Pilot-scale testing of renewable biocatalyst for swine manure treatment and mitigation of odorous VOCs, ammonia and hydrogen sulfide emissions

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Abstract
Comprehensive control of odors, hydrogen sulfide (H$_2$S), ammonia (NH$_3$), and greenhouse gas (GHG) emissions associated with swine production is a critical need. A pilot-scale experiment was conducted to evaluate surface-applied soybean peroxidase (SBP) and calcium peroxide (CaO$_2$) as a manure additive to mitigate emissions of odorous volatile organic compounds (VOC) including dimethyl disulfide/methanethiol (DMDS/MT), dimethyl trisulfide, $n$-butyric acid, valeric acid, isovaleric acid, $p$-cresol, indole, and skatole. The secondary impact on emissions of NH$_3$, H$_2$S, and GHG was also measured. The SBP was tested at four treatments (2.28–45.7 kg/m$^2$ manure) with CaO$_2$(4.2% by weight of SBP) over 137 days. Significant reductions in VOC emissions were observed: DMDS/MT (36.2%–84.7%), $p$-cresol (53.1%–89.5%), and skatole (63.2%–92.5%). There was a corresponding significant reduction in NH$_3$ (14.6%–67.6%), and significant increases in the greenhouse gases CH$_4$ (32.7%–232%) and CO$_2$ (20.8%–124%). The remaining emissions (including N$_2$O) were not statistically different. At a cost relative to 0.8% of a marketed hog it appears that SBP/CaO$_2$ treatment could be a promising option at the lowest (2.28 kg/m$^2$) treatment rate for reducing odorous gas and NH$_3$ emissions at swine operations, and field-scale testing is warranted.

Keywords
Swine manure, Biocatalyst, Mitigation, Soybean peroxidase, Odor

Disciplines
Agriculture | Bioresource and Agricultural Engineering

Comments

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Pilot-scale testing of renewable biocatalyst for swine manure treatment and mitigation of odorous VOCs, ammonia and hydrogen sulfide emissions

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HIGHLIGHTS

• Soybean peroxidase (SBP) is a bio-based, soybean-derived, low cost product.
• Topical treatment using SBP/CaO2 to mitigate gas emissions from manure was tested.
• Emissions reduced up to 68% (NH3), 85% (DMDS/MT), 90% (p-cresol), & 93% (skatole).
• There was a corresponding increase in CO2 & CH4 emissions.
• The remaining target gas emissions (including N2O) were not statistically different.

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ABSTRACT

Comprehensive control of odors, hydrogen sulfide (H2S), ammonia (NH3), and greenhouse gas (GHG) emissions associated with swine production is a critical need. A pilot-scale experiment was conducted to evaluate surface-applied soybean peroxidase (SBP) and calcium peroxide (CaO2) as a manure additive to mitigate emissions of odorous volatile organic compounds (VOC) including dimethyl disulfide/methanethiol (DMDS/MT), dimethyl trisulfide, n-butyric acid, valeric acid, isovaleric acid, p-cresol, indole, and skatole. The secondary impact on emissions of NH3, H2S, and GHG was also measured. The SBP was tested at four treatments (2.28–45.7 kg/m2 manure) with CaO2 (4.2% by weight of SBP) over 137 days. Significant reductions in VOC emissions were observed: DMDS/MT (36.2%–84.7%), p-cresol (53.1%–89.5%), and skatole (63.2%–92.5%). There was a corresponding significant reduction in NH3 (14.6%–67.6%), and significant increases in the greenhouse gases CH4 (32.7%–232%) and CO2 (20.8%–124%). The remaining emissions (including N2O) were not statistically different. At a cost relative to 0.8% of a marketed hog it appears that SBP/CaO2 treatment could be a promising option at the lowest (2.28 kg/m2) treatment rate for reducing odorous gas and NH3 emissions at swine operations, and field-scale testing is warranted.

1. Introduction

Emissions of odorous volatile organic compounds (VOCs), ammonia (NH3), and hydrogen sulfide (H2S) are a problematic
byproduct of pork production (Van Huffel et al., 2016; Cai et al., 2015; Stinn et al., 2014). Mitigation of these emissions is a current issue due to their effect on local and regional air quality. In addition, emissions of greenhouse gases (GHG) (CH₄, N₂O and CO₂) are a potential contribution to climate change.

