Agricultural and Biosystems Engineering Publications

Agricultural and Biosystems Engineering

2016

Surface Application of Soybean Peroxidase and Calcium Peroxide for Reducing Odorous VOC Emissions from Swine Manure Slurry

David B. Parker
United States Department of Agriculture

Morgan Hayes
University of Illinois at Urbana-Champaign

Tami M. Brown-Brandl
United States Department of Agriculture

Bryan L. Woodbury
United States Department of Agriculture

Mindy Spiehs
United States Department of Agriculture

Follow this and additional works at: http://lib.dr.iastate.edu/abe_eng_pubs

See next page for additional authors

Part of the Agriculture Commons, and the Bioresource and Agricultural Engineering Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/abe_eng_pubs/765. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

Surface Application of Soybean Peroxidase and Calcium Peroxide for Reducing Odorous VOC Emissions from Swine Manure Slurry

Abstract

A laboratory experiment was conducted to evaluate and compare surface-applied versus fully-mixed treatments of soybean peroxidase (SBP) plus calcium peroxide (CaO_2) for reducing odorous volatile organic compound (VOC) emissions from swine manure slurry. Industrial-grade SBP (5-50 g L^{-1}) and powdered CaO_2 (0.16-1.6 g L^{-1}) were applied to swine manure slurry in 7.6 L containers, and odorous VOC emission rates (phenolics, indolics, volatile fatty acids, methyl sulfides) were measured over a 14 d period using sorbent tubes and gas chromatography. The five treatments consisted of a control, the fully-mixed rate of 50 g L^{-1} SBP plus 1.6 g L^{-1} CaO_2, and three surface-applied treatments of 10%, 50%, and 100% of the fully-mixed application rate. The odorants 4-methylphenol and skatole accounted for the majority of the odor activity value (OAV). The 10% surface-applied rate was as effective as the 100% surface-applied and fully-mixed application rates at reducing 4-methylphenol and skatole emissions for up to 10 d (P2 every 4-7 d. Future pilot- and field-scale research should focus on surface application of SBP and CaO_2 at a rate equal to 10% of the fully-mixed rate.

Disciplines
Agriculture | Bioresource and Agricultural Engineering

Authors
David B. Parker, Morgan Hayes, Tami M. Brown-Brandl, Bryan L. Woodbury, Mindy Spiehs, and Jacek A. Koziel

Surface Application of Soybean Peroxidase and Calcium Peroxide for Reducing Odorous VOC Emissions from Swine Manure Slurry

D. B. Parker, M. Hayes, T. Brown-Brandl, B. L. Woodbury, M. J. Spiehs, J. A. Koziel

ABSTRACT. *A laboratory experiment was conducted to evaluate and compare surface-applied versus fully-mixed treatments of soybean peroxidase (SBP) plus calcium peroxide (CaO_2) for reducing odorous volatile organic compound (VOC) emissions from swine manure slurry. Industrial-grade SBP (5-50 g L^{-1}) and powdered CaO_2 (0.16-1.6 g L^{-1}) were applied to swine manure slurry in 7.6 L containers, and odorous VOC emission rates (phenolics, indolics, volatile fatty acids, methyl sulfides) were measured over a 14 d period using sorbent tubes and gas chromatography. The five treatments consisted of a control, the fully-mixed rate of 50 g L^{-1} SBP plus 1.6 g L^{-1} CaO_2, and three surface-applied treatments of 10%, 50%, and 100% of the fully-mixed application rate. The odorants 4-methylphenol and skatole accounted for the majority of the odor activity value (OAV). The 10% surface-applied rate was as effective as the 100% surface-applied and fully-mixed application rates at reducing 4-methylphenol and skatole emissions for up to 10 d (P<0.05). Emission rates for the treatments were greater than the control on d 14, indicating the need for reapplication of $SBP+CaO_2$ every 4-7 d. Future pilot- and field-scale research should focus on surface application of SBP and CaO_2 at a rate equal to 10% of the fully-mixed rate.*

Keywords. *Manure, Odor, Soybean peroxidase, Swine, Volatile organic compound.*

A large number of volatile organic compounds (VOC) are emitted from animal feeding operations (Kai and Schafer, 2004; Lo et al., 2008; Akdeniz et al., 2010; Ni et al., 2012; Parker et al., 2013a; Cai et al., 2015). Since many of these VOCs are odorous, they are an important aspect of air quality downwind of many animal feeding operations. As a result of growing concerns with odors near industrial and agricultural facilities, several states have enacted ambient odor regulations (Sweeten, 1995; CAQCC, 1999; Chen et al., 1999; Redwine and Lacey, 2000).

Many VOCs are generated from the degradation of amino acids, which occurs both in the intestines of animals and during the anaerobic decomposition of manure (Mata-

Alvarez et al., 2000; Kai and Schafer, 2004; Koziel et al., 2006; Cai et al., 2006; Chen et al., 2008). Commonly reported odorants from manure sources include ammonia, volatile fatty acids (VFA), sulfides, 4-methylphenol (aka p-cresol), phenol, indole, and skatole. While many odorous compounds are emitted from manure, the phenolic and indolic compounds have been shown most responsible for manure odors at distance from the source (Wright et al., 2005; Bulliner et al., 2006; Koziel et al., 2006; Parker, 2008).

Several researchers have investigated the use of peroxidase enzymes for the abatement of phenolic contaminants in wastewaters (Wu et al., 1997; Caza et al., 1999; Flock et al., 1999; Morawski et al., 2001; Steevensz et al., 2014). Peroxidases are naturally occurring enzymes isolated from plant roots and above ground biomass. In the presence of peroxides, the peroxidase enzyme polymerizes some of the phenolic and indolic compounds, making them less odorous (Tonegawa et al., 2003). The chemical reaction first produces free phenoxyl radicals, which then couple to produce dimers. Steevensz et al. (2014) presents an example of this chemical reaction for phenol as shown in figure 1.
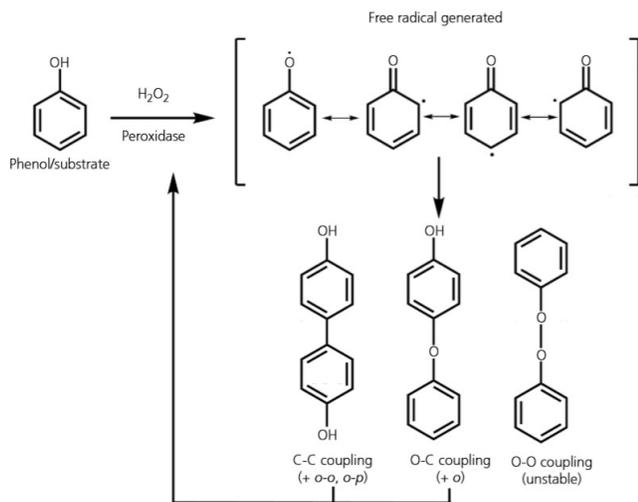
There are many different kinds of peroxidase enzymes, but horseradish peroxidase (HRP) and soybean peroxidase (SBP) have been the most studied for treatment of animal manures. Govere et al. (2007) showed a considerable reduction in odor intensity when minced horseradish root was applied to swine manure. One drawback with using horseradish root at the commercial scale is the limited supply. Ye et al. (2009) demonstrated considerable

The authors are **David B. Parker, ASABE Member,** Research Agricultural Engineer, USDA-ARS, Bushland, Texas; **Morgan Hayes,** Assistant Professor, University of Illinois, Urbana, Illinois; **Tami Brown Brandl, ASABE Member,** Research Agricultural Engineer, **Bryan L. Woodbury, ASABE Member,** Research Agricultural Engineer, and **Mindy J. Speihs**, Research Animal Scientist, USDA-ARS, Clay Center, Nebraska; and **Jacek A. Koziel, ASABE Member,** Associate Professor, Iowa State University, Ames, Iowa. **Corresponding author:** David B. Parker, USDA-ARS, Conservation and Production Research Laboratory, 2300 Experiment Station Rd., Bushland, TX 79012; phone 806-356-5744; e-mail: david.parker@ars.usda.gov.

