RESEARCHREPORT

ENVIRONMENT

Title: Testing soybean peroxidase for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions – **NPB #12-108**

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Industry Summary

The control of odor, odorous volatile organic compounds (VOCs), hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gases (GHGs) emissions associated with commercial swine production is a critical need. Manure storage is the major source of gaseous emissions. This study aimed for the most comprehensive, to date, assessment of a manure additive for mitigation of gaseous emissions of all major compounds of interest from swine manure. This study assessed *topical* application of manure additive treatment in controlled pilot and farm scales (soybean peroxidase (SBP); product code 516-IND; Bio-Research Products, Inc.). This research builds on the previous published study where SBP product was *mixed* into manure and resulted in significant mitigation of odorous VOCs in lab scale. In this research both pilot and farm scale testing of topical SBP treatment (and ~23.5:1 weight/weight mix of SBP:CaO_2 catalyst) was conducted over ~5 month and ~1.5 month, respectively. Effects of SBP dose and time were tested on pilot scale. The effects of time were tested on farm scale using the lowest SBP dose selected from the pilot study. This work aimed at providing a comprehensive

assessment of SBP treatment efficacy to mitigate emissions of odorous VOCs, odor, H_2S, NH_3, and GHGs, i.e., a set of target gases of concern to swine industry. Results of farm scale testing were, in general consistent with the results of pilot scale controlled tests.

Specifically, farm scale testing of SBP resulted in mitigation of many important gases:

1. Ammonia emissions were reduced by 21.7% and were statistically significant.
2. Hydrogen sulfide emissions were reduced by 79.7% and were statistically significant.
3. Greenhouse gas emissions were reduced for nitrous oxide (N_2O) at 9.8% and were not statistically significant. Both methane (CH_4) and carbon dioxide (CO_2) emissions were reduced by 6.2% and 3.0%, respectively, and were not statistically significant.
4. Sulfur VOCs emissions were significantly increased by 30.6% for dimethyl disulfide. Effects on dimethyl trisulfide could not be assessed.
5. Volatile fatty acids emissions were significantly reduced by 37.2% (butyric acid), 47.7% (valeric acid) and 39.3% (isovaleric acid).
6. Phenolics emissions were reduced by 14.4% (*p*-cresol), 31.2% (indole) and 43.5% (skatole) and were statistically significant for indole and skatole.

The estimated cost of treatment (additives only) was estimated at $1.45 per marketed pig and $2.62 per marketed pig when the cost of labor was added. Similarly, the estimated cost was $2.19/pig space/year of the (additives only) and $3.95 when the cost of labor was included (2014 price benchmarking). The cost estimate was at the lower range of comparable products tested for air quality mitigation ($0.01 to $18.2 per marketed pig). The SBP treatment also resulted in a more comprehensive mitigation of a greater number of gases of concern for swine industry.

Keywords:

Swine, manure, storage, air quality, emissions, mitigation, soybean peroxidase, odor, volatile organic compounds, ammonia, hydrogen sulfide, greenhouse gases.

Scientific Abstract:

The control of odor, odorous volatile organic compounds (VOCs), hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gases (GHGs) emissions associated with commercial swine production is a critical need. Manure storage is the major source of gaseous emissions. This study aimed for the most comprehensive, to date, assessment of a manure additive for mitigation of gaseous emissions of all major compounds of interest from swine manure. This study tested *topical* application of manure additive treatment in controlled pilot and farm scales (soybean peroxidase (SBP); product code 516-IND; Bio-Research Products, Inc.). This research builds on the previous published study where SBP product was *mixed* into manure and resulted in significant mitigation of odorous VOCs in lab scale. In this research both pilot and farm scale testing of topical SBP treatment (and ~23.5:1 weight/weight mix of SBP:CaO_2 catalyst) was conducted over ~5 month and ~1.5 month, respectively. This work aimed at providing a comprehensive assessment of SBP treatment efficacy to mitigate emissions of odorous VOCs, odor, H_2S, NH_3, and GHGs, i.e., a set of target gases of concern to swine industry.

The soybean based additive was first tested in **pilot scale** (Objective 1). Effects of SBP dose and time were tested. The following topical doses (mass per manure surface area) with three replicates of each: 0, 2.28, 4.57, 22.8 and 45.7 kg/m^2 (equivalent of 0, 0.467, 0.936, 4.67 and 9.36 lbs/ft^2; and equivalent of 0, 2.5, 5.0, 25 and 50 g/L of swine manure) were evaluated. Emissions of VOCs, H_2S, NH_3, and GHGs were monitored over the course of 21 days pre-application and 136 days post SBP application. Pilot scale tests resulted in

reduction of gaseous emissions for some compounds, while no difference or increase in emissions for others for the entire SBP testing period of 136 days. Specifically:

1. **Ammonia** emissions were reduced by 14.6% to 67.6% and were statistically significant except for the lowest SBP dose. The percent reduction was correlated with the SBP dose. The apparent effectiveness of SBP treatment was decreasing over time.
2. **H_2S** emissions were highly variable and not correlated with the SBP dose.
3. **GHGs** emissions were not significantly changed for nitrous oxide (N_2O). Methane (CH_4) and CO_2 emissions increased by 32.7% to 232% and 20.8% to 124%, respectively. The percent increase was statistically significant (except for CH_4 and the lowest dose) and was correlated with the SBP dose. The increase of CO_2 and CH_4 emissions may be inferred considering biochemical breakdown of VOCs as a result of SBP treatment.
4. **Sulfur VOC** emissions were generally reduced by 36.2% to 84.7% (DMDS) and 10.7% to 16.9% (DMTS). However, the only statistically significant reduction was for DMDS at the mid-range SBP doses.
5. **Volatile fatty acids** emissions were reduced by 8.5% to 19.5% (butyric acid), 79.2% to 88.5% (valeric acid) and 42.7% to 59.2% (isovaleric acid) except for the highest SBP dose for butyric and isovaleric acids. However, none of the reductions were statistically significant.
6. **Phenolics** emissions were reduced by 53.1% to 89.5% (*p*-cresol), 52.6% to 81.8% (indole, except for the highest SBP dose), and 63.2% to 92.5% (skatole) and were statistically significant for *p*-cresol and skatole. Indole emission's reductions were not statistically significant. The apparent effectiveness of SBP treatment on phenolics was decreasing over time.

The soybean based additive was then tested at **farm scale** (Objective 2). Effects of time were tested using one (the lowest) SBP dose selected from the pilot study. A topical dose of 2.28 kg/m^2 (equivalent of 0.467 lbs/ft^2, equivalent of 12 g/L of swine manure was used. VOCs, H_2S, NH_3, and GHGs emissions were monitored over the course of 42 days post SBP application. In general, mitigating effects of SBP treatment were similar at the farm and the pilot scales (especially, when the similar, 42 day treatment periods at the pilot and farm scales were compared). Overall, the SBP treatment was effective in mitigating major gases of concern on the farm scale. NH_3 showed a significant 22% overall reduction in emissions in the treated room compared to the untreated room. Hydrogen sulfide emissions in the treated room resulted in a significant 80% overall reduction compared to the untreated room. Greenhouse gas emissions in the treated room showed an insignificant reduction compared to the untreated room. Non sulfur VOCs emissions from the treated room showed an average reduction of 36% based on the average overall means. Specifically:

1. **Ammonia** emissions were reduced by 21.7% and were statistically significant. The reduction at the farm scale was slightly higher than that observed at the pilot scale (15.3%) over the same treatment time at the same SBP dose.
2. **H_2S** emissions were reduced by 79.7% and were statistically significant. However, it was only the 22.8 kg/m^2 SBP dose at pilot scale that resulted in H_2S emissions reduction (62.9%). Effects of other pilot scale doses were highly variable.
3. **GHGs** emissions were reduced for N_2O at 9.8%. However, the reduction was not statistically significant. Similarly, a statistically insignificant change was also observed at the pilot scale for N_2O (2.9% increase) at the same SBP dose. Both methane and CO_2 emissions were reduced by 6.2% and 3.0%, respectively. However, the reduction was not statistically significant. Significant increase in CO_2 (24.6%) was observed at the same SBP dose at the pilot scale. This apparent discrepancy could be explained by contribution of exhaled CO_2 at the farm scale and its effect on significant increase in measured concentrations. Increased levels of CO_2 made it more challenging to measure the changes in CO_2 emissions from the manure. Methane also increased at the pilot scale for the same SBP dose (32.2%), however it was not significant.

4. **Sulfur VOC** emissions were significantly increased by 30.6% for DMDS. The pilot scale flux estimates resulted in a reduction of DMDS (65.1%) at the same SBP dose. DMTS was only present in high enough concentrations to be measured for one day in one room during the trial so the effect of the SBP could not be assessed.
5. **Volatile fatty acids** emissions were significantly reduced by 37.2% (butyric acid), 47.7% (valeric acid) and 39.3% (isovaleric acid). Similar reductions were observed (17.7%, 5.6% and 46.9%, respectively) at the pilot scale for the same SBP dose, however they were not significant.
6. **Phenolics** emissions were reduced by 14.4% (*p*-cresol), 31.2% (indole) and 43.5% (skatole) and were statistically significant for indole and skatole. The pilot scale resulted in reductions of 58.3% (*p*-cresol), 82.9% (indole) and 81.4% (skatole) at the same SBP dose, with significant reductions in *p*-cresol and skatole.

The estimated cost of treatment (additives only) was estimated at $1.45 per marketed pig and $2.62 per marketed pig when the cost of labor was added. Similarly, the estimated cost was $2.19/pig space/year of the (additives only) and $3.95 when the cost of labor was included (2014 price benchmarking). The cost estimate was at the lower range of comparable products tested for air quality mitigation ($0.01 to $18.2 per marketed pig). The SBP treatment with similar cost resulted in a more comprehensive mitigation of greater number of gases of concern for swine industry. It also may have a potential benefit to U.S. soybean farmers as the active ingredient is derived from soybean hulls, a low value by-product of soybean utilization.

Introduction:

Pork production affects regional and local air quality by emissions of odor and volatile organic compounds (VOCs), ammonia (NH_3), hydrogen sulfide (H_2S), greenhouse gases (GHGs) (CH_4, N_2O and CO_2), and particulate matter (PM). The current interest in mitigation and adaptation focuses on GHGs emissions and climate change and variability. However, it is important to recognize that sustainable mitigation and adaptation requires holistic approach to mitigation of gaseous emissions and lowering the carbon/nitrogen/water footprint per pig. Specifically, for air quality, this implies comprehensive mitigation of all crucial gases of concern without significantly detrimental impact on emissions of any of the key target gases: i.e., NH_3, H_2S, odor, VOCs and GHGs. To date, no feasible technology to address all target gases have emerged to full scale application.

It has been shown that nearly 300 chemical compounds have been reported in air emissions from swine manure. These VOC originate from the degradation of amino acids in the intestines of animals and through anaerobic decomposition of stored manure. Ammonia, hydrogen sulfide, volatile fatty acids, sulfides, *p*-cresol, phenol, indole, and skatole are among the most commonly reported odorants associated with animal manures. Though many compounds are emitted at animal feeding operations, the phenolic and indolic compounds are most dominant at a distance from these area sources. Recently, greenhouse gas (GHGs) effect gases such as CO_2, CH_4 and N_2O have gained attention due to climate change concerns.

Peroxidase enzymes have been investigated for abatement of phenolic contaminants in wastewaters. In the presence of a peroxide such as hydrogen peroxide (H_2O_2) or calcium peroxide (CaO_2), the peroxidase enzyme polymerizes the phenolic and indolic compounds in wastewater to produce insoluble and non-volatile compounds, thereby reducing the odor (Aitken et al., 1994; Tonegawa et al., 2003). There are many different kinds of peroxidase enzymes, but horseradish peroxidase (HRP) and soybean peroxidase (SBP) have been the most studied. HRP and SBP are naturally occurring enzymes isolated from roots or other plant materials.

While there has been considerable research on peroxidase enzymes for treatment of wastewaters, only recently was the technology applied to treatment of manure for odor control. Govere et al. (2005, 2007) demonstrated the removal of phenolic compounds from swine manure using minced horseradish roots, while Ye et al. (2009) showed that purified HRP was efficient at reducing concentrations of phenol, *p*-cresol, indole, and skatole in swine manure. The primary drawbacks to using raw horseradish root or purified HRP are the limited supply and excessive cost.

As opposed to HRP, **soybean peroxidase (SBP)** is more plentiful due to the fact that soybeans are one of the most plentiful crops produced in the U.S. SBP has been shown to be effective at removing phenolic compounds from wastewater (Caza et al., 1999), and given the plentiful supply of soybean farming in the U.S., it is more economical than HRP. HRP is an enzyme isolated from horseradish roots that oxidizes a variety of aromatic substrates using H_2O_2 as an oxidant (Morawski et al., 2001). Numerous formulations of HRP have been used to remediate industrial wastewaters from contaminants such as polychlorophenols (Wagner and Nicell, 2002; Nicell et al., 1993) and *p*-cresol from swine manure (Govere et al., 2005). Thus, the focus of this research is on the SBP treatment of manure and aim at the possibility comprehensive solution to mitigating gaseous emissions from swine operations.

Objectives:

Objective 1. *Test the effectiveness of soybean peroxidase (**SBP**) for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in pilot scale.*

Objective 2. *Test the effectiveness of soybean peroxidase for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in production scale.*

Materials and Methods

Objective 1. *Test the effectiveness of soybean peroxidase (**SBP**) for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in pilot scale.*

Pilot scale setup

Deep pit swine manure from an Iowa State University swine finisher was pumped in to fifteen 1.22 m (4 ft) tall, 0.38 m (15 in) diameter sealed manure storage simulators (**Figure 1 and 2**). One hundred and four liters (27.5 gal) of swine manure was the starting volume followed by 9.46 L (2.5 gal) weekly manure additions for two weeks after SBP addition resulting in a final volume of 123 L (32.5 gal). The simulated ventilation was controlled via rotameters in order to achieve a ventilation rate of 7.5 headspace exchanges per hour. The rate was adjusted when fresh manure was added to keep the 7.5 headspace exchanges per hour constant. Air exchange rates were consistent with typical values for air exchange rates of manure pit storage areas in swine barns with fully slatted floors (Harmon, 2013). Storage temperature was kept between 9 and 20 °C (average = 15.6 ± 3.7 °C) to simulate the temperature of deep pit storage (Andresen, 2013).

Baseline measurements where taken for two weeks *prior to SBP addition* in order to evaluate emissions from each of the 15 storage simulators so that the treatments could be randomized to eliminate storage simulator variation.

SBP was then applied in doses of 0, 2.28, 4.57, 22.8 and 45.7 kg/m^2 (0, 0.467, 0.936, 4.67 and 9.36 lbs/ft^2, respectively. These doses are also equivalent to 0, 2.5, 5.0, 25 and 50 g/L on mass of SBP per volume of manure on the day of application. These mass/volume rates are only reported here for comparison with previous studies where SBP was added on per volume of manure basis (Parker et al, 2012). Total duration of pilot experiment was 136 days. Manure samples were collected before SBP application and again after the 136 days of monitoring for analysis. Effectiveness of SBP treatment was statistically analyzed by comparing estimated emissions of target gases between the control and each treatment dose. Ammonia, H_2S, CH_4, CO_2, nitrous oxide (N_2O) and relative humidity measurements were collected on selected 33 days after SBP application (approximately twice a week, with more frequent sampling in the first two months). VOC measurements were collected on selected 30 days over the 136 day monitoring after the SBP application (approximately twice a week, with more frequent sampling in the first two months).

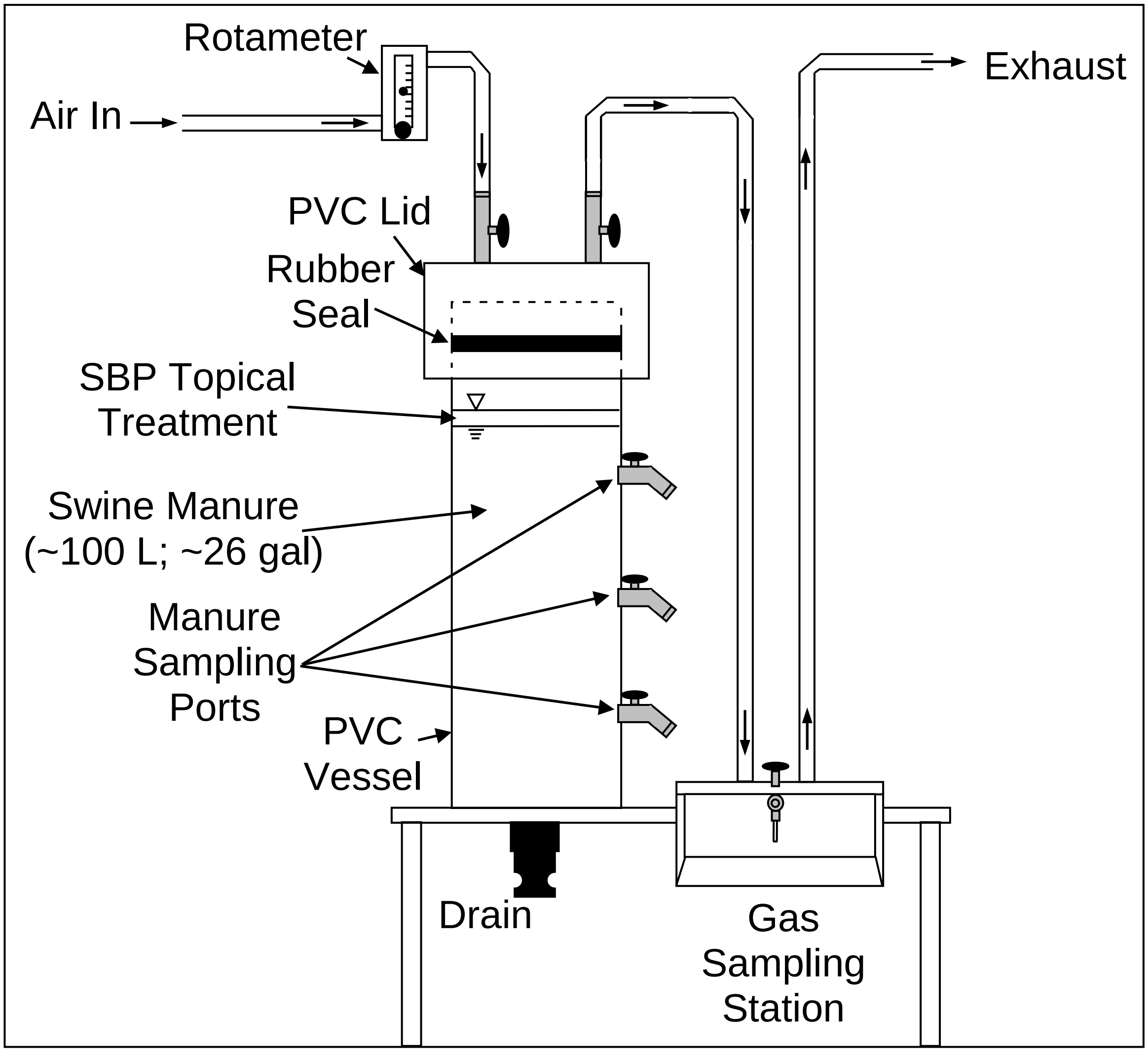

Figure 1. Pilot scale manure storage setup.

Figure 2. Pilot scale reactor setup. Fifteen 36 gal PVC reactors to hold swine manure with adjustable ventilation flow control and emission sampling stations.

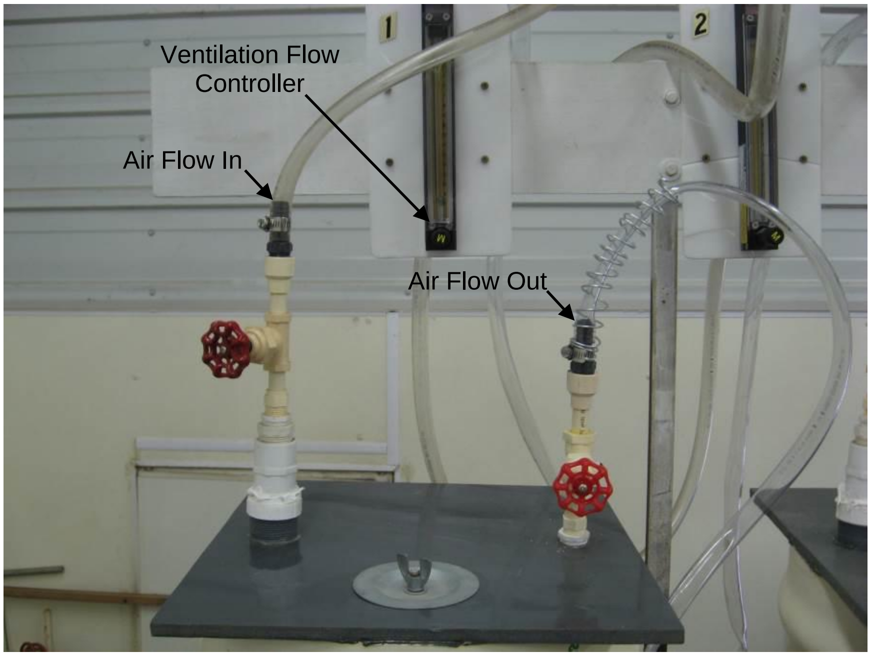

Figure 3. Pilot scale ventilation control and plumbing of each reactor. The air in is supplied via air compressor, the flow rate to each reactor is controlled via individual rotameters, and the air out flow is directed to gas sampling stations before being vented outside.

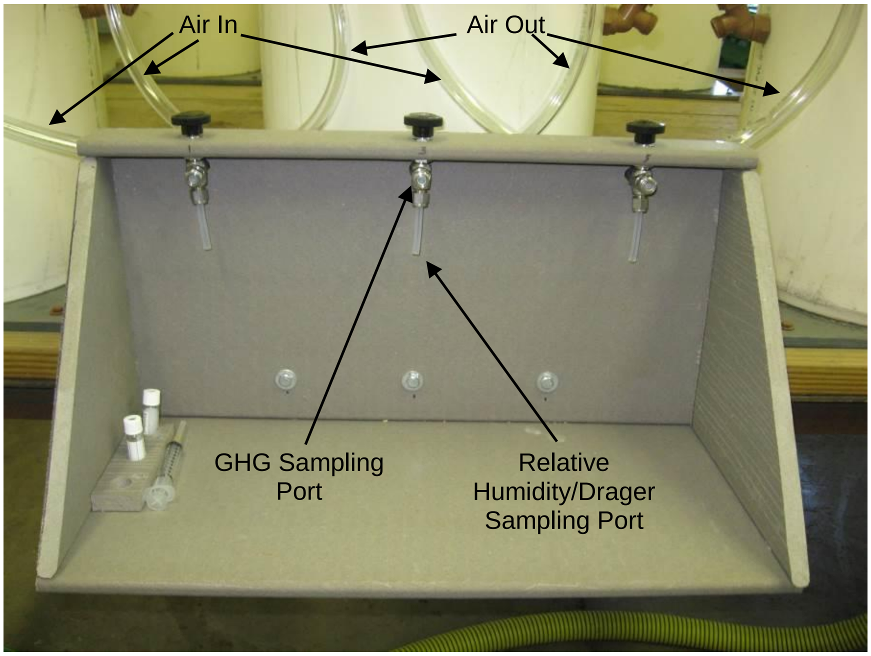

Figure 4. Pilot scale gas sampling station. Gas sampling stations were setup in the "Air In" venting emissions flow from each reactor with the ability to take gas samples for GHG analysis at anytime and the ability to open a line in the vent stream to collect NH_3 and H_2S via the Drager analyzer or to collect VOCs via sorbent tubes.

Relative Humidity

Figure 5. Pilot scale gas sampling station setup for relative humidity. Sample pump pulls air from the reactor vent line through sealed tube containing relative humidity probe.

Percent relative humidity was monitored in order to account for the vented air’s ability to hold other compounds relative to the amount of water in the vented air (**Figure 5**).

Greenhouse gases

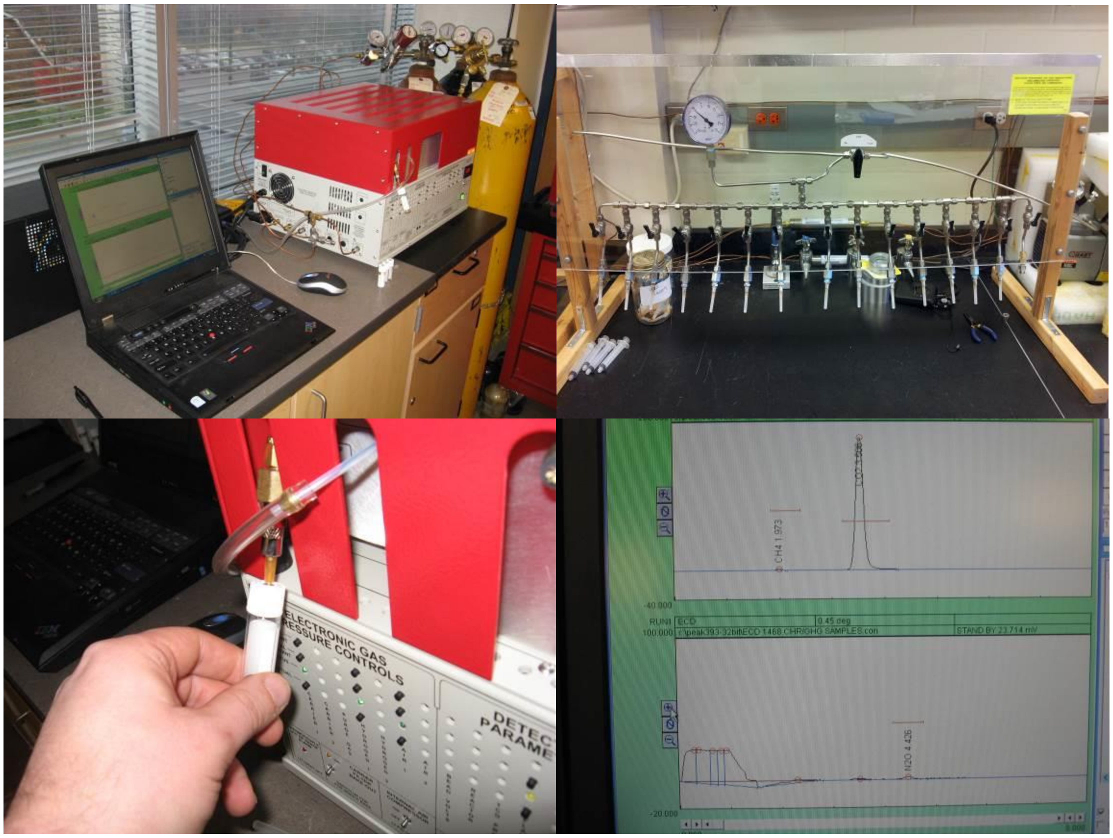

Figure 6. Top Left: SRI Greenhouse Gas GC. Top Right: Sample vial cleaning system. Sample analysis of GHGs. Bottom Left: Gas sample is injected on the GC. Bottom Right: Chromatogram of gas sampling showing CH_4, CO_2 and N_2O.

Gas samples collected (**Figure 8**) in the field via syringe and 5.9 ml Exetainer vials (Labco Limited, UK) were analyzed for GHG concentrations on a GHG GC (SRI Instruments, Torrance, CA, USA) equipped with FID and ECD detectors (**Figure 7**). Gas method detection limits were 1.99 ppm, 170 ppb, and 20.7 ppb for CO_2, CH_4 and N_2O, respectively. Standard curves were constructed daily using 2 ppm and 10.3 ppm methane, 510 ppm, 1010 ppm and 2010 ppm carbon dioxide, and 0.101 ppm, 1.02 ppm and 10.1 ppm nitrous oxide (Air Liquide America, Plumsteadville, PA, USA). Standards used for standard curve construction were done in duplicate for CH_4 and CO_2 while N_2O standards were done in triplicate. The conversions to gas concentrations (ppm) for the samples were based on peak area for CH_4 and CO_2 and on peak height for N_2O (peak height was a more consistent measure due to smaller peaks).

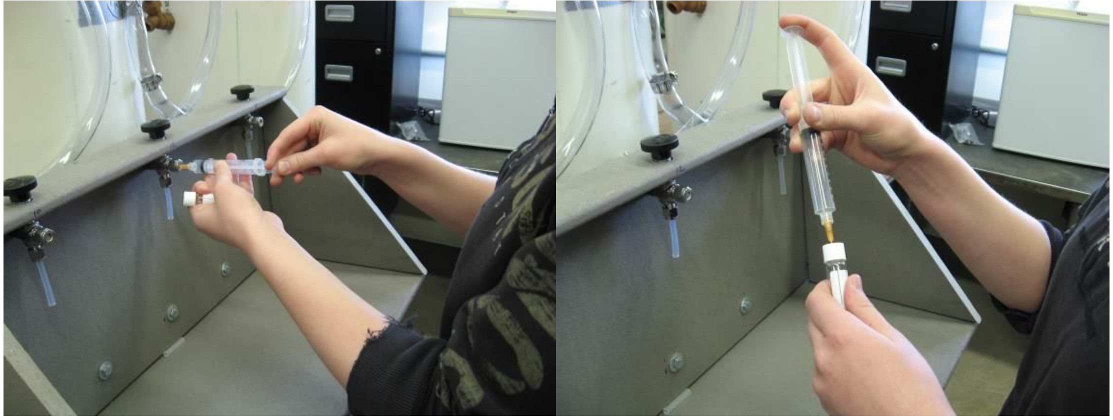

Figure 7. Pilot scale sampling station GHG collection. Left: GHG sample was collected from reactor vent line from pilot scale swine manure storage. Right: GHG sample was transferred to vial for transport to lab for analysis.

