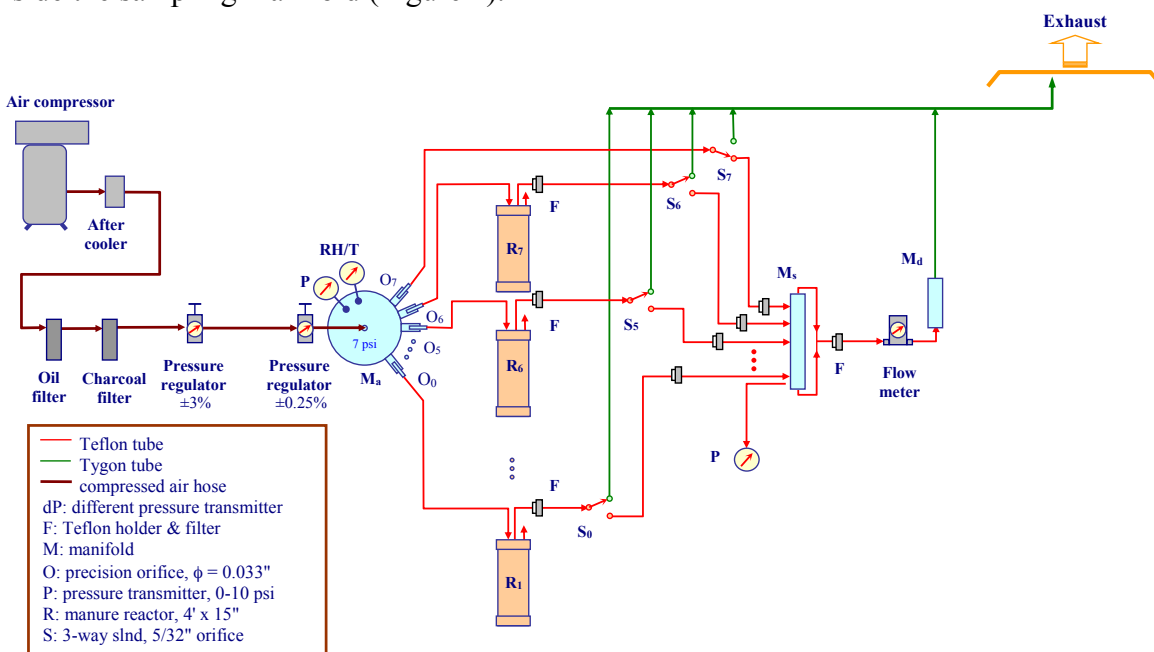


Figure 1. Diagram of the test setup.

Manure Reactors

There were seven manure reactors used in this test (Figure 2). Reactors 1-5 and 7 contained manure and reactor 6 contained tap water. Reactor 6 was used for testing bag sampling methods without disturbing the manure reactors.



Figure 2. Reactors or simulated pits.

The reactors were 61 cm (24 in.) tall with an inside diameter of 15 in. (37.9 cm). Each one had a sealed slip cap on the bottom and a removable slip cap on the top (Figure 3). The reactors were lined with 0.05 mm thick Tedlar® film on the top 14 in. (64 cm) of the inside walls. The air inlet opening was adjusted to a height of 6 in. (15 cm) above the manure surface. The air inlet included a baffle to direct air radially in all directions (Figure 3).

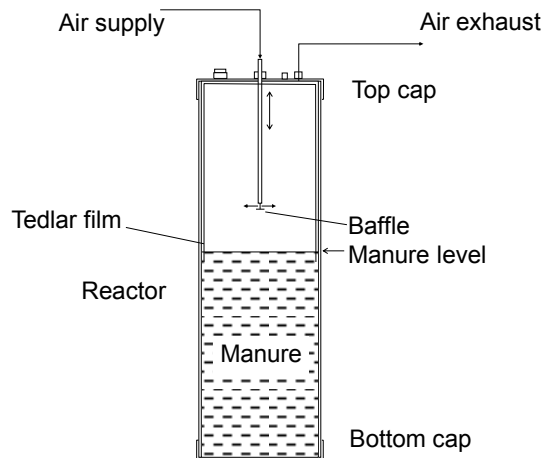


Figure 3. Schematic of the manure reactor.

Test Manure

On July 14, 2015 (day 0), about 90 gallons of manure was pumped out of under-floor deep pits of one of the finishing buildings (Grow-Finish #1) at the Purdue University Animal Science

Research Farm into two 55 gallon barrels and hauled to the ABE Building on the Purdue University campus in West Lafayette, Indiana. The manure was thoroughly mixed in the first barrel before randomly adding six inches of manure into each of six reactors. After adding DryLet as prescribed amounts to four of the reactors (see below) and collecting manure samples from the control reactors (in addition to samples taken from the 55 gallon barrels), the reactors were filled to a depth of 12 inches using well-mixed manure from the second barrel. On day 42, prior to taking manure samples, the depths of the manure in each reactor were measured to determine evaporation loss. Manure samples were submitted to Midwest Labs in Kansas City for analysis.