Applied Engineering in Agriculture

Vol. 32(4): 389-398   2016 American Society of Agricultural and Biological Engineers ISSN 0883-8542 DOI 10.13031/aea.32.11672   389

Figure 1. In the presence of peroxidase enzyme and peroxide, phenolic compounds are first converted to phenoxyl radicals, then to dimers (from Steevensz et al., 2014).

reductions in odorous phenolic and indolic compounds in swine manure treated with purified HRP. The primary drawback for using purified HRP for odor abatement at the commercial scale is the cost.

Soybeans are one of the most abundant crops produced in the world. A considerable amount of SBP is found in soybean hulls (Gijzen et al., 1993), and SBP has been shown to be water soluble (Steevensz et al., 2013). Steevensz et al. (2014) summarized the various methods of using SBP for industrial wastewater treatment. The U.S. produced about 81 million metric tons of soybeans in 2007, compared to only 10,000 metric tons of horseradish (Masuda and Goldsmith, 2009; Bratsch, 2009).

We recently reported on a laboratory experiment where SBP and powdered CaO_2 were used to treat swine manure (Parker et al., 2012a). In this earlier research, the SBP (50 g L^{-1}) + CaO_2 (1.6 g L^{-1}; 22.1 mM) were fully-mixed in the swine manure, and the emissions of the primary odorant 4-methylphenol were reduced by 92% to 98% over the 48 h monitoring period. The Parker et al. (2012a) experiments demonstrated the efficacy of SBP+CaO_2 for fully-mixed conditions. However, it was also determined that surface-application would be more economical than fully-mixed if it resulted in similar treatment efficiency. Therefore, a follow-up laboratory study was completed but at a larger scale (7.6 L vs. 200 mL), longer time period (14 d as compared to 2 d) and including both surface-applied and fully-mixed applications. The objective of this study was to compare three rates of surface application of SBP+CaO_2 with the fully-mixed treatment over a time period of 14 d for their effectiveness in mitigating odorous VOC emissions from swine manure.

MATERIALS AND METHODS
EXPERIMENTAL DESIGN
The laboratory experiment consisted of a completely randomized design (CRD) with five treatments (TRTs):
- TRT 1) a control with no amendments (Control),

- TRT 2) 50 g L^{-1} SBP plus 1.6 g L^{-1} CaO_2 (22.1 mM CaO_2) fully mixed in the manure slurry (100% Mixed),
- TRT 3) 50 g L^{-1} SBP plus 1.6 g L^{-1} CaO_2 applied to the surface (100% Surficial; equivalent to 5 kg m^{-2}),
- TRT 4) 25 g L^{-1} SBP plus 0.80 g L^{-1} CaO_2 applied to the surface (50% Surficial), and
- TRT 5) 5 g L^{-1} SBP plus 0.16 g L^{-1} CaO_2 applied to the surface (10% Surficial).

There were three replicates of each treatment, and VOC emissions were measured at times of 0.02, 1, 2, 4, 7, 10, and 14 d following application.

REAGENTS, SOYBEAN PEROXIDASE, AND SWINE MANURE
The SBP used in this study was an industrial grade product (Cat. No. X516-IND; Bio-Research Products Inc., North Liberty, Iowa) and consisted of a reddish-tan, fine powder with a reported nominal activity of 0.77 U mg^{-1} (U=guaiacol activity units). Powdered calcium peroxide (20%, American Chemical Society grade) was obtained from Fisher Scientific (St. Louis, Mo.).

Swine manure was collected from a barn at the USDA-ARS U.S. Meat Animal Research Center in Clay Center, Nebraska. The mechanically-ventilated gestation barn had 470 m^2 pen surface and a maximum capacity of 288 animals. The manure collection system was shallow-pit with fresh water makeup. At the time of sampling, the barn housed approximately 200 gestating sows with an average weight of 215 kg. The diet was corn-based with soybean meal (82.6% ground corn, 13.7% soybean meal, and supplements).

VOC CONCENTRATION AND FLUX MEASUREMENT
Each 7.6 L plastic container was initially filled with 3.8 L of swine slurry, such that half of the container was slurry and half was headspace. The enclosed cylindrical plastic containers had dimensions of 22.0 cm diameter and 20.0 cm height, with a swine slurry surface area of 0.038 m^2. Sweep air entered the container through a port in the center of the lid. The entrance port had 6.35 mm-O.D. Teflon tubing approximately 9 cm long inside the container to release air just above the surface. To assist in mixing, the tubing was sealed on the bottom with a setscrew, and four 1.6 mm holes were drilled at right angles to move air equally in all four directions. Exhaust air was sampled at a point 5.5 cm downstream from the outside of the lid. Sweep air was passed continuously through the headspace at a rate of 1 L/min to assure adequate mixing in the headspace. Fresh swine slurry was added daily to each container (38 mL, equivalent to 1% of initial volume), and the slurry was gently mixed for 20 s to simulate the small amount of mixing that occurs in the shallow pit from rising gas bubbles. The stirring apparatus was inserted through the surface each day in the same location to prevent disrupting the surface more than necessary. The sweep air flow rate was kept constant over the 14 d evaluation period, while the headspace decreased slightly each day as additional manure was added. The initial sweep air exchange rate was 15.7 exchanges h^{-1}, and increased to 18.3 exchanges h^{-1} at

14 d, which approximated exchange rates in the shallow pit of the swine barn.

Prior to entering the containers, the sweep air was passed through activated carbon and Drierite[TM] filters to remove VOCs and moisture (fig. 2). The sweep air was verified as VOC-free through GC-MS analyses. The sweep air flow rate in each container was controlled using a dedicated valved rotameter with scale of 0 to 1.2 L min^{-1} and standard accuracy of ±5% of full scale (Omega Engineering, Stamford, Conn.). Because VOC flux is linearly correlated to sweep air flow rate (Parker et al., 2013b), similar uncertainties (±5%) would be expected for individual VOC flux measurements.

A fraction of the air exiting the container was sampled using stainless steel sorbent tubes (89 mm × 6.4 mm OD) packed with 200 mg Tenax TA® sorbent. Conditioned and capped tubes were purchased new from the manufacturer (Markes International Inc., Wilmington, Del.). Prior to first use, tubes were conditioned for 2 h at 230°C and verified to be clean before sampling. Air was pulled by vacuum through the sorbent tubes at a flow rate of 75 mL min^{-1} for 8 min for a sample volume of 600 mL using a vacuum pump (Pocket pump 210 series, SKC Inc., Eighty Four, Pa.). All sampling was conducted in a temperature- and humidity-controlled chamber at 50% RH and 21.0°C. The initial air sampling was conducted 30 min (0.02 d) after the treatments were applied. Subsequent air sampling was conducted on d 1, 2, 4, 7, 10, and 14. Each air sampling was conducted 3 h after the daily addition of swine slurry. Two sorbent tubes were collected from each container during each sampling period.

GC/MS with Thermal Desorption

Sorbent tube samples were analyzed using a thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) system. The TD system consisted of a Markes Unity 2 thermal desorber with Ultra 2 autosampler (Markes International Inc., Wilmington, Del.). Samples were quantified with an Agilent 7890A GC with Agilent 5975C MS (Agilent Technologies, Inc., Santa Clara, Calif.).