Volatile Organic Compounds (VOCs)

Figure 8. Thermal desorption - multidimensional gas chromatograph – mass spectrometer – olfactometer (TD-MDGC-MS-O) for VOCs analysis. Gas samples were collected on sorbent tubes in the field (e.g., reactor vent line or barn room exhaust fan), brought to the lab and desorbed/introduced to MDGC-MS-O for

analysis via thermal desorption (TD) autosampler. Quantified mass of VOCs and volume of gas sample was used to estimate gas concentration.

VOCs were collected via (4 mm O.D., 0.10 m long) sorbent tubes constructed of 304-grade stainless steel that had been double passivated with a proprietary surface-coating process. Tubes were packed with 65 mg Tenax TA sorbent. Silanized glass wool plugs and stainless steel screens were placed in the two ends of the tubes to hold the sorbent. Before the first use, sorbent tubes were conditioned by thermal desorption (260 °C for 5 h) under a 100 mL/min flow of He. For subsequent uses, pre-conditioning at 260 °C for 30 min was tested as sufficient and applied for all tubes. Field air samples were taken using a portable sampling pump with a set flow rate of 50 mL/min for 15 min, and analysis within two days. The sampling flow rates were checked with a NIST-traceable digital flow meter (Bios International, Butler, NJ, USA) (**Figure 9**).

Chemical analyses of swine odorants were completed using the TD-MDGC–MS/O system (**Figure 8**). The TD system consists of a Model 3200 automated thermal desorption inlet for Agilent 6890 GC developed by Microanalytics (Round Rock, TX, USA) based on a PAL® autosampler. The unique design of the Model 3200 system allows for gentle purging of air and water from sorbent tubes prior to a single-step sample desorption and introduction to GC. This system eliminates desorption followed by a separate step of cryotrapping and subsequent rapid desorption. Instead, samples are desorbed directly onto the front of GC column, then directly swept column, eliminating problems associated with a typical desorption–trapping–desorption and problems with the presence of water/air in sorbent tubes.

Multidimensional GC–MS/O (Microanalytics) was equipped with two columns connected in series. The non-polar pre-column was 12 m, 0.53mm i.d.; film thickness, 1_m with 5% phenyl methylpolysiloxane stationary phase (SGE BP5) and operated with constant pressure mode at 8.5 psi (0.58 atm). The polar analytical column was a 25m×0.53mm fused silica capillary column coated with poly (ethylene glycol) (WAX; SGE BP20) at a film thickness of 1_m. The column pressure was constant at 5.8 psi (0.39 atm). System automation and data acquisition software were MultiTraxTM V. 6.00 and AromaTraxTM V. 7.02 (Microanalytics) and ChemStationTM (Agilent, Santa Clara, CA, USA). The general GC run parameters used were as follows: injector, 260 °C; FID, 280 °C , column, 40 °C initial, 3 min hold, 7 °C/min, 220 °C final, 10 min hold; carrier gas, GC-grade helium. The GC was operated in a constant pressure mode where the mid-point pressure, i.e., pressure between pre-column and column, was always at 5.8 psi (0.39 atm) and the heart-cut sweep pressure was 5.0 psi. The MS scan range was 33 to 280 m/z. Spectra were collected at 6 scans/s using scan and selective ion monitoring (SIM) simultaneously. Mass calculations were based on SIM scans. Electron multiplier voltage was set to 1000 V. MS tuning was performed using the default autotune setting using perfluorotributylamine (PFTBA) daily. (Cai, 2010)

Figure 9. Pilot scale sampling setup for VOCs collection via sorbent tubes. Sampling pump pulls gas sample from the reactor vent line through the sorbent tube (4 mm O.D., 0.10 m long, packed with Tenax TA) and the gas flow rate is monitored via inline flow meter for the predetermined sampling time. Total gas sample volume can be estimated as a product of measured flow rate and sampling time.

Ammonia and Hydrogen Sulfide

Figure 10. Drager portable gas analyzer used to measure NH_3 and H_2S from the vent line of the manure storage reactor via the gas sampling station.

Ammonia and H_2S concentrations were measured via a Drager X-am 5600 portable gas analyzer (**Figure 10**) with NH_3 and low range H_2S XS sensors. Analyzer was calibrated using Drager calibration software, Environics 4040 gas dilution system (Tolland, CT, USA) and standard gases (Praxair, Ames, IA, USA) (NH_3: 102 ppm and H_2S: 15.6 ppm).

Ammonia measurement needed compensation for H_2S to avoid false readings. The Drager 5600 analyzer manual briefly mentions that the H_2S may interfere with NH_3 measurement. Thus, the following compensation was developed to account for H_2S interference on NH_3 concentration (Eq. 1). Compensation determination was accomplished with standard gases.

$$C_a = C_m - (C_{H_2Sm} S + b) \qquad \text{Eq. 1}$$

Where:

C_a is the corrected NH_3 concentration in ppm,
C_m is the measured NH_3 concentration in ppm,
C_{H2Sm} is the measured H_2S concentration in ppm,
S and b are the best fit coefficients with S being the slope and b being the y intercept of the standard curve of the NH_3 response to H_2S.

The NH_3 response to H_2S (**Figure 11**) was determined by reading standard concentration of H_2S with the Drager analyzer and observing the NH_3 response over the H_2S concentration range of 0 to15.6 ppm. This was done in duplicate to determine the correction needed for accurate NH_3 measurements in the presence of H_2S (i.e., a typical situation in livestock housing with manure storage).

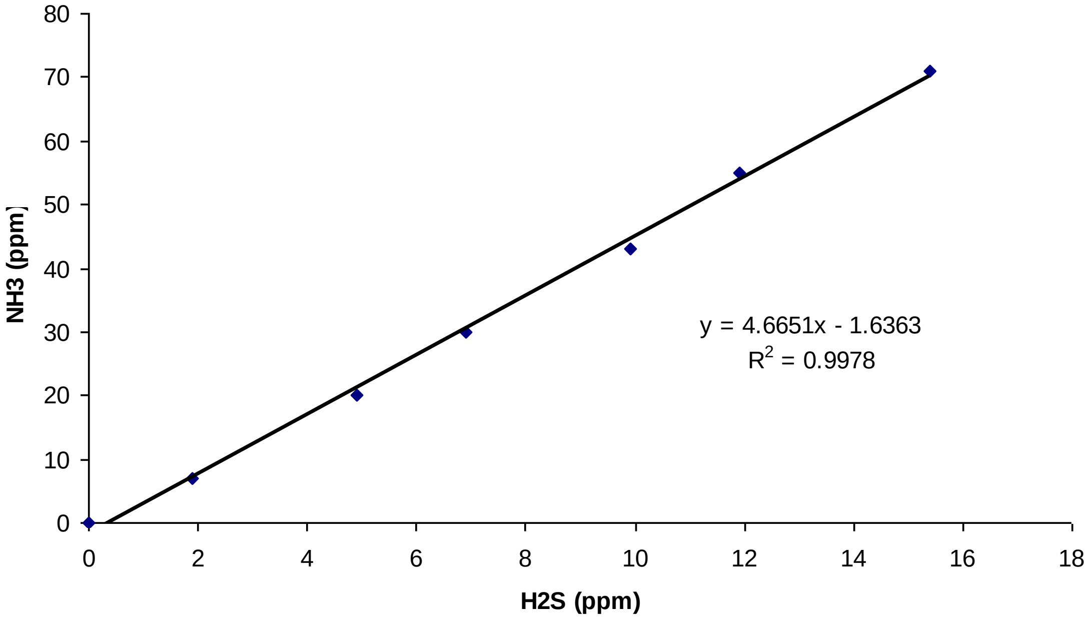

Figure 11. Standard curve used to adjust the Drager analyzer response to NH_3 in the presence of H_2S (0-15.6 ppm).

Swine Manure Analysis

Swine manure analysis was completed using the following standard methods:

- TKN – Standard Method 2001-11 (AOAC, 2000) –Kjeldahl digestion in block digester with Fisher digestion tablets as a catalyst followed by steam distillation and titrimetric analysis.
- Ammonia (NH_3) – Standard Method 4500-NH_4 B & C- Preliminary steam distillation followed by titrimetric analysis (APHA, 1998).

- Dissolved reactive phosphorus – Standard Method 4500-P E (APHA, 1998) – Filtration to 0.45 µm to remove particulates followed by the ascorbic acid method.

- Total phosphorus – Standard Method 4500-P B.4 & E (APHA, 1998) Sulfuric acid-nitric acid digestion in a block digester followed by the ascorbic acid method.

- pH –Standard method 4500-H+B. Electrode method (APHA, 1998).

- Total solids/moisture content and volatile solids – Standard Method 2540 G (APHA, 1998) – dried for 24 hours at 105°C for 24 hours (constant weight) for total solids followed by ignition at 550°C for 1 hour for volatile solids.

- Percent carbon, hydrogen, nitrogen, sulfur - Elemental analysis results were acquired using a PE 2100 Series II combustion analyzer (Perkin Elmer Inc., Waltham, MA) with a cysteine calibration standard, with a expected precision and accuracy of the measurements being +/- 0.3% for each element, and the combustion and reduction temperatures were 975 ^{o}C and 975 ^{o}C respectively. All standards and reagents are from Perkin Elmer and/or Elementar America's Inc.

Soybean Peroxidase Activity

SBP was extracted by acetic acid hydrolysis at room temperature and vortexing periodically over 1 h followed by centrifugation. The extract was then diluted 20x in water and assayed with guaiacol and H_2O_2 substrate at 30 °C and 470 nm for 3 min using a UV-Vis spectrometer. Calculations for SBP activity are shown in Eq. 2.

$$A = \frac{S * 0.4 * 20}{0.005} \qquad \text{Eq. 2}$$

Where:

A is the SBP activity in IU (international units)/mL.
S is the slope of the linear part of the curve from the UV-Vis spectrometer in absorption$_{470}$/min.
0.4 is the SBP absorption factor at 470 nm.
0.005 is the volume of enzyme assayed in mL.
20 is the dilution factor of the enzyme assayed.

Estimation of Gas Flux (emissions from manure in mass/time/area)

Pilot scale

Measured gas concentrations were used for estimation of flux, i.e., emissions from manure based on time and surface area of manure. Gas concentrations were measured at field conditions and required conversions to standard conditions.

Conversion to gas concentration in mass per volume from measured ppm for NH_3, H_2S, CH_4, CO_2 and N_2O in µg/mL is shown in Eq. 3.

$$C = \frac{C_a * P}{R * T * 1000} molwt \qquad \text{Eq. 3}$$

Where:

C is the gas concentration in µg/mL.
C_a is the measured (for NH_3 it is the adjusted) concentration in ppm.
P is the atmospheric pressure in atmospheres.
R is the ideal gas constant, 0.082057 L atm K^{-1} mol^{-1}.
T is the measured temperature in Kelvin.
molwt is the molecular weight of the gas.

Eq. 4 was used to convert C (mass/volume) to EPA standard conditions (1 atm, 25 °C, dry air) with humidity adjustment to dry air:

$$C_{std} = \frac{C}{(\frac{P_m}{760})(\frac{298}{T_m})(\frac{1}{1-H})} \qquad \text{Eq. 4}$$

Where:

C_{std} is standardized and humidity factored in gas concentration in µg/mL.
C is the concentration in µg/ml from Eq. 3.
P_m is the measured atmospheric pressure in mmHg.
T_m is the measured temperature in Kelvin.
H is the humidity ratio determined by measured relative humidity and the use of a psychrometric calculator.

Ventilation rate of the pilot scale storage simulators using the inline rotameters is shown in Eq. 5.

$$Qair = \frac{R_m * S + b}{\sqrt{\frac{P * 14.7}{530 * T}}} \qquad \text{Eq. 5}$$

Where:

Qair is the ventilation rate in ml/min.
R_m is the measured reading from the rotameter.
S is the slope from the factory rotameter calibration data (111.81).
B is the y intercept from the factory rotameter calibration data (127.11).
P is the measured pressure in psi.
T is the measured temperature in Rankine.

Qair was then adjusted to EPA standard conditions with humidity adjustment to dry air as C_{std} using Eq. 6

$$Qair_{std} = Qair(\frac{P_m}{760})(\frac{298}{T_m})(\frac{1}{1-H}) \qquad \text{Eq. 6}$$

Where:

$Qair_{std}$ is standardized to dry air and gas concentration in mL/min.

Qair is the ventilation in mL/min from Eq. 5.
P_m is the measured atmospheric pressure in mmHg.
T_m is the temperature in Kelvin.
H is the Humidity Ratio determined by measured relative humidity and the use of a psychrometric calculator.

Emissions may then be calculated with Eq. 7:

$$E = \frac{Qair_{std} * C_{std} * 60}{1000} \qquad \text{Eq. 7}$$

Where:
E is emissions in mg/h.
$Qair_{std}$ is from Eq. 6.
C_{std} is from Eq. 4.

The flux (emissions) were then related to the manure surface area Eq. 8.

$$E_{surface} = \frac{E}{A} \qquad \text{Eq. 8}$$

Where:
$E_{surface}$ is in mg/h/m^2.
E is from Eq. 7.
A is the surface area of manure in square meters.

Concentrations of VOCs were estimated based on gas sampling with sorbent tubes. Mass of VOCs trapped on sorbent tubes was estimated using GC-MS. Volume of air sample pumped through a sorbent tube was based on the measured air flow rate and sampling time (Eq. 9):

$$V_s = F * t \qquad \text{Eq. 9}$$

Where:
V_s is the volume of air that was sampled trough the tube in mL.
F is the average of the measured flow rate trough the tube in mL/min.
t is the time in min in which the sampling was taken.

The sample volume was then adjusted to standard conditions with Eq. 10.

$$V_{s_{std}} = V_s \left(\frac{P_m}{760}\right)\left(\frac{298}{T_m}\right)\left(\frac{1}{1-H}\right) \qquad \text{Eq. 10}$$

Where:
$V_{s\ std}$ is the standardized volume of air that was sampled through the tube in mL.
V_s is from Eq. 9.
P_m is the measured atmospheric pressure in mmHg.
T_m is the temperature in Kelvin.

H is the Humidity Ratio determined by measured relative humidity and the use of a psychrometric calculator.

The concentration of the VOC were calculated with the volume of air sampled and the mass that was determined by GC-MS and the determined MS detector response factor in Eq. 11.

$$C_{std} = \frac{m}{V_{s_{std}}} \qquad \text{Eq. 11}$$

Where:

C_{std} is the standardized concentration of VOC in ng/mL.
m is the mass determine by GC-MS in ng.
$V_{s\ std}$ is from Eq. 10.

Emissions then were calculated in Eq. 12.

$$E = Qair_{std} * C_{std} * 60 \qquad \text{Eq. 12}$$

Where:

E is emissions in ng/h.
$Qair_{std}$ is from Eq. 6.
C_{std} is from Eq. 11.

The VOC emissions (flex) were then related to the manure surface area Eq. 13.

$$E_{surface} = \frac{E}{A} \qquad \text{Eq. 13}$$

Where:

$E_{surface}$ is in ng/h/m^2.
E is from Eq. 12.
A is the surface area of manure in square meters.

Objective 2. *Test the effectiveness of soybean peroxidase for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in production scale.*

Farm Scale Setup

Farm scale testing was carried out at ISU Allen E. Christian Swine Teaching Farm. One barn consisting of separate rooms, two of which housed 89 pigs each (treatment room had 90 pigs but one pig died on day 6 after SBP application) (**Figure 13 and 14**). Shallow manure pit (0.61 m, 2 ft) under one room was used as control and manure pit under the other room was treated with topical application of SBP at a dose of 2.28 kg/m^2 (0.467 lb/ft^2, 12 g/L), i.e. the lowest dose (mass/area) tested in the pilot scale. Based on the pilot-scale tests and the feasibility of SPB topical application was the 2.28 kg/m^2 dose which resulted in approx. ¼ inch (6 mm) thick layer of SPB. Considering the manure pit dimensions (36' x 36') and approx. ¼ inch layer of SPB, was accomplished with 275 kg of SBP and 12 kg of CaO2 (**Figures 16 – 18**).

Gas samples were collected directly from primary exhaust fan in each room. Gas samples were collected (**Figure 12**) and analyzed for relative humidity, NH_3, H_2S in real-time while air samples for GHGs odorous VOCs concentrations were collected and analyzed in the lab. Farm scale experiment lasted for 2 weeks before SBP application and 6 weeks after SBP application (8 weeks total). Barn ventilation airflow rate were determined by anemometer profiling of air flow through the primary fans in each room (**Figure 15**). Primary fans of each room were the only ventilation (~5.4 air exchanges per hour) that was considered for each room due to the outside temperature at the time of the study was that that the primary fans were the only ones operating. In addition, room control was manually set so that the primary fan was the only one running for the duration of the gas sampling.

Gas emissions were estimated as a product of measured concentrations and the total airflow rate through each room, both adjusted for standard conditions. Effectiveness of SBP treatment was statistically analyzed by comparing estimated emissions of target gases in the two rooms. Environmental data was collected along with manure for quality evaluation (manure was collected before SBP application, immediately after SBP application, and again at the end of the study). Ammonia, H_2S and relative humidity were measurements were collected on 28 days after SBP application (approx. every other day). Methane, CO_2 and N_2O were measurements were collected on 24 days after SBP application (approx. every other day on average). VOC measurements were collected on 19 days over the 42 day monitoring after the SBP application.

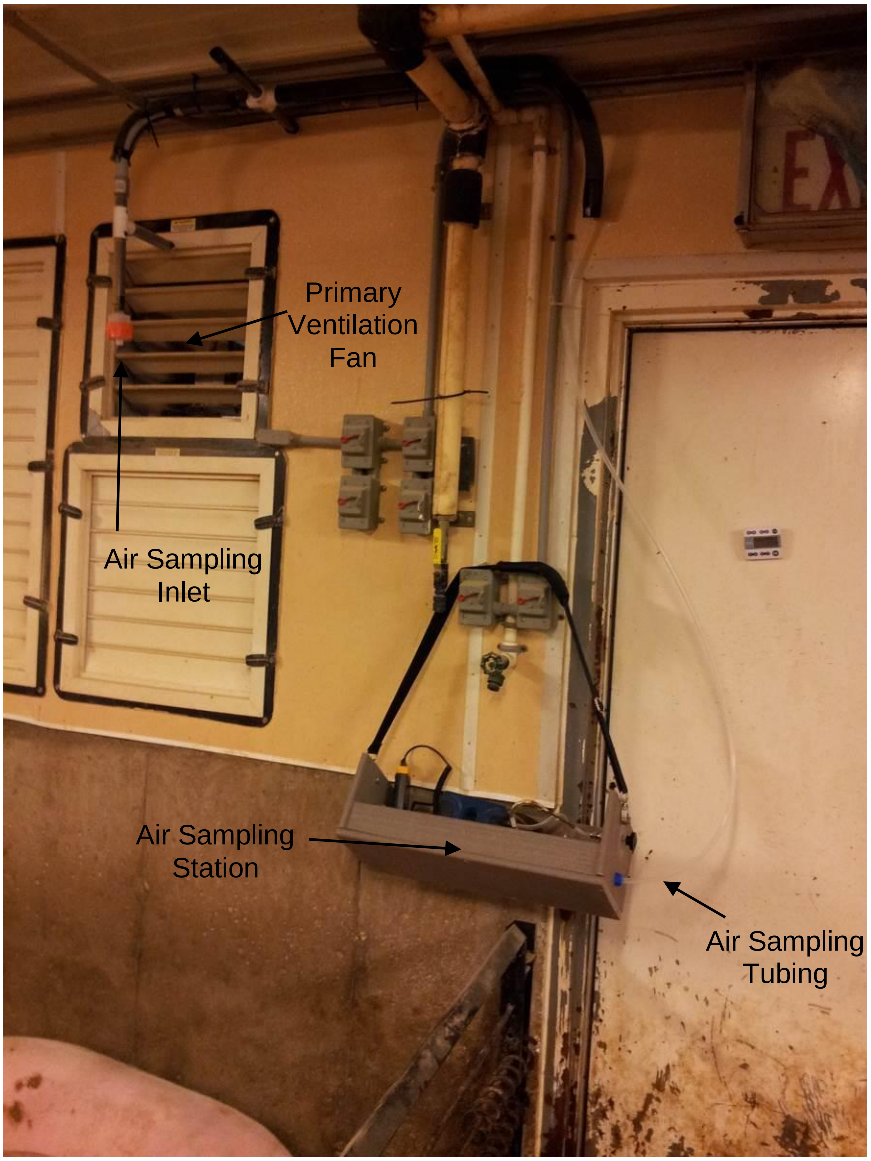

Figure 12: Farm scale gas sampling setup. Air sampling line is situated in front of primary ventilation fan. Gas samples for measurement of all target gas concentrations (NH_3, H_2S, GHGs, and VOCs) and relative humidity were collected at this location.

Figure 13: Farm scale testing room. Two identical rooms (control and treatment) were used to test the effects of SBP applied to manure surface on gaseous emissions.

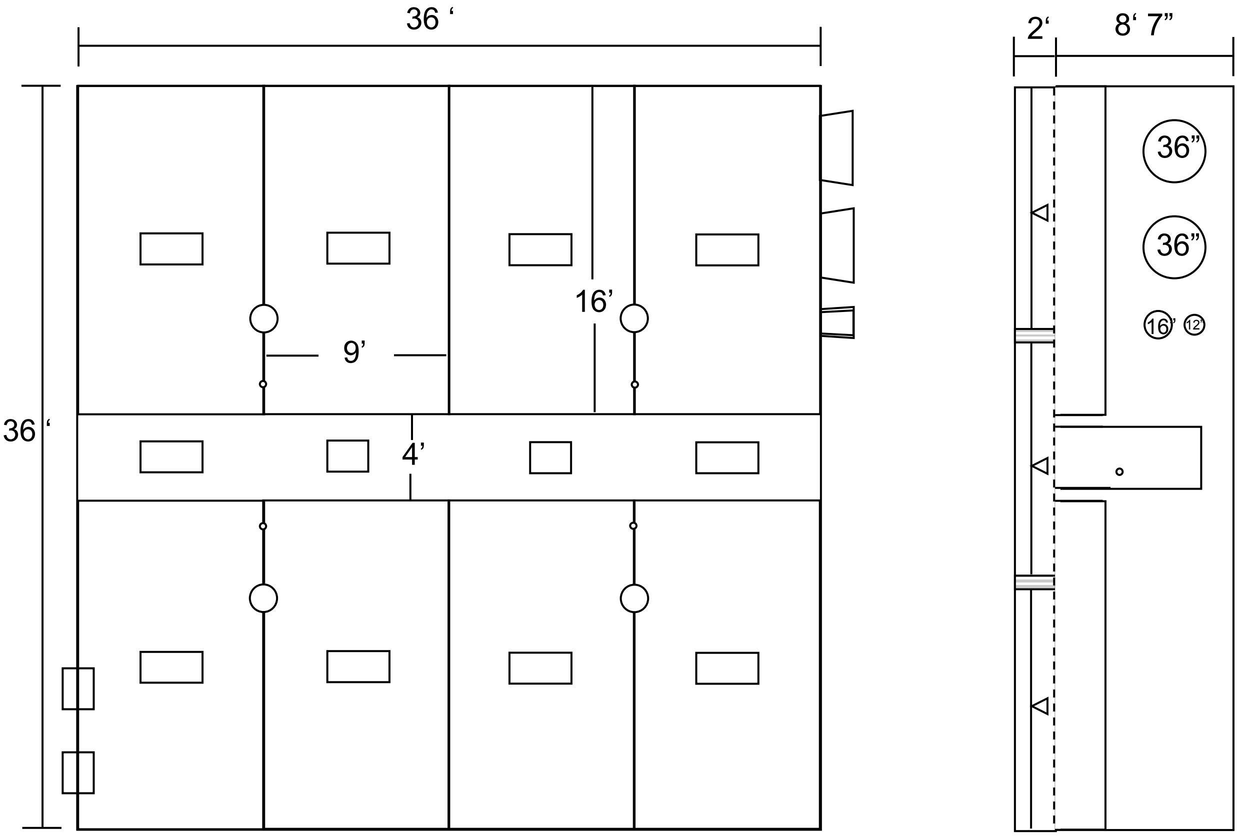

Figure 14: Farm scale testing room schematics.

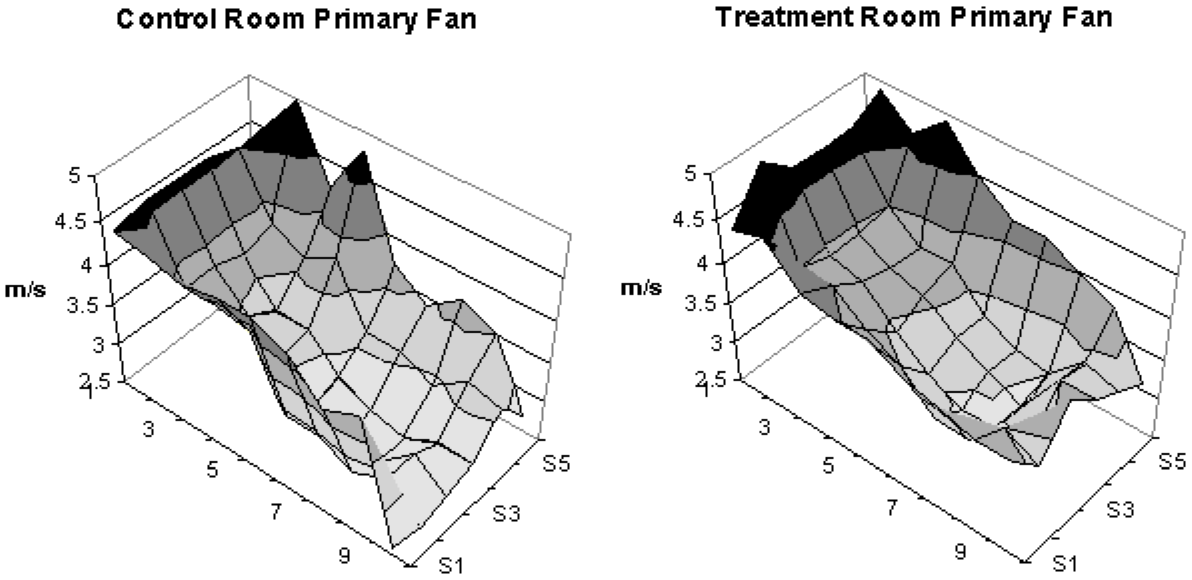

Figure 15: Farm scale primary fan air velocity profiles used for air flow estimates. Each data point represent an average of n = 3 measurements of air velocity on the grid of 54 (9 by 6) sections of the cross sectional fan area perpendicular to the flow. Air flow and measured concentrations were used to estimate gaseous emissions.

Application of SBP treatment

Figure 16. Farm scale - premixing of weighted ratio (~23.5:1 w/w) of soybean peroxidase treatment and CaO_2 catalysts.

Figure 17. Farm scale - application of premixed soybean peroxidase treatment and CaO_2 catalysts through slats to the manure pit. Special funnel device was assembled to accelerate the application, to minimize losses and to apply treatment uniformly over the entire manure pit surface area.

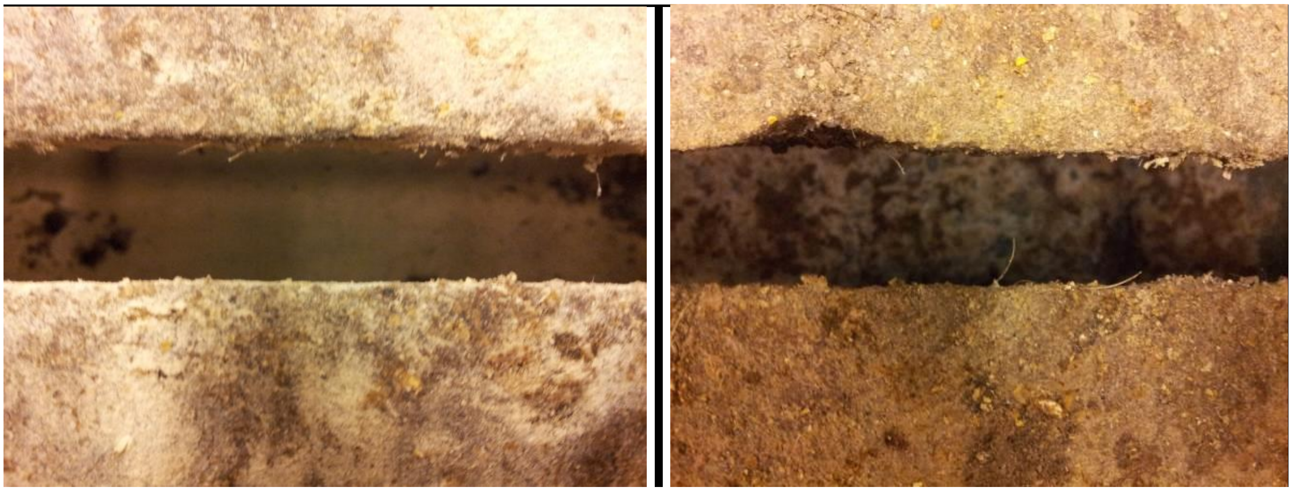

Figure 18. Farm scale - close-up of soybean peroxidase treatment on the surface of manure (left) and control (non-treated manure on the right) as seen through slat opening.