Manure additives are one of 12 types of technologies that have been proposed to mitigate gaseous emissions from livestock manure storage and handling (Iowa State University Extension and Outreach, 2015; Maurer et al., 2016). However, a limitation of most mitigation technology research is that only about 25% of all research has been evaluated beyond the lab- and pilot-scale and tested in the field. In addition, most research has focused on a limited number of gases. Because of these limitations, it is difficult to rank and adopt mitigation technologies without comprehensive treatment data and an understanding of impact beyond those single or few target gases (Maurer et al., 2016). It is always possible that reducing emissions of one target pollutant can have the opposite effect on other important target pollutants.

The report by Heber et al. (2001) is still the largest pilot-scale study comparing efficacy of 35 swine manure additives for mitigation of NH₃ and H₂S emissions over 42 days. Portejoie et al. (2003) reported a 93% and 92% reduction in NH₃ emissions from manure treated with SBP/CaO₂ and either mixed throughout the manure or applied to the surface (Parker et al., 2012, 2016). While familiar with soybeans as they are a common animal feed, soybean hulleds, a low value and low utility byproduct. Swine farmers are very soybean-derived product. It is produced by shredding soybean husks, a low value and low utility byproduct. Swine farmers are very familiar with soybeans as they are a common animal feed. Thus, the potential for nutrient retention. Percent relative humidity in manure storage and handling (Iowa State University Extension and Outreach, 2015; Stinn et al., 2014). Mitigation of these emissions is a current issue due to their effect on local and regional air quality. In addition, emissions of greenhouse gases (GHG) (CH₄, N₂O and CO₂) are a potential contribution to climate change.

2. Materials and methods

2.1. Experimental design

The pilot-scale study was designed to simulate manure conditions in a deep pit swine manure system. Deep-pit manure storage is commonly used for manure storage under barns in Midwest U.S. The experimental design was a completely randomized design (CRD) with five treatments and three replications per treatment, for a total of 15 experimental units. The five treatments consisted of SBP application rates of 0, 2.28, 4.57, 22.8 and 45.7 kg/m² (0–9.36 lbs/ft²), respectively. CaO₂ was mixed with the SBP at a rate equivalent to 4.2% CaO₂/SBP w/w. The SBP/CaO₂ mixture was surface-applied to the manure. The highest application rate of 45.7 kg/m² (SBP mass/manure surface area) was equivalent to the 50 g/L (SBP mass/volume of manure) application rate tested in the lab-scale studies of Parker et al. (2012, 2016).

2.2. Manure storage simulators

Deep pit swine manure from an Iowa State University swine finisher operation was pumped into fifteen 1.22 m (4 ft) tall, 0.38 m (15 in) diameter sealed manure storage simulators (Fig. 1; Fig. S1). Each simulator initially received 104 L (27.5 gal) of swine manure followed by 9.5 L (2.5 gal) weekly manure additions for two weeks after SBP/CaO₂ addition resulting in a final volume of 123 L (32.5 gal). The ventilation in each simulator was controlled via valves with rotameters (Fig. S2) in order to achieve a ventilation rate of 7.5 headspace exchanges per h. The rate was adjusted when fresh manure was added to keep a constant exchange rate. Air exchange rates were consistent with recommended values for less than half full manure pit storage (assuming cool season; minimum ventilation, growing (34–68 kg) pigs, in swine barn with fully slatted floor) (MWPS, 1983). Storage temperature was kept between 9 and 20 °C (average = 15.6 ± 3.7 °C) to simulate the temperature of deep pit storage (Da Silva Batista et al., 2013).

Baseline gas emissions measurements were taken for two weeks prior to SBP/CaO₂ addition to evaluate emissions from each of the 15 pilot manure storage simulators to make sure that there were no significant difference in emissions due to the system prior to randomly assigning treatments to the experimental units. Total duration of the pilot experiment was 137 days. Manure samples were collected and analyzed before SBP/CaO₂ application and at the end of the experiment to determine effects on manure quality and potential for nutrient retention. Percent relative humidity in manure headspace was monitored via an 850071 Environmental Quality meter (Sper Scientific, Scottsdale, AZ, USA) every day that gas emission samples were collected (Fig. S3).