Based on randomized selection, reactors 3 and 5 were controls and therefore did not have any product added to the manure. A measured 0.1 g of DryLet was introduced into reactors 4 and 7, and 1 and 2 g were introduced into reactors 2 and 1, respectively. Product inclusions of 0.1, 1 and 2 g are denoted as low, medium and high, respectively.

Gas Sampling and Concentration Measurement

The data acquisition and control (DAC) system consisted of a desktop computer, FieldPoint data acquisition and control hardware (National Instruments Co., Austin, TX), and DAC software. The DAC program for this test, AirDAC, was written in LabVIEW DAC software (National Instrument, Inc.). AirDAC sampled output signals from the sensors every second. It then calculated the signals, averaged them every minute before saving them in data files. The AirDAC also controlled the solenoids for automatic air sampling. Each reactor was sampled for flow rate, temperature, humidity, and pressure once per cycle for 10 min at a time, and there are four 360-min cycles per day.

Tedlar bags (50-L) were filled with gas from the reactor headspace on days 6, 17, 23, 30, 35 and 40, respectively and taken to the Purdue Swine Environmental Research Laboratory (SERB) for analysis of the gas concentrations in the bags (Table 1). The SERB's gas sampling system pumped air out of the bags at 5 L/min into a Teflon analyzer manifold from which gas analyzers drew continuous subsamples.

Hydrogen sulfide was measured with a 0-10,000 ppb pulsed fluorescence SO₂ analyzer (Model 340, TEI, Inc., Mansfield, MA). Carbon dioxide, ammonia, and methane measured with a photoacoustic infrared multigas analyzer (INNOVA 1412, LumaSense Technologies, Copenhagen, Denmark) and a gas filter correlation analyzer (Teledyne Model 320EU) was used to measure nitrous oxide. The gas analyzers at SERB were calibrated weekly using certified gases in cylinders. The cylinder gases were diluted to desired concentrations using a gas dilution system (Envionics 4040, Envionics, Toland, CT). These instruments and calibration method were also used in the National Air Emissions Monitoring Study (Cortus et al., 2013).

Odor Sampling and Evaluation

On days 24 and 42, odor samples were collected into two 10-L Tedlar bags from each reactor. Each bag was filled directly from the headspace to minimize losses and absorption to tubing.

Positive pressure within each reactor forced the headspace air into the bags over a period of 75 min. The air from the air distribution manifold was also sampled.

All sample bags were preconditioned in a similar manner. Each bag was filled twice to 1/3 its fullness with nitrogen gas and emptied using a vacuum pump. The evaluations of all odor samples were conducted within 30 h of collection to minimize storage losses.

Odor samples taken from the laboratory test were evaluated at the Purdue Agricultural Air Quality Lab using an odor panel and a dynamic olfactometer. Lim et al. (2003) described the detailed standardized procedure of odor evaluation.

The strength or concentration of an odor is measured by determining the dilution factor required to reach the odor detection threshold (ODT). As odor strength increases, ODT also increases because more odor-free air is needed to dilute the sample to its ODT.

The ODTs were measured with a dynamic dilution forced-choice olfactometer (a dilution apparatus). This olfactometer (ACSCENT International Olfactometer, St. Croix Sensory, Stillwater, MN) met the olfactometry standards of the United States (ASTM, 1992) and Europe (ECN, 2000). The odor panel consisted of four trained human subjects that were screened to determine their odor sensing ability (ASTM, 1981). The odor panel was managed in accordance with ASTM STP 758, Guidelines for the Selection and Training of Sensory Panel Members (ASTM, 1981) and ANSI/ASQC Q2-1991, Quality Management and Quality System Elements for Laboratories (ANSI, 1991). All panel members were non-smokers.

The olfactometer delivered a precise mixture of sample and dilution air to the panelist through a Teflon-coated presentation mask at 20 Lpm. The dilution ratio of the mixture is the ratio of total diluted sample volumetric flow rate to the volumetric flow rate of the sample. For example, a dilution ratio of 1000 is achieved with 20 mL/min of sample flow and 20 L/min of total diluted flow.

The olfactometer diluted the odor sample starting with a high dilution ratio, and presented a step by step series of ascending concentrations (step factor = 2) to each panelist. A triangle test was conducted whereby the panelist sniffed all three sequential sample coded gas streams at each dilution ratio. One gas stream was randomly assigned to have the odor while the other two gas streams were odor-free. The three gas streams were directed one at a time to the mask. The panelist selected which of the three presentations was “different” (even if no difference was perceived) and thus contained the odor (ASTM, 1992). The panelist declared by pressing a button whether the selection was a “guess” (no perceived difference), “detection” (selection is different from the other two), or “recognition” (selection smells like something). The sample at the initial dilution steps are so dilute that they cannot be distinguished from odor-free air. Higher and higher odor concentrations (2-fold increases), or lower and lower sample dilutions (50% reductions), were presented to each panelist until the sample was correctly detected and/or recognized in two consecutive steps.

An individual best-estimate ODT estimate was calculated by taking the geometric mean of the last nondetectable dilution ratio and the first detectable dilution ratio. The panel ODT was

calculated as the geometric mean of the individual ODTs. Retrospective screening of each panelist threshold was applied to the panel ODT (ECN, 2000).