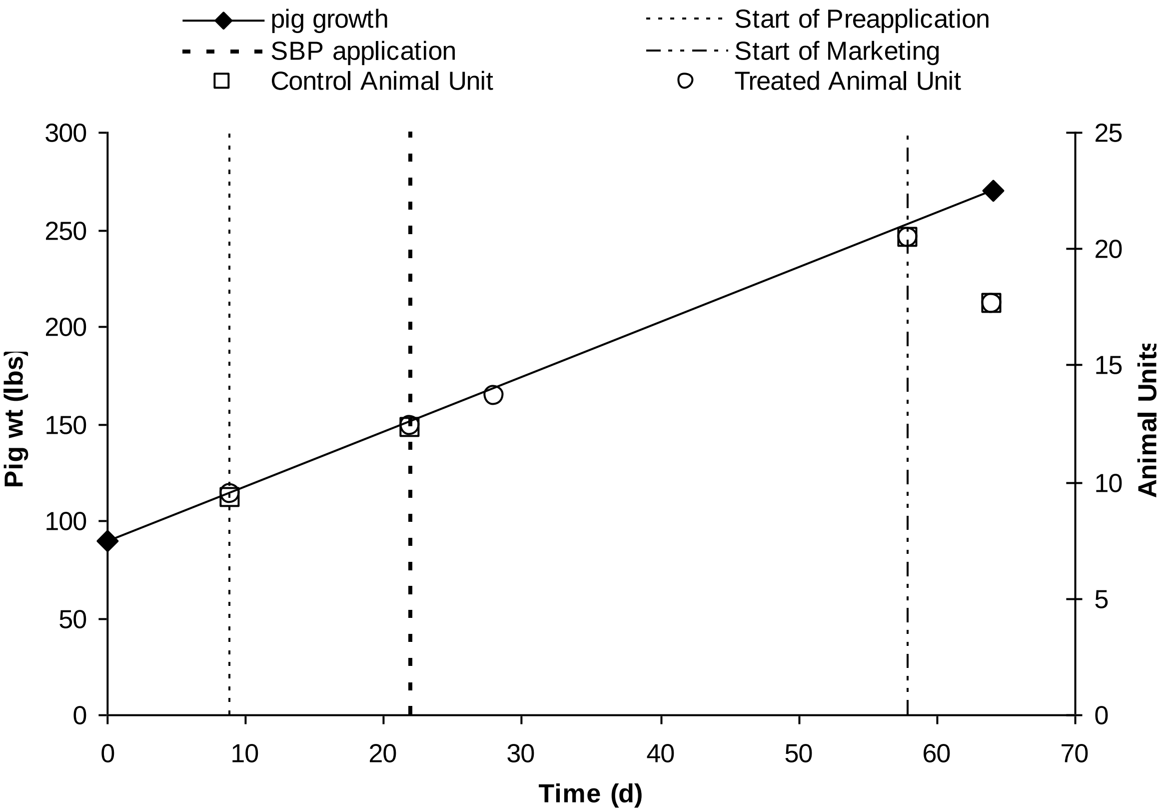

Figure 19. Farm scale – pig weight and animal units progression during testing period.

Estimation of Gas Flux (emissions from manure in units of mass/time/area)

Estimates of gas emissions for the farm scale were completed using the same equations listed above except for Eq. 5 (not used due to the fact that the rotameters where not used to determine the ventilation rate in the barn). Instead, the ventilation rates in the barn were determined by measuring air velocities (m/s) of a 54 block grid of each fan. The Qair was then determined in Eq. 14.

$$Qair = \frac{V * A * 1000000}{0.016667} \qquad \text{Eq. 14}$$

Where:

Qair is the ventilation in mL/min.
V is the measured air velocity in m/s.
A is the cross-sectional area of a fan in m^2.

Estimates of gas emissions for the farm scale were adjusted to account for the differences observed during the baseline measurements collected for the two week prior to SBP treatment for reduction calculations by adding the average difference between the rooms prior to SBP treatment (excluding the first two days of measurements to allow for equilibration) to the emissions from the control room in order to normalize the rooms (Eq. 15).

$$E_{adj} = (E_{tb} - E_{cb}) + E_{ca} \qquad \text{Eq. 15}$$

Where:

E_{adj} is the adjusted flux estimate.
E_{tb} is the flux estimate for the treated room before SBP application.
E_{cb} is the flux estimate for the control room before SBP application.
E_{ca} is the flux estimate for the control room after SBP application.

Percent reduction in gas emission estimates were completed using Eq. 16.

$$\%R = \frac{E_{Con} - E_{Treat}}{E_{Con}} * 100 \qquad \text{Eq. 16}$$

Where:
%R is the % of reduction.
E_{Con} is the average flux estimate of the desired time interval (day, week, biweek or overall) of the control.
E_{Treat} is the average flux estimate of the desired time interval (day, week, biweek or overall) of the treated.

Statistical Analysis for Pilot and Farm 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, $p<0.05$ was used as the cut off for statistical significance.

Results

Objective 1. *Test the effectiveness of soybean peroxidase (**SBP**) for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in pilot scale.*

*Pilot Scale – Effects of Treatment **Time***

The SBP surface coverage of the swine manure stored in the pilot scale simulated storage is depicted in **Figures 20-24.** The two lowest SBP doses of 2.28 and 4.57 kg/m^2 resulted in nearly complete SBP settling into the manure over the 137 days. The higher SBP doses of 22.8 and 45.7 kg/m^2 had more of the SBP still on the surface of the manure after 137 days. The 22.8 kg/m^2 SBP dose still had some dry SBP covering the complete surface of the manure after 137 days. The highest SBP dose of 45.7 kg/m^2 was ~5 inches thick. This relatively heavy layer of SBP had forced the SBP to crack the crust and roll into the top layer during periodic additions of "fresh" manure. This resulted in less manure surface coverage with the largest SBP dose over time.

Figure 20: Simulated manure storage – **control** (no SBP). Left: Day 14 after treatment, Right: Day 137 after treatment.

Figure 21: Simulated manure storage treated with **2.28 kg/m^2** SBP dose. Left: Day 14 after treatment, Right: Day 137 after treatment.

Figure 22: Simulated manure storage treated with **4.57 kg/m^2** SBP dose. Left: Day 14 after treatment, Right: Day 137 after treatment.

Figure 23: Simulated manure storage treated with **22.8 kg/m^2** SBP dose. Left: Day 14 after treatment, Right: Day 137 after treatment.

Figure 24: Simulated manure storage treated with **45.7 kg/m^2** SBP dose. Left: Day 14 after treatment, Right: Day 137 after treatment. This relatively heavy layer of SBP had forced the SBP to crack the crust and roll into the top layer during periodic additions of "fresh" manure. This resulted in less manure surface coverage with the largest SBP dose over time.

Greenhouse Gases - Pilot scale

Methane and CO_2 estimates of flux (mass/time/emitting manure surface area) were significantly higher overall for all SBP treatment over the 136 day monitoring period. Nitrous oxide flux estimates showed no significant difference for all SBP treatment levels over the 136 day period after treatment (**Figures 25, 26 and 27**). Generation of CO_2 and CH_4 is likely a result of biochemical breakdown of VOCs and illustrated in the *Manure-Air Biochemical Cycles of Target Gases* section later in the document (**Figures 67-69**). 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_2O (Montes 2013), i.e., manure bacteria can either suppress CH_4 generation at the expense of increased N_2O or vice versa. Closer inspection of the CH_4 and N_2O flux (**Figures 25** and **27**) supports this apparent trend, i.e., increased and re-equilibrating CH_4 and decreased and re-equilibrating N_2O for both the control and treatment. These apparent trends for CH_4 and N_2O in control suggest that oxygen availability in manure due to pump-out and transfer to storage simulators have influenced variations in bacterial growth early in the experiment. Methane and CO_2 flux was inversely proportional to the SBP dose. In-depth analysis of the effects of the dose is presented in a later section.

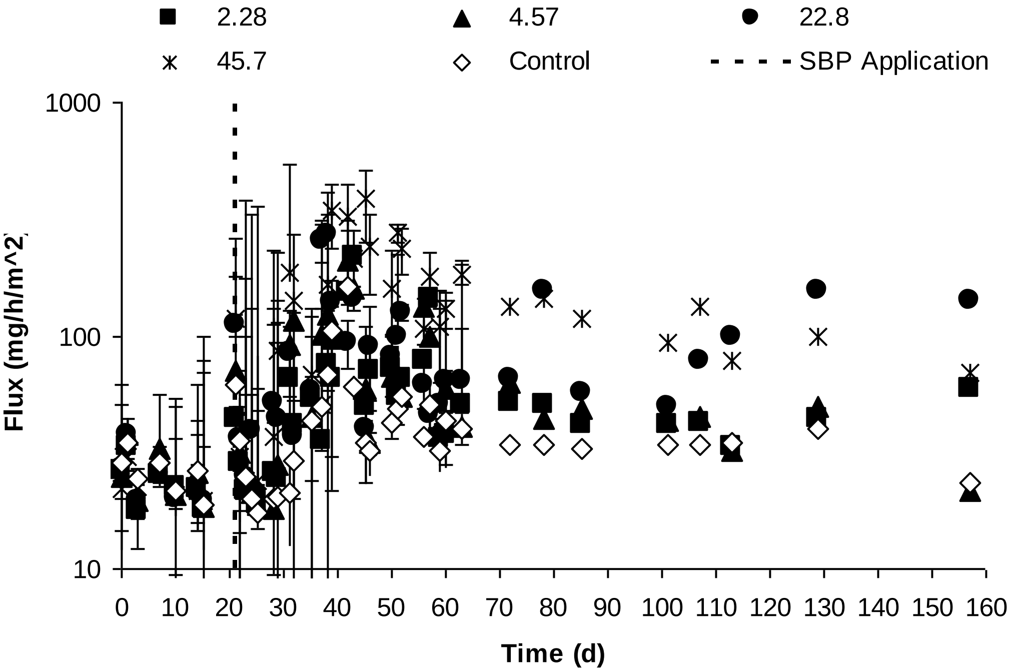

Figure 25: Pilot scale – measured methane flux. Note: SBP treatments are in kg/m^2.

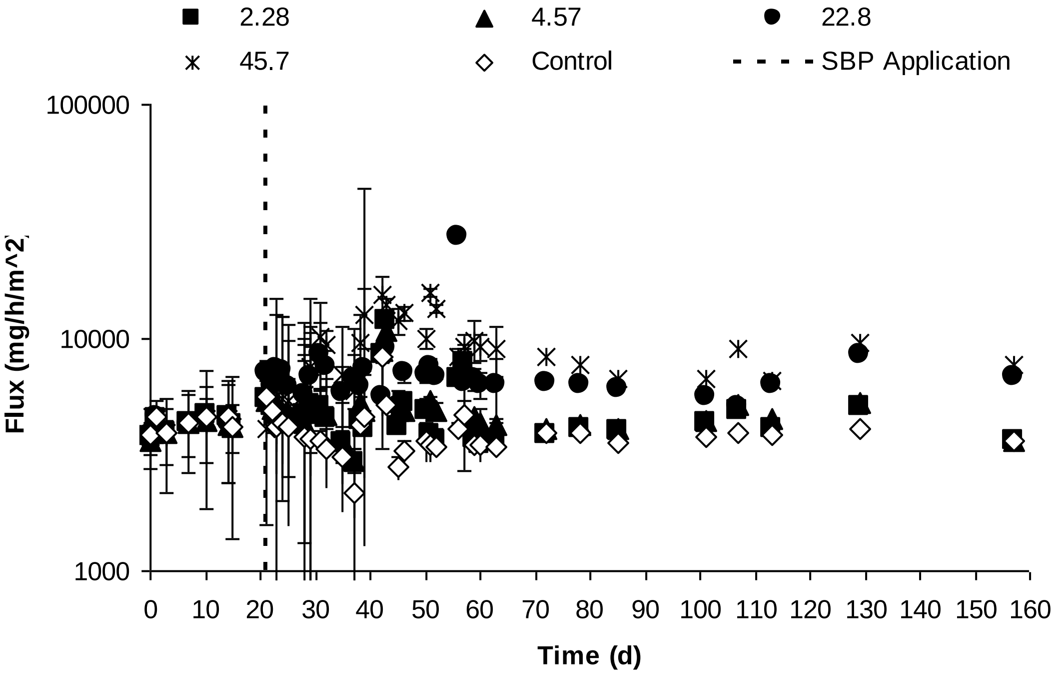

Figure 26: Pilot scale – measured carbon dioxide flux. Note: SBP treatments are in kg/m^2.

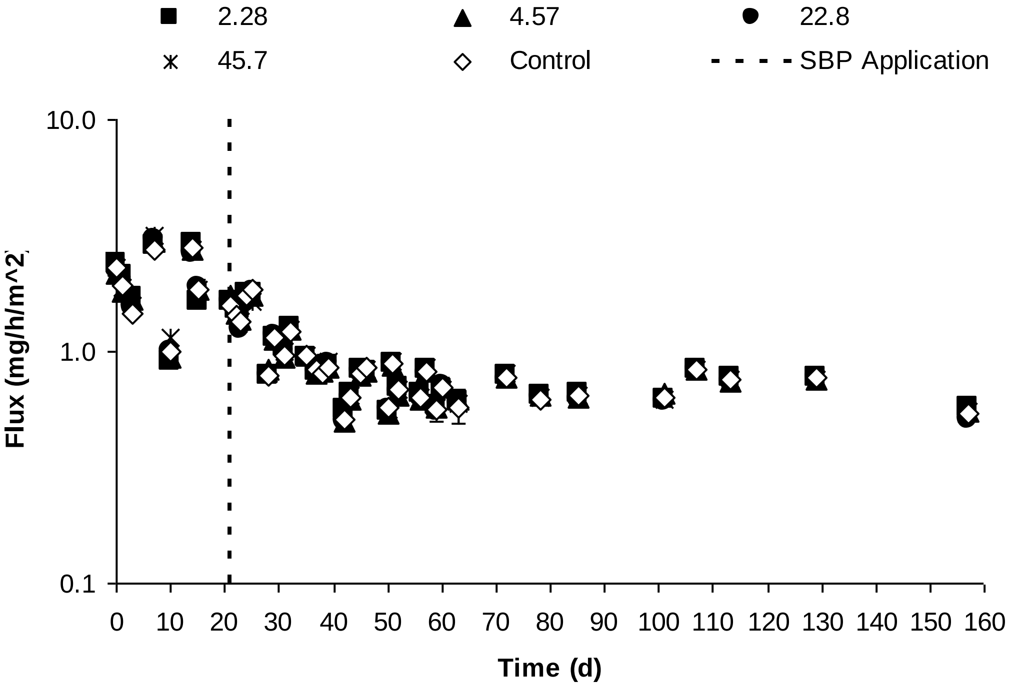

Figure 27: Pilot scale – measured nitrous oxide flux. Note: SBP treatments are in kg/m^2.

Ammonia and Hydrogen Sulfide - Pilot scale

Ammonia flux was consistently reduced for all SBP treatment levels with higher dose resulted in more significant reductions. The higher reductions in NH_3 flux estimates occurred immediately after SBP application with the SBP effect wearing off over time. (**Figure 28**) In-depth analysis of the effects of the dose is presented in a later section.

Measured concentrations of H_2S in both control and treatment were generally low (~0.1 to 25 ppm). Thus, the estimates of flux and the mitigation effect were challenging to assess. Mitigation effect was highly variable and not well correlated with the dose. SBP treatments of 2.28 and 22.8 kg/L resulted in a decrease in H_2S flux estimates while 4.57 and 45.7 kg/L SBP treatment resulted in an increase in H_2S flux estimates (**Figure 29**). In-depth analysis of the effects of the dose is presented in a later section.

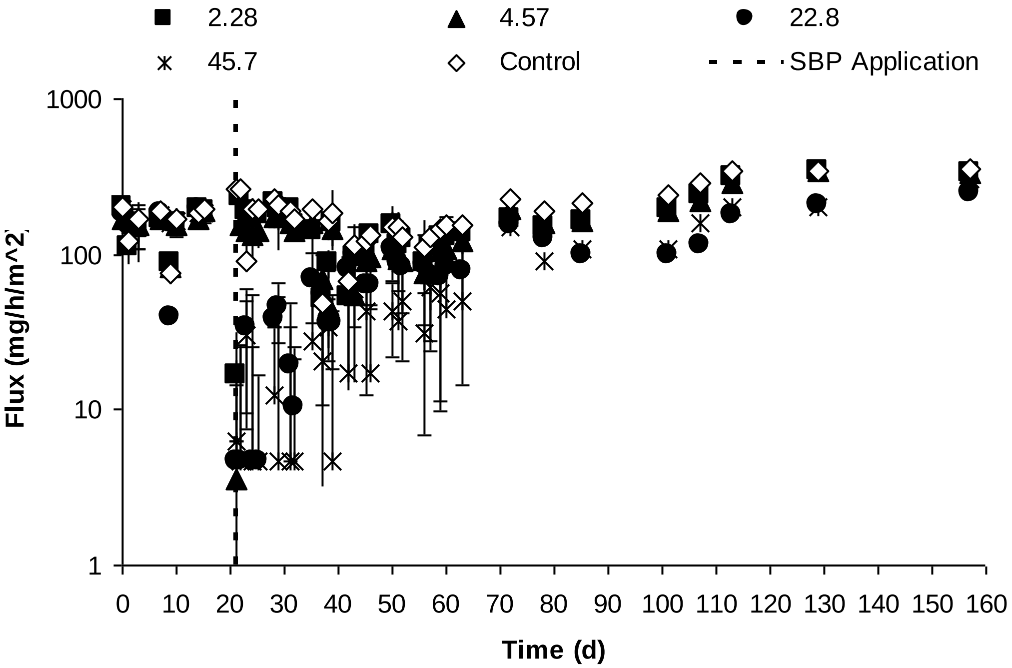

Figure 28: Pilot scale – measured ammonia flux. Note: SBP treatments are in kg/m^2.

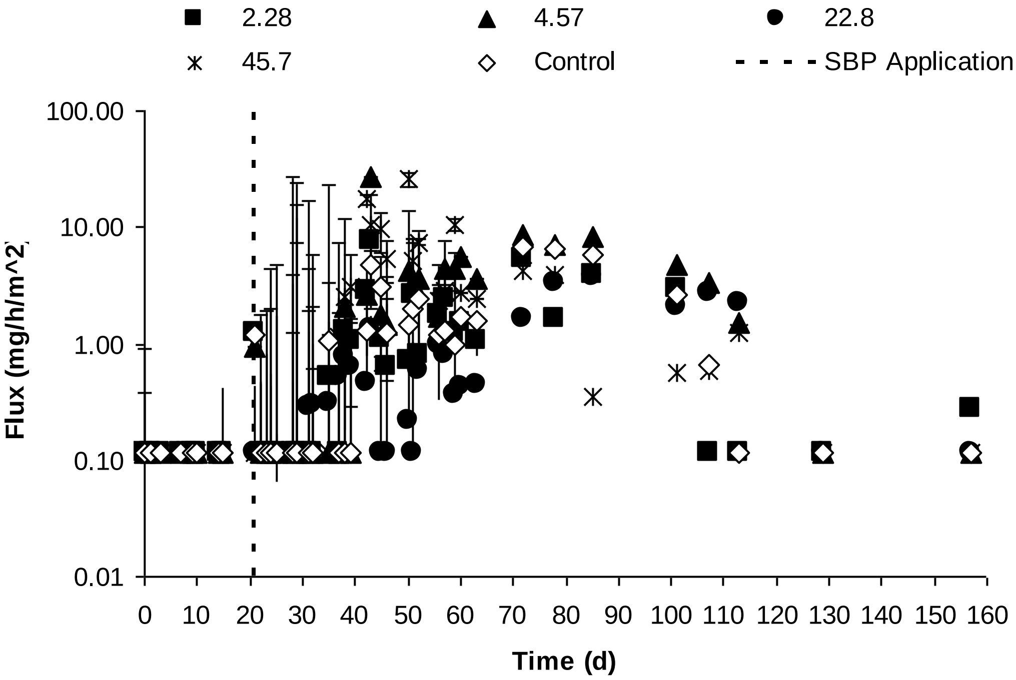

Figure 29: Pilot scale – measured hydrogen sulfide flux. Note: SBP treatments are in kg/m^2.

Volatile Organic Compounds - Pilot scale

Sulfur containing VOCs were mitigated with the SPB treatment. DMDS flux estimates were significantly reduced with the 4.57 and 22.8 kg/m^2 SBP treatments. Treatments doses of 2.28 and 45.7 kg/m^2 SBP resulted in reductions of DMDS also but not at a significant level. There was also a trend in dosing level for DMDS with higher dose resulting in higher reduction in flux estimates. In-depth analysis of the effects of the dose is presented in a later section. Fluxes of H_2S and DMDS were simultaneously higher in months 2 and 3 of the trial with the H_2S flux peaking at the end of month 1. In-depth analysis of the effects of the dose is presented in a later section.

The resulting flux estimates for DMTS did not show any significant effect in regards to any of the SBP treatments. (**Figures 30 and 31**) In-depth analysis of the effects of the dose is presented in a later section.

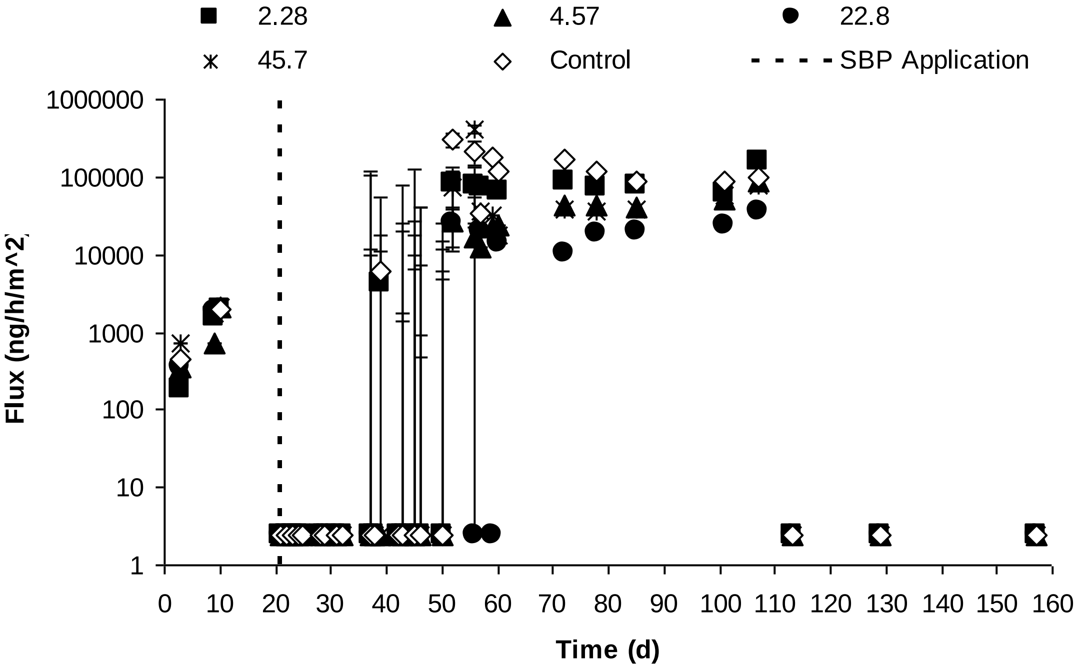

Figure 30: Pilot scale – measured DMDS flux. Note: SBP treatments are in kg/m^2.

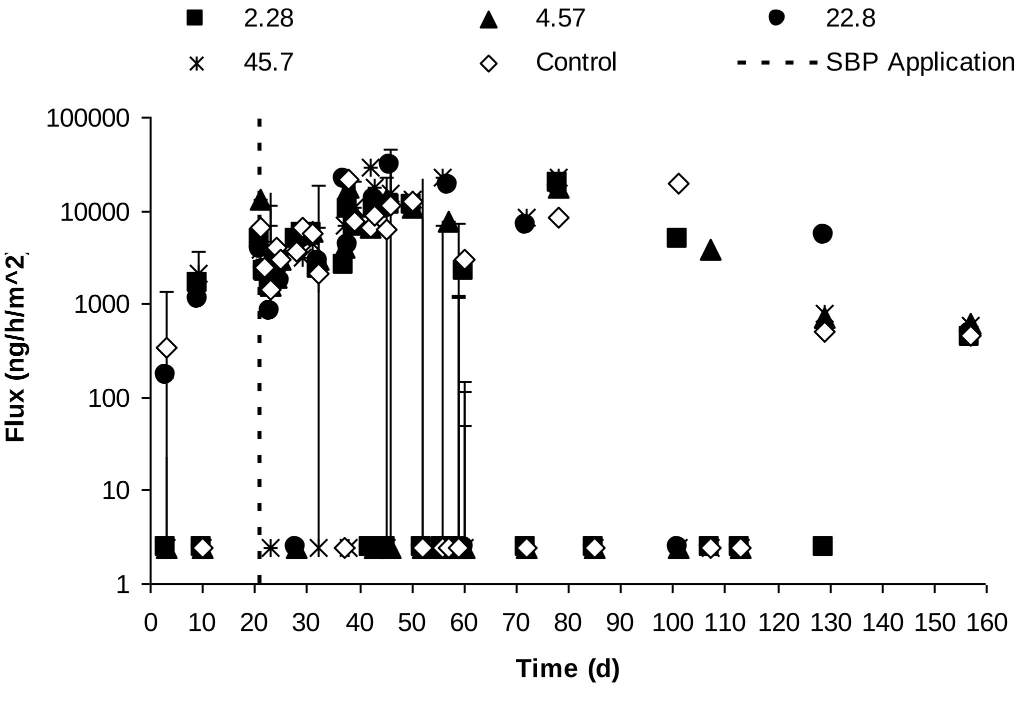

Figure 31: Pilot scale – measured DMTS flux. Note: SBP treatments are in kg/m^2.

Measured flux for the target short chain organic fatty acids did not result in any significant differences for the SBP treatments. The only exception was the highest dose (45.7 kg/m^2 of SBP) with significant increase for *n*-butyric acid and isovaleric acid flux. (**Figures. 32, 33 and 34**) In-depth analysis of the effects of the dose is presented in a later section.

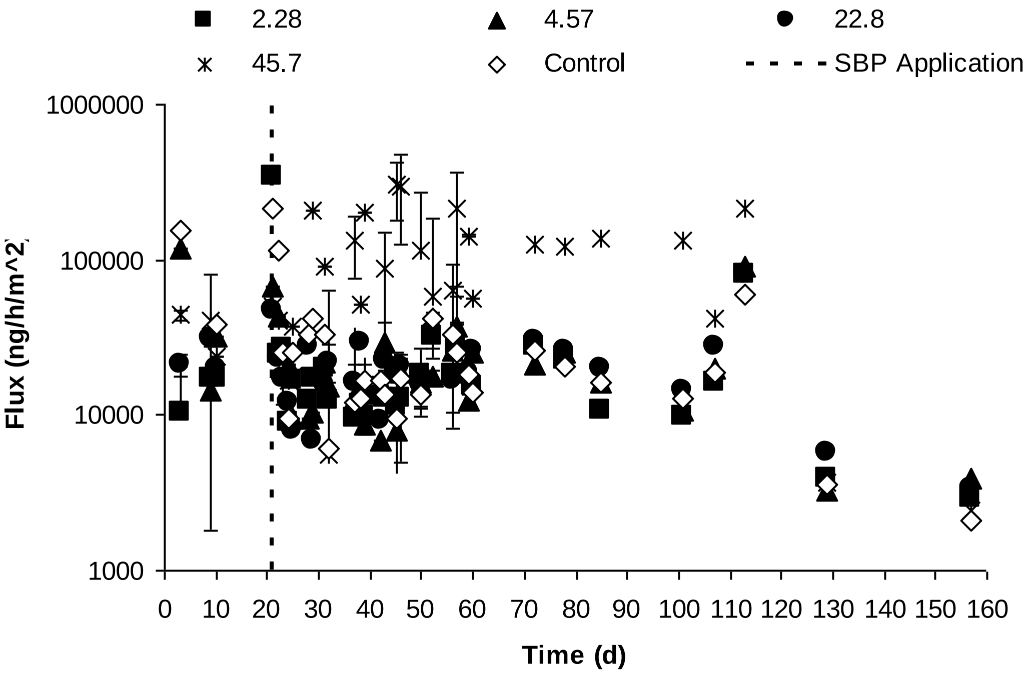

Figure 32: Pilot scale – measured *n*-butyric acid flux. Note: SBP treatments are in kg/m^2.