In the TD system, samples were initially purged for 2 min (40 mL min^{-1}, 20°C) to remove water and air. The tube was desorbed for 10 min at 280°C with a carrier gas flow of 50 mL min^{-1} and trapped on the cold trap maintained at -10°C. The cold trap was heated to 320°C for 3 min with a carrier gas flow of 20 mL min^{-1}, and 1.4 mL min^{-1} was transferred to the column in the GC-MS. In the GC oven, the column was held at 40°C for 3 min, ramped to 230°C at 8°C min^{-1}, then held at 230°C for 5 min for a total run time of 31.8 min. The polar analytical column was an Agilent Innowax, 30 m × 0.25 mm ID capillary column (polyethylene glycol, 0.25 μm film thickness).

Standards and Calibration

Samples were analyzed for eight VFAs (acetic, propionic, isobutyric, butyric, isovaleric, valeric, hexanoic, heptanoic), three phenolics (phenol, 4-methylphenol, 4-ethylphenol), two indolics (indole, skatole), and two sulfides (dimethyl disulfide, DMDS; dimethyl trisulfide, DMTS). Standard solutions were prepared by diluting known masses of pure chemicals with methanol. Standards were prepared using serial dilutions, and injected onto clean tubes using a calibration solution loading rig (CSLR; Markes International Inc., Wilmington, Del.). The liquid calibration standard was
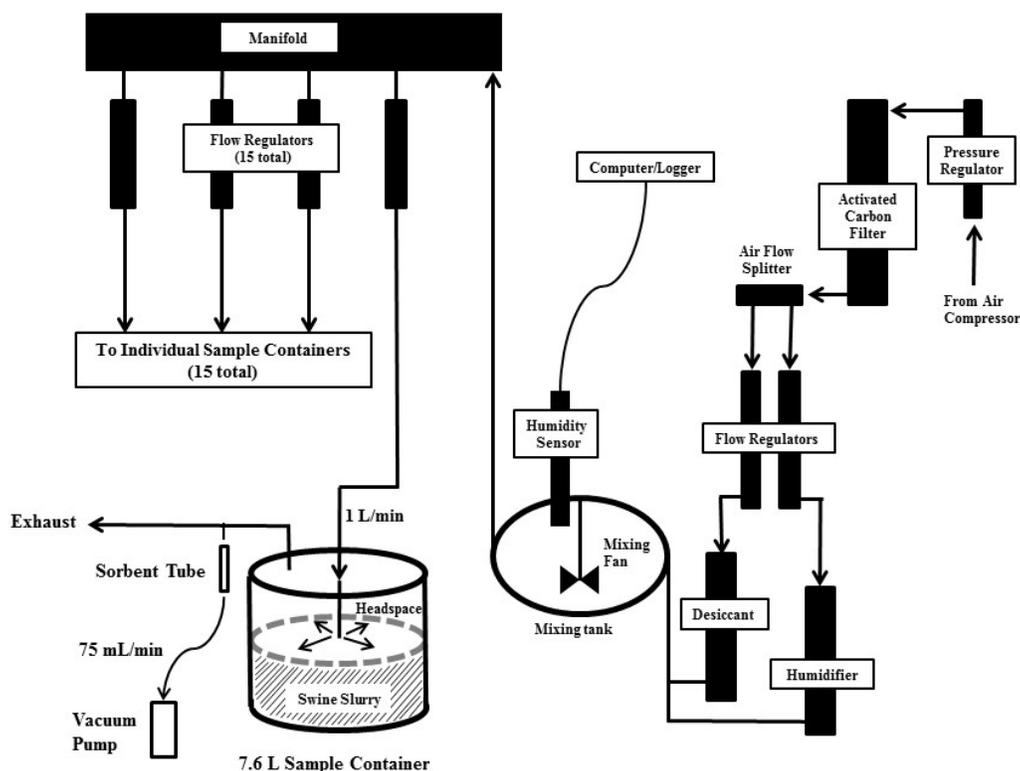

Figure 2. Schematic of the sampling system used to measure VOC emissions from swine slurry.

introduced through the CSLR injector septum in clean bottled air carrier gas (75 mL min^{-1}) using a standard GC syringe. Within the linear range, standard curves were fit using linear regression with the curve forced through the origin.

All sorbent tubes were conditioned with the TD system and analyzed on the GC-MS prior to sampling to verify that clean tubes were used in the experiment. Regression slopes and r^2 values for each compound are shown in table 1. All standard curves were linear throughout the range shown in table 1.

STATISTICAL ANALYSIS

The data were analyzed as a CRD with repeated measures in time using the SAS MIXED Procedure (SAS Inst. Inc., Cary, N.C.). Fixed effects were treatment, replicate, time, and the treatment × time interaction. Replicate × treatment was the subject of the repeated measures, and several covariance structures were tested. The covariance structure resulting in the smallest Akaike and Schwarz Bayesian criteria was considered most appropriate for analysis. When significant (P ≤ 0.05) treatment × time interactions were detected using single-degree-of-freedom F-tests, pairwise comparisons of the simple-effects means were conducted within the PDIFF option of SAS.

ODOR ACTIVITY VALUE

Odor activity values (OAV), defined as the ratio of the concentration of a compound to the human odor detection threshold (ODT) for that compound (Guadagni et al., 1963; Leffingwell and Leffingwell, 1991; Parker et al., 2012b; Zhang et al., 2015), were calculated to assess the relative importance of individual chemical compound reductions (or increases) on odor. Compounds with large OAVs are more likely to contribute to the overall odor of a complex odor mixture. Odor activity values were calculated using the geometric mean odor detection thresholds (ODT) as summarized in the comprehensive review presented in Parker et al. (2012b). The relative contribution of each compound was calculated by dividing the OAV for the individual compound by the sum of the OAVs for all compounds (Guadagni et al., 1963; Leffingwell and Leffingwell, 1991).

RESULTS AND DISCUSSION

STATISTICAL COMPARISONS

The treatment × time interactions were significant (P ≤ 0.05) for all compounds. Therefore, only the treatment × time means were statistically compared. Mean emission rates for each compound and time period are presented in table 2. Because of the significant treatment × time interactions, comparisons between time periods or between compounds were not statistically appropriate and therefore were not conducted.

PHENOLIC AND INDOLIC COMPOUNDS

The OAV analysis revealed that the primary odorous compounds were among the five phenolic and indolic compounds, which accounted for 83% to 98% of the summed OAV. The two compounds 4-methylphenol and skatole alone accounted for summed OAVs of 35-235 (fig. 3a), and 79%-97% of the overall OAV (fig. 3b).

The 50% and 100% surficial treatments (TRT 3 and 4) had the greatest reduction in overall OAV (fig. 3a), primarily because of the 80% and 86% reduction in 4-methylphenol for these two treatments, respectively. These reductions in 4-methylphenol emissions are comparable to those of Parker et al. (2012a), who reported 92% reduction in 4-methylphenol after 2 d for SBP+CaO$_2$ in a fully-mixed application. Similarly, Ye et al. (2009) reported almost complete reduction in 4-methylphenol for up to 2 d after application when swine slurry was surface sprayed with purified horseradish peroxidase and peroxide solutions.

The SBP+CaO$_2$ treatment effect was most evident at 4 d after application, when all of the treatments had statistically lower 4-methylphenol emission rates than the control (table 2). This trend continued on d 7 and 10 (fig. 4a), but no statistical difference was measured between the treatments and the control on these days because of the variability among replicates.