2.3. Volatile organic compounds (VOCs)

VOCs were collected in 304-grade stainless steel sorbent tubes (4 mm O.D., 0.10 m long) filled with 65 mg Tenax TA. Air samples were collected using a portable sampling pump (50 mL/min for 15 min), and were analyzed within two days (Fig. S4). The sampling flow rates were verified with a NIST-traceable digital flow meter (Bios International, Butler, NJ, USA). Chemical analyses of swine odorants were completed using the TD-MDGC–MS/O system (Agilent 6890 GC; Microanalytics, Round Rock, TX, USA) (Fig. S5) using procedures previously described (Zhang et al., 2012) (Olfactometry port was not used in this study). An additional sorbent tube to test for breakthrough was used during each sampling set. Work by Andersen et al. (2012) has shown that methanethiol (MT) can convert to dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) using sorbent tubes and thermal desorption. It is not possible to determine the extent of that conversion with field air samples and determine the exact fraction of DMDS or DMTS that resulted from MT conversion. Additional experiment was conducted post project to determine the extent of MT to DMDS/DMTS conversion using moist and dry air (Cai et al., 2015). It was determined that complete conversion of MT to DMDS (97.5–99.5%) and DMTS (0.5–2.5%) is possible for moist standard gas stored on sorbent tubes from 1 to 3 days. Thus, caution should be exercised while...
interpreting measured DMDS and DMTS concentrations as they are likely confounded by conversion of MT and fluxes of these compounds are reported as DMDS/MT and DMTS/MT throughout the manuscript.

2.4. Ammonia and hydrogen sulfide

Ammonia and H2S concentrations were measured via a Drager X-am 5600 portable gas analyzer (Luebeck, Germany) with NH3 and low range H2S XS sensors (Fig. S6). The analyzer was calibrated using Drager calibration software, Environics 4040 gas dilution system (Tolland, CT, USA) and standard gases (Praxair, Ames, IA, USA) (NH3: 102 ppm and H2S: 15.6 ppm). Calibration details are in SI.

2.5. Greenhouse gases

Gas samples were collected via syringe and 5.9 mL Exetainer vials (Labco Limited, UK) and were analyzed for GHG concentrations on a gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with FID and ECD detectors, and CO2-to-CH4 catalytic convertor (Figs. S7–S9). Gas method detection limits were 1.99 ppm for CO2, 170 ppb for CH4, and 20.7 ppb for N2O. Standard curves were constructed daily using 2 ppm and 10.3 ppm CO2; 510 ppm, 1010 ppm and 2010 ppm CH4; and 0.101 ppm, 1.01 ppm, and 10.1 ppm N2O (Air Liquide America, Plumsteadville, PA, USA). Daily standards used for standard curve construction were completed in duplicate for CH4 and CO2 while N2O standards were constructed in triplicate.

2.6. Swine manure analysis

Swine manure analysis was completed using standard methods described in greater detail in SI. Total Kjeldahl nitrogen (TKN) was quantified by digestion followed by steam distillation and titrimetric analysis (AOAC, 2000). Ammonia (NH3) was quantified by steam distillation followed by titrimetric analysis (APHA, 1998). Dissolved reactive phosphorus was quantified by the ascorbic acid method (APHA, 1998). Total phosphorus was determined by sulfuric acid-nitric acid digestion followed by the ascorbic acid method (APHA, 1998), while pH was determined using the electrode method (APHA, 1998). Total solids/moisture content and volatile solids were determined by oven drying method (APHA, 1998). Percent C, H, N, and S were acquired with a combustion analyzer (Perkin Elmer Inc., Waltham, MA) with a cysteine calibration standard. Conceptual schematics of target gas emissions potential sources and possible fates in the C, N, and S cycles are presented in Figs. S10–S12.

2.7. Soybean peroxidase activity

SBP was extracted by 3% acetic acid hydrolysis at room temperature and vortexed periodically over 1 h followed by centrifugation. The extract was then assayed based on modified guaiacol assay (Baker et al., 2002) at 30 °C and 470 nm for 3 min using a UV–Vis spectrometer. Details are presented in SI.

2.8. Estimation of target gas flux

Measured gas concentrations were used for calculation of flux (E), i.e., emissions based on time and emitting surface area of manure (mass/(time × area)). Gas concentrations were measured at field conditions and were converted to standard conditions (1 atm, 25 °C, dry air). Methodology of gas flux estimations based
on measured variables is presented in SI (Equations S3 to S13). Overall mean % reduction (\%R) for each target gas was calculated using Eq. (1).

\[
\%R = \frac{E_{\text{Con}} - E_{\text{Trt}}}{E_{\text{Con}}} \times 100\% \tag{1}
\]

where \(E_{\text{Con}}\) is the average flux estimate of the desired time interval (day, week, biweekly or overall) of the control, and \(E_{\text{Trt}}\) is the corresponding average flux estimate of the treatment.