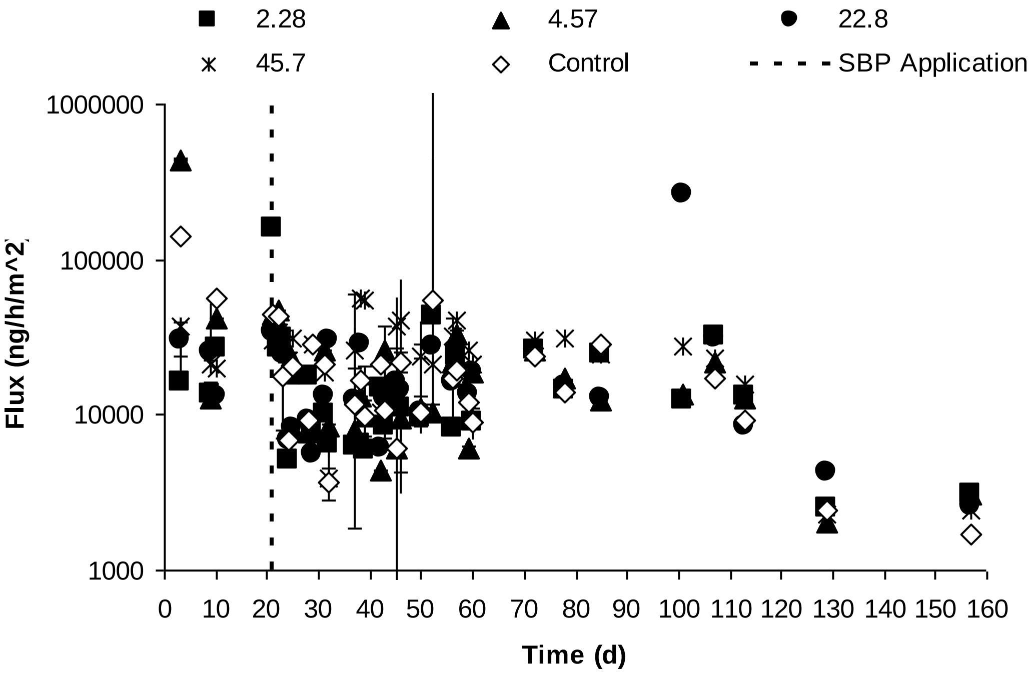

Figure 33: Pilot scale – measured valeric acid flux. Note: SBP treatments are in kg/m^2.

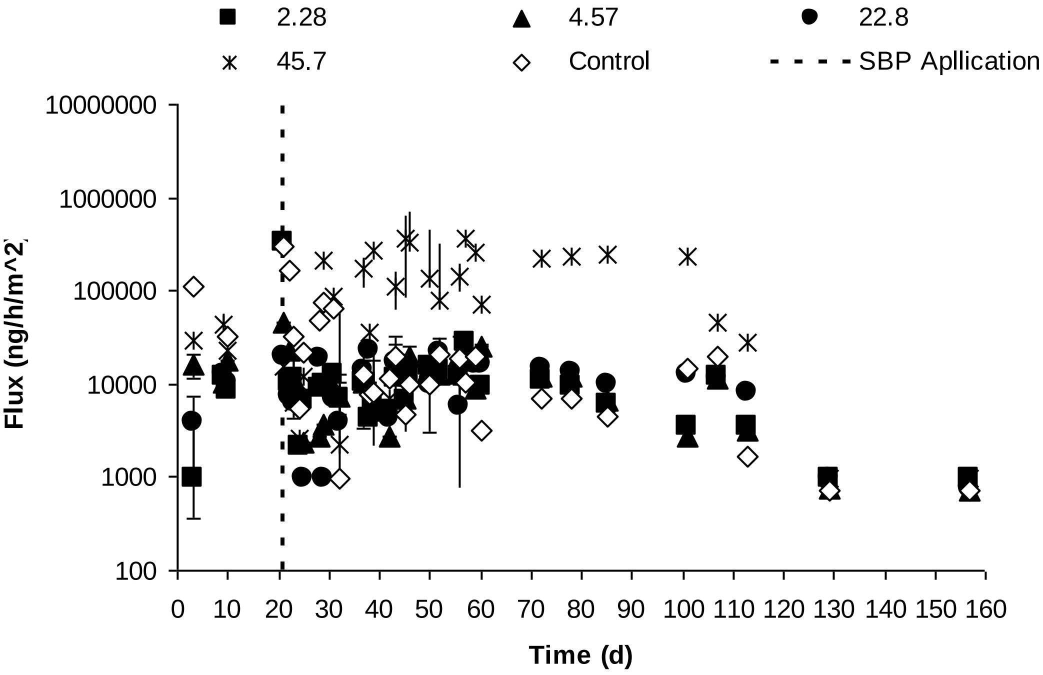

Figure 34: Pilot scale – measured isovaleric acid flux. Note: SBP treatments are in kg/m^2.

p-Cresol and skatole flux estimate was significantly reduced for all SBP treatments with no apparent benefit with higher SBP dosing. Indole flux did not result in significant reductions for any of the SBP treatments – this was likely due to the inconsistent emission of that compound at the pilot scale tests. (**Figure. 35, 36 and 37**) In-depth analysis of the effects of the dose is presented in a later section.

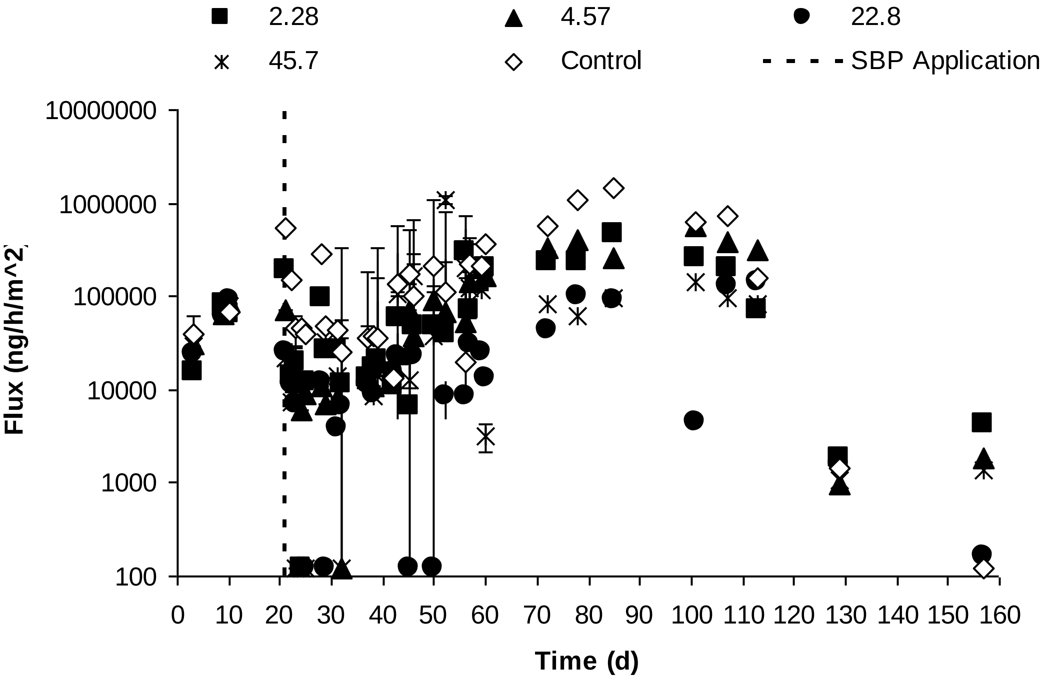

Figure 35: Pilot scale – measured *p*-cresol flux. Note: SBP treatments are in kg/m^2.

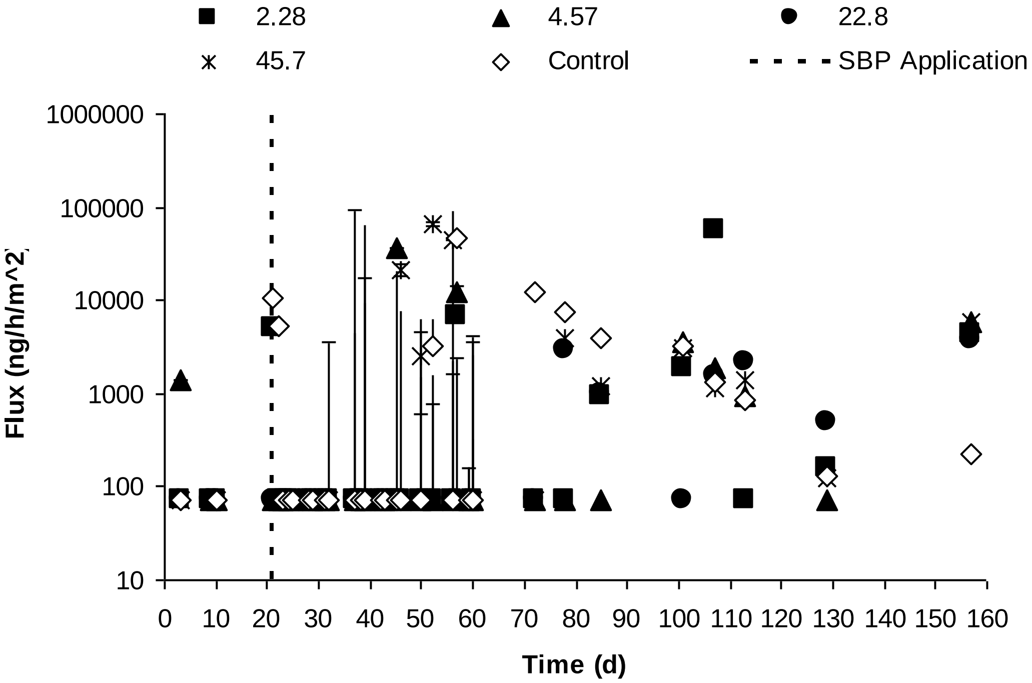

Figure 36: Pilot scale – measured indole flux. Note: SBP treatments are in kg/m^2.

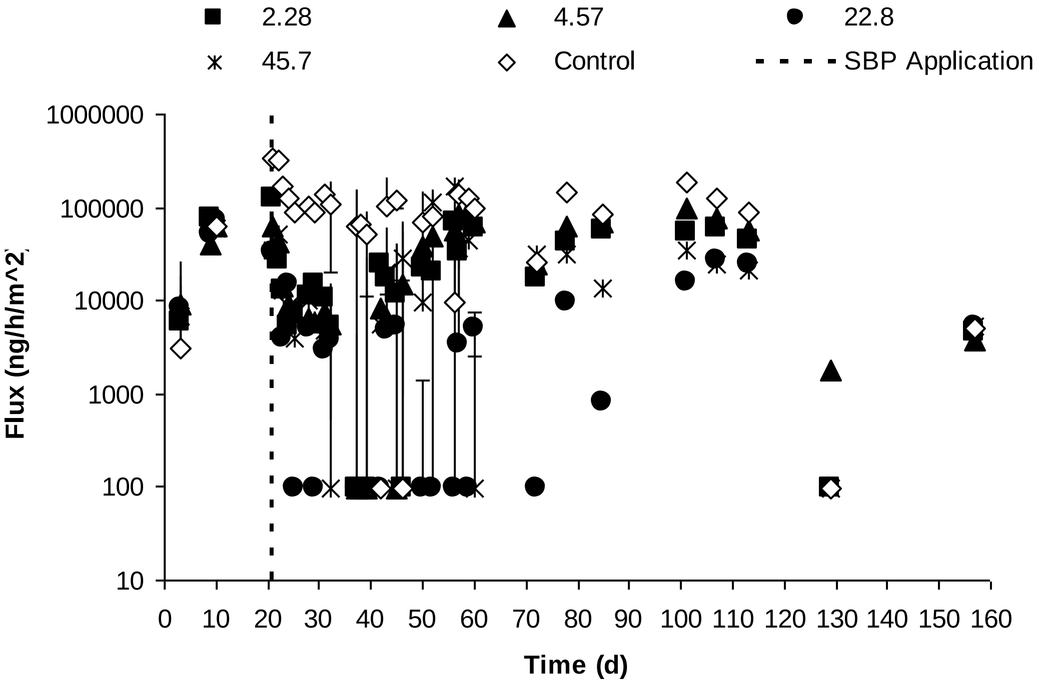

Figure 37: Pilot scale – measured skatole flux. Note: SBP treatments are in kg/m^2.

Environmental and Physicochemical Parameters - Pilot scale

Relative humidity (RH) inside simulated storage headspace and manure pH were also monitored. The SBP caused a decrease in manure pH coinciding with the dose. Decrease in pH was consistent with the observed decrease in NH_3 emissions and increase in CO_2 and CH_4 emissions (**Figures 68 and 70**).

The same could be seen for RH, i.e. RH was correlated with the dose, with the exception of the RH of the SBP treated re-converging with the control levels over the course of ~ 90 days. This apparent convergence pattern was consistent with the one observed for NH_3 flux in **Figure 28**.

Room temperature was maintained between 10 to 20 °C. (**Figure 38, 39 and 40**)

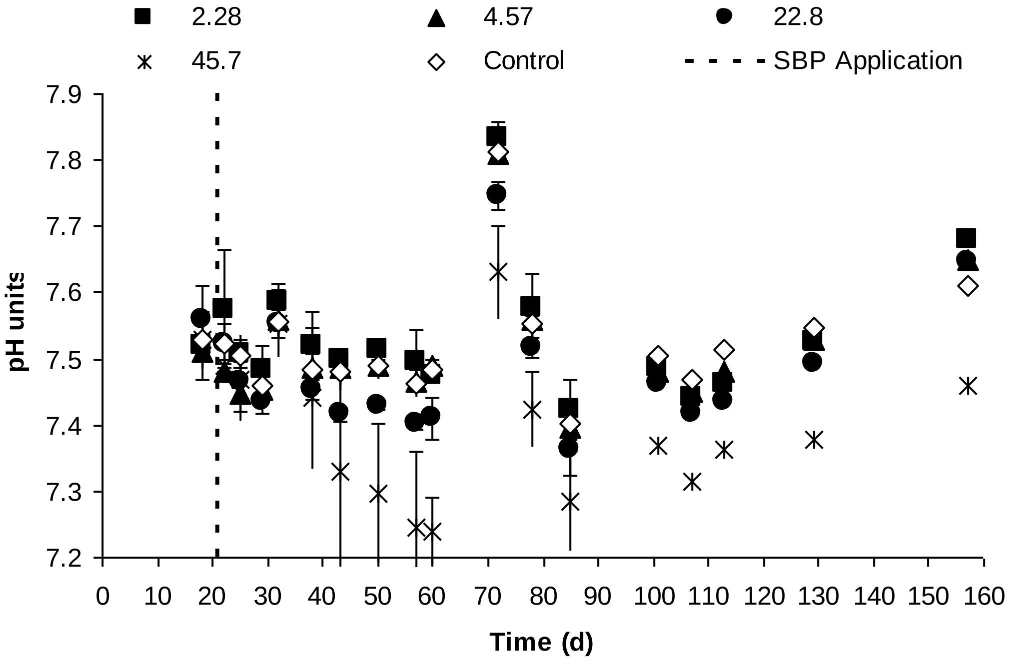

Figure 38: Pilot scale – manure pH evolution over time. Note: SBP treatments are in kg/m^2.

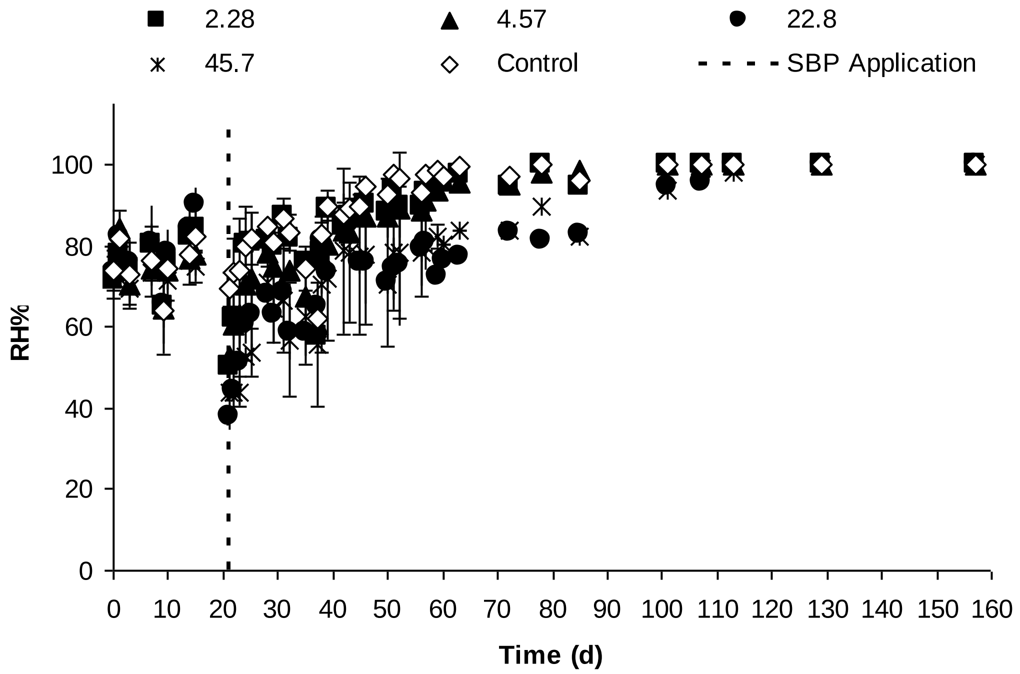

Figure 39: Pilot scale – relative humidity of headspace air above manure inside simulated storage. Note: SBP treatments are in kg/m^2.

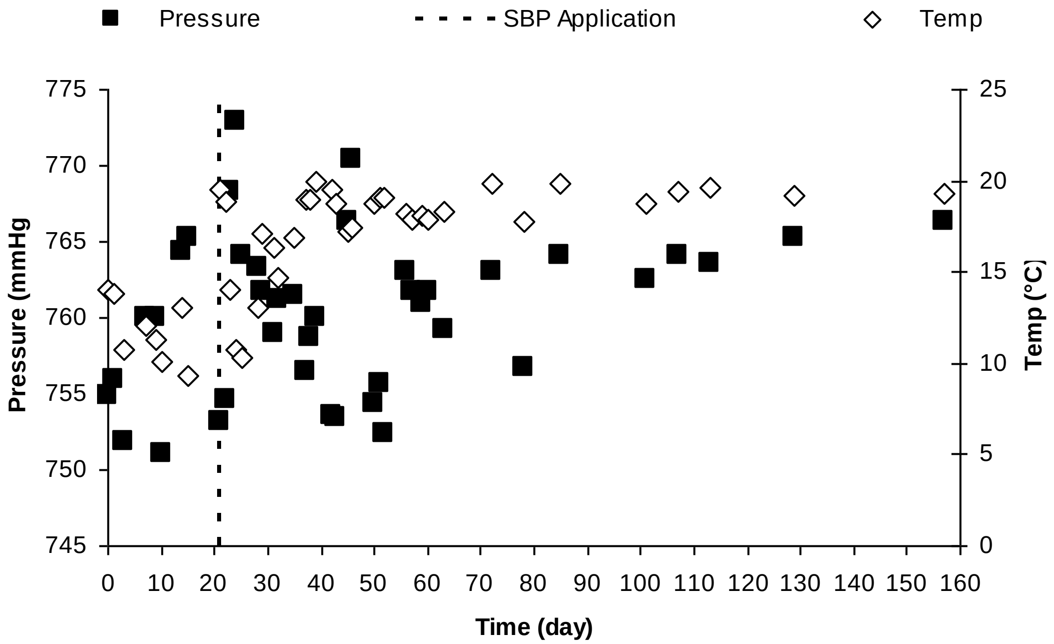

Figure 40: Pilot scale – pilot scale test room temperature and pressure.

Summary of gas measured concentrations and gas flux (emission) – pilot scale

The mean and the range (minimum and maximum) measured concentrations and estimated gas flux for pilot scale are presented in **Table 1** and **Table 2**, respectively. The mean is the average of all measured concentrations and resulting flux in headspace of rectors simulating manure storage.

Table 1: Pilot scale – Summary of measured gas concentrations.

Compound	Mean	St.dev.	Min	Max
NH_3	92.7	66.9	4.00*	302
H_2S	1.50	4.31	0.100*	44.8
CH_4	60.1	83.3	1.85	721
CO_2	1,650	1,420	245	23,200
N_2O	0.266	0.0664	0.102	0.490
DMDS	3.76	8.37	0.000400*	68.7
DMTS	0.422	0.866	0.000300*	4.95
n-Butyric Acid	5.36	8.72	0.144*	61.6
Valeric Acid	6.02	55.3	0.268*	967
Isovaleric Acid	4.14	11.3	0.131*	90.8
p-Cresol	16.0	34.5	0.0154*	274
Indole	0.324	1.72	0.00850*	19.6
Skatole	3.61	5.27	0.0102*	29.4

*limit of detection value. NH_3, H_2S, CH_4, CO_2 and N_2O concentrations in ppm. DMDS, DMTS, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole and skatole concentrations in ppb.

Table 2: Pilot scale – Summary of estimated flux ranges.

Compound	Mean	St.dev.	Min	Max
NH_3	132	83.6	4.72*	358
H_2S	1.70	4.76	0.118*	48.1
CH_4	69.8	86.2	1.96	786
CO_2	5,690	3,810	748	68,600
N_2O	1.10	0.611	0.439	3.27
DMDS	24.8	53.7	0.00240*	419
DMTS	4.00	7.61	0.00240*	45.1
n-Butyric Acid	39.1	62.2	0.911*	412
Valeric Acid	50.1	410	1.97*	7120
Isovaleric Acid	33.9	86.2	0.959*	684
p-Cresol	129	266	0.120*	2130
Indole	2.67	13.8	0.0719*	166
Skatole	39.7	56.3	0.0959*	331

*limit of detection value. NH_3, H_2S, CH_4, CO_2 and N_2O flux mg/h/m^2. DMDS, DMTS, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole and skatole flux in µg/h/m^2.

Summary of gas flux (emission) reduction – pilot scale

Summary of overall mean % reduction for each target gas before and after application of pilot scale SBP treatment (Eq. 16) for each dose tested and (n=3) replicates for control and treatment. The overall mean was estimated using all measured flux for either "Before" or "After" period. "Before SBP application" represent the 3 week period of baseline testing while "After SBP application" represent the 136 days post treatment application. The baseline testing was conducted to determine if the flux from treatment and control are statistically similar, i.e., no significant difference. No significant difference "Before SBP application: was observed for all treatments with the exception of butyric acid (at 22.8 kg/m^2).

Pilot scale tests resulted in reduction of gaseous emissions (flux) for some compounds, while no difference or increase in emissions for others for the entire SBP testing period of 136 days.

1. **Ammonia** emissions were reduced by 14.6% to 67.6% and were statistically significant except for the lowest SBP dose. The percent reduction was correlated with the SBP dose. The apparent effectiveness of SBP treatment was decreasing over time.
2. **H_2S** emissions were highly variable and not correlated with the SBP dose.
3. **GHGs** emissions were not significantly changed for N_2O. Methane and CO_2 emissions increased by 32.7% to 232% and 20.8% to 124%, respectively. The percent increase was statistically significant (except for CH_4 and the lowest dose) and was correlated with the SBP dose. The increase of CO_2 and CH_4 emissions may be inferred considering biochemical breakdown of VOCs as a result of SBP treatment.
4. **Sulfur VOC** emissions were generally reduced by 36.2% to 84.7% (DMDS) and 10.7% to 16.9% (DMTS). However, the only statistically significant reduction was for DMDS at the mid-range SBP doses.
5. **Volatile fatty acids** emissions were reduced by 8.5% to 19.5% (butyric acid), 79.2% to 88.5% (valeric acid) and 42.7% to 59.2% (isovaleric acid) except for the highest SBP dose for butyric and isovaleric acids. However, none of the reductions were statistically significant.
6. **Phenolics** emissions were reduced by 53.1% to 89.5% (*p*-cresol), 52.6% to 81.8% (indole, except for the highest SBP dose), and 63.2% to 92.5% (skatole) and were statistically significant for *p*-cresol and skatole. Indole emission's reductions were not statistically significant. The apparent effectiveness of SBP treatment on phenolics was decreasing over time.

Specifically:

- **NH_3** flux (emissions) were reduced by 67.6% ($p<0.0001$), 58.4% ($p<0.0001$), 25.2% ($p=0.008$) for 45.7, 22.8, 4.57 kg/m^2 SBP dose, respectively. NH_3 flux was also reduced by 14.6% for the lowest 2.28 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.120$).
- **H_2S** flux (emissions) were highly variable and not correlated with the dose. H_2S flux was reduced by 48.3% ($p=0.036$) for 22.8 kg/m^2 SBP dose. H_2S flux was also reduced by 10.9% for the lowest 2.28 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.688$). H_2S flux increased by 144.4% ($p=0.024$) for 45.7 kg/m^2 SBP dose. H_2S flux also increased by 105.9% for the 4.57 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.062$).
- **CH_4** flux (emissions) increased by 232% ($p<0.0001$), 107% ($p<0.0001$), 52.1% ($p=0.009$) for 45.7, 22.8, 4.57 kg/m^2 SBP doses, respectively. CH_4 flux also increased by 32.7% for the lowest 2.28 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.077$).
- **CO_2** flux (emissions) increased by 124% ($p<0.0001$), 83.5% ($p<0.0001$), 27.4% ($p=0.0003$), 20.8% ($p=0.013$) for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively.
- **N_2O** flux (emissions) were highly variable and not correlated with the dose. N_2O flux was slightly reduced by 0.4% for 22.8 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.97$). N_2O flux slightly increased by 1.3%, 0.2%, 2.6% for 45.7, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.913$, $p=0.985$, $p=0.919$, respectively).
- **DMDS** flux (emissions) were reduced by 84.7% ($p=0.006$) and 67.5% ($p=0.021$) for 22.8, 4.57 kg/m^2 SBP doses, respectively. DMDS flux was also reduced by 50.3% and 36.2% for the 45.7 and 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.335$ and $p=0.212$, respectively).
- **DMTS** flux (emissions) were highly variable and not correlated with the dose. DMTS flux was reduced by 10.7% and 16.9% for 4.57 and 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.577$ and $p=0.495$, respectively). DMTS flux slightly increased by 6.2% and 9.2% for 45.7 and 22.8 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.631$ and $p=0.632$, respectively).
- ***n*-Butyric Acid** flux (emissions) were highly variable and not correlated with the dose. *n*-Butyric acid flux increased by 235% ($p=0.0002$) for 45.7 kg/m^2 SBP dose. *n*-Butyric acid flux was reduced by

17.5%, 19.5%, 8.5% for the 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.270, p=0.225, p=0.944, respectively).

- **Valeric acid** flux (emissions) were highly variable and not correlated with the dose. Valeric acid flux was reduced by 83.5%, 79.2%, 88.5%, 87.5% for the 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.356, p=0.362, p=0.301, p=0.331 respectively).
- **Isovaleric acid** flux (emissions) were highly variable and not correlated with the dose. Isovaleric acid flux increased by 355% (p=0.0003) for 45.7 kg/m^2 SBP dose. Isovaleric acid flux was reduced by 58.8%, 59.2%, and 42.7% for the 22.8, 4.57, and 2.28 kg /m2 SBP doses, respectively. However, the treatment was not significant (p=0.071, p=0.064, p=0.474, respectively).
- ***p*-Cresol** flux (emissions) were reduced by 78.2% (p=0.023), 89.5% (p=0.001), 53.1% (p=0.040), 64.9% (p=0.020) for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively.
- **Indole** flux (emissions) were highly variable and not correlated with the dose. Indole flux was reduced by 81.8% and 52.6% for 22.8 and 4.57 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.093 and p=0.571, respectively). Indole flux increased by 24.2% and slightly increased by 3.2% for 45.7 and 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.544 and p=0.811, respectively).
- **Skatole** flux (emissions) was reduced by 77.2% (p<0.0001), 92.5% (p<0.0001), 63.2% (p<0.0001), 72.6% (p<0.0001) for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively.

Table 3: Pilot scale – overall statistical significance of emissions reduction of SBP treatment over 136 days.