The SBP+CaO$_2$ treatment had limited effect on phenol emissions. This same phenomenon was observed in Parker

Table 1. Summary of compounds quantified by GC/MS in the study, linear range and regression statistics for standard curves.

Compound	MW[a]	Retention Time (min)	Linear Range (ng)	Linear Regression Slope	Linear Regression (r^2)	Odor Detection Threshold[b] (µg m^{-3})
Phenol	94.1	20.2	5.7-1105	1.31E-04	0.99	206
4-Methylphenol	108.1	21.1	5.2-1045	1.37E-04	0.97	1.3
4-Ethylphenol	122.2	22.2	5.2-1055	8.50E-05	0.97	6.3
Indole	117.1	25.2	6.3-1283	6.60E-05	0.99	2.1
Skatole	131.2	25.6	7.1-722	4.30E-05	0.97	0.48
Acetic acid	60.0	12.4	2.6-2602	8.18E-04	0.99	578
Propanoic acid	74.1	13.8	2.5-2485	7.58E-04	0.99	106
Isobutyric acid	88.1	14.2	2.3-2344	4.53E-04	0.99	38
Butyric acid	88.1	15.1	2.4-2401	2.94E-04	0.99	6.9
Isovaleric acid	102.1	15.7	2.3-2290	2.69E-04	0.99	2.3
Valeric acid	102.1	16.7	2.3-2342	2.51E-04	0.99	8.8
Hexanoic acid	116.2	18.1	2.3-2348	2.97E-04	0.98	69
Heptanoic acid	130.2	19.5	2.3-2278	3.57E-04	0.98	60
Dimethyl disulfide	94.2	5.2	2.4-1281	1.83E-04	0.99	12
Dimethyl trisulfide	126.2	11.0	0.4-587	1.83E-04	0.99	2.0

[a] MW=molecular weight.
[b] Geometric mean odor detection thresholds from Parker et al. (2012b).

Table 2. Least squares means (µg m^{-2} min^{-1}) for the control with no additives (TRT 1), 50 g L^{-1} soybean peroxidase (SBP) mixed throughout (100% Mixed; TRT 2), 50 g L^{-1} SBP applied to the surface (100% Surficial; TRT 3), 25 g L^{-1} SBP applied to the surface (50% Surficial; TRT 4), and 5 g L^{-1} SBP applied to the surface (10% Surficial; TRT 5).

Compound	Treatment	Time Since Application of Treatment (Days)[a]						
		0.02 d	1 d	2 d	4 d	7 d	10 d	14 d
4-methylphenol	Control (TRT 1)	29 a	1.1 a	0.43 ab	0.31 a	0.54 a	1.49 a	0.28 b
4-methylphenol	100% Mixed (TRT 2)	28 a	0.56 ab	0.15 c	0.04 b	0.13 a	0.94 a	0.38 b
4-methylphenol	100% Surficial (TRT 3)	1.5 c	0.33 b	0.52 a	0.10 b	0.077 a	0.73 a	3.4 a
4-methylphenol	50% Surficial (TRT 4)	2.1 c	0.16 b	0.20 bc	0.027 b	0.077 a	0.75 a	1.2 b
4-methylphenol	10% Surficial (TRT 5)	22 b	0.44 b	0.17 c	0.12 b	0.053 a	0.35 a	3.9 a
Phenol	Control (TRT 1)	0.72 a	0.47 a	0.26 a	0.33 a	0.50 a	0.34 b	0.37 b
Phenol	100% Mixed (TRT 2)	0.72 a	0.32 a	0.30 a	0.32 a	0.34 a	0.46 b	0.37 b
Phenol	100% Surficial (TRT 3)	0.31 a	0.20 a	0.40 a	0.37 a	0.54 a	1.4 a	2.44 a
Phenol	50% Surficial (TRT 4)	0.46 a	0.25 a	0.41 a	0.10 a	0.60 a	1.3 a	1.0 b
Phenol	10% Surficial (TRT 5)	0.62 a	0.41 a	0.34 a	0.20 a	0.33 a	0.28 b	0.57 b
4-ethylphenol	Control (TRT 1)	0.93 a	0.42 a	0.085 a	0.081 a	0.087 a	0.21 a	0.12 c
4-ethylphenol	100% Mixed (TRT 2)	0.78 a	0.095 b	0.024 b	0.007 b	0.010 b	0.070 b	0.27 b
4-ethylphenol	100% Surficial (TRT 3)	0.039 c	0.022 b	0.059 b	0.020 b	0.014 ab	0.069 b	0.41 a
4-ethylphenol	50% Surficial (TRT 4)	0.062 c	0.022 b	0.041 b	0.009 b	0.010 b	0.067 b	0.21 b
4-ethylphenol	10% Surficial (TRT 5)	0.57 b	0.14 b	0.033 b	0.036 b	0.008 b	0.028 b	0.43 a
Indole	Control (TRT 1)	0.29 a	0.048 a	0.028 a	0.021 a	0.021 a	0.080 ab	0.082 b
Indole	100% Mixed (TRT 2)	0.25 a	0.12 a	0.060 a	0.026 a	0.019 a	0.11 a	0.014 b
Indole	100% Surficial (TRT 3)	0.032 b	0.026 a	0.045 a	0.010 a	0.023 a	0.13 a	0.42 a
Indole	50% Surficial (TRT 4)	0.044 b	0.037 a	0.040 a	0.011 a	0.012 a	0.16 a	0.34 a
Indole	10% Surficial (TRT 5)	0.24 a	0.085 a	0.023 a	0.025 a	0.007 a	0.012 b	0.020 b
Skatole	Control (TRT 1)	1.2 a	2.0 a	1.11 a	1.3 a	0.31 a	1.2 a	1.4 ab
Skatole	100% Mixed (TRT 2)	0.57 b	0.36 b	0.12 b	0.14 b	0.018 b	0.20 b	0.90 bc
Skatole	100% Surficial (TRT 3)	0.08 c	0.051 b	0.12 b	0.098 b	0.025 b	0.33 b	1.9 a
Skatole	50% Surficial (TRT 4)	0.10 c	0.056 b	0.16 b	0.055 b	0.022 b	0.26 b	0.77 c
Skatole	10% Surficial (TRT 5)	0.65 b	1.8 a	0.24 b	0.097 b	0.019 b	0.082 b	1.0 bc
VFAs	Control (TRT 1)	7.5 a	3.1 a	2.7 a	2.6 a	2.5 a	1.8 a	1.3 a
VFAs	100% Mixed (TRT 2)	2.6 b	3.1 a	3.9 a	2.2 ab	1.6 a	1.8 a	1.9 a
VFAs	100% Surficial (TRT 3)	2.2 b	2.0 ab	3.3 a	1.2 b	1.8 a	0.88 b	2.0 a
VFAs	50% Surficial (TRT 4)	3.2 b	1.9 ab	2.5 a	1.3 b	2.8 a	1.3 ab	2.2 a
VFAs	10% Surficial (TRT 5)	1.9 b	1.6 b	3.2 a	2.0 ab	2.1 a	1.7 ab	2.2 a
Sulfides	Control (TRT 1)	0.21 a	0.04 a	0.14 a	0.67 a	0.99 c	0.71 b	0.67 ab
Sulfides	100% Mixed (TRT 2)	0.24 a	0.20 a	0.83 a	1.3 a	1.1 c	0.44 b	0.43 b
Sulfides	100% Surficial (TRT 3)	0.11 a	0.12 a	0.080 a	0.50 a	10 a	2.0 a	1.4 a
Sulfides	50% Surficial (TRT 4)	0.14 a	0.12 a	0.074 a	0.68 a	4.6 b	1.4 a	0.61 ab
Sulfides	10% Surficial (TRT 5)	0.50 a	0.12 a	0.26 a	1.3 a	0.80 c	0.32 b	0.24 b

[a]   a, b, c   Means within a column (for a specific compound and time period only), with different letters differ (P≤0.05).

et al. (2012a) for both aqueous solutions of phenol+4-methylphenol and swine slurry. In terms of odor control, the targeting of 4-methylphenol is a benefit because the ODT for 4-methylphenol is about 160× lower than that for phenol. Thus, in terms of overall odor reduction success, the reduction of 4-methylphenol emissions is more important than reduction of phenol emissions. Phenol emission rates increased considerably at d 10 and 14 for the two highest surficial rates (TRT 3 and 4) (fig. 4b), but the overall effect on the OAV was minimal.