To assess panelist performance, a reference odorant n-butanol (40 ppm) was included in each odor session and was evaluated like the other samples. The n-butanol evaluations were used to document olfactometer and panelist performance (ECN, 2000) by calculating the odor detection concentration (ODC) for the n-butanol and comparing it to the target value of 40 ppb (ECN, 2000). The odor concentration in terms of European odor units (OU_E) was calculated by multiplying the ODT by the ratio of the n-butanol ODC by 40 ppb. The evaluation of effects on odor was based on the difference between exhaust air odor concentration and the odor concentration in the air supply, or the net odor concentration.

Results and Discussion

Manure Characteristics

The analysis results of the source manure at the initial reactor filling are shown in Table 2. The samples showed reasonably good uniformity among samples indicated by the low relative standard deviations, which ranged from 0.6% for pH to 55% for organic nitrogen and averaged 18.4%.

The samples taken from the reactors on day 42 exhibited relative uniformity as the relative standard deviations ranged from 0.8 for pH to 19.4% for total sulfur (

Table 3). DryLet M2[®] therefore had no apparent effect on the fertilizer value of the manure nor any other analyzed characteristic (

Table 3). However, the analysis of solids in reactor 4 (R4) was significantly higher ($P<0.05$) at 5.0% as compared with the overall average of 3.9%. This reactor could potentially be considered an outlier and its data removed from the analysis.

The manure depths on day 42 were 10.0, 9.8, 10.5, 9.8, 10.0 and 10.5 inches in reactors 1-5 and 7, respectively. The water loss ranged from 12.5 to 18.8% and averaged 15.8%, which was an average depth reduction of 1.2 mm per day.

The average daily mean temperature of the reactor room during the test was $23\pm1^\circ\text{C}$. The overall average hourly mean reactor ventilation rate was 7.25 ± 0.10 L/min.

Table 2. Characteristics of source manure on the first day, mg/L.

Sample	R1	R2	R3	R4	R5	R7	Mean \pm SD
Ammonia nitrogen (total)	0.22	0.28	0.27	0.27	0.28	0.28	0.27 \pm 0.03
Organic nitrogen	0.14	0.16	0.12	0.12	0.35	0.12	0.17 \pm 0.10
TKN	0.36	0.44	0.39	0.39	0.63	0.40	0.44 \pm 0.11
Phosphorus	0.21	0.23	0.16	0.18	0.21	0.18	0.20 \pm 0.03
Potassium	0.16	0.19	0.19	0.20	0.19	0.25	0.20 \pm 0.02
Total solids	4.6	5.6	3.6	3.6	4.4	3.6	4.3 \pm 0.8
pH	7.00	7.00	7.00	7.00	7.10	7.70	7.1 \pm 0.05
Sulfur (total), %	0.03	0.03	0.02	0.03	0.03	0.02	0.03 \pm 0.004

Table 3. Characteristics of reactor manure on last day, mg/L.

Parameter	Controls			DryLet M2 [®]				
				Low	Med	High	Treated	
	R3	R5	Avg	R4	R7	R2	R1	Avg
Ammonia nitrogen (total)	0.28	0.28	0.28	0.29	0.28	0.28	0.28	0.28
Organic Nitrogen	0.12	0.14	0.13	0.16	0.12	0.14	0.13	0.14
TKN	0.40	0.42	0.41	0.45	0.40	0.42	0.41	0.42
Phosphorus	0.18	0.21	0.195	0.23	0.18	0.21	0.18	0.20
Potassium	0.26	0.26	0.26	0.26	0.25	0.25	0.26	0.25
Total solids	3.5	4.0	3.75	5.0	3.6	4.1	3.5	4.1
pH	7.6	7.6	7.6	7.5	7.7	7.6	7.6	7.6
Sulfur (total), %	0.02	0.03	0.025	0.03	0.02	0.03	0.03	0.03

Odor Concentration

The panel average n-butanol concentrations were 54.7 and 13.8 ppb for the two odor sessions and days 24 and 42, respectively. From these data, the European odor units were calculated. The average net concentrations for two samples per reactor are shown in Table 4. The odor concentrations of the air supply were 301 and 96 OU_E/m³ on days 24 and 42, respectively.

Assuming odor concentration is correlated with H₂S concentrations, it is expected that the maximum odor concentrations will occur in the third week and gradually decrease until the end of the test. This is confirmed by the differences in odor concentrations of all reactors between days 24 and 42 (Table 4 and Figure 4). The average decrease in reactor headspace odor concentration from days 24 to 42 ranged from 60 to 73% and averaged 68%. As the emissions subsided as fresh manure was not added after the initial fill (Figure 5).

Table 4. Net odor concentrations of the reactor headspaces (n=2), OU_E/m³.

Day	R3	R5	R4	R7	R2	R1	Ctrl	Low	Med	High	Trt
24	4038	3338	2760	1520	2273	2060	3672	2049	2273	2060	2106
42	1094	903	819	550	903	672	994	671	903	672	723

On day 24, the low, medium and high reactors reduced the odor by 44.2, 38.1 and 43.9%, respectively (P>0.05). The overall average net odor concentration of all four treated reactors on day 24 was 2106 OUE/m³, which is a statistically significant 42.7% less (P<0.05) than the control reactors on the same day. If the high solids reactor R4 is removed from the analysis, the reduction of the combined treated reactors was 48% (P<0.05). The reduction of odor in the combined treated reactors was 27.3% (P>0.05) on day 42.