		Pilot scale test							
SBP dose (kg/m^2)		**45.7**		**22.8**		**4.57**		**2.28**	
SBP dose (lb/ft^2)		**9.36**		**4.67**		**0.936**		**0.467**	
SBP dose (g/L)		**50**		**25**		**5.0**		**2.5**	
Gas	**Before / After SBP Application**		p value		p value		p value		p value
NH_3	Before	-4.4	0.836	3.7	0.853	1.5	0.945	3.1	0.887
NH_3	After	**67.6**	**<.0001**	**58.4**	**<.0001**	**25.2**	**0.008**	14.6	0.120
H_2S	Before	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000
H_2S	After	**-144.4**	**0.024**	**48.3**	**0.036**	-105.9	0.062	10.9	0.688
CH_4	Before	10.5	0.936	6.7	0.939	1.7	0.981	9.5	0.880
CH_4	After	**-231.7**	**<.0001**	**-107.1**	**<.0001**	**-52.1**	**0.009**	-32.7	0.077
CO_2	Before	1.4	0.956	1.3	0.968	2.9	0.844	0.1	0.996
CO_2	After	**-123.6**	**<.0001**	**-83.5**	**<.0001**	**-27.4**	**0.000**	**-20.8**	**0.013**
N_2O	Before	-3.9	0.726	-2.3	0.838	-0.5	0.967	-2.7	0.814
N_2O	After	-1.3	0.913	0.4	0.970	-0.2	0.985	-2.6	0.919
DMDS	Before	-21.5	0.999	-5.6	0.997	-4.7	0.997	-3.3	0.999
DMDS	After	50.3	0.335	**84.7**	**0.006**	**67.5**	**0.021**	36.2	0.212
DMTS	Before	-77.5	0.992	-36.5	0.999	98.6	0.973	-150.7*	0.933
DMTS	After	-6.2	0.631	-9.2	0.632	10.7	0.577	16.9	0.495
***n*-Butyric Acid**	Before	64.2	0.251	**77.5**	**0.008**	32.6	0.138	85.0	0.089
***n*-Butyric Acid**	After	**-235.0**	**0.000**	17.5	0.270	19.5	0.225	8.5	0.944
Valeric Acid	Before	72.3	0.776	77.8	0.767	-110.8	0.819	80.3	0.771
Valeric Acid	After	83.5	0.356	79.2	0.362	88.5	0.301	87.5	0.331
Isovaleric Acid	Before	60.1	0.563	88.9	0.092	77.5	0.125	90.8	0.226

Isovaleric Acid	After	**-354.7**	**0.000**	58.8	0.071	59.2	0.064	42.7	0.474
***p*-Cresol**	Before	-6.6	0.971	-9.9	0.972	-9.3	0.973	5.9	0.999
***p*-Cresol**	After	**78.2**	**0.023**	**89.5**	**0.001**	**53.1**	**0.040**	**64.9**	**0.020**
Indole	Before	0.0	0.999	0.0	0.998	-809.2*	0.952	0.0	1.000
Indole	After	-24.2	0.544	81.8	0.093	52.6	0.571	-3.2	0.811
Skatole	Before	-17.0	0.956	-25.8	0.989	-12.0	0.937	-33.1	0.786
Skatole	After	**77.2**	**<.0001**	**92.5**	**<.0001**	**63.2**	**<.0001**	**72.6**	**<.0001**

Bold: Statically significantly at a 95% confidence level.

*gas was not detected consistently enough at high enough levels to achieve reproducible results.

Soybean Peroxidase Activity – Pilot scale

Table 4: Pilot scale – soybean peroxidase activity and layer thickness before and after 87 days of treatment.

Treatment	2.28 kg/m^2	4.57 kg/m^2	22.8 kg/m^2	45.7 kg/m^2	"fresh"
Activity (U/ml)	0.00016	0.00032	0.00148	0.0006	0.76533
Starting Thickness (mm)	6	13	64	127	
Dry Thickness (mm)	2	9	31	15	
Wet Thickness (mm)	24	40	31	15	

Note: The starting thickness is that of the SBP at application. The dry thickness is that of the thickness of dry SBP on the surface of the manure after 87 days. The wet thickness is that of the thickness of the SBP that had soaked up moisture from the surface of the manure.

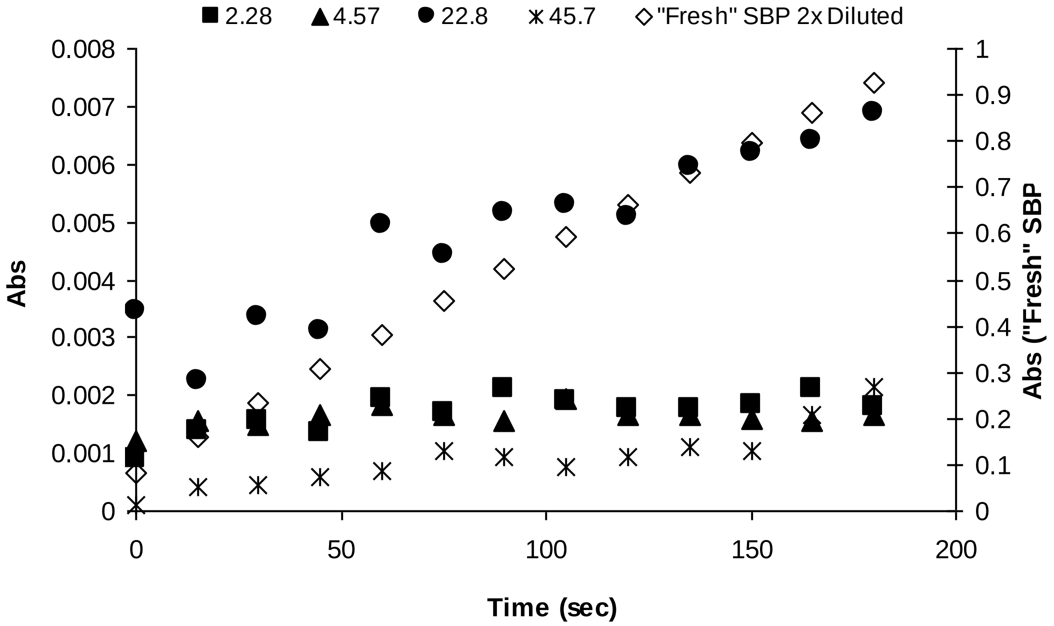

Figure 41: Pilot scale – day 87 after SBP treatment SBP activity. Note: SBP treatments are in kg/m^2.

The soybean peroxidase activity was determined on the SBP that had been applied to manure for 87 days to determine if there was still enzymatic activity after that duration of exposure to the swine manure. The resulting activities showed that the SBP that had sank into the manure, thus being directly in contact with the manure (does 2.28, 4.57 and 45.7 kg/m^2 SBP), were much lower than that of the 22.8 kg/m^2 SBP dose, which had dry SBP still floating on the surface of the manure. (**Figure. 41 and Table 4**)

Manure Analysis - Pilot Scale

Table 5: Pilot scale – manure analysis data.

SBP Treatment (kg/m^2)	TS%		VS %		Volatility %		COD mg/L		pH		NH3-N mg/L		TKN mg/L		PO4-P mg/L		TP mg/L	
	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137	Before	Day 137
0	9.7 a	4.3 b	8.4 a	2.9 b	86.0 a	66.8 b	41935.3 a	17550.0 a	7.5 a	7.6 a	8550.3 a	6836.7 a	11481.7 a	7323.3 c	147.0 a	NA	392.7 a	NA
2.28	6.6 a	4.0 b	5.3 a	2.7 b	79.7 ab	65.7 b	39372.7 a	17201.7 a	7.5 a	7.6 a	11872.7 a	7299.7 a	14999.0 a	7686.0 bc	146.0 a	NA	413.0 a	NA
4.57	8.7 a	3.9 b	7.4 a	2.6 b	82.7 ab	65.5 b	39197.3 a	17694.3 a	7.5 a	7.6 a	11195.0 a	6679.0 a	15169.3 a	7686.3 bc	145.3 a	NA	395.0 a	NA
22.8	5.9 a	4.1 b	4.7 a	2.7 b	77.7 b	66.3 b	39136.7 a	19036.3 a	7.6 a	7.6 a	10364.3 a	7996.7 a	12990.0 a	7967.7 b	151.7 a	NA	413.0 a	NA
45.7	7.7 a	5.2 a	6.4 a	3.6 a	81.3 ab	69.4 a	41867.0 a	19623.0 a	7.5 a	7.4 b	11185.7 a	7280.7 a	13031.7 a	8641.3 a	157.0 a	NA	386.0 a	NA

Means for each value followed by different letter are significantly different at $p < 0.05$ for each column.

The SBP treatment did not result in nitrogen lose decreases for any of the SBP treatment levels but the SBP itself added nitrogen to the manure relative to the dosing level. (**Figure. 42 and Table 6**)

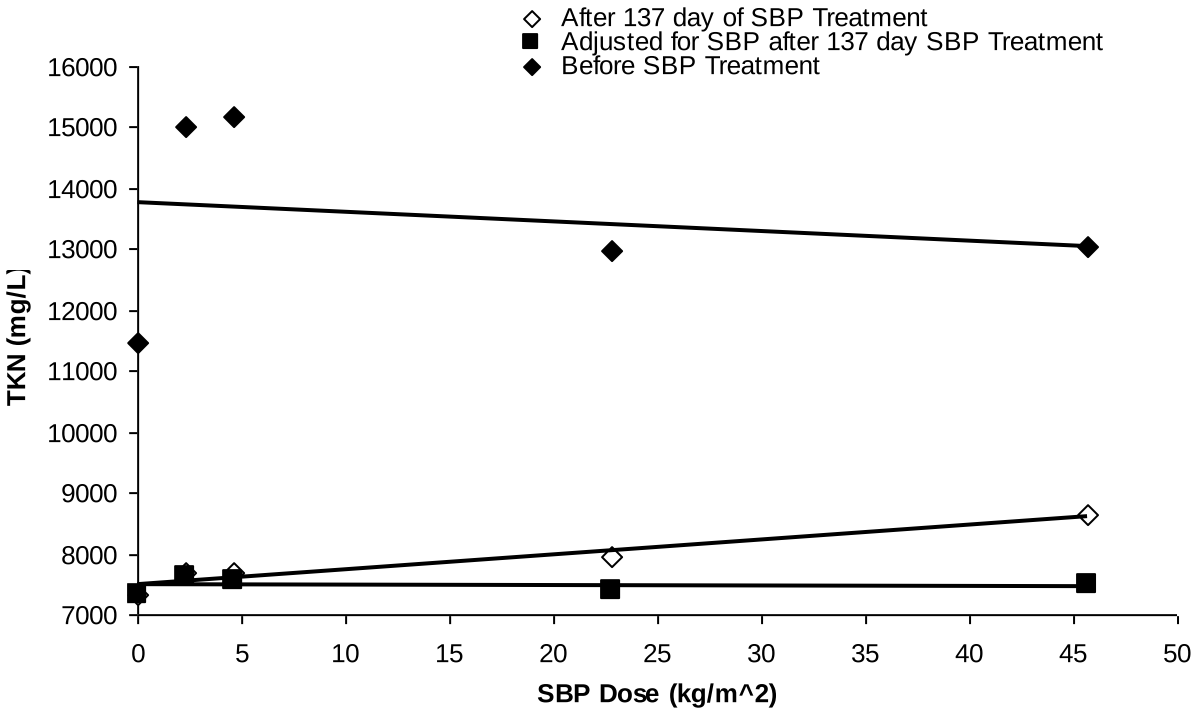

Figure 42: Pilot scale – total Kjeldahl nitrogen (TKN) of manure after 137 days of treatment as is and adjusted to account for N that was added by the SBP itself.

Table 6: Pilot scale – nitrogen loss from manure.

SBP kg/m^2	TKN Loss (g)	% TKN Lost	% of lost as NH_3	% of lost as N_2O	% of loss as NH_3 and N_2O
0	511.57	36.22	14.79	0.04	14.82
2.28	899.65	48.76	7.47	0.02	7.49
4.57	920.56	49.33	7.01	0.02	7.02
22.8	617.84	38.66	6.50	0.03	6.53
45.7	540.11	33.69	7.34	0.03	7.37

Effects of SBP ***Dose*** *- Pilot scale*

The % reduction showed strong linear correlation with the SBP dose for the overall pilot scale treatment period for NH_3, CH_4, and CO_2 (**Table 7**). For the rest of the gases the SBP dose effect starts to plateau for SBP doses > 4.57 kg/m^2 (**Figure 43**). Strong linear correlation between SBP dose and % reduction was also observed for H_2S, DMDS, *n*-butyric acid, valeric acid, isovaleric acid and *p*-cresol for the lowest three SBP doses, i.e., when 0, 2.28, and 4.57 kg/m^2 were taken in to account (**Table 7**).

Table 7: Pilot scale – overall % reduction correlation with SPB dose.

Doses*	**NH_3**	**H_2S**	**CH_4**	**CO_2**	N_2O	**DMDS**	DMTS	**BA**	**VA**	**IVA**	***p*-Cresol**	Indole	Skatole
5	**0.884**	0.406	**0.940**	**0.957**	0.003	0.013	0.363	0.658	0.605	0.587	0.084	0.328	0.196
4	**0.917**	0.260	0.739	**0.960**	0.142	0.381	0.544	0.493	0.718	0.423	0.612	0.483	0.389
3	**1.000**	**0.818**	**0.998**	**0.898**	0.001	**0.925**	0.053	**0.997**	**0.885**	**0.941**	**0.790**	0.344	0.689

Notes: Bold values are R^2 values >0.75 showing high correlation. BA: *n*-butyric acid, VA: valeric acid, IVA: isovaleric acid. * doses were 0, 2.28, 4.57, 22.8 and 45.7 kg/m^2 with 5 being all five doses factored in and 4 being the lowest four doses factor in, and 3 being the lowest three doses factored in.

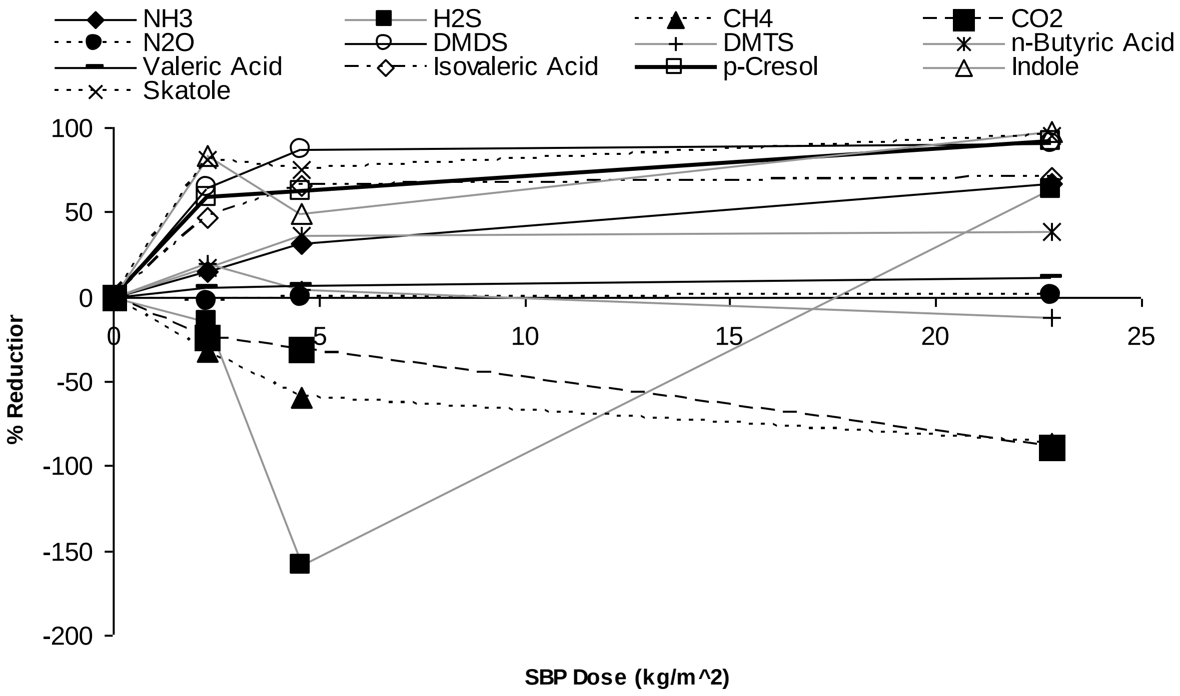

Figure 43: Pilot scale – target gas reduction as a result of SBP dose. Highest dose not shown due to no or only minor improvement in target gas reduction.

Correlations (R^2 values) were also calculated on weekly and biweekly basis in order to observe any change in SBP dose effects over the monitoring period (**Figures 44-49**). There is a fall off of correlation observed after week 14 when all SBP doses are considered.

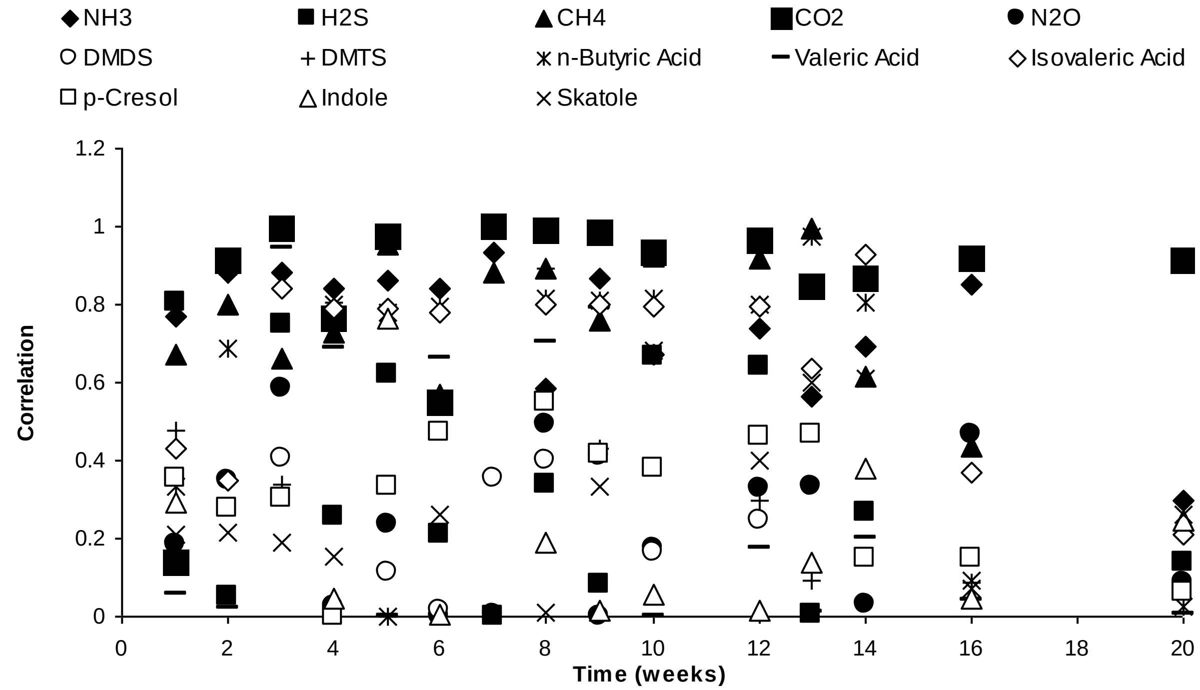

Figure 44: Pilot scale – weekly correlations incorporating all five SBP doses.

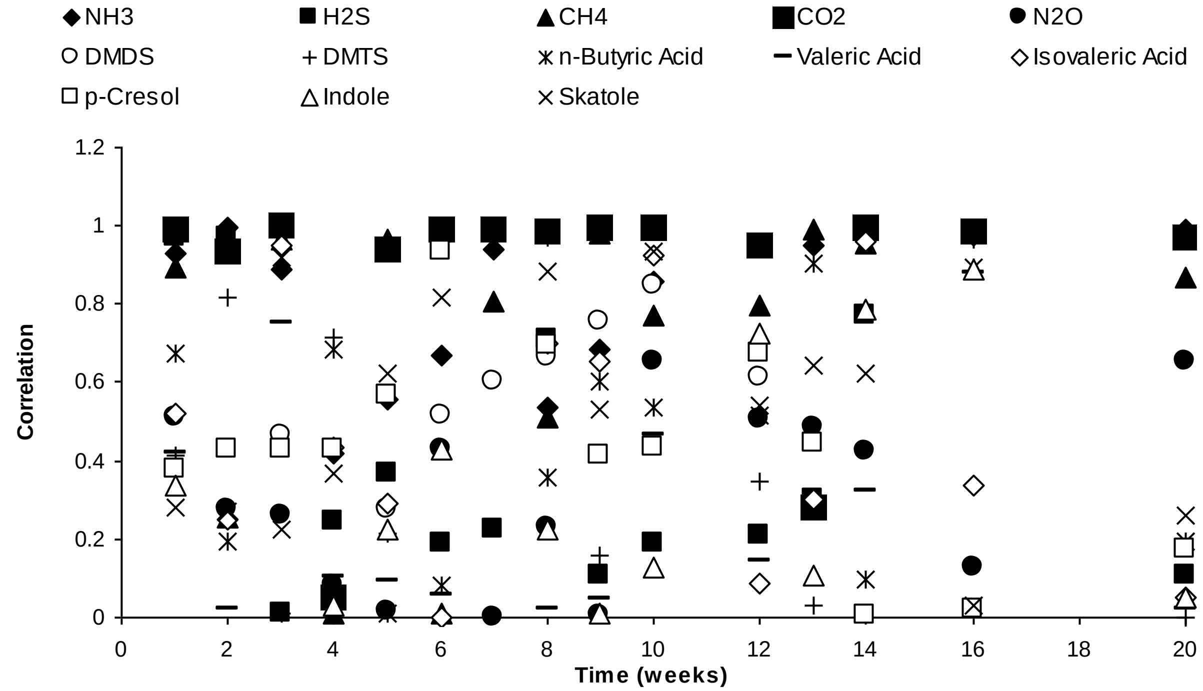

Figure 45: Pilot scale – weekly correlations incorporating the four lowest SBP doses.

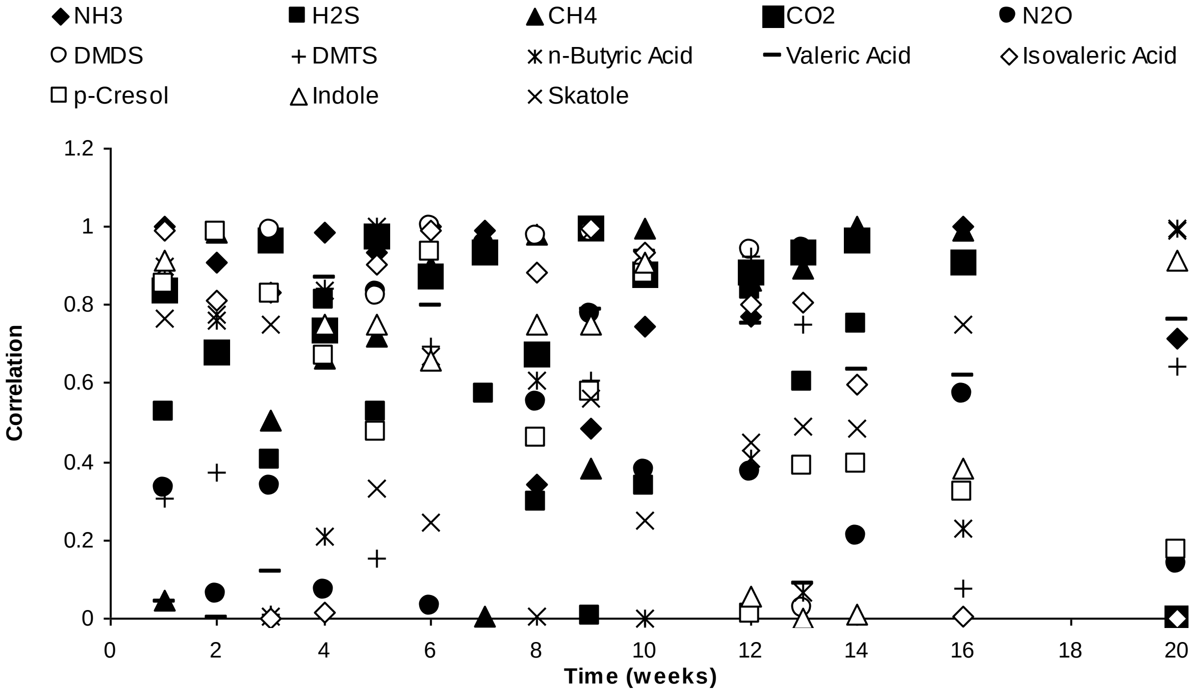

Figure 46: Pilot scale – weekly correlations incorporating the three lowest SBP doses.

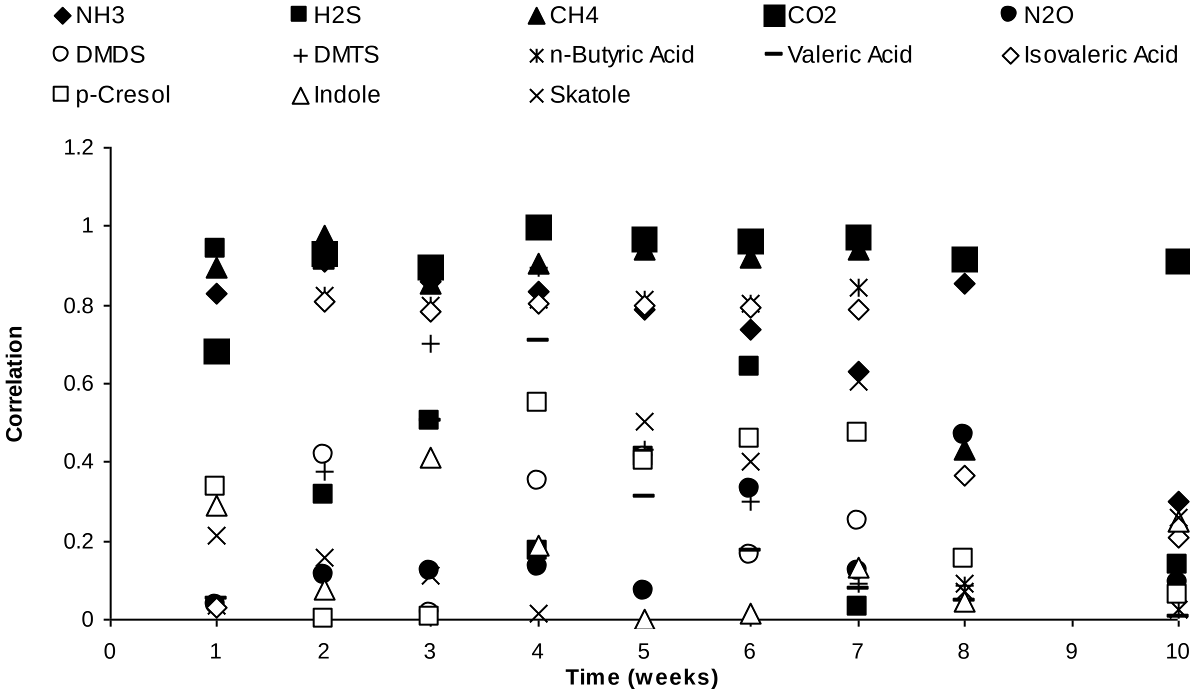

Figure 47: Pilot scale – biweekly correlations incorporating all five SBP doses.

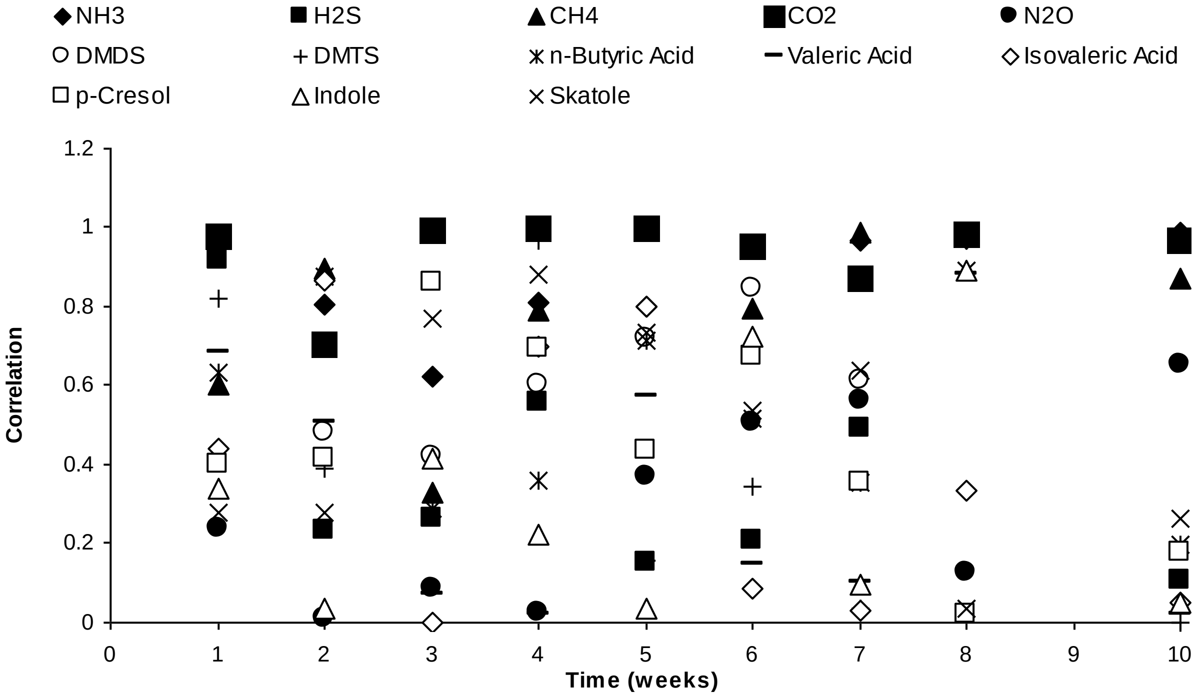

Figure 48: Pilot scale – biweekly correlations incorporating the four lowest SBP doses.