The emission rates of 4-ethylphenol were significantly lower in all SBP+CaO$_2$ treatments at all sampling periods except for 14 d (table 2, fig. 4c). The overall importance of 4-ethylphenol emissions is somewhat unknown because of limited information on its odor threshold. A single reference quotes an odor threshold for 4-ethylphenol about 5× higher than the geometric mean threshold for 4-methylphenol (Parker et al., 2012b). At the 4-ethylphenol concentrations observed in this research, 4-ethylphenol accounted for less than 1% of the overall OAV. Nevertheless, the statistically significant reductions of both

4-methylphenol and 4-ethylphenol is a promising observation related to the overall odor reduction efficacy of SBP+CaO$_2$ and the preeminence of 4-methylphenol as the characteristic downwind odorant of livestock facilities (Wright et al., 2005; Bulliner et al., 2006; Koziel et al., 2006).

The SBP+CaO$_2$ treatment reduced the indole emissions for the first 24 h, but had little effect on indole past that time (fig. 4d). However, SBP+CaO$_2$ treatment had a more pronounced effect on reduction of skatole emissions, with statistically significant reduction at all time periods except for d 14 (table 2, fig. 4e). Given that the odor threshold for skatole is about 4× less than that of indole, the significant reductions in skatole emissions is fortuitous to overall odor reduction.

Overall, both the fully-mixed (TRT 2) and surface-applied (TRT 3-5) applications of SBP+CaO$_2$ were effective at reducing 4-methylphenol and skatole emissions for up to 10 d. The 5 g L^{-1} surface-applied (10% Surficial) application was as effective as the 50 g L^{-1} surface-applied (100% Surficial) and 50 g L^{-1} fully-mixed (100% Mixed)
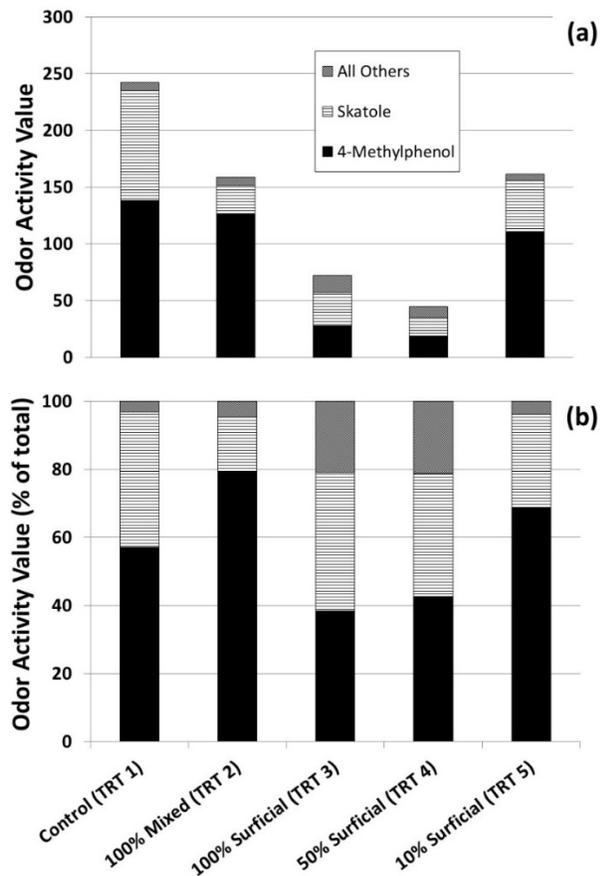
Figure 3. A comparison of average odor activity value (OAV) among treatments over the 14-d experiment, showing the calculated total OAVs (top) and the relative OAV as a percentage of the summed OAVs of all compounds (bottom). The OAV was dominated by 4-methylphenol and skatole.

application rates for up to 10 d (P<0.05). For this reason, future pilot- and field-scale research with SBP on swine manure slurry should focus on this lower rate of surface application. Most of the phenolic and indolic emission rates were greater than the control on d 14, indicating the need for reapplication of SBP+CaO$_2$ every 4 to 7 d. In a shallow pit system with fresh water makeup where the pit is drained every seven days, application would probably be required twice over the 7 d period.

VOLATILE FATTY ACIDS

The VFA emission rates were considerably lower than the phenolic and indolic emissions. The summed VFAs impact only accounted for 0.9% to 3.5% of the OAV, an indication that the VFAs did not contribute appreciably to the overall odor of the swine slurry (fig. 3). The VFAs were dominated by butyric and isovaleric acids, which accounted for about 67% of all the VFAs. This differed from the VFA emissions reported by Parker et al. (2012a), where the swine manure VFA emissions were dominated by acetic, propionic, and butyric acids. Others have reported acetic

acid as the dominant VFA in swine manure as well (Spoelstra, 1980; Conn et al., 2007), but acetic acid was not the most prevalent VFA in this research. Researchers have reported variation in VOC emissions from swine manure depending on type of operation, manure storage type, age of manure, and differing diets. Conn et al. (2007) showed a considerable difference in manure chemistry among three operation types of finishing, sow, and mixed. Likewise, emissions of VFA and odor from swine manure are affected by diet (Miller and Varel, 2003; Shriver et al., 2003; Velthof et al., 2005; Leek et al., 2007).

The total VFA emissions were about two orders of magnitude lower in this latest experiment than was reported in Parker et al. (2012a). Given that the manure collection system was a shallow-pit with fresh water makeup, it is possible that the sampling time since application of the fresh water was different between the two studies.

The pH of the manure was measured on d 3, 10, and 14. The pH of the control was 7.3 on d 3, and the lowest pH was 6.7 in one of the SBP treatments. The pH values increased slightly on d 10 and 14. For comparison, the pH of the control in our earlier research was 6.0 and decreased to 5.1 after 2 d (Parker et al., 2012a). The pH of the manure in this latest experiment was about 2 pH units higher than the previous experiment. Since VFAs are more volatile in their non-ionized form at lower pH values, the difference in VFA emissions between the two experiments was likely due to differences in manure pH (Miller and Berry, 2005).

The SBP+CaO$_2$ treatments had marginal long-term effect on VFA emissions as compared to the control (table 2). All of the SBP+CaO$_2$ treatments had a VFA reduction of about 60% for the first 24 h, but the effect did not last past d 1 (fig. 4f). There was little difference in VFA emissions among the three rates of surface treatment.

SULFIDES

While SBP+CaO$_2$ treatment reduced the 4-methylphenol emissions, it had limited effect on the sulfides. This is not surprising, given that the enzymatic treatment focuses on aromatic compounds and not sulfides (Steevensz et al., 2014). The SBP+CaO2 treatment first converts the aromatic compounds to free radicals, which are then combined to form dimers. Because most sulfur-containing odorous compounds emitted from animal manures are not aromatics, the likelihood of SBP+CaO$_2$ treatment having a positive odor-reducing effect due to dimerization is negligible.