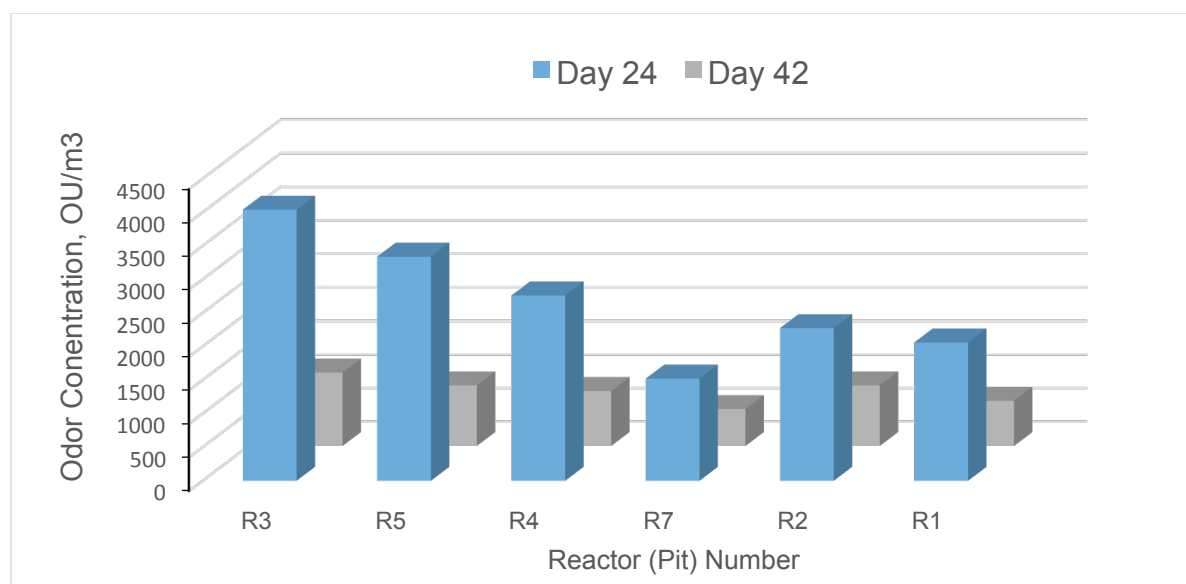


Figure 4. Odor concentrations measured on days 24 and 42 by a human olfactometry panel.

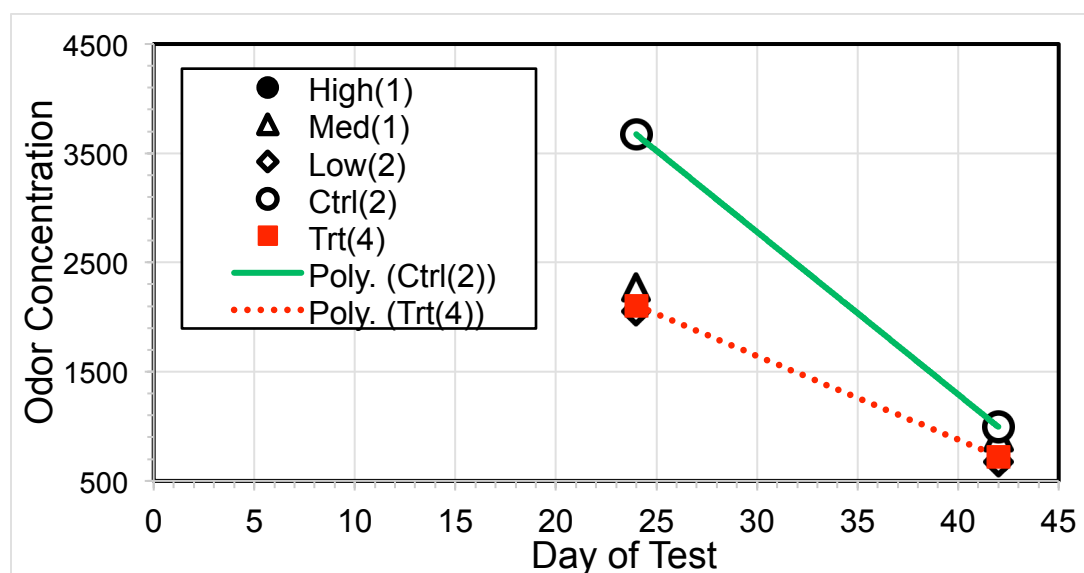


Figure 5. Average odor concentrations for control and treated reactors.

Effect on Hydrogen Sulfide Concentrations

The H_2S concentrations of each bag sample along with averages of control and treatment reactors are given in Table 5. As observed in previous studies of stored manure, the release of H_2S from all reactors increased to a maximum on day 17 and decreased gradually to the end of the test. The concentrations were similarly low on the first and last sampling events on days 7 and 41, respectively. The scientific explanation for the low initial values on day 7 is that the original H_2S was released from the manure during the pumping, transport and delivery to the reactors and it requires several days for the microbial population to become established once again in the manure. The explanation for the releases to return to day 7 levels on day 41 is that since no new

manure was added to the reactors after the first day, the microbial nutrients became depleted. Thus, the focus for evaluating the efficacy of the product in reducing H₂S was the middle four sampling days (days 17, 24, 31 and 36).