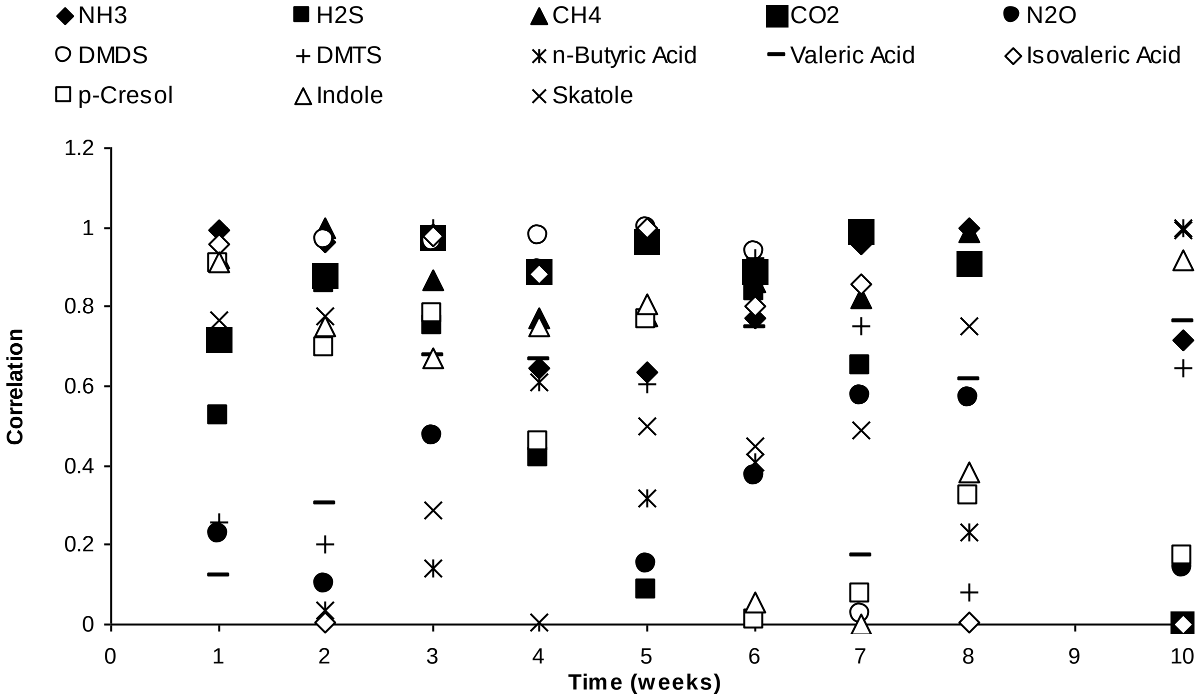

Figure 49: Pilot scale – biweekly correlations incorporating the three lowest SBP doses.

Objective 2. *Test the effectiveness of soybean peroxidase for swine manure treatment and mitigation of odorous VOCs, ammonia, hydrogen sulfide and greenhouse gas emissions in production scale.*

Farm Scale

Table 8: SBP treatment application rates

	SBP Concentration*		**Surface Application**		**SBP Surface Layer Thickness**	
	g/L	**lb/gal**	**kg/m^2**	**lb/ft^2**	**cm**	**in**
Pilot Scale**	50.0****	0.417	45.7	9.36	12.7	5.00
Pilot Scale	25.0	0.209	22.8	4.67	6.35	2.50
Pilot Scale	5.00	0.042	4.57	0.936	1.27	0.50
Pilot Scale	2.50	0.021	2.28	0.467	0.635	0.25
Swine Farm***	12.0	0.100	2.28	0.467	0.635	0.25

*Based on topical application estimated for comparison between (Parker et al) study in which SBP was mixed with manure. Values signify the ratio of the mass of SBP applied to the surface (without mixing) to the initial volume of manure.

**PVC columns: height/diameter 1.2 m/0.38 m (4 ft/1.2 ft), sealed headspace with ventilation rate of 7.5 exchanges/h, initial/final manure depth 0.91/1.2 m (3.0/3.8 ft).

***Swine finisher room: fully slated floor, 100% mechanical ventilation, initial/final amount of pigs 90/89, initial/final depth of manure in pit 0.18/0.51 m (0.58/1.7 ft), initial stocking density 1pig/0.75 m^2, initial/final pig weight.

****This concentration of SBP treatment was tested as mixed with manure (Parker et al)

Treatment application rates for SBP are shown in **Table 8** with equivalent units in metric and standard units along with concentration and surface equivalences. In previous work (Parker 2012) the SBP was mixed into the manure so treatments were determined as a concentration (g/L) of SBP in manure. This study was based on surface application of the SBP, which would be the practical way of applying the treatment in real world applications, so the surface application units of kg/m^2 were used.

Greenhouse Gases - Farm Scale

There were no statistically significant differences in estimated flux for the three GHGs at the farm scale as a result of the SBP treatment. (**Figures. 50, 51 and 52**)

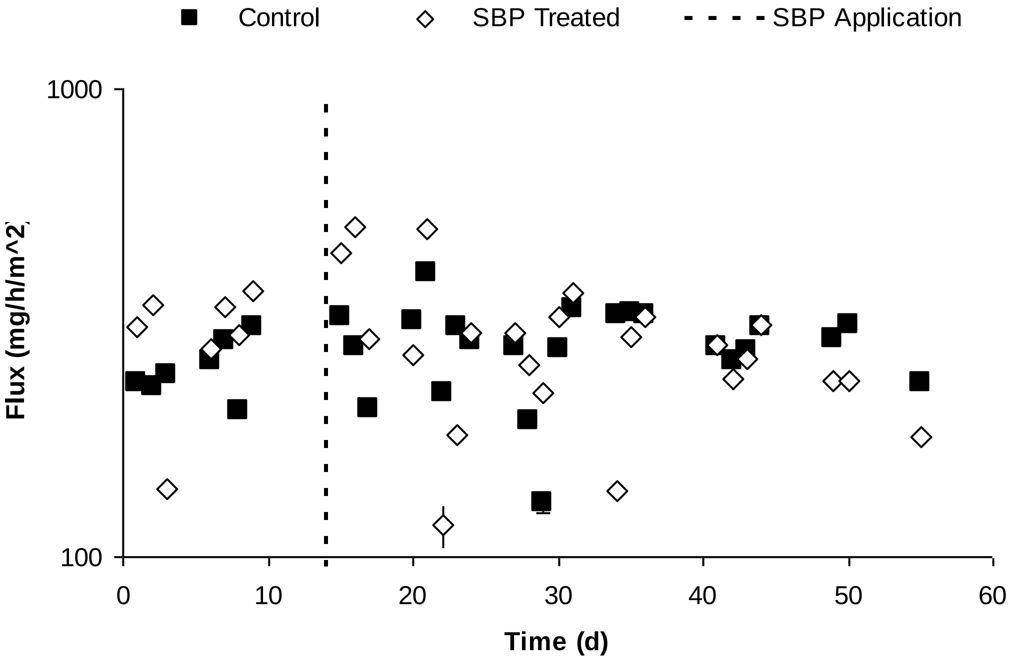

Figure 50: Farm Scale – measured methane flux.

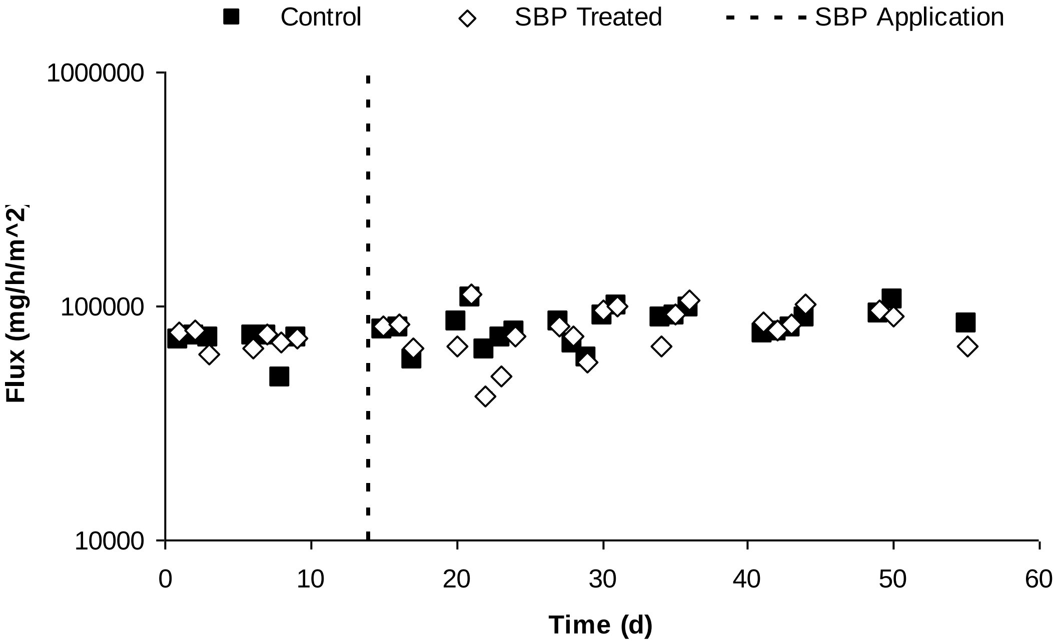

Figure 51: Farm Scale – measured carbon dioxide flux.

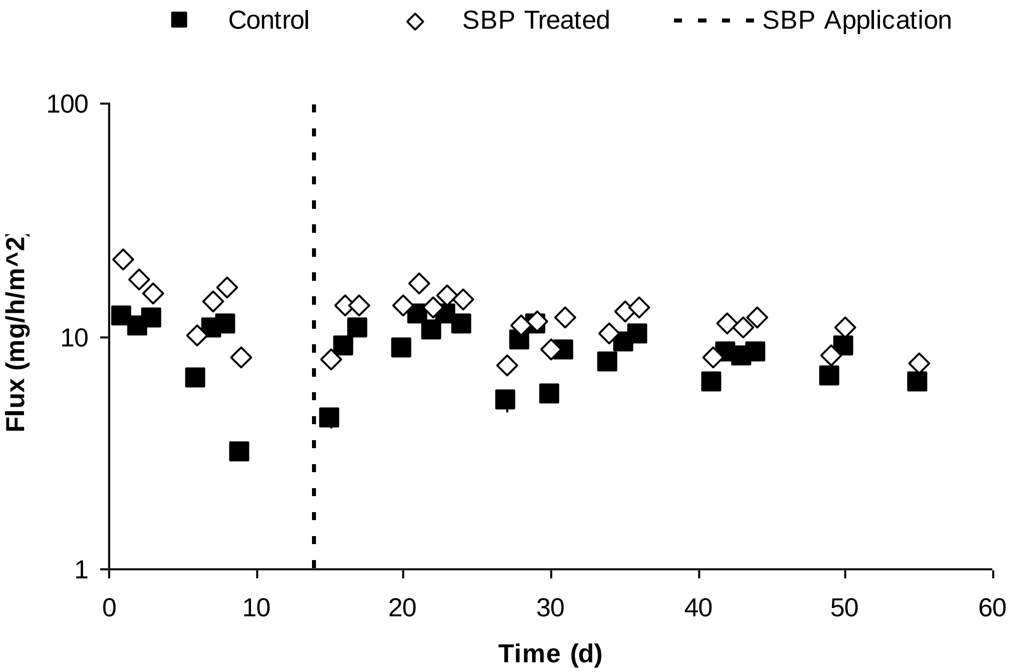

Figure 52: Farm Scale – measured nitrous oxide flux.

Ammonia and Hydrogen Sulfide - Farm Scale

There was a statistically significant reduction in NH_3 flux estimates after the SBP treatment (**Figure 53**). The SBP treatment resulted in statistically significant reduction in regards to H_2S for every sampling period over the 42 days after application (**Figure 54**).

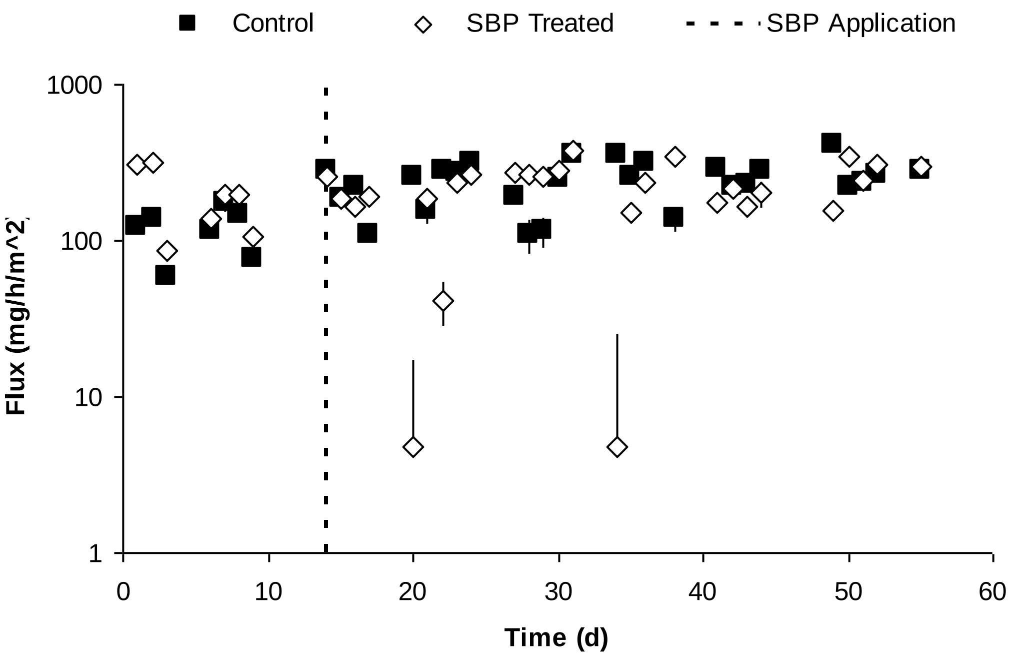

Figure 53: Farm Scale – measured ammonia flux.

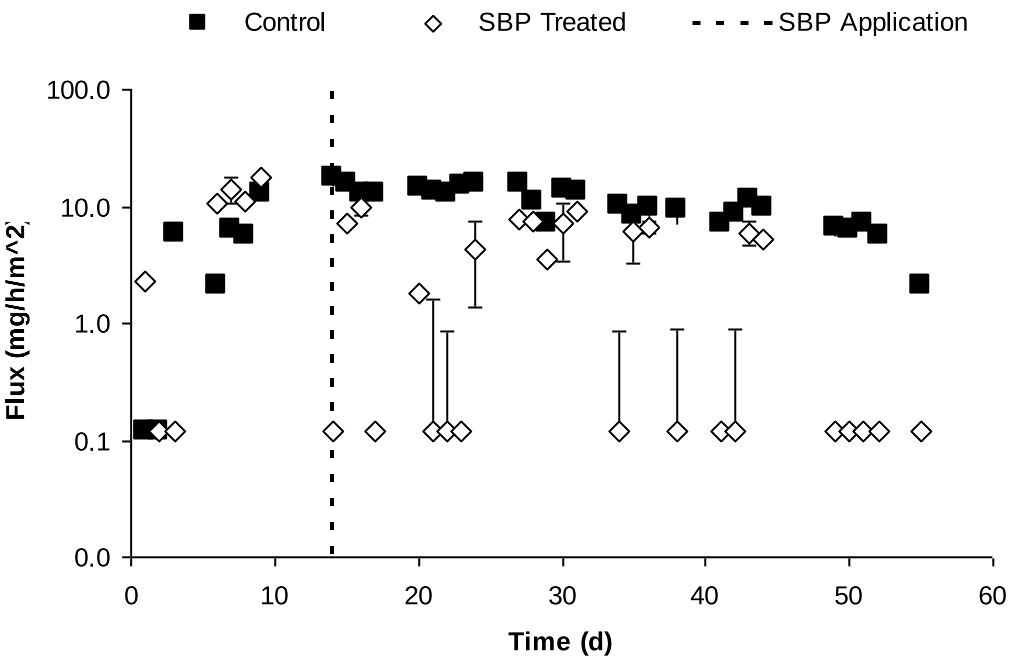

Figure 54: Farm Scale – measured hydrogen sulfide flux.

Volatile Organic Compounds - Farm Scale

Dimethyl disulfide flux estimates showed a significant increase as a result of the SBP treatment (**Figure. 55**). Dimethyl trisulfide flux estimates resulted in no statistically significant differences as a result of the SBP treatment (**Figure. 56).**

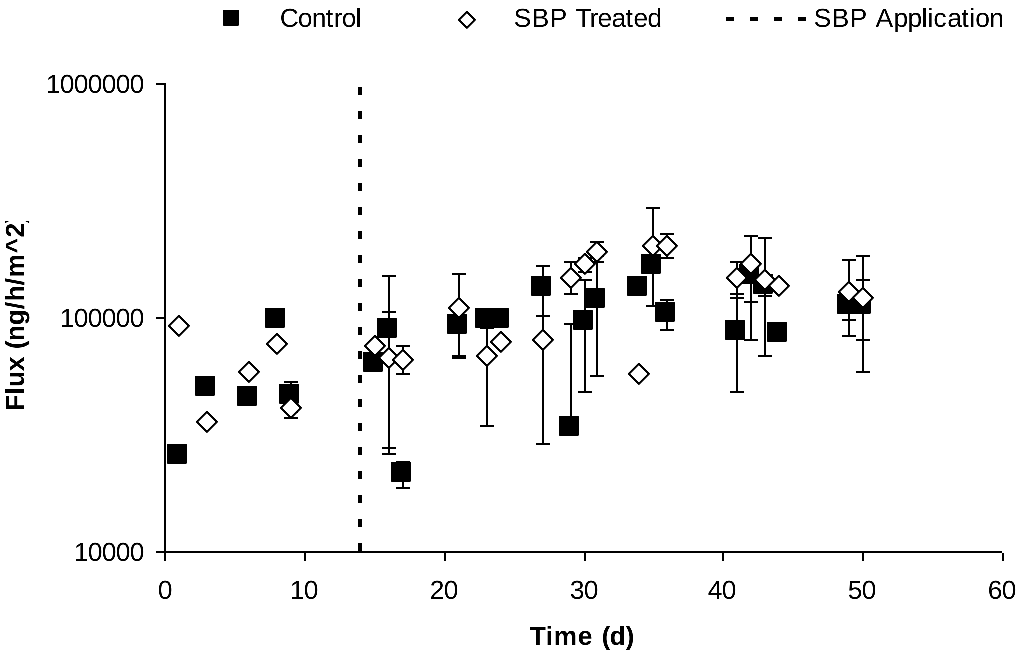

Figure 55: Farm Scale – measured DMDS flux.

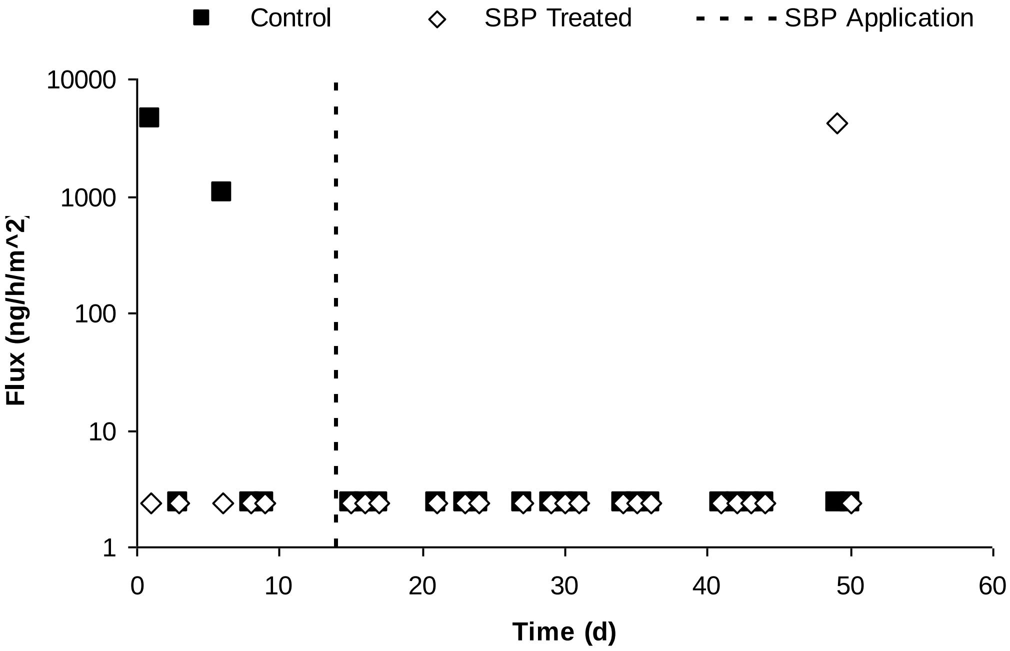

Figure 56: Farm Scale – measured DMTS flux.

n-Butyric acid, valeric acid and isovaleric acid flux estimate showed similar statistically significant reduction for the SBP treated room.

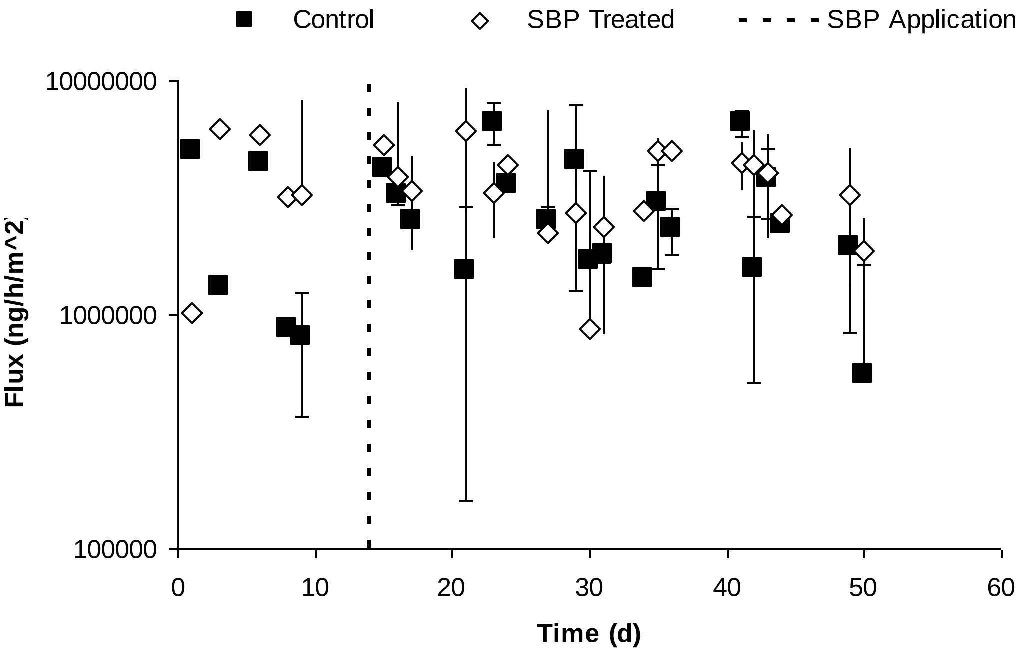

Figure 57: Farm Scale – measured *n*-butyric acid flux.

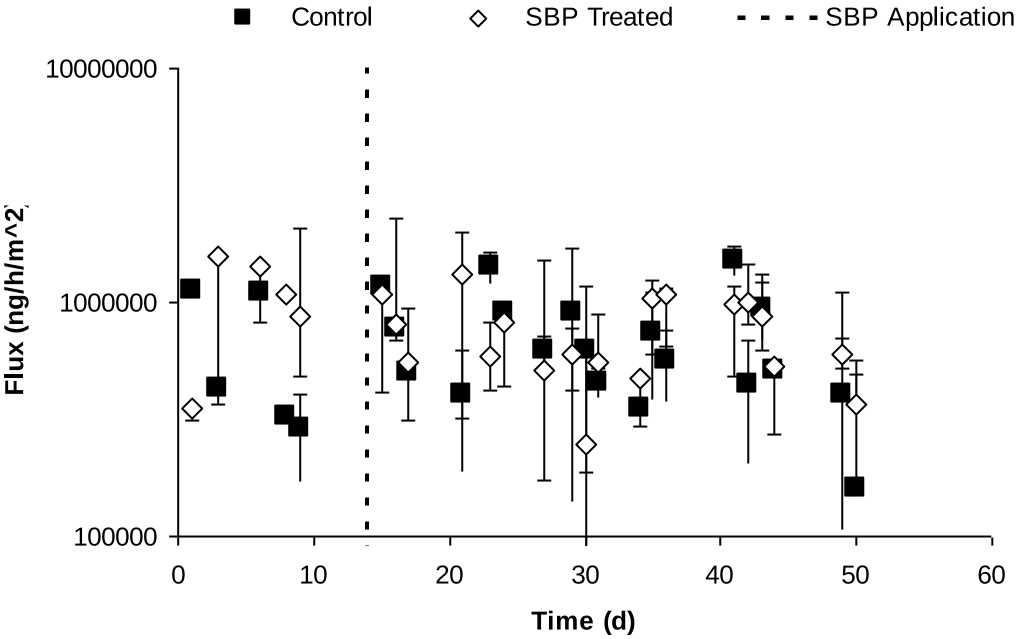

Figure 58: Farm Scale – measured valeric acid flux.

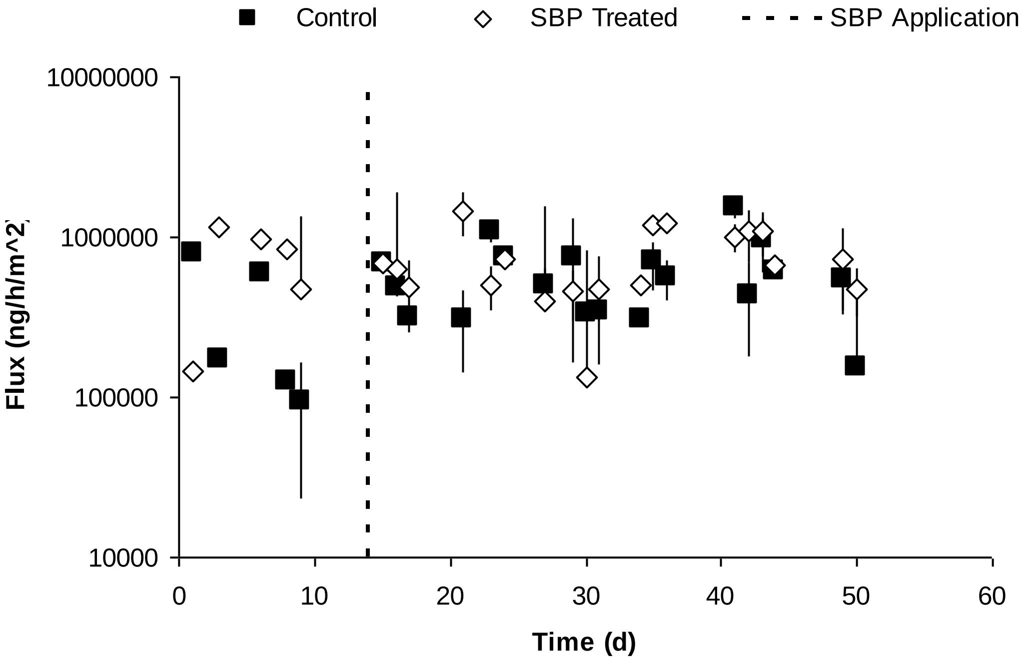

Figure 59: Farm Scale – measured isovaleric acid flux.

p-Cresol flux estimates did not show a statistically significant reduction in regards to the SBP treatment at the farm scale (**Figure 60**). Indole and skatole both showed statistically significant reduction as a result of the SBP treatment (**Figures 61 and 62**)

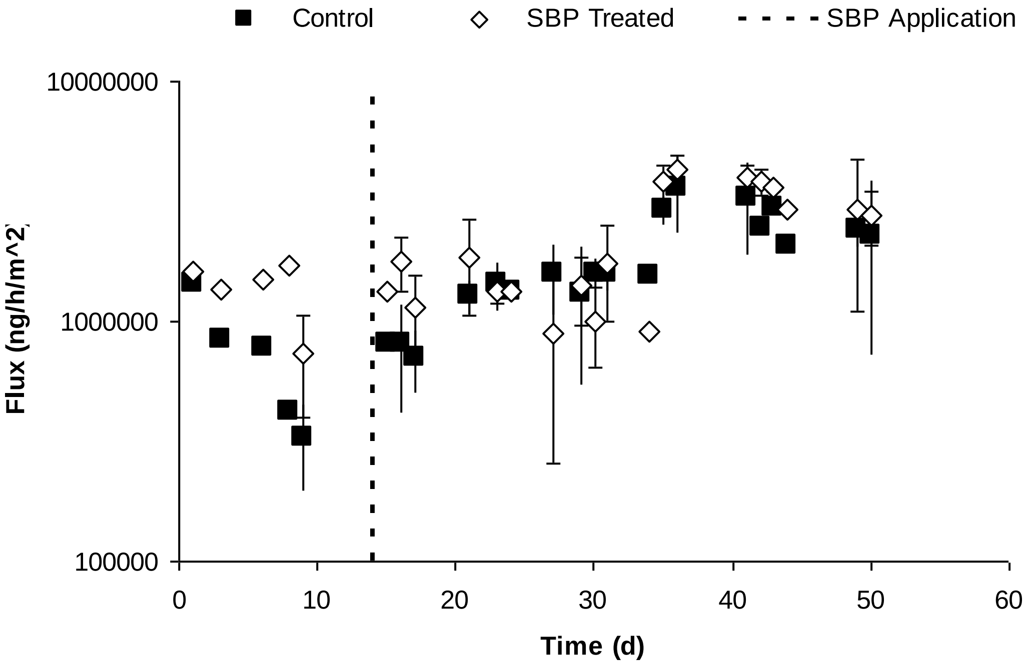

Figure 60: Farm Scale – measured *p*-cresol flux.