There was little difference in sulfide emissions among the treatments for the first four d. For an unknown reason, there was a spike in the sulfide emissions on d 7 and 10 for the two highest surface-applied treatments only (TRT 3 and 4; fig. 4g, 3h). The average OAVs for the two sulfides ranged from 2 to 11, which accounted for a maximum of 15% of the overall OAV.
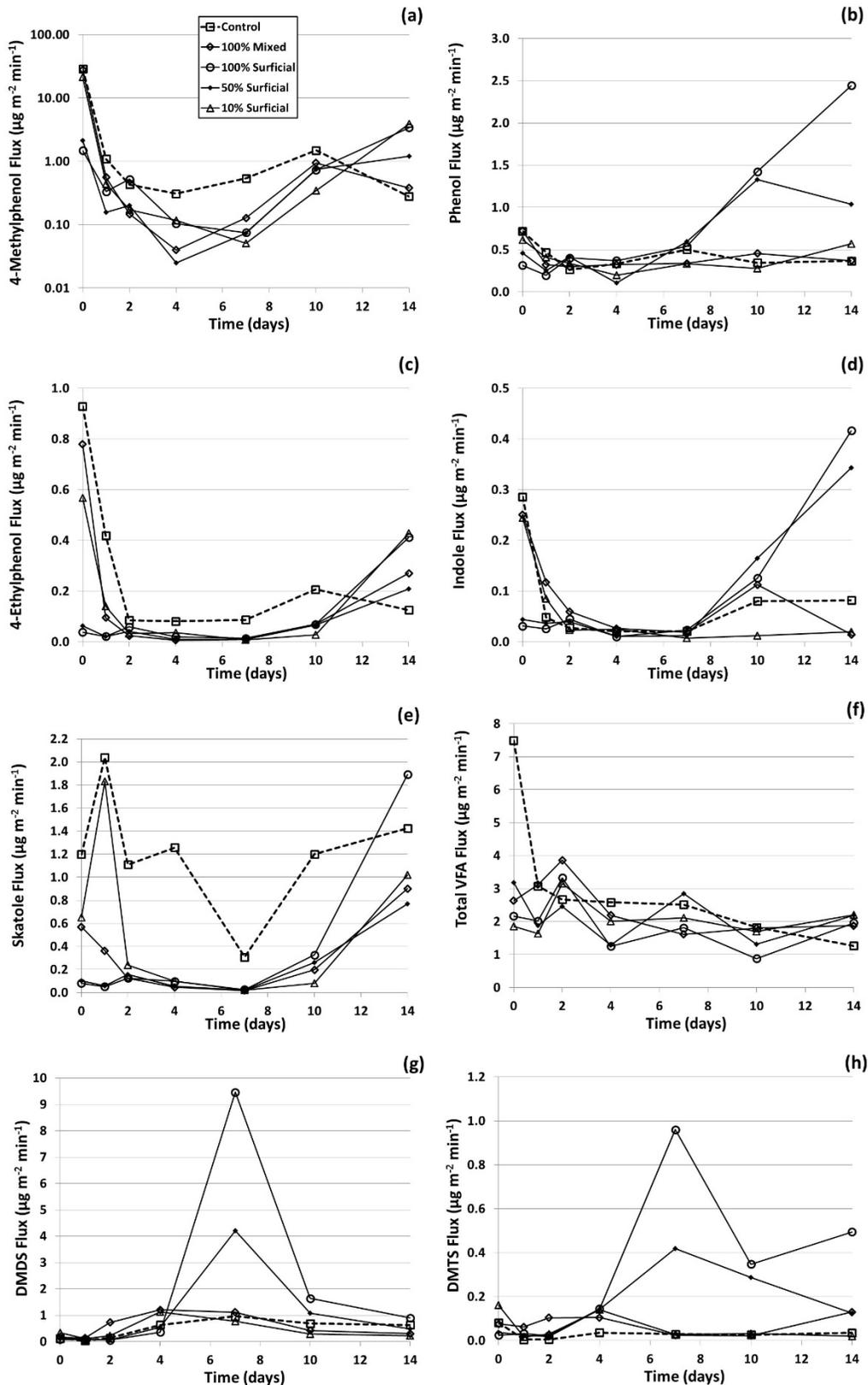
Figure 4. Lux of odorous compounds over the 14-d time period for the control (TRT 1); fully-mixed rate at 50 g L^{-1} SBP (100% Mixed, TRT 2); 50 g L^{-1} rate surface-applied (100% Surficial, TRT 3); 25 g L^{-1} rate surface-applied (50% Surficial, TRT 4); and 5 g L^{-1} rate surface-applied (10% Surficial, TRT 5).

The measured DMDS emissions were about 8× that of DMTS emissions (fig. 4g, 4h). Cai et al. (2015) also reported higher DMDS than DMTS in a swine finisher barn, but cautioned about potential interference with methanethiol when using thermal desorption to measure sulfide compounds. While the sulfides are presented as DMDS and DMTS in this research, other researchers have demonstrated that both DMDS and DMTS can be produced when methanethiol is heated to approximately 300°C in a thermal desorption system (Andersen et al., 2012). For this reason, with the current thermal desorption system, there is no way to determine whether the VOC originated as methanethiol, DMDS, DMTS, or in combination. The geometric mean odor threshold for methanethiol is about 5× and 31× lower than DMTS and DMDS, respectively, which would result in OAV 5× to 31× higher if the odor originated from methanethiol instead of DMDS or DMTS (Woodbury et al., 2015). If all of the DMDS and DMTS originated from methanethiol, the OAV would range from 48 to 203, and would potentially account for up to 77% of the OAV. Mean DMDS and DMTS concentrations among all treatments over the 14 d experiment were 32 and 4.6 $\mu g\ m^{-3}$, which are in the same range as the methanethiol concentrations measured at a research swine barn exhaust and reported by Feilberg et al. (2010), who measured methanethiol concentrations up to 10 ppbv (20 $\mu g\ m^{-3}$) using the PTR-MS method which is not affected by thermal conversion.

Given that we personally observed a notable reduction in odor for the SBP treatments on this project and that of Parker et al. (2012a), we believe it unlikely that a majority of the DMDS and DMTS originated from methanethiol in the thermal desorption process. If all of the DMDS and DMTS originated from methanethiol, then it is unlikely that the reduction in 4-methylphenol emissions would have been apparent to the human nose, as the methanethiol would have likely overwhelmed the other compounds in the mix. It is possible that CaO_2 could oxidize some methanethiol in the manure to produce DMDS and DMTS prior to thermal desorption. Nevertheless, further research on this subject is warranted to definitively quantify the sulfides sources and their final products. It is evident that SBP+CaO_2 was not effective in treating sulfide emissions, thus this treatment would not be appropriate for swine manures which are known to be dominated by sulfide emissions (such as some deep pit management systems).

SAFETY AND ECONOMICS

As discussed previously, soybean peroxidase is a fine organic powder similar to grain dust, which can be explosive if suspended in air and ignited. Therefore, soybean peroxidase should be applied with minimal air dispersion. Also, because CaO_2 can be ignited by grinding (FMC, 2009), the CaO_2 should always be added after grinding the soybean hulls.

The use of highly purified SBP such as that discussed in Hailu et al. (2010) is cost-prohibitive at this point, as the cost to treat the manure from a single pig would exceed $100 USD (Parker et al., 2012a). The use of ground soybean hulls would be more economical. As discussed in

Steevensz et al. (2013), there is a wide variation in SBP enzyme activity among soybean cultivars. Selection of soybean hulls with high enzyme activity, together with self-grinding at or near the swine farm, could reduce the cost of SBP+CaO_2 treatment.