A clear trend of lower mean H₂S concentrations in the treated reactors as compared with the control reactors is apparent in Figure 6. The overall group-mean H₂S concentrations for days 17-36 were 1489 ppb for the control reactors and 1189, 885 and 1078 ppb (20, 41 and 28% lower than the controls) for the low, medium and high dosages of DryLet.

The average H₂S concentrations of the treated reactors were 20, 37, 29 and 24% lower than the average of the control reactors on days 17, 24, 31 and 26, respectively. The overall average H₂S concentration of all four treated reactors on the middle four sampling days was 1085 ppb which is 27% less than the 1489 ppb average concentration in the control reactors on the same days. If the high solids reactor R4 is removed from the analysis, the reduction is 34%.

The average cumulative release of H₂S reached 630 and 467 mg for the control and treated reactors (Figure 7), a 26% difference.

The results strongly suggest that DryLet reduces H₂S released from swine manure pits around 30% and at the same time reduces odor by around 30%.

The dose of DryLet M2[®] used seemed to have little impact on H₂S/odor reduction. Reactor R4 may have underperformed simply due to the difficulties associated with the delivery of tiny amounts of the solid particles and because the solids content were unusually high as compared with the other reactors. Still, the average values for H₂S concentration amongst all treated reactors was about 27% reduction, without regard to the dose applied.

The best DryLet M2[®] performance was obtained with a medium dosage of 1 g, achieving a reduction of H₂S relative to the controls of about 51% after 24 days.

Table 5. Hydrogen sulfide concentrations in pit headspace (ppb).

Day	Controls		DryLet M2 [®] Low		DryLet M2 [®] Medium		DryLet M2 [®] High		Averages				
	R3	R5	R4	R7	R2	R1	Controls	Low	Med	High	Treated		
7	645	337	684	472	381	603	491	578	381	603	535		
17	2445	1686	1798	1722	1411	1719	2066	1760	1411	1719	1663		
24	1818	-	1621	853	895	1178	1818	1237	895	1178	1137		
31	877	784	907	413	516	536	831	660	516	536	593		
36	1359	1122	1171	1028	720	878	1241	1099	720	878	949		
41	491	419	689	328	410	342	455	508	410	342	442		

Concentrations of Other Gases

The average gas concentrations for the various reactor groupings were calculated for ammonia (Figure 8), methane (Figure 9), nitrous oxide (Figure 10), and carbon dioxide (Figure 11). The treatment had no apparent effect on these gases, as expected, but the data proves that the random order in which the reactors were filled was effective in establishing similar manure characteristics among the reactors.

The overall average ammonia concentration of all four treated reactors on the middle four sampling days was 56 ppm as compared with 58 ppm for the control reactors. The average mass of ammonia released was 12.2 and 12.6 g for the treated and control reactors, respectively. The change in ammonia concentration production is about 3% and may not be significant.

The overall average methane concentration of all four treated reactors on the middle four sampling days was 411 ppm as compared with 409 ppm for the control reactors. The average mass of methane released was 85 and 83 g for the treated and control reactors, respectively.

The overall average nitrous oxide concentration of all four treated reactors on the middle four sampling days was 342 as compared with 340 ppb for the control reactors. The average mass of nitrous oxide released was 25 and 24 mg (assume 300 ppb ambient concentration) from the treated and control reactors, respectively.

The overall average carbon dioxide concentration of all four treated reactors on the middle four sampling days was 953 as compared with 957 ppm for the control reactors. The average mass of carbon dioxide released was 535 and 529 g (assume 380 ppm ambient concentration) from the treated and control reactors, respectively.

The results strongly suggest that DryLet M2[®] reduces H₂S released from swine manure pits around 30% and at the same time reduces odor by around 30%.

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The olfactometry with a trained sensory panel revealed that this estimate is in line with the perceived odor contained in these same samples and adds credibility to the analytical findings. Further tests would certainly require more frequent and more extensive data collection.