2.9. Statistical analysis for pilot-scale

The General Linear Model procedure, PROC GLM, in SAS System (version 9.3, SAS Institute, Inc., Cary, NC, USA) was used to analyze the data and determine the p values. A significance level of 0.05 was used as the cut off for statistical significance.

3. Results and discussion

3.1. Visual observations of the SBP surface layer over time

For the two lowest SBP/CaO2 application rates of 2.28 and 4.57 kg/m², there was almost complete wetting and absorption of the SBP/CaO2 into the manure surface progressing from the day of application (Day 1) to Day 137 (Fig. 2). At the higher SBP/CaO2 application rates of 22.8 and 45.7 kg/m², some of the SBP was still visible on the surface of the manure on Day 137 (Fig. 3). The 22.8 kg/m²...
m² SBP/CaO₂ application rate still had some dry SBP/CaO₂ covering the complete surface of the manure on Day 137 (Fig. 3). The highest SBP/CaO₂ application rate of 45.7 kg/m² was ~13 cm thick. The weight of this relatively thick layer of SBP/CaO₂ caused the SBP crust to roll into the top layer during periodic additions of new manure (Fig. 3). This resulted in less manure surface coverage with the largest SBP application rate over time. Assessment of the distribution of dry and wet SBP/CaO₂ layer thickness in the midpoint of treatment (Day 88) is presented in Table 1 and Fig. S13. These visual observations of the surface SBP layer are important because they provide a better understanding on the mechanisms responsible for the mitigation effect (e.g., chemical activation of peroxidase, biofilm/biofilter layer interface between manure and air, or the combination of both).

3.2. Treatment effects on odorous volatile organic compounds

The p-cresol and skatole fluxes were significantly reduced for all SBP treatments with no apparent benefit with higher SBP application rates (Table 2, Fig. 4B and C). These p-cresol results compare favorably to the laboratory studies of Ye et al. (2009) and Parker et al. (2012, 2016); Ye et al. (2009) reported almost 100% reduction in p-cresol emissions when 2 kg batch of swine slurry was treated with horseradish peroxidase and peroxides. Likewise, Parker et al. (2012) reported reductions in p-cresol of 62–92% for swine manure treated with SBP/CaO₂ mixed throughout the manure. Parker et al. (2012) also reported a short-term reduction in skatole and indole emissions that were apparent at 24 h after treatment but negligible after 48 h. However, our surface application demonstrated a longer-term reduction in skatole up to 137 d, an important consideration for possible farm-scale application.

There were no significant differences in indole flux for any of the SBP treatments (Fig. S14), likely due to the highly variable emission of that compound. DMDS/MT and DMTS/MT were simultaneously higher in months 2 and 3 of the SBP treatments (Fig. S15). Measured flux for the target short chain organic fatty acids did not result in any significant differences for the SBP treatments with only one exception at the highest application rate (45.7 kg/m² of SBP) with significant (p = 0.0002 and p = 0.0003, respectively) increase for n-butyric acid and isovaleric acid flux (Figs. S16–S18).

Summary of measured gas concentrations and flux ranges of monitored gases are presented in Tables S1 and S2.

Table 1

<table>
<thead>
<tr>
<th>Treatment (kg/m²)</th>
<th>2.28</th>
<th>4.57</th>
<th>22.8</th>
<th>45.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet thickness on d 88 (mm)</td>
<td>24</td>
<td>40</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>Dry thickness on d 88 (mm)</td>
<td>2</td>
<td>9</td>
<td>31</td>
<td>15</td>
</tr>
<tr>
<td>Starting (initial application) thickness on d 1 (mm)</td>
<td>6</td>
<td>13</td>
<td>64</td>
<td>127</td>
</tr>
</tbody>
</table>

3.3. Treatment effects on ammonia and hydrogen sulfide

Ammonia flux was consistently reduced for all SBP/CaO₂ treatment levels, with the higher application rates resulting in more significant reductions (67.6% (p < 0.0001), 58.4% (p < 0.0001), and 25.2% (p = 0.008) for the 45.7, 22.8, and 4.57 kg/m² SBP/CaO₂ application rates, respectively) (Table 2). NH₃ flux was also reduced by 14.6% for the lowest 2.28 kg/m² SBP/CaO₂ application rate, but was not significant (p = 0.120) (Fig. 4A).