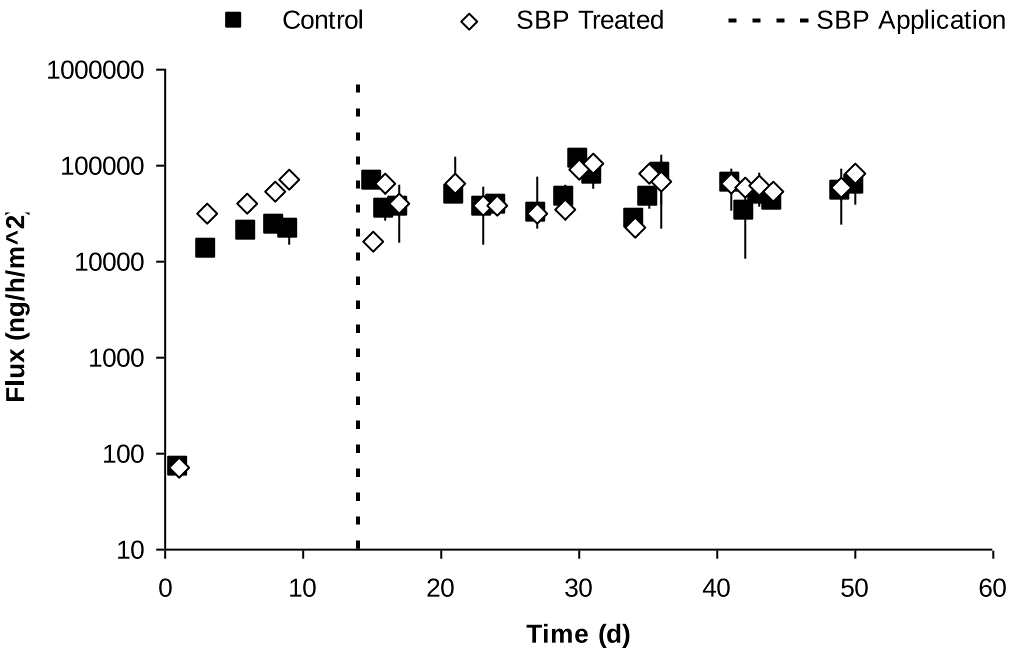

Figure 61: Farm Scale – measured indole flux.

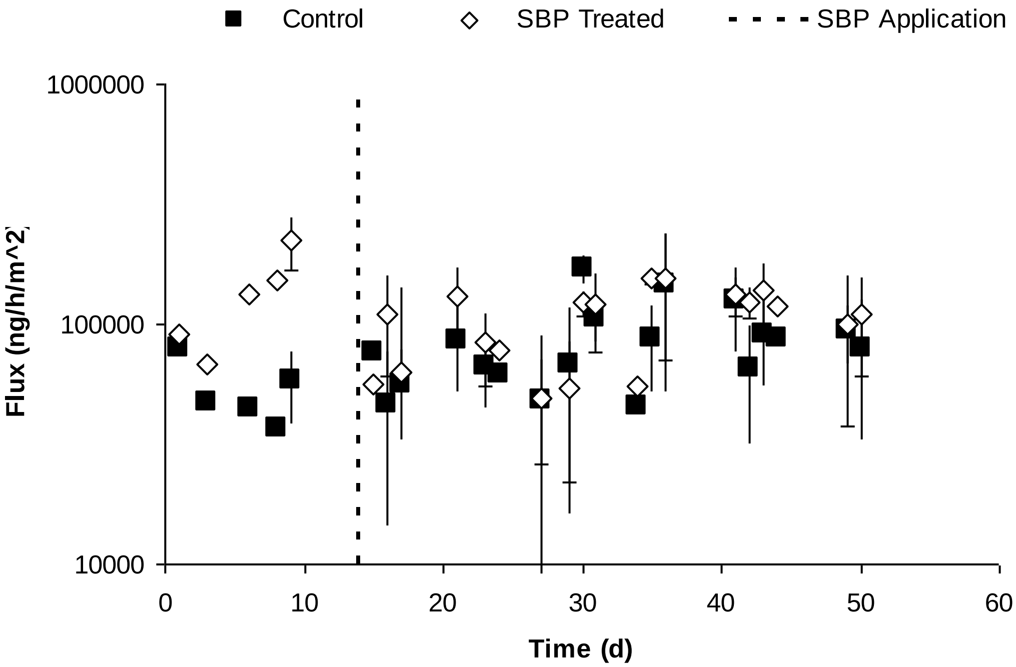

Figure 62: Farm Scale – measured skatole flux.

Environmental and Physicochemical Parameters - Farm Scale

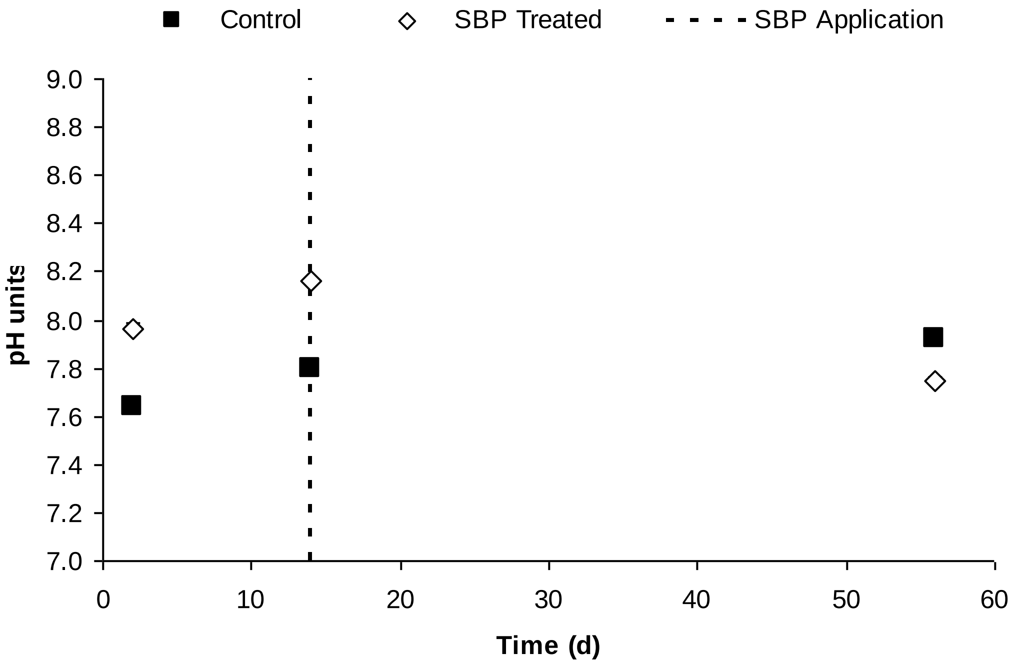

Figure 63: Farm Scale – measured pH.

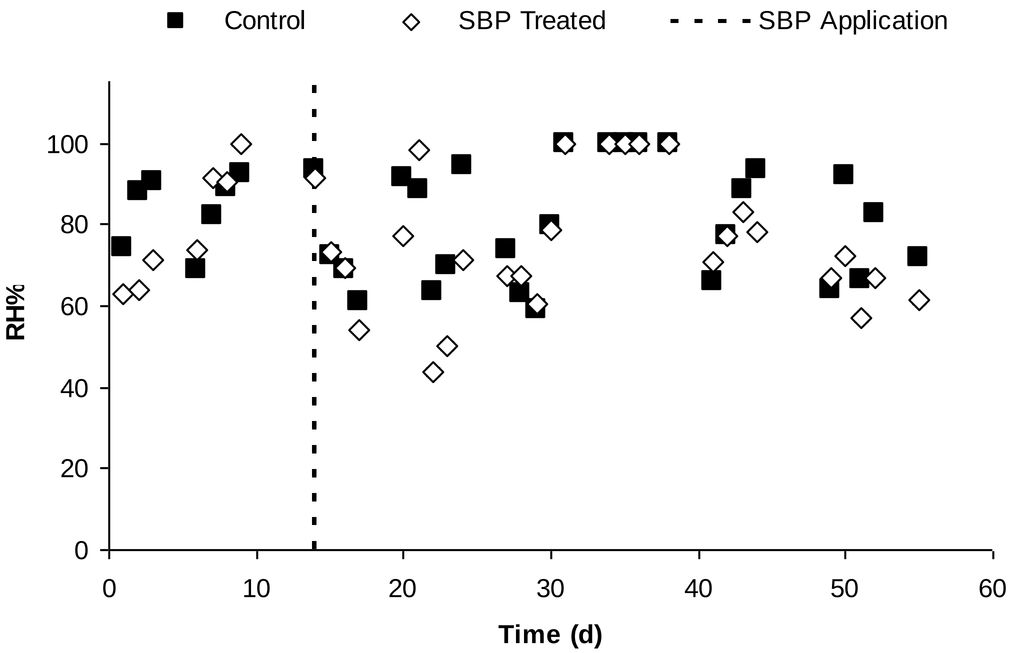

Figure 64: Farm Scale – measured relative humidity.

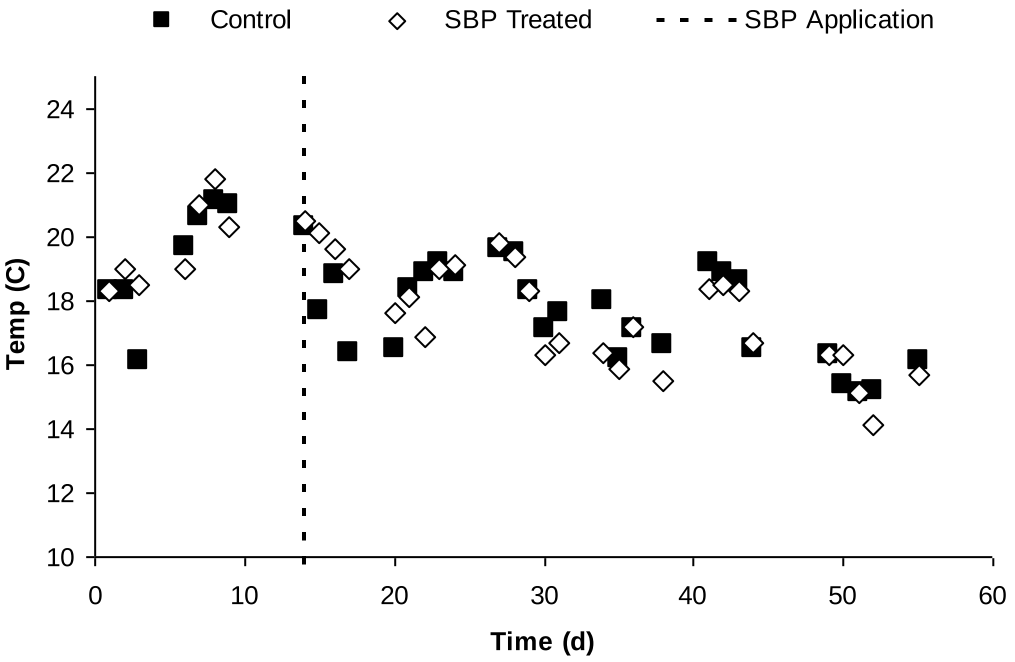

Figure 65: Farm Scale – measured room temperature profile.

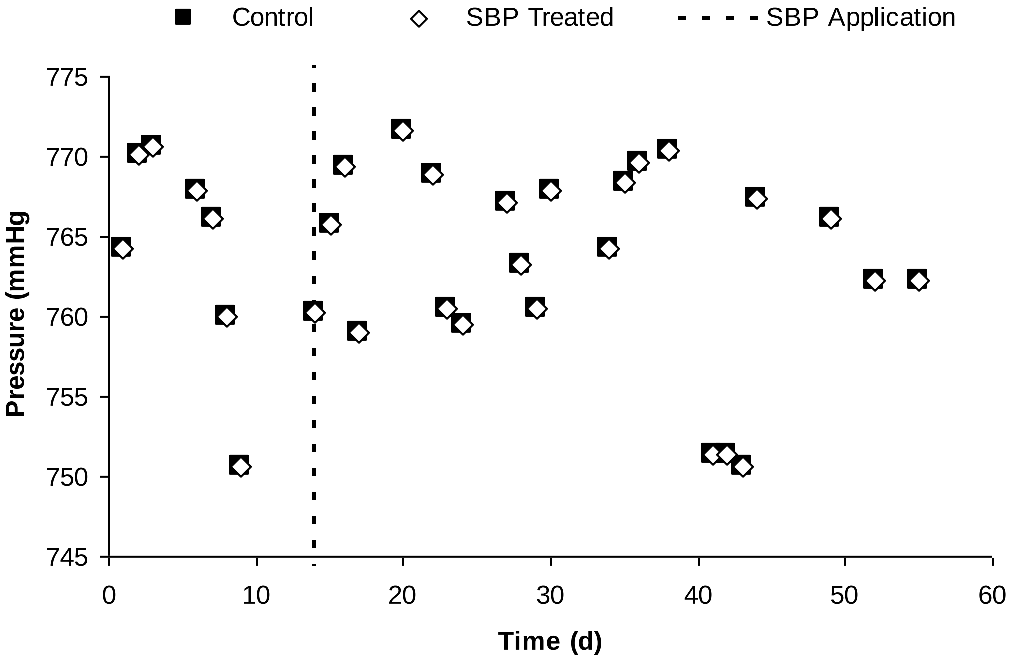

Figure 66: Farm Scale – measured atmospheric pressure.

Summary of gas measured concentrations and gas flux (emission) – farm scale

The mean and the range (minimum and maximum) measured concentrations and estimated gas emissions for farm scale are presented in **Table 9** and **Table 10**, respectively. The mean is the average of all measured concentrations and emissions.

Table 9: Farm scale – measured concentration ranges.

Compound	Mean	St.dev.	Min	Max
NH_3	17.2	6.78	4.00*	33.9
H_2S	0.570	0.420	0.100*	1.60
CH_4	23.7	6.21	9.30	42.7
CO_2	2,440	438	1,210	3,380
N_2O	0.323	0.0960	0.0994	0.650
DMDS	1.39	0.789	0.124	3.67
DMTS	0.00242	0.0121	0.000300*	0.113
n-Butyric Acid	48.2	34.6	4.53	174
Valeric Acid	9.62	6.77	0.943	35.5
Isovaleric Acid	8.16	6.11	0.748	29.8
p-Cresol	22.4	13.7	0.175	61.7
Indole	0.534	0.342	0.00850*	1.85
Skatole	0.922	0.514	0.0102*	2.91

*limit of detection value. NH_3, H_2S, CH_4, CO_2 and N_2O concentrations in ppm. DMDS, DMTS, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole and skatole concentrations in ppb.

Table 10: Farm scale – measured barn emissions (flux estimates, mass/time/manure area).

Compound	Mean	St.dev.	Min	Max
NH_3	216	89.1	4.72*	417
H_2S	6.70	5.59	0.118*	19.2
CH_4	281	75.7	116	524
CO_2	79,600	14,600	41,400	114,000
N_2O	10.6	3.33	3.04	21.9
DMDS	101	58.3	8.67	283
DMTS	0.210	1.17	0.00240*	10.6
n-Butyric Acid	3,270	2,350	313	11,600
Valeric Acid	755	532	75.5	2,800
Isovaleric Acid	643	484	56.7	2,520
p-Cresol	1,870	1,150	14.1	5,100
Indole	48.4	31.4	0.0719*	162
Skatole	93.6	52.7	0.0959*	290

*limit of detection value. NH_3, H_2S, CH_4, CO_2 and N_2O flux mg/h/m^2. DMDS, DMTS, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole and skatole flux in µg/h/m^2.

The ratio of measured concentrations and estimated emissions is presented in **Tables 11** and **12**, respectively.

Table 11: Farm/pilot scale measured concentration ratio.

Compound	**Mean**	**Min**	**Max**
NH_3	0.19	1.54	0.11
H_2S	0.38	1.00	0.04
CH_4	0.39	5.04	0.06
CO_2	1.48	4.93	0.15
N_2O	1.21	0.98	1.33
DMDS	0.37	309.98	0.05
DMTS	0.01	1.00	0.02
n-Butyric Acid	8.99	31.51	2.83
Valeric Acid	1.60	4.65	0.04
Isovaleric Acid	1.97	28.17	0.33
p-Cresol	1.40	11.38	0.23
Indole	1.65	1.00	0.09
Skatole	0.26	1.00	0.10

Table 12: Farm/pilot scale estimated emissions (flux) ratio.

Compound	**Mean**	**Min**	**Max**
NH_3	1.6	1.2	1.2
H_2S	4.0	1.0	0.4
CH_4	4.0	59.4	0.7
CO_2	14.0	55.4	1.7
N_2O	9.6	6.9	6.7
DMDS	4.1	3,610	0.7
DMTS	0.1	1.0	0.2
n-Butyric Acid	83.6	344	28.1
Valeric Acid	15.1	50.1	0.4
Isovaleric Acid	19.0	232	3.7
p-Cresol	14.5	117	2.4
Indole	18.2	1.0	1.0
Skatole	2.4	1.0	0.9

Table 13: Farm Scale – measured % reduction and statistical significance.

			Pilot scale test								Farm scale test			
SBP dose (topical) (SBP mass/manure surface area), kg/m^2			**45.7**		**22.8**		**4.57**		**2.28**		**2.28**		**2.28**	
SBP dose (topical) (SBP mass/manure surface area), lb/ft^2			**9.36**		**4.67**		**0.936**		**0.467**		**0.467**		**0.467**	
SBP dose equivalent (SBP mass/manure volume), g/L			**50**		**25**		**5.0**		**2.5**		**12**		**12**	
Gas	**Interval**	**After Treatment**		Stdev		Stdev		Stdev		Stdev	**Adjusted**	Stdev	**Non Adjusted**	Stdev
NH_3	Daily	Days of Reduction (%)	**100**		**93.9**		**93.9**		**87.9**		**67.9**		**53.6**	
		Days of Significant Reduction (%)	**90.9**		**81.8**		**33.3**		**12.1**		**57.1**		**46.4**	
		Average Significant Reduction	**72.0**	21.0	**63.3**	22.5	**42.0**	24.3	**48.3**	31.7	**43.9**	28.4	**44.8**	30.8
		Average Non Significant Reduction	**48.6**	31.6	**25.5**	10.7	**20.6**	8.51	**12.9**	7.00	**4.84**	2.01	**6.56**	3.50
		Average Overall Reduction	**69.9**	22.5	**54.0**	30.1	**23.4**	26.6	**11.8**	28.5	**12.0**	50.0	**-2.44**	63.3
	Weekly	Weeks of Reduction (%)	**100**		**100**		**100**		**100**		**100**		**100**	
		Weeks of Significant Reduction (%)	**86.7**		**66.7**		**6.67**		**0.0**		**0.00**		**0.00**	
		Average Significant Reduction	**64.1**	19.1	**58.1**	20.1	**42.9**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**24.1**	15.1	**36.2**	7.88	**20.4**	9.51	**14.9**	8.03	**22.7**	8.44	**13.0**	9.01
		Average Overall Reduction	**58.7**	22.9	**50.8**	19.8	**21.9**	10.9	**14.9**	8.03	**22.7**	8.44	**13.0**	9.01
	Biweekly	Biweeks of Reduction (%)	**100**		**100**		**100**		**100**		**100**		**100**	
		Biweeks of Significant Reduction (%)	**88.9**		**88.9**		**11.1**		**0.00**		**33.3**		**0.00**	
		Average Significant Reduction	**59.9**	19.0	**51.1**	18.4	**32.4**	a	**0.00**	a	**29.9**	a	**0.00**	a
		Average Non Significant Reduction	**13.5**	a	**38.9**	a	**18.2**	10.8	**14.2**	7.32	**17.5**	3.47	**11.9**	8.08
		Average Overall Reduction	**54.8**	23.6	**49.7**	17.7	**19.7**	11.1	**14.2**	7.32	**21.6**	7.57	**11.9**	8.08
H_2S	Daily	Days of Reduction (%)	**21.2**		**54.6**		**9.1**		**33.3**		**100**		**96.4**	
		Days of Significant Reduction (%)	**0.00**		**12.1**		**0.00**		**3.03**		**100**		**89.3**	
		Average Significant Reduction	**0.00**	a	**73.7**	18.9	**0.00**	a	**75.6**	a	**81.3**	21.1	**74.6**	28.3
		Average Non Significant Reduction	**63.2**	32.5	**63.5**	25.8	**50.7**	35.1	**46.1**	22.1	**0.00**	a	**59.7**	49.2
		Average Overall Reduction	**-341**	666	**-78.8**	354	**-155**	354	**-53.8**	224	**81.3**	21.1	**70.9**	31.8
	Weekly	Weeks of Reduction (%)	**40.0**		**60.0**		**6.67**		**40.0**		**100**		**100**	
		Weeks of Significant Reduction (%)	**0.00**		**33.3**		**0.00**		**6.67**		**100**		**100**	
		Average Significant Reduction	**0.00**	a	**65.3**	21.4	**0.00**	a	**75.6**	a	**79.6**	11.8	**71.8**	16.6
		Average Non Significant Reduction	**54.6**	30.0	**52.1**	21.4	**14.4**	a	**39.7**	24.4	**0.00**	a	**0.00**	a
		Average Overall Reduction	**-147**	300	**-116**	485	**-162**	300	**-2.42**	58.3	**79.6**	11.8	**71.8**	16.6
	Biweekly	Biweeks of Reduction (%)	**44.4**		**66.7**		**11.1**		**33.3**		**100**		**100**	
		Biweeks of Significant Reduction (%)	**0.00**		**44.4**		**0.00**		**11.1**		**100**		**100**	
		Average Significant Reduction	**0.00**	a	**62.6**	13.9	**0.00**	a	**55.2**	a	**79.8**	9.78	**71.1**	13.3
		Average Non Significant Reduction	**53.9**	25.0	**28.1**	7.0	**11.2**	a	**46.7**	33.1	**0.00**	a	**0.00**	a
		Average Overall Reduction	**-72.7**	180	**-25.3**	193	**-111**	168	**-3.1**	58.6	**79.8**	9.78	**71.1**	13.3
CH_4	Daily	Days of Reduction (%)	**6.06**		**6.06**		**21.2**		**24.2**		**60.0**		**45.8**	
		Days of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**3.03**		**56.0**		**41.7**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**5.26**	a	**23.8**	17.8	**25.2**	18.0
		Average Non Significant Reduction	**8.90**	6.68	**25.7**	22.8	**7.64**	3.34	**20.5**	11.9	**0.95**	a	**1.38**	a
		Average Overall Reduction	**-250**	221	**-125**	131	**-57.1**	87.8	**-42.8**	71.0	**4.74**	29.9	**-3.92**	33.7
	Weekly	Weeks of Reduction (%)	**0.00**		**0.00**		**13.3**		**20.0**		**83.3**		**66.7**	
		Weeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**0.00**	a	**0.00**	a	**6.99**	0.770	**10.8**	6.27	**12.3**	5.65	**7.10**	4.60

		Average Overall Reduction	**-242**	104	**-152**	137	**-43.2**	49.7	**-39.1**	44.1	**6.30**	15.6	**-1.51**	16.9
	Biweekly	Biweeks of Reduction (%)	**0.00**		**0.00**		**11.1**		**0.0**		**66.7**		**33.3**	
		Biweeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**0.00**	a	**0.00**	a	**6.44**	a	**0.0**	a	**12.1**	6.34	**9.31**	a
		Average Overall Reduction	**-225**	63.5	**-172**	150	**-35.5**	25.4	**-41.6**	45.9	**7.20**	9.57	**-0.560**	10.0
CO_2	Daily	Days of Reduction (%)	**3.03**		**3.03**		**6.06**		**9.09**		**37.5**		**37.5**	
		Days of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**37.5**		**33.3**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**18.4**	12.3	**19.3**	11.9
		Average Non Significant Reduction	**27.0**	a	**32.5**	a	**1.77**	2.47	**4.61**	5.04	**0.00**	a	**2.57**	a
		Average Overall Reduction	**-133**	87.5	**-91.0**	96.2	**-28.6**	24.6	**-22.1**	28.3	**3.16**	14.6	**2.02**	14.8
	Weekly	Weeks of Reduction (%)	**0.00**		**0.00**		**6.67**		**6.67**		**66.7**		**66.7**	
		Weeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**0.00**	a	**0.00**	a	**0.020**	a	**0.600**	a	**5.91**	4.48	**4.82**	4.55
		Average Overall Reduction	**-123**	57.5	**-79.1**	40.5	**-23.1**	15.8	**-16.1**	15.3	**1.84**	7.22	**0.720**	7.29
	Biweekly	Biweeks of Reduction (%)	**0.00**		**0.00**		**11.1**		**0.00**		**100**		**33.3**	
		Biweeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**0.00**	a	**0.00**	a	**0.020**	a	**0.00**	a	**2.78**	4.72	**7.13**	a
		Average Overall Reduction	**-118**	42.2	**-79.6**	35.6	**-21.2**	14.1	**-15.7**	10.8	**2.78**	4.72	**1.67**	4.73
N_2O	Daily	Days of Reduction (%)	**33.3**		**60.6**		**54.5**		**27.3**		**84.0**		**0.00**	
		Days of Significant Reduction (%)	**3.03**		**0.00**		**0.00**		**0.00**		**76.0**		**0.00**	
		Average Significant Reduction	**10.6**	a	**0.00**	a	**0.00**	a	**0.00**	a	**12.9**	6.98	**0.00**	a
		Average Non Significant Reduction	**1.48**	0.890	**2.63**	2.12	**2.57**	1.66	**2.21**	0.960	**5.72**	2.05	**0.00**	a
		Average Overall Reduction	**-1.50**	3.67	**0.430**	3.34	**-0.100**	3.89	**-2.31**	3.88	**10.3**	8.42	**-34.7**	15.1
	Weekly	Weeks of Reduction (%)	**26.7**		**73.3**		**53.3**		**20.0**		**100**		**0.00**	
		Weeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**2.16**	0.890	**2.08**	1.88	**1.87**	1.00	**1.14**	0.810	**9.76**	5.68	**0.00**	a
		Average Overall Reduction	**-1.10**	2.58	**0.870**	2.67	**-0.650**	3.54	**-2.28**	2.60	**9.76**	5.68	**-33.4**	8.26
	Biweekly	Biweeks of Reduction (%)	**33.3**		**77.8**		**44.4**		**11.1**		**100**		**0.00**	
		Biweeks of Significant Reduction (%)	**0.00**		**0.00**		**0.00**		**0.00**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**2.19**	1.28	**2.21**	2.19	**1.82**	0.40	**2.01**	a	**10.29**	4.93	**0.00**	a
		Average Overall Reduction	**-0.620**	2.59	**1.49**	2.39	**-0.680**	2.66	**-2.14**	2.42	**10.29**	4.93	**-32.3**	4.30
DMDS	Daily	Days of Reduction (%)	**31.0**		**34.5**		**37.9**		**27.6**		**26.3**		**26.3**	
		Days of Significant Reduction (%)	**17.2**		**31.0**		**20.7**		**6.90**		**0.00**		**5.26**	
		Average Significant Reduction	**77.5**	6.17	**85.6**	12.5	**81.4**	11.2	**68.0**	6.87	**0.00**	a	**56.8**	a
		Average Non Significant Reduction	**52.0**	35.2	**40.6**	a	**53.4**	32.1	**32.6**	14.0	**29.6**	16.4	**28.3**	8.70
		Average Overall Reduction	**16.6**	39.5	**28.0**	40.6	**25.2**	37.0	**5.34**	34.2	**-64.9**	127	**-44.9**	94.1
	Weekly	Weeks of Reduction (%)	**57.1**		**57.1**		**57.1**		**50.0**		**16.7**		**16.7**	
		Weeks of Significant Reduction (%)	**0.00**		**21.4**		**14.3**		**7.14**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**91.8**	1.71	**87.6**	5.09	**81.9**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**54.9**	31.2	**79.4**	13.6	**56.9**	29.9	**33.9**	13.1	**14.4**	a	**19.7**	a
		Average Overall Reduction	**31.4**	36.3	**48.0**	44.1	**36.9**	39.4	**16.0**	33.6	**-32.0**	28.8	**-22.9**	26.9
		Biweeks of Reduction (%)	**66.7**		**66.7**		**66.7**		**55.6**		**33.3**		**33.3**	