OPPORTUNITIES FOR FUTURE RESEARCH

We have shown that surface application of SBP+CaO_2, at a rate 10% of the fully-mixed rate reported in Parker et al. (2012a), is effective in reducing odors from swine slurry in a laboratory setting. Future studies are warranted at pilot- and field-scale, and using more manure with greater odor potential to simulate deep pit storage, to optimize and test this promising treatment technology. Research on appropriate application methods at the field-scale is also needed. Engineering protocols need to be developed to apply the SBP+CaO_2 safely and uniformly over the manure surface in the deep-pit area.

CONCLUSIONS

Surface-applied and fully-mixed applications of SBP+CaO_2 were equally effective at reducing emissions of odorous VOCs from swine slurry for up to 10 d. Of the phenolic and indolic compounds, the SBP+CaO_2 treatment was most effective in reducing concentrations of 4-methylphenol and skatole, which together accounted for 79% to 97% of the OAV. The surface-applied treatment of SBP+CaO_2 appears to be a promising technology for reducing odor emissions from swine manure collected from a shallow-pit system with fresh water makeup. The SBP+CaO_2 treatment was effective in reducing odors for 10 d. Reapplication of SBP+CaO_2 will likely be required every 4 to 7 d. Future pilot- and field-scale research should focus on surface application of SBP+CaO_2 at a rate equal to 10% of the fully-mixed rate, with additional testing in deep pit swine barns.

REFERENCES

Akdeniz, N., Koziel, J. A., Ahn, H.-K., Glanville, T. D., & Crawford, B. P. (2010). Field scale evaluation of volatile organic compound production inside biosecure swine mortality composts. *Waste Manag., 30*(10), 1981-1988. http://dx.doi.org/10.1016/j.wasman.2010.05.022

Andersen, K. B., Hansen, M. J., & Feilberg, A. (2012). Minimisation of artefact formation of dimethyl disulphide during sampling and analysis of methanethiol in air using solid sorbent materials. *J. Chromatogr. A, 1245*, 24-31. http://dx.doi.org/10.1016/j.chroma.2012.05.020

Bratsch, A. (2009). Specialty crop profile: Horseradish. Virginia Coop. Ext., Publ. 438-104. Virginia Polytechnic Institute and State University. Retrieved from http://pubs.ext.vt.edu/438/438-104/438-104_pdf.pdf

Bulliner, E. A., Koziel, J. A., Cai, L., & Wright, D. (2006). Characterization of livestock odors using steel plates, solid-phase microextraction, and multidimensional gas chromatography-mass spectrometry-olfactometry. *J. Air & Waste Manag. Assoc., 56*(10), 1391-1403. http://dx.doi.org/10.1080/10473289.2006.10464547

Cai, L., Koziel, J. A., Davis, J., Lo, Y.-C., & Xin, H. (2006). Characterization of volatile organic compounds and odors by in-vivo sampling of beef cattle rumen gas, by solid-phase microextraction, and gas chromatography-mass spectrometry-olfactometry. *Anal. Bioanal. Chem., 386*(6), 1791-1802. http://dx.doi.org/10.1007/s00216-006-0799-1

Cai, L., Koziel, J. A., Zhang, S., Heber, A. J., Cortus, E. L., Parker, D.,... Lim, T. T. (2015). Odor and odorous chemical emissions from animal buildings: Part 3. Chemical emissions. *Trans. ASABE, 58*(5), 1333-1347. http://dx.doi.org/10.13031/trans.58.11199

CAQCC. (1999). Colorado Air Quality Control Commission Regulation No. 2.

Caza, N., Bewtra, J. K., Biswas, N., & Taylor, K. E. (1999). Removal of phenolic compounds from synthetic wastewater using soybean peroxidase. *Water Res., 33*(13), 3012-3018. http://dx.doi.org/10.1016/S0043-1354(98)00525-9

Chen, L., Hoff, S. J., Koziel, J. A., Cai, L., Zelle, B., & Sun, G. (2008). Performance evaluation of a wood-chip based biofilter using solid-phase microextraction and gas chromatography-mass spectroscopy-olfactometry. *Bioresour. Technol., 99*(16), 7767-7780. http://dx.doi.org/10.1016/j.biortech.2008.01.085

Chen, Y., Bundy, D. S., & Hoff, S. J. (1999). Using olfactometry to measure intensity and threshold dilution ratio for evaluating swine odor. *J. Air & Waste Manag. Assoc., 49*(7), 847-853. http://dx.doi.org/10.1080/10473289.1999.10463855

Conn, K. L., Topp, E., & Lazarovits, G. (2007). Factors influencing the concentration of volatile fatty acids, ammonia, and other nutrients in stored liquid pig manure. *JEQ, 36*(2), 440-447. http://dx.doi.org/10.2134/jeq2006.0222

Feilberg, A., Dorno, N., & Nyord, T. (2010). Odour emissions following land spreading of animal slurry assessed by proton-transfer-reaction mass spectrometry (PTR-MS). *Chem. Eng. Trans., 23*, 111-116.

Flock, C., Bassi, A., & Gijzen, M. (1999). Removal of aqueous phenol and 2-chlorophenol with purified soybean peroxidase and raw soybean hulls. *J. Chem. Technol. Biotechnol., 74*(4), 303-309. http://dx.doi.org/10.1002/(SICI)1097-4660(199904)74:4<303::AID-JCTB38>3.0.CO;2-B

FMC. (2009). Material safety data sheet, calcium peroxide. FMC Corp., CAS No. 1305 79 9. Retrieved from http://msdsviewer.fmc.com/

Gijzen, M., van Huystee, R., & Buzzell, R. I. (1993). Soybean seed coat peroxidase: A comparison of high-activity and low-activity genotypes. *Plant Physiol., 103*(4), 1061-1066. http://dx.doi.org/10.1104/pp.103.4.1061

Govere, E. M., Tonegawa, M., Bruns, M. A., Wheeler, E. F., Kephart, K. B., Voigt, J. W., & Dec, J. (2007). Using minced horseradish roots and peroxides for the deodorization of swine manure: A pilot scale study. *Bioresour. Technol., 98*(6), 1191-1198. http://dx.doi.org/10.1016/j.biortech.2006.05.012

Guadagni, D. G., Buttery, R. G., Okano, S., & Burr, H. K. (1963). Additive effect of sub-threshold concentrations of some organic compounds associated with food aromas. *Nature, 200*(4913), 1288-1289.

Hailu, G., Weersink, A., & Cahlik, F. (2010). Examining the prospects for commercialization of soybean peroxidase. *AgBioForum, 13*, 263-273.

Kai, P., & Schafer, A. (2004). Identification of key odour components in pig house air using hyphenated gas chromatography olfactometry. *Agric. Eng. Int.: CIGR J. Sci. Res. Dev., 6*, 1-11.

Koziel, J. A., Cai, L., Wright, D. W., & Hoff, S. J. (2006). Solid-phase microextraction as a novel air sampling technology for improved, GC-olfactometry-based assessment of livestock odors. *J. Chromatogr. Sci., 44*(7), 451-457. http://dx.doi.org/10.1093/chromsci/44.7.451

Leek, A. B. G., Hayes, E. T., Curran, T. P., Callan, J. J., Beattie, V. E., Dodd, V. A., & O'Doherty, J. V. (2007). The influence of manure composition on emissions of odour and ammonia from finishing pigs fed different concentrations of dietary crude protein. *Bioresour. Technol., 98*(18), 3431-3439. http://dx.doi.org/10.1016/j.biortech.2006.11.003

Leffingwell, J. C., & Leffingwell, D. (1991). GRAS flavor chemicals-detection thresholds. *Perfumer & Flavorist, 16*(1), 1-19.