The higher reductions in NH₃ flux estimates occurred immediately after SBP/CaO₂ application, with the SBP/CaO₂ effect wearing off over time. There could be several modes of action responsible for the NH₃ reductions. At least part of the treatment effect could have been the result of the SBP covering the manure surface. Because NH₃ flux is strongly correlated to evaporation rate, anything that inhibits evaporation would also decrease the NH₃ flux (Parker et al., 2013). It is also possible that the SBP binds or absorbs the NH₄⁺ or NH₃ in solution. Apparent lowering of pH and relative humidity in simulators headspace is documented in section 3.5. Further research is required to assess the primary mode of action.

Measured concentrations of H₂S in both the control and treatments were between ~0.1 and 25 ppm and were highly variable (Fig. S19). Thus, the estimates of flux and the mitigation effect were challenging to assess and were not correlated with the application rate. SBP treatments of 2.28 and 22.8 kg/m² resulted in a decrease in H₂S flux estimates while 45.7 kg/m² SBP treatment resulted in an increase in H₂S flux.

Table 2

<table>
<thead>
<tr>
<th>Pilot-scale test</th>
<th>2.28</th>
<th>4.57</th>
<th>22.8</th>
<th>45.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas % Reductions</td>
<td>36.2</td>
<td>67.5</td>
<td>84.7</td>
<td>50.3</td>
</tr>
<tr>
<td>p value</td>
<td>0.212</td>
<td>0.021</td>
<td>0.006</td>
<td>0.335</td>
</tr>
<tr>
<td>DMDS/MT</td>
<td>16.9</td>
<td>10.7</td>
<td>79.2</td>
<td>83.5</td>
</tr>
<tr>
<td>n-Butyric Acid</td>
<td>87.5</td>
<td>88.5</td>
<td>92.3</td>
<td>83.5</td>
</tr>
<tr>
<td>Valeric Acid</td>
<td>42.7</td>
<td>59.2</td>
<td>58.8</td>
<td>354.7</td>
</tr>
<tr>
<td>p-cresol</td>
<td>64.9</td>
<td>53.1</td>
<td>48.5</td>
<td>78.2</td>
</tr>
<tr>
<td>Indole</td>
<td>72.6</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
<tr>
<td>Skatole</td>
<td>14.6</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
<tr>
<td>NH₃</td>
<td>10.9</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
<tr>
<td>H₂S</td>
<td>32.7</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>20.8</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
<tr>
<td>N₂O</td>
<td>2.6</td>
<td>115.0</td>
<td>92.5</td>
<td>77.2</td>
</tr>
</tbody>
</table>

Bold font signifies statistical significance (p < 0.05) between each treatment and the control. DMDS and DMTS reductions are likely confounded by conversion of MT and are reported as DMDS/MT and DMTS/MT.
3.4. Treatment effects on greenhouse gases

Methane and CO$_2$ flux were significantly ($p \leq 0.013$) higher overall for all SBP treatments over the 137 day monitoring period except for methane at the lowest application rate ($p = 0.077$) (Fig. 5A and B). Nitrous oxide flux was not significantly different ($p = 0.913$ to $p = 0.985$) for all SBP treatment levels over the 137 day period after treatment (Fig. 5C). The increase in generation of CO$_2$ and CH$_4$ is likely a result of biochemical breakdown of the SBP. In essence, mitigation of VOCs resulted in increased emissions of CO$_2$ and CH$_4$. It is also important to recognize the role of bacteria population that might be controlling the generation of CH$_4$ vs. N$_2$O (Montes et al., 2013). For example, manure bacteria can either suppress CH$_4$ generation at the expense of increased N$_2$O or vice versa.

Closer inspection of the CH$_4$ and N$_2$O flux (Fig. 5A and C) supports this apparent trend, i.e., increased and re-equilibrating CH$_4$ and decreased and re-equilibrating N$_2$O for both the control and treatment. These apparent trends for CH$_4$ and N$_2$O in the control suggest that oxygen availability in manure due to pump-out and transfer to storage simulators has influenced variations in bacterial growth early in the experiment. Methane and CO$_2$ flux was inversely proportional to the SBP application rate.