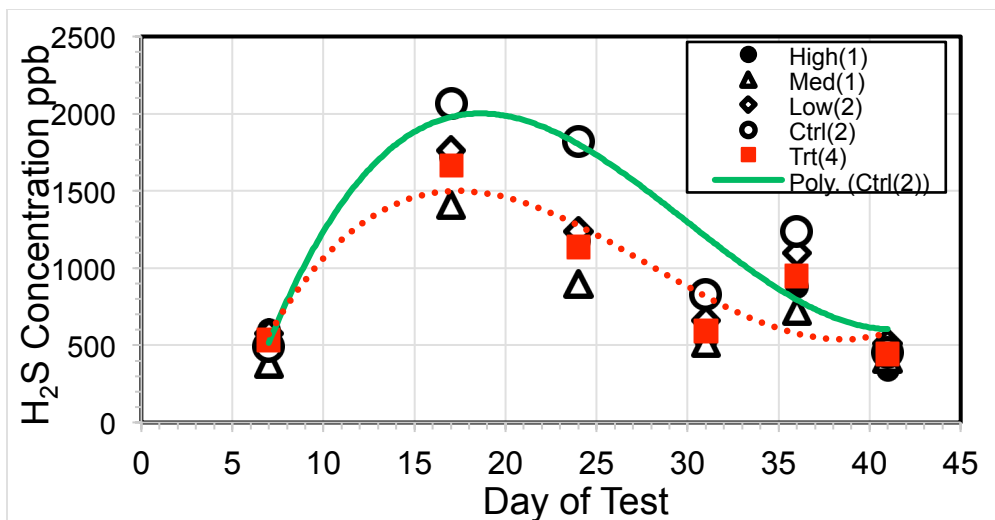


Figure 6. Average H_2S concentrations of treated and untreated manure.

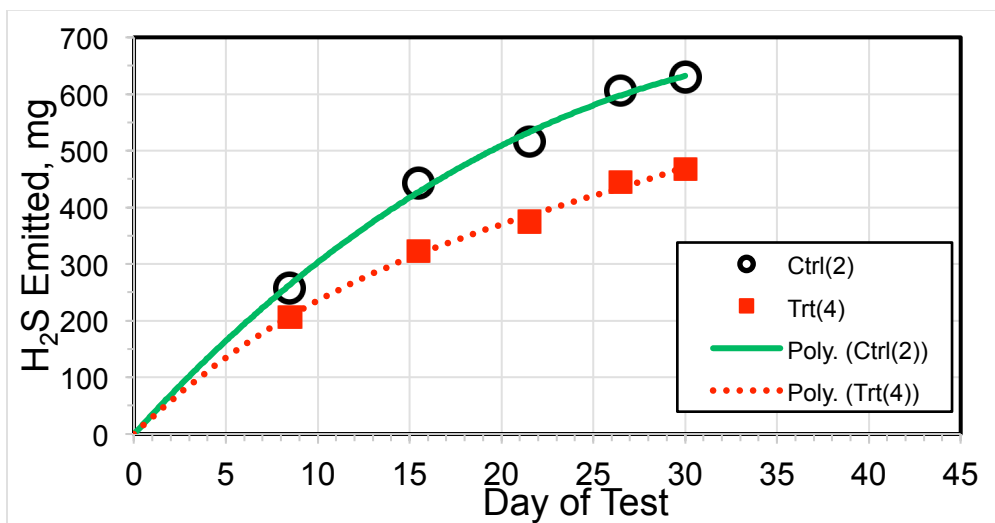


Figure 7. Mass of H_2S emitted from treated and untreated manure over time.

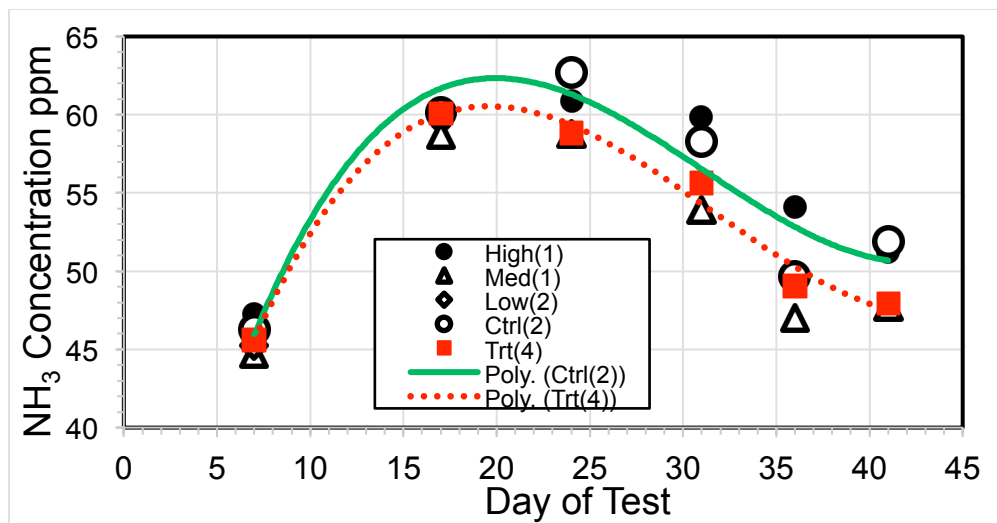


Figure 8. Average NH_3 concentrations of treated and untreated manure.