Lo, Y.-C. M., Koziel, J. A., Cai, L., Hoff, S. J., Jenks, W. S., & Xin, H. (2008). Simultaneous chemical and sensory characterization of VOCS and semi-VOCS emitted from swine manure using SPME and multidimensional gas chromatography-mass spectrometry-olfactometry system. *JEQ, 37*(2), 521-534. http://dx.doi.org/10.2134/jeq2006.0382

Masuda, T., & Goldsmith, P. D. (2009). World soybean production: Area harvested, yield, and long-term projections. *Int. Food and Agribusiness Manag. Rev., 12*(4), 143-162.

Mata-Alvarez, J., Mace, S., & Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresour. Technol., 74*(1), 3-16. http://dx.doi.org/10.1016/S0960-8524(00)00023-7

Miller, D. N., & Berry, E. D. (2005). Cattle feedlot soil moisture and manure content: I. Impacts on greenhouse gases, odor compounds, nitrogen losses, and dust. *JEQ, 34*(2), 644-655. http://dx.doi.org/10.2134/jeq2005.0644

Miller, D. N., & Varel, V. H. (2003). Swine manure composition affects the biochemical origins, composition, and accumulation of odorous compounds. *J. Anim. Sci., 81*(9), 2131-2138.

Morawski, B., Quan, S., & Arnold, F. H. (2001). Functional expression and stabilization of horseradish peroxidase by directed evolution in Saccharomyces cerevisiae. *Biotechnol. Bioeng., 76*(2), 99-107. http://dx.doi.org/10.1002/bit.1149

Ni, J.-Q., Robarge, W. P., Xiao, C., & Heber, A. J. (2012). Volatile organic compounds at swine facilities: A critical review. *Chemosphere, 89*(7), 769-788. http://dx.doi.org/10.1016/j.chemosphere.2012.04.061

Parker, D. B. (2008). Reduction of odor and VOC emissions from a dairy lagoon. *Appl. Eng. Agric., 24*(5), 647-655. http://dx.doi.org/10.13031/2013.25272.

Parker, D. B., Cai, L., Kim, K.-H., Hales, K. E., Spiehs, M. J., Woodbury, B. L.,... Patefield, K. D. (2012a). Reducing odorous VOC emissions from swine manure using soybean peroxidase and peroxides. *Bioresour. Technol., 124*, 95-104. http://dx.doi.org/10.1016/j.biortech.2012.08.031

Parker, D. B., Koziel, J. A., Cai, L., Jacobson, L. D., Akdeniz, N., Bereznicki, S. D.,... Hetchler, B. P. (2012b). Odor and odorous chemical emissions from animal buildings: Part 6. Odor activity value. *Trans. ASABE, 55*(6), 2357-2368. http://dx.doi.org/10.13031/2013.42498

Parker, D. B., Gilley, J., Woodbury, B. L., Kim, K.-H., Galvin, G., Bartelt-Hunt, S. L.,... Snow, D. D. (2013a). Odorous VOC emission following land application of swine manure slurry. *Atmos. Environ., 66*, 91-100. http://dx.doi.org/10.1016/j.atmosenv.2012.01.001

Parker, D. B., Ham, J., Woodbury, B., Cai, L., Spiehs, M., Rhoades, M.,... Cole, A. (2013b). Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile organic compound and ammonia emissions from area sources at animal feeding operations. *Atmos. Environ., 66*, 72-83. http://dx.doi.org/10.1016/j.atmosenv.2012.03.068

Redwine, J., & Lacey, R. (2000). A summary of state odor regulations pertaining to confined animal feeding operations. *Proc. 2nd Int. Conf. Air Pollution Agric. Oper.* (pp. 33-41). St. Joseph, MI: ASAE.

Shriver, J. A., Carter, S. D., Sutton, A. L., Richert, B. T., Senne, B. W., & Pettey, L. A. (2003). Effects of adding fiber sources to reduced-crude protein, amino acid-supplemented diets on nitrogen excretion, growth performance, and carcass traits of finishing pigs. *J. Anim. Sci., 81*(2), 492-502.

Spoelstra, S. F. (1980). Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. *Agric. Environ., 5*(3), 241-260. http://dx.doi.org/10.1016/0304-1131(80)90004-1

Steevensz, A., Cordova Villegas, L. G., Feng, W., Taylor, K. E., Bewtra, J. K., & Biswas, N. (2014). Soybean peroxidase for industrial wastewater treatment: A mini review. *J. Environ. Eng. Sci., 9*(3), 181-186. http://dx.doi.org/10.1680/jees.13.00013

Steevensz, A., Madur, S., Al-Ansari, M. M., Taylor, K. E., Bewtra, J. K., & Biswas, N. (2013). A simple lab-scale extraction of soybean hull peroxidase shows wide variation among cultivars. *Ind. Crops Prod., 48*, 13-18. http://dx.doi.org/10.1016/j.indcrop.2013.03.030

Sweeten, J. M. (1995). Odor measurement technology and applications: A state-of-the-art review. In C. C. Ross (Ed.), *7th Int. Symp. Agric. Food Proc. Wastes* (pp. 214-229). St. Joseph, MI: ASAE.

Tonegawa, M., Dec, J., & Bollag, J.-M. (2003). Use of additives to enhance the removal of phenols from water treated with horseradish and hydrogen peroxide. *JEQ, 32*(4), 1222-1227. http://dx.doi.org/10.2134/jeq2003.1222

Velthof, G. L., Nelemans, J. A., Oenema, O., & Kuikman, P. J. (2005). Gaseous nitrogen and carbon losses from pig manure derived from different diets. *JEQ, 34*(2), 698-706. http://dx.doi.org/10.2134/jeq2005.0698

Woodbury, B. L., Gilley, J. E., Parker, D. B., Marx, D. B., & Eigenberg, R. A. (2015). VOC emissions from beef feedlot pen surfaces as affected by within-pen location, moisture and temperature. *Biosyst. Eng., 134*, 31-41.

Wright, D. W., Eaton, D. K., Nielsen, L. T., Kuhrt, F. W., Koziel, J. A., Spinhirne, J. P., & Parker, D. B. (2005). Multidimensional gas chromatography-olfactometry for the identification and prioritization of malodors from confined animal feeding operations. *J. Agric. Food. Chem., 53*(22), 8663-8672. http://dx.doi.org/10.1021/jf050763b

Wu, Y., Taylor, K. E., Biswas, N., & Bewtra, J. K. (1997). Comparison of additives in the removal of phenolic compounds by peroxidase-catalyzed polymerization. *Water Res., 31*(11), 2699-2704. http://dx.doi.org/10.1016/S0043-1354(97)00119-X

Ye, F. X., Zhu, R. F., & Li, Y. (2009). Deodorization of swine manure slurry using horseradish peroxidase and peroxides. *J. Hazard. Mater., 167*(1-3), 148-153. http://dx.doi.org/10.1016/j.jhazmat.2008.12.096

Zhang, S., Koziel, J. A., Cai, L., Hoff, S. J., Heathcote, K. Y., Chen, L.,... Bereznicki, S. D. (2015). Odor and odorous chemical emissions from animal buildings: Part 5. Simultaneous chemical and sensory analysis with gas chromatography-mass spectrometry-olfactometry. *Trans. ASABE, 58*(5), 1349-1359. http://dx.doi.org/10.13031/trans.58.11123