Emissions of GHGs from stored swine manure occur naturally during storage. The increase in CO$_2$ and CH$_4$ flux from SBP treatment is small when put into the context of total GHG emissions from a US commercial swine finisher and swine gestation barn with a deep pit storage. The increase in CO$_2$ as a result of the SBP/CaO$_2$ treatments of 2.28, 4.57, 22.8 and 45.7 kg/m$^2$ equates to 0.52–0.68, 0.66–0.86, 2.01–2.62, and 2.97–3.88% of the total CO$_2$ emitted from a typical swine finisher with deep pit, respectively (Sun et al., 2008; Ni et al., 2008). There is much greater CO$_2$ contribution from pigs’ respiration, combustion from natural gas-fired space heaters, and from microbial activity in manure. The increase in CH$_4$ is small for the two lowest SBP/CaO$_2$ treatments that could be considered feasible for farm applications, i.e., 2.28 and 4.57 kg/m$^2$, with 5.38 and 8.02% of the total CH$_4$ resulting emitted from a typical deep pit swine finisher barn. The higher, much less practical for farm application SBP/CaO$_2$ application rates 22.8 and 45.7 kg/m$^2$ resulted in a larger increase of CH$_4$ that equated to 16.5 and 35.6% of the total CH$_4$ emitted from a typical deep pit swine finisher barn (Ni et al., 2008).

3.5. Treatment effects on environmental and physicochemical parameters

Relative humidity (RH) in the headspace of the simulators and manure pH were also monitored besides test room temperature and pressure (summarized in Fig. S20). The SBP caused a decrease in manure pH coinciding with the application rate (Fig. 6A). This decrease in pH was consistent with the observed decrease in NH$_3$ emissions. Lower pH promotes the formation of the non-volatile ammonium ion leading to lower NH$_3$ emissions (Fig. 4). The lower pH also supported the apparent increase in CO$_2$ and CH$_4$ emissions (Fig. 5). The RH was also correlated with the application rate (Fig. 6B; $R^2 = 0.82$), the SBP layer seemed to provide a barrier, suppressing evaporation and trapping the moisture in the manure. The effect was greater with higher SBP application rate (with the
possible exception of the highest dose and the reasons discussed in 3.1), and faded over time as the SBP became more incorporated into the top layer of the manure. This apparent convergence pattern was consistent with the one observed for NH₃ flux in Fig. 4A.

3.6. Soybean peroxidase activity

The soybean peroxidase activity was determined on the SBP that had been applied to manure for 88 days to determine if there was still an enzymatic activity after that duration of exposure to the swine manure. The resulting activities for the SBP that had formed a moist crust on the manure, thus being directly in contact with the manure (i.e., doses 2.28, 4.57 and 45.7 kg/m² SBP), were much lower, i.e., 3.2 × 10⁻⁶, 6.4 × 10⁻⁶ and 12 × 10⁻⁶ U/mg respectively, than that of the 22.8 kg/m² SBP/CaO₂ application rate (29.6 × 10⁻⁶ U/mg), which had dry SBP still floating on the surface of the manure. All SBP activity after 88 days of exposure to swine manure were considerably lower than that of unexposed SBP, which had an activity of 0.0153 U/mg. This suggests that SBP activity is affected by contact with manure and is likely responsible for the treatment effect. Steevensz et al. (2013) reported that grinding/mixing preparation of the SBP and soybean variety affects its useful activity based on the survey of 65 different cultivars. Thus, it is important to consider these variables for optimal treatment effectiveness.

3.7. Manure analysis

Nutrient conservation is an important parameter for any type of manure treatment that will be later used for field application. As compared to the control, this study resulted in significantly higher TKN levels in the manure for the two highest application rates, but no significant difference for the two lower application rates (p ≥ 0.218). These differences were not due to the SBP conserving the N that was in the manure but that the SBP was contributing N to the manure. If the TKN levels are adjusted for the amount of N contributed by the level of SBP there was no statistical difference between the SBP treatments. The observed reduction in NH₃ does
not add up a high enough percentage to have an effect on the TKN levels in the manure (Table 3).