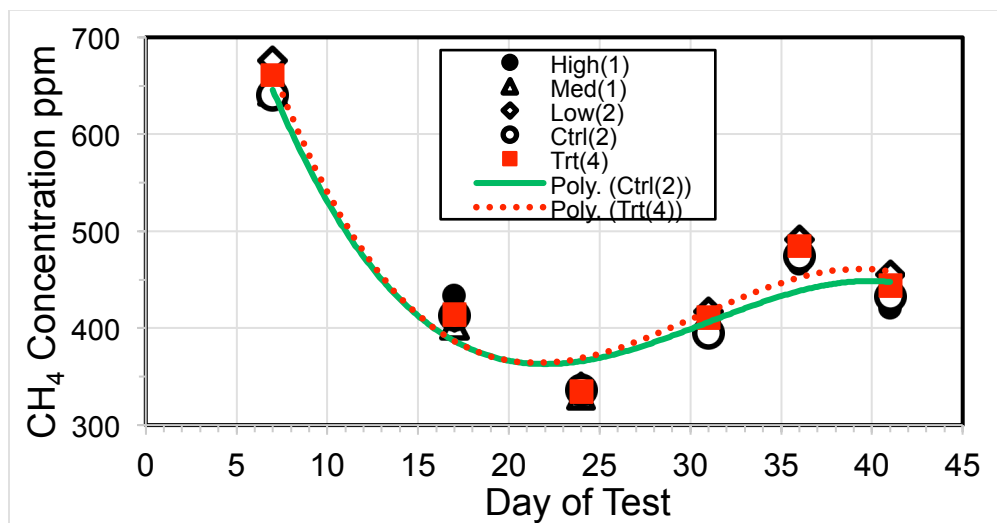


Figure 9. Average concentration of CH_4 measured in the treated and control reactors.

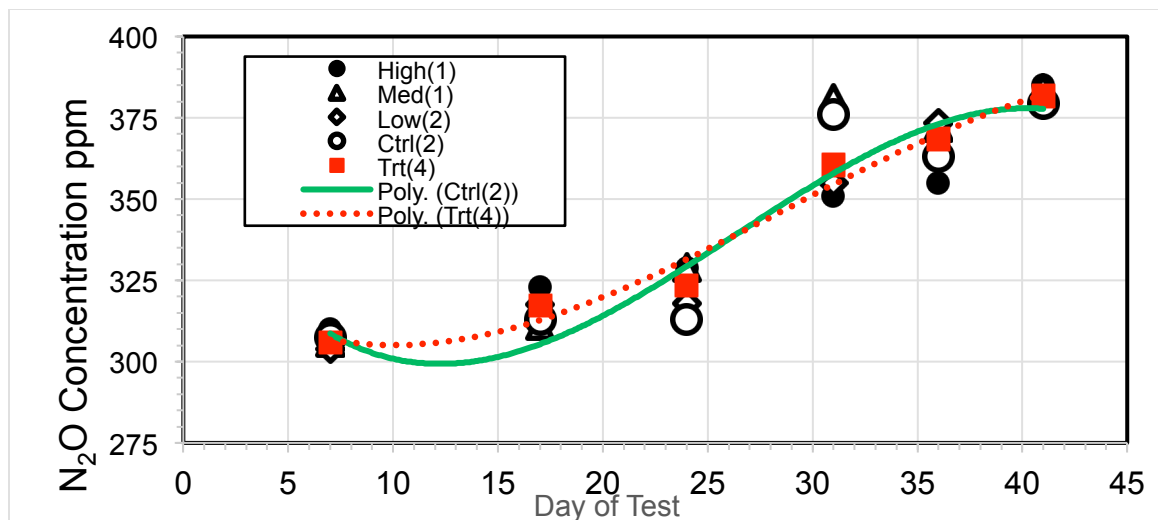


Figure 10. Average concentration of N_2O measured in the treated and control reactors.

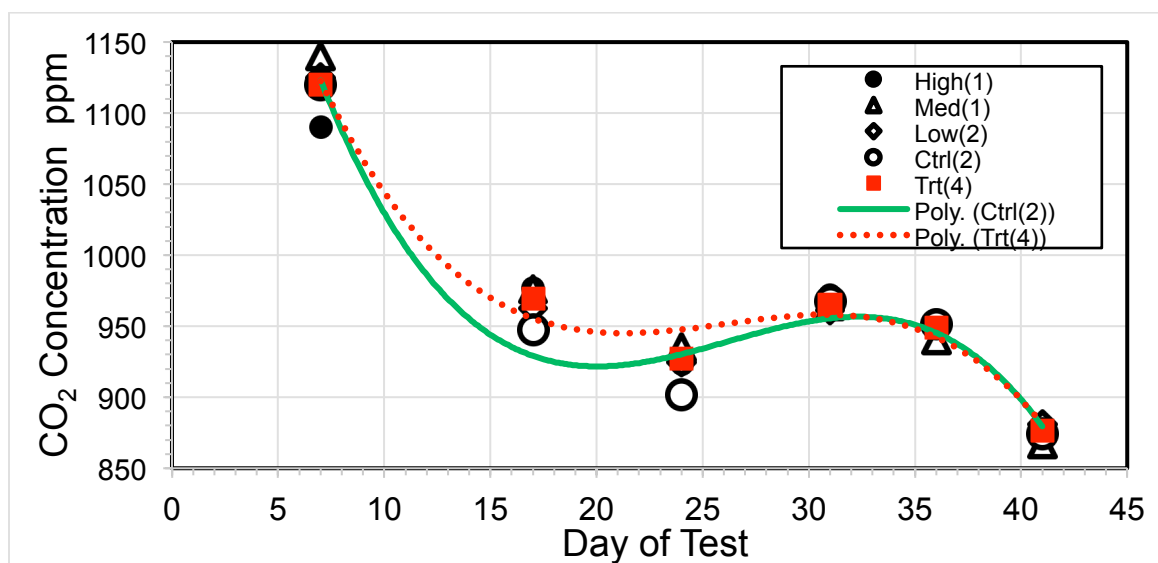


Figure 11. Average concentration of CO_2 measured in the treated and control reactors.