3.8. Effects of SBP application rate

There was a positive correlation between % reduction and SBP application rate for NH3 and a negative correlation between % reduction and SBP application rate for CH4 and CO2. For the rest of the gases, the treatment effect starts to reach an apparent plateau at higher SBP application rates, i.e., when 0, 2.28, and 4.57 kg/m² were taken into account (Fig. 7). A strong correlation was also observed for H2S, DMDS/MT, n-butyric acid, valeric acid, isovaleric acid, and p-cresol for the lowest three SBP application rates, i.e., when 0, 2.28, and 4.57 kg/m² were taken into account (Table S3). This suggests that larger SBP application rates are not necessarily resulting in a proportional treatment effect. Lower SBP application rate might be sufficiently effective especially when economic feasibility for farm application are considered.

3.9. Economics of SBP/CaO2 treatment

The resulting treatment costs range from $1.45 to $29.06 per marketed pig for the lowest to highest SBP application rate, respectively. These costs are based on $191/ton for grinding of bulk soybeans (University of Missouri Extension, 2014), $4.00/ton for grinding of bulk CaO2 (American International Chemical, Inc., Framingham, MA). These costs do not include labor required to apply the treatments, which could vary greatly depending on method of application. Cost estimates for mitigation additives are relatively few and often limited to one or few target gases reported. The $1.45/market pig price estimate is within the range of $0.01 to $18.2 price estimates (Table S4) with an average additive cost of $4.28 ± $5.80 for manure additive treatment of odor, VOCs, NH3, and H2S (Balsari et al., 2006; Heber et al., 2000, 2001; Moreno et al., 2010). With the average carcass weight of a hog from 2010 through 2015 (USDA-AMS, 2016) being 94.9 kg (209.3 lbs) and the average market price over the same period of $83.60/carcass hundredweight (Iowa State University Extension and Outreach, 2016), the estimated cost percentage equates to 0.8–16.6% for the range of treatment rates (2.28–45.7 kg/m²) in this study.

4. Conclusions

This study provided a comprehensive assessment of a manure additive for mitigation of gaseous emissions of all major compounds of interest from swine manure. Significant reductions in NH3, DMDS/MT, p-cresol and skatole were observed, with corresponding increases in greenhouse gases CH4 and CO2 and no effect on N2O emissions. The SBP/CaO2 treatment resulted in mitigation of most gases of concern to the swine industry, considering the complex physical/chemical/biological processes that are at work in swine manure emissions. At a cost relative to 0.8% of a marketed hog it appears that SBP/CaO2 treatment could be a promising option at the lowest (2.28 kg/m²) treatment rate for reducing odorous gas and NH3 emissions at swine operations, and field-scale testing is warranted.

Associated content

Supporting Information. Includes photos demonstrating treatment, details of methods and theory, emissions mitigation effects for gases where no significant effect was observed, and explanation of gas emissions from manure as a part of C, N and S cycles.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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Disclaimer

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.11.021.

Abbreviations

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>mdGC-MS-O</td>
<td>multidimensional gas chromatography-mass spectrometry-olfactometry</td>
</tr>
<tr>
<td>TD</td>
<td>thermal desorption</td>
</tr>
<tr>
<td>SBP/CaO2</td>
<td>soybean peroxidase/calcium peroxide</td>
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<tr>
<td>GHG</td>
<td>greenhouse gas</td>
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<tr>
<td>TKN</td>
<td>total Kjeldahl nitrogen</td>
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<tr>
<td>CRD</td>
<td>completely randomized design</td>
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<tr>
<td>VOCs</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>AMPAT</td>
<td>Air Management Practices Assessment Tool</td>
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<tr>
<td>RH</td>
<td>relative humidity</td>
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<tr>
<td>FID</td>
<td>flame ionization detector</td>
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<tr>
<td>ECD</td>
<td>electron capture detector</td>
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<tr>
<td>NH3</td>
<td>ammonia</td>
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<tr>
<td>H2S</td>
<td>hydrogen sulfide</td>
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<tr>
<td>CO2</td>
<td>carbon dioxide</td>
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<tr>
<td>CH4</td>
<td>methane</td>
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<tr>
<td>N2O</td>
<td>nitrous oxide</td>
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<tr>
<td>DMDS</td>
<td>dimethyl disulfide</td>
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<tr>
<td>DMTS</td>
<td>dimethyl trisulfide</td>
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<tr>
<td>MT</td>
<td>methanethiol</td>
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</tbody>
</table>

References


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