Summary and Conclusions

A 42-day laboratory test was conducted to evaluate the efficacy of three different dosages of DryLet M2[®] in reducing odor and hydrogen sulfide release from swine manure. The approach was to conduct a limited-scope pilot study with only six ventilated reactors (simulated deep pits) and off-line analysis of a limited number of discrete headspace samples to determine whether a more comprehensive test with greater statistical power is warranted. Other analyzers had been calibrated and sampling from the same manifold for another project which allowed the measurement of ammonia, methane, nitrous oxide and carbon dioxide in six “weekly” samples from each reactor. The reactors were sampled twice for odor for evaluation by dynamic forced-choice olfactometry. The conclusions of the study were as follows:

1. The release of H₂S from swine manure that is handled and then subsequently stored without further additions will increase for about three weeks and then decrease to relatively low levels by day 42. Odor release from the manure appears to follow a similar pattern as H₂S.
2. DryLet M2[®] significantly ($P < 0.05$) reduced odor release by 43% on day 24 of the test and apparently ($P > 0.05$) reduced odor release by 27% on day 42.
3. DryLet M2[®] reduced the release of hydrogen sulfide by 27% based on the collective samples taken from all treated reactors on days 17, 24, 31 and 36.
4. DryLet M2[®] had no observable effect on manure fertilizer value.
5. The effectiveness of DryLet M2[®] on H₂S and odor release was not influenced by the dosage level in these tests.
6. The best DryLet M2[®] performance was obtained with a medium dose, achieving a reduction of H₂S relative to the controls of about 50% after 24 days.
7. The results of this study indicate that ammonia, methane, carbon dioxide and nitrous oxide gas production are not significantly changed by the use of DryLet M2[®] relative to the controls.

Based on the positive results with the small data set, further testing is warranted and recommended, with emphasis on more frequent odor samples, continuous gas sampling and analysis, and more experimental replicates to increase the statistical power of the test.

Recommendations for Future Research

The limitations of small data sets notwithstanding, the data clearly supports significant H₂S and odor reduction.

Further testing is warranted and recommended, with emphasis on more frequent odor samples, continuous gas sampling and analysis, and more experimental replicates to increase the statistical power of the test.

References

- ASTM. 1981. Guidelines for the selection and training of sensory panel members. ASTM special technical publication 758. Philadelphia: American Society for Testing and Materials.
- ASTM. 1992. Standard practices for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limits. E 679 - 91. In Annual Book of ASTM Standards. vol. 15.07. pp. 35-39. Philadelphia: ASTM.
- Bereznicki, S.D. et al. 2012. Odor and odorous chemical emissions from animal bldgs: Pt. 1 – Project overview, collection methods, & quality control. Trans. ASABE 55(6):2325-2334.
- Chénard, L., S.P. Lemay, and C. Laguë. 2003. Hydrogen sulfide assessment in shallow-pit swine housing and outside manure storage. J. Agricultural Safety and Health 9(4):285-302.
- Cortus, E.L., L.D. Jacobson, B.P. Hetchler, A.J. Heber, and B.W. Bogan. 2015. Methane and nitrous oxide analyzer comparison and emissions from dairy freestall barns with manure flushing and scraping. Atmospheric Environment 100:57-65.
- ECN. 2000. Air quality - Determination of Odour Concentration by Dynamic Olfactometry. UDC 543.271.2:628.52. Reference document (draft prEN for translation), document CEN/TC264/WG2/N222/e. Brussels: CEN, European Committee for Standardisation, Central Secretariat: Rue de Stassart 36, B-1050.
- Groot Koerkamp, P.W.G., J.H.M. Metz, et al. 1998. Concentrations and emissions of ammonia in livestock buildings in northern Europe. J. Agric. Eng. Res. 70(1):79-95.
- Heber, A. J., J.-Q. Ni, A. L. Sutton, J. A. Patterson, K. J. Fakhoury, D. T. Kelly, and P. Shao. 2001. Manure Pit Additive Evaluation. Des Moines, Iowa: National Pork Board.
- Lim, T. T., A. J. Heber, J.-Q. Ni, A. L. Sutton, and P. Shao. 2003. Odor and gas release from anaerobic treatment lagoons for swine manure. J. Environ. Qual. 32(2): 406-416.
- Mitloehner, F.M. and M.S. Calvo. 2008. Worker health and safety in concentrated animal feeding operations. Journal of Agricultural Safety and Health 14(2):163-187.
- NIOSH. 2005. NIOSH pocket guide to chemical hazards. Washington, D.C.: National Institute for Occupational Safety and Health. Available at: www.cdc.gov/niosh/npg/npgd0028.html. Accessed 18 January 2016.
- Tengman, C.L., R.N. Goodwin, A.K. Gralap-Gonzalez, A.J. Heber, J.Q. Ni, K.J. Fakhoury and A.L. Sutton. 2002. Odor solutions initiative manure pit additive testing results. J. Animal Science, p. 51, Midwest ASAS/ADSA meeting.