	Biweekly	Biweeks of Significant Reduction (%)	**0.00**		**33.3**		**22.2**		**11.11**		**0.00**		**0.00**	
		Average Significant Reduction	**0.00**	a	**88.5**	6.54	**80.9**	9.1	**57.91**	a	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**55.8**	29.7	**78.7**	18.6	**52.5**	36.6	**33.9**	9.4	**0.11**	a	**7.79**	a
		Average Overall Reduction	**37.2**	36.5	**55.7**	43.2	**41.3**	40.1	**14.6**	35.5	**-28.6**	31.1	**-20.4**	29.8
DMTS	Daily	Days of Reduction (%)	**37.9**		**44.8**		**31.0**		**48.3**		**100**		**0.00**	
		Days of Significant Reduction (%)	**6.90**		**6.90**		**3.45**		**3.45**		**5.26**		**0.00**	
		Average Significant Reduction	**100**	a	**90.3**	13.7	**100**	a	**74.8**	a	**1670**	a	**0.00**	a
		Average Non Significant Reduction	**61.0**	39.5	**44.1**	38.7	**59.8**	45.2	**36.2**	37.7	**101**	0.00	**0.00**	a
		Average Overall Reduction	**-52300**	185000	**-67600**	220000	**-21900**	71300	**-3710**	20100	**184**	360	**-9220**	40200
	Weekly	Weeks of Reduction (%)	**28.6**		**35.7**		**35.7**		**50.0**		**100**		**0.00**	
		Weeks of Significant Reduction (%)	**7.14**		**7.14**		**7.14**		**7.14**		**16.7**		**0.00**	
		Average Significant Reduction	**100**	a	**100**	a	**100**	a	**74.8**	a	**886**	a	**0.00**	a
		Average Non Significant Reduction	**36.6**	14.2	**20.5**	7.90	**17.2**	16.1	**36.4**	35.1	**101**	0.00	**0.00**	a
		Average Overall Reduction	**-24800**	92700	**-20900**	77800	**-11700**	43700	**10.1**	51.2	**232**	321	**-14600**	35800
	Biweekly	Biweeks of Reduction (%)	**22.2**		**22.2**		**22.2**		**55.6**		**100**		**0.0**	
		Biweeks of Significant Reduction (%)	**11.11**		**11.11**		**11.11**		**11.11**		**33.3**		**0.0**	
		Average Significant Reduction	**100**	a	**100**	a	**100**	a	**74.83**	a	**415**	a	**0.0**	a
		Average Non Significant Reduction	**28.4**	a	**23.9**	a	**19.6**	a	**38.2**	44.7	**101**	0	**0.0**	a
		Average Overall Reduction	**-38600**	116000	**-32500**	97000	**-9100**	27300	**10.4**	63.2	**206**	181	**-11700**	20200
n-Butyric Acid	Daily	Days of Reduction (%)	**17.2**		**34.5**		**55.2**		**58.6**		**89.5**		**26.3**	
		Days of Significant Reduction (%)	**0.00**		**6.90**		**3.45**		**3.45**		**21.1**		**0.00**	
		Average Significant Reduction	**0.00**	a	**79.1**	1.10	**68.6**	a	**78.4**	a	**65.0**	11.7	**0.00**	a
		Average Non Significant Reduction	**41.1**	31.7	**45.6**	23.4	**38.9**	24.8	**28.9**	17.5	**34.1**	15.1	**36.3**	15.8
		Average Overall Reduction	**-456**	647	**-17.0**	70.9	**-2.71**	60.1	**7.09**	38.5	**34.8**	27.8	**-53.9**	95.6
	Weekly	Weeks of Reduction (%)	**7.14**		**21.4**		**50.0**		**64.3**		**100**		**16.7**	
		Weeks of Significant Reduction (%)	**0.00**		**7.14**		**7.14**		**0.00**		**33.3**		**0.00**	
		Average Significant Reduction	**0.00**	a	**72.0**	a	**56.2**	a	**0.00**	a	**47.5**	15.1	**0.00**	a
		Average Non Significant Reduction	**51.0**	a	**26.3**	22.6	**21.4**	17.2	**20.2**	12.4	**31.8**	3.46	**10.3**	a
		Average Overall Reduction	**-405**	377	**-19.6**	40.9	**-1.10**	37.6	**6.38**	23.3	**37.0**	10.9	**-32.5**	38.7
	Biweekly	Biweeks of Reduction (%)	**0.00**		**11.1**		**55.6**		**55.6**		**100**		**0.00**	
		Biweeks of Significant Reduction (%)	**0.00**		**11.1**		**11.1**		**0.00**		**66.7**		**0.00**	
		Average Significant Reduction	**0.00**	a	**64.8**	a	**53.3**	a	**0.00**	a	**38.6**	5.70	**0.00**	a
		Average Non Significant Reduction	**0.00**	a	**0.00**	a	**11.5**	7.06	**16.2**	5.9	**33.0**	a	**0.00**	a
		Average Overall Reduction	**-388**	390	**-22.0**	38.8	**-4.62**	39.1	**0.97**	20.8	**36.7**	5.19	**-27.6**	25.8
Valeric Acid	Daily	Days of Reduction (%)	**31.0**		**51.7**		**48.3**		**55.2**		**94.7**		**42.1**	
		Days of Significant Reduction (%)	**3.45**		**3.45**		**3.45**		**3.45**		**42.1**		**5.26**	
		Average Significant Reduction	**98.9**	a	**88.9**	a	**99.4**	a	**99.5**	a	**59.0**	13.4	**59.0**	a
		Average Non Significant Reduction	**25.3**	21.2	**32.2**	27.4	**41.6**	28.6	**36.4**	19.1	**42.5**	17.4	**24.3**	19.9
		Average Overall Reduction	**-79.2**	136	**-28.7**	145	**-13.0**	78.9	**-7.83**	73.5	**46.2**	23.2	**-26.5**	72.5
	Weekly	Weeks of Reduction (%)	**35.7**		**50.0**		**50.0**		**42.9**		**100**		**50.0**	
		Weeks of Significant Reduction (%)	**7.14**		**7.14**		**7.14**		**7.14**		**66.7**		**0.00**	
		Average Significant Reduction	**98.9**	a	**88.9**	a	**99.4**	a	**99.5**	a	**49.0**	11.5	**0.00**	a
		Average Non Significant Reduction	**13.5**	12.0	**26.6**	17.5	**30.2**	25.6	**32.9**	16.0	**45.6**	7.53	**8.85**	12.2
		Average Overall Reduction	**-39.6**	78.9	**-4.95**	51.1	**3.01**	48.4	**-0.630**	51.4	**47.9**	9.67	**-13.7**	32.8
		Biweeks of Reduction (%)	**22.2**		**44.4**		**55.6**		**44.4**		**100**		**66.7**	
		Biweeks of Significant Reduction (%)	**11.1**		**11.1**		**11.1**		**11.1**		**100**		**0.00**	

	Biweekly	Average Significant Reduction	**98.9**	a	**88.9**	a	**99.4**	a	**99.5**	a	**47.2**	3.38	**0.00**	a
		Average Non Significant Reduction	**3.96**	a	**22.7**	9.43	**21.3**	6.22	**23.0**	14.3	**0.0**	a	**3.14**	1.46
		Average Overall Reduction	**-23.1**	61.5	**-5.09**	50.8	**6.54**	48.5	**-1.54**	54.4	**47.2**	3.38	**-10.1**	23.0
Isovaleric Acid	Daily	Days of Reduction (%)	**24.1**		**44.8**		**51.7**		**55.2**		**84.2**		**31.6**	
		Days of Significant Reduction (%)	**0.00**		**10.3**		**6.90**		**3.45**		**26.3**		**0.00**	
		Average Significant Reduction	**0.00**	a	**92.7**	3.17	**85.1**	0.870	**93.7**	a	**67.8**	11.9	**0.00**	a
		Average Non Significant Reduction	**69.2**	23.8	**56.0**	31.8	**61.3**	27.8	**54.0**	22.1	**40.1**	11.8	**34.9**	20.6
		Average Overall Reduction	**-1330**	1860	**-40.9**	141	**-37.1**	190	**-17.6**	138	**37.6**	32.6	**-49.6**	104
	Weekly	Weeks of Reduction (%)	**7.14**		**28.6**		**42.9**		**50.0**		**100**		**16.7**	
		Weeks of Significant Reduction (%)	**0.00**		**7.14**		**7.14**		**0.00**		**33.3**		**0.00**	
		Average Significant Reduction	**0.00**	a	**92.4**	a	**82.6**	a	**0.00**	a	**51.5**	17.0	**0.00**	a
		Average Non Significant Reduction	**90.0**	a	**47.9**	35.6	**44.2**	396	**41.1**	29.1	**33.7**	9.40	**12.8**	a
		Average Overall Reduction	**-1470**	1600	**-48.1**	120	**-5.62**	63.3	**-5.02**	55.4	**39.6**	14.0	**-27.2**	29.1
	Biweekly	Biweeks of Reduction (%)	**11.1**		**33.3**		**44.4**		**44.4**		**100**		**0.00**	
		Biweeks of Significant Reduction (%)	**0.00**		**11.1**		**11.1**		**0.00**		**66.7**		**0.00**	
		Average Significant Reduction	**0.00**	a	**90.4**	a	**84.0**	a	**0.00**	a	**42.5**	0.83	**0.00**	a
		Average Non Significant Reduction	**46.2**	a	**12.1**	4.5	**37.8**	40.8	**45.7**	25.6	**29.8**	a	**0.00**	a
		Average Overall Reduction	**-1310**	1490	**-22.5**	60.8	**1.93**	56.1	**-0.01**	46.7	**38.2**	7.38	**-25.7**	20.9
p-Cresol	Daily	Days of Reduction (%)	**82.8**		**89.7**		**82.8**		**89.7**		**79.0**		**26.3**	
		Days of Significant Reduction (%)	**13.8**		**17.2**		**0.00**		**10.3**		**15.8**		**0.00**	
		Average Significant Reduction	**87.8**	8.17	**91.7**	6.27	**0.00**	a	**72.6**	5.71	**59.8**	2.66	**0.00**	a
		Average Non Significant Reduction	**72.7**	27.3	**84.1**	20.6	**61.3**	26.3	**60.8**	18.3	**16.5**	13.6	**26.2**	20.7
		Average Overall Reduction	**-18.4**	278	**74.6**	37.5	**-4.84**	281	**-115**	708	**17.6**	24.5	**-21.4**	40.2
	Weekly	Weeks of Reduction (%)	**85.7**		**85.7**		**85.7**		**85.7**		**66.7**		**33.3**	
		Weeks of Significant Reduction (%)	**35.7**		**50.0**		**28.6**		**35.7**		**33.3**		**0.00**	
		Average Significant Reduction	**87.3**	7.15	**92.0**	5.20	**69.0**	18.5	**67.3**	8.31	**41.3**	6.14	**0.00**	a
		Average Non Significant Reduction	**58.4**	26.5	**72.1**	35.6	**48.3**	25.1	**58.7**	16.1	**7.48**	1.79	**11.4**	10.7
		Average Overall Reduction	**-21.1**	303	**68.4**	45.0	**-63.9**	405	**-198**	951	**15.2**	21.1	**-23.4**	35.5
	Biweekly	Biweeks of Reduction (%)	**88.9**		**77.8**		**88.9**		**77.8**		**66.7**		**0.00**	
		Biweeks of Significant Reduction (%)	**11.1**		**66.7**		**22.2**		**33.3**		**0.00**		**0.00**	
		Average Significant Reduction	**93.9**	a	**90.1**	10.6	**80.5**	9.2	**66.8**	6.64	**0.00**	a	**0.00**	a
		Average Non Significant Reduction	**57.8**	32.9	**81.8**	a	**34.2**	19.6	**58.8**	12.9	**22.2**	5.82	**0.00**	a
		Average Overall Reduction	**-62.8**	376	**64.0**	50.7	**-122**	503	**-343**	1180	**14.8**	13.5	**-20.0**	11.0
Indole	Daily	Days of Reduction (%)	**31.0**		**27.6**		**27.6**		**31.0**		**89.5**		**42.1**	
		Days of Significant Reduction (%)	**3.45**		**3.45**		**3.45**		**3.45**		**21.1**		**5.26**	
		Average Significant Reduction	**99.9**	a	**99.9**	a	**73.9**	a	**85.7**	a	**53.5**	21.7	**77.3**	a
		Average Non Significant Reduction	**54.2**	43.3	**89.9**	15.4	**90.8**	20.9	**82.1**	23.1	**28.6**	17.7	**11.9**	10.5
		Average Overall Reduction	**-3350**	12600	**-43.9**	300	**-1750**	9260	**-178**	821	**30.3**	23.4	**-14.0**	40.5
	Weekly	Weeks of Reduction (%)	**57.1**		**50.0**		**50.0**		**57.1**		**100**		**33.3**	
		Weeks of Significant Reduction (%)	**0.00**		**7.14**		**0.00**		**0.00**		**16.7**		**0.00**	
		Average Significant Reduction	**0.00**	a	**99.6**	a	**0.00**	a	**0.00**	a	**37.6**	a	**0.00**	a
		Average Non Significant Reduction	**46.9**	39.1	**87.7**	15.8	**86.7**	21.1	**82.5**	19.4	**28.5**	13.0	**12.2**	2.90
		Average Overall Reduction	**-829**	2090	**-98.3**	433	**-1040**	3420	**-375**	1170	**30.1**	12.2	**-10.5**	21.5
	Biweekly	Biweeks of Reduction (%)	**55.6**		**55.6**		**55.6**		**55.6**		**100**		**66.7**	
		Biweeks of Significant Reduction (%)	**0.00**		**11.1**		**0.00**		**0.00**		**66.7**		**0.00**	
		Average Significant Reduction	**0.00**	a	**99.3**	a	**0.00**	a	**0.00**	a	**36.5**	6.79	**0.00**	a
		Average Non Significant Reduction	**51.2**	47.1	**89.6**	15.9	**82.4**	23.9	**77.5**	22.5	**17.3**	a	**1.14**	0.500

		Average Overall Reduction	**-737**	1570	**-160**	537	**-934**	2190	**-438**	983	**30.1**	12.1	**-10.4**	20.0
Skatole	Daily	Days of Reduction (%)	**79.3**		**86.2**		**89.7**		**86.2**		**100**		**15.8**	
		Days of Significant Reduction (%)	**24.1**		**34.5**		**20.7**		**24.1**		**73.7**		**0.00**	
		Average Significant Reduction	**86.1**	6.71	**93.1**	6.06	**76.6**	19.1	**79.6**	12.4	**51.1**	11.7	**0.00**	a
		Average Non Significant Reduction	**89.8**	11.2	**96.0**	7.56	**62.8**	35.1	**71.6**	28.2	**23.4**	4.65	**25.0**	4.24
		Average Overall Reduction	**-1160**	5480	**81.5**	34.5	**-822**	3210	**-817**	4640	**43.8**	16.1	**-28.1**	41.8
	Weekly	Weeks of Reduction (%)	**78.6**		**85.7**		**92.9**		**92.9**		**100**		**16.7**	
		Weeks of Significant Reduction (%)	**14.3**		**28.6**		**14.3**		**14.3**		**100**		**0.00**	
		Average Significant Reduction	**92.2**	4.89	**94.8**	3.04	**90.9**	4.81	**88.4**	3.75	**43.2**	10.8	**0.00**	a
		Average Non Significant Reduction	**71.6**	23.8	**92.1**	11.0	**43.5**	28.9	**56.2**	25.1	**0.00**	a	**12.2**	a
		Average Overall Reduction	**57.4**	41.4	**79.3**	35.9	**-79.9**	490	**56.8**	29.8	**43.2**	10.8	**-24.7**	22.3
	Biweekly	Biweeks of Reduction (%)	**66.7**		**77.8**		**88.9**		**88.9**		**100**		**0.00**	
		Biweeks of Significant Reduction (%)	**22.2**		**55.6**		**22.2**		**11.1**		**100**		**0.00**	
		Average Significant Reduction	**86.5**	6.23	**95.3**	2.55	**91.6**	2.81	**87.4**	a	**42.8**	7.35	**0.00**	a
		Average Non Significant Reduction	**71.3**	21.5	**87.7**	16.9	**31.4**	16.0	**52.8**	25.5	**0.00**	a	**0.00**	a
		Average Overall Reduction	**48.0**	45.5	**71.7**	43.1	**-156**	609	**50.8**	31.3	**42.8**	7.35	**-25.8**	18.4

Interval (Daily, Weekly, and Biweekly): Data analyses based on all daily, weekly or biweekly means.
Days/weeks/biweeks of reduction: Percent of days/weeks/biweeks over the entire measurement period at which a mitigating effect was observed after SBP application (i.e., reduction of gas emissions).
Days of significant reduction: Percent of days/weeks/biweeks over the entire measurement period at which a statistically significant mitigating effect was observed after SBP application (i.e., reduction of gas emissions).
Average Significant Reduction: Mean percent reduction in gas emissions based solely on statistically significant mitigation effect to gas emissions at either daily, weekly or biweekly intervals(i.e., mitigation was observed and it was statistically significant).
Average Non significant Reduction: Mean percent reduction in gas emissions based solely on non-statistically significant mitigation effect to gas emissions at either daily, weekly or biweekly intervals (i.e., mitigation effect on emissions was observed but it was not statistically significant).
Average Overall Reduction: Mean percent reduction of gas emissions for all measurements analyzed on daily, weekly mean and biweekly mean intervals.
Adjusted: Estimates of mitigation effect on emissions were adjusted to compensate for mean differences measured in control and treatment rooms before SBP treatment (i.e., in the 2 week period of baseline emissions measurements before SBP application).
Non Adjusted: Estimates of mitigation effect on emissions were not adjusted for differences between control and treatment rooms that were measured before treatment.
a: Standard deviation could not be calculated because of single or no occurrence observed.

Summary of gas flux (emission) reduction – farm scale

Summary of overall mean % reduction for each target gas before and after application of SBP treatment (Eq. 16) for one dose tested (2.28 kg/m^2) and (n=3) replicates of gaseous emissions measurements for control and treatment at farm. The pilot scale emissions mitigation results are also presented for side-by-side comparisons in **Table 14** – however, *only the first 42 days of pilot scale after treatment to match the trial period of the farm scale* are presented. Full summary of the product efficacy in pilot scale and 136 days in presented in earlier section of this report.

The overall mean % reduction was estimated using all measured flux for either "Before" or "After" period. "Before SBP application" represents the 3 week period (pilot scale) or 2 week period (farm scale) of baseline testing while "After SBP application" represents the 42 days post treatment application. The baseline testing was conducted to determine if the flux from treatment and control are statistically similar, i.e., no significant difference.

Significant differences “Before SBP application for the farm scale was observed for N_2O, DMTS and skatole. High non-significant differences were also observed for the majority of other gases also so an adjustment was used to normalize the differences between rooms at the farm scale (Eq. 15).

The overall results of the farm scale showed that topical SBP treatment statistically significantly reduced emissions of NH_3 (21.7%), H_2S (79.7), *n*-butyric acid (37.2%), valeric acid (47.7%), isovaleric acid (39.3%), indole (31.2%) and skatole (43.5%). Emissions of *p*-cresol were also reduced by14.4% and were not statistically significant.

In general, mitigating effects of SBP treatment were similar at the farm and the pilot scales (when the similar, 42 day treatment is compared). Specifically:

1. **Ammonia** emissions were reduced by 21.7% and were statistically significant. The reduction at the farm scale was slightly higher than that observed at the pilot scale (15.3%) over the same treatment time at the same SBP dose.
2. **H_2S** emissions were reduced by 79.7% and were statistically significant. However, it was only the 22.8 kg/m^2 SBP dose at pilot scale that resulted in H_2S emissions reduction (62.9%). Effects of other pilot scale doses were highly variable.
3. **GHGs** emissions were reduced for N_2O at 9.8%. However, the reduction was not statistically significant. Similarly, a statistically insignificant change was also observed at the pilot scale for N_2O (2.9% increase) at the same SBP dose. Both methane and CO_2 emissions were reduced by 6.2% and 3.0%, respectively. However, the reduction was not statistically significant.
   Significant increase in CO_2 (24.6%) was observed for the same SBP dose at the pilot scale. This apparent discrepancy could be explained by contribution of exhaled CO_2 at the farm scale and its effect on significant increase in measured concentrations. Increased levels of CO_2 made it more challenging to measure the changes in CO_2 emissions from the manure. Methane also increased at the pilot scale and same SBP dose (32.2%), however it was not significant.
4. **Sulfur VOC** emissions were significantly increased by 30.6% for DMDS. The pilot scale flux estimates resulted in a reduction of DMDS (65.1%) at the same SBP dose. DMTS was only present in high enough concentrations to be measured for one day in one room during the trail so the effect of the SBP could not be assessed.
5. **Volatile fatty acids** emissions were significantly reduced by 37.2% (butyric acid), 47.7% (valeric acid) and 39.3% (isovaleric acid). Similar reductions were observed (17.7%, 5.6% and 46.9%, respectively) at the pilot scale for the same SBP dose, however they were not significant.
6. **Phenolics** emissions were reduced by 14.4% (*p*-cresol), 31.2% (indole) and 43.5% (skatole) and were statistically significant for indole and skatole. The pilot scale resulted in reductions of 58.3% (*p*-cresol), 82.9% (indole) and 81.4% (skatole) at the same SBP dose, with significant reductions in *p*-cresol and skatole.

Specifically, emissions and mitigating effects of SBP treatment at the farm scale (and comparable 42 day period at the pilot scale were as follows:

- **NH_3** flux (emissions) at pilot scale were reduced by 83.6% ($p<0.0001$), 66.8% ($p<0.0001$), 31.9% ($p=0.001$) for 45.7, 22.8, 4.57 kg/m^2 SBP dose, respectively. NH_3 flux was also reduced by 15.3% for the lowest 2.28 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.110$). NH_3 flux at farm scale was reduced by 21.7% ($p=0.008$).
- **H_2S** flux (emissions) at pilot scale were highly variable and not correlated with the dose. H_2S flux was reduced by 62.9% ($p=0.004$) for 22.8 kg/m^2 SBP dose. H_2S flux increased by 330.6% ($p=0.005$) for 45.7 kg/m^2 SBP dose. H_2S flux also increased by 105.9 and 14.3% for the 4.57 and 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.1.04 and $p=0.680$, respectively). H_2S flux at farm scale was reduced by 79.7% ($p<0.0001$).
- **CH_4** flux (emissions) at pilot scale were increased by 228.8% ($p<0.0001$), 86.4% ($p=0.004$), 59.4% ($p=0.012$) for 45.7, 22.8, 4.57 kg/m^2 SBP doses, respectively. CH_4 flux also increased by 32.2% for the lowest 2.28 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.161$). CH_4 flux at farm scale was reduced by 6.2%. However, the treatment was not significant ($p=0.404$).
- **CO_2** flux (emissions) at pilot scale increased by 128.8% ($p<0.0001$), 88.7% ($p<0.0001$), 31.1% ($p=0.001$), 24.6% ($p=0.023$) for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. CO_2 flux at farm scale was reduced by 3.0%. However, the treatment was not significant ($p=0.545$).
- **N_2O** flux (emissions) were highly variable and not correlated with the dose. N_2O flux was reduced by 0.2 and 0.1% for 22.8 and 4.57 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.990$ and $p=0.997$, respectively). N_2O flux increased by 1.4, 2.9%for 45.7, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.916$, $p=0.944$, respectively). N_2O flux at farm scale was reduced by 9.8%. However, the treatment was not significant ($p=0.121$).
- **DMDS** flux (emissions) at pilot scale were reduced by 45.1, 90.6, 87.3, 65.1% for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.628$, $p=0.051$, $p=0.058$, $p=0.205$, respectively). DMDS flux at farm scale increased by 30.6% ($p=0.029$).
- **DMTS** flux (emissions) at pilot scale were highly variable and not correlated with the dose. DMTS flux was reduced by 4.7 and 19.5% for 4.57 and 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.613$ and $p=0.458$, respectively). DMTS flux increased by 5.4 and 12.4%for 45.7 and 22.8 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.610$ and $p=0.590$, respectively). DMTS flux at farm scale was reduced by 185%. However, the treatment was not significant ($p=0.084$).
- ***n*-Butyric Acid** flux (emissions) at pilot scale were highly variable and not correlated with the dose. *n*-Butyric acid flux increased by 168.3% ($p=0.004$) for 45.7 kg/m^2 SBP dose. *n*-Butyric acid flux was reduced by 38.4, 36.5, 17.7% for the 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.169$, $p=0.156$, $p=0.922$, respectively). *n*-Butyric acid flux at farm scale was reduced by 37.2% ($p=0.0002$).
- **Valeric acid** flux (emissions) at pilot scale were highly variable and not correlated with the dose. Valeric acid flux was reduced by 10.9, 6.9, 5.6% for the 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant ($p=0.539$, $p=0.858$, $p=0.781$, respectively). Valeric acid increased by 33.4 for 45.7 kg/m^2 SBP dose. However, the treatment was not significant ($p=0.108$). Valeric acid flux at farm scale was reduced by 47.7% ($p<0.0001$).

- **Isovaleric acid** flux (emissions) at pilot scale were highly variable and not correlated with the dose. Isovaleric acid flux increased by 170.2% (p=0.007) for 45.7 kg/m^2 SBP dose. Isovaleric acid flux was reduced by 70.1, 65.5, and 46.9% for the 22.8, 4.57, and 2.28 kg /m2 SBP doses, respectively. However, the treatment was not significant (p=0.059, p=0.059, p=0.485, respectively). Isovaleric acid flux at farm scale was reduced by 39.3% (p<0.0001).
- ***p*-Cresol** flux (emissions) at pilot scale were reduced by 92.0% (p<0.0001), 61.7% (p=0.006), 58.3% (p=0.030) for 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. *p*-Cresol flux was also reduced by 46.8% for the highest 45.7 kg/m^2 SBP dose. However, the treatment was not significant (p=0.460). *p*-Cresol flux at farm scale was reduced by 14.4%. However, the treatment was not significant (p=0.222).
- **Indole** flux (emissions) at pilot scale were highly variable and not correlated with the dose. Indole flux was reduced by 98.2, 49.0, 82.9% for 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. However, the treatment was not significant (p=0.169, p=0.767, p=0.267, respectively). Indole flux increased by 75%for 45.7 kg/m^2 SBP dose. However, the treatment was not significant (p=0.450). Indole flux at farm scale was reduced by 31.2% (p=0.001).
- **Skatole** flux (emissions) at pilot scale were reduced by 78.0% (p<0.0001), 95.4% (p<0.0001), 75.4% (p<0.0001), 81.4% (p<0.0001) for 45.7, 22.8, 4.57, 2.28 kg/m^2 SBP doses, respectively. Skatole flux at farm scale was reduced by 43.5% (p<0.0001).

Comparison of pilot scale and field scale emissions reduction

1. The pilot scale and the farm scale flux estimates for the 2.28 kg/m^2 SBP dose resulted in reductions of NH_3, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole and skatole, with more statistical significance observed on the farm scale (**Table 14**).
2. Flux estimates for sulfur containing compounds were drastically different between the pilot scale and the farm scale. Flux estimates at the pilot scale showed an increase in H_2S and a reduction in DMDS, while the farm scale resulted in the opposite. This observation illustrates the delicate balance of chemical and microbial processes that are at work in a complex system such as manure.
3. The GHGs, CO_2 and CH_4, also showed differences between pilot and farm scale. The pilot scale resulted in increases in both gases due to the oxidation byproducts of VOCs as a result of the SBP treatment, while at the farm scale this was not observed. This observation of CO_2 and CH_4 not increasing on the farm scale was most likely due to the overall increase of both gases in the sampled air due to the pigs themselves that were present on the farm scale which drowned out the increases resulting from the manure.

Table 14: Farm Scale – measured overall statistical significance of emissions reduction of SBP treatment over 42 days of treatment. Pilot scale flux data was based on 42 days of treatment only to match the length of farm scale testing.

		Pilot scale test								**Farm scale test**			
SBP dose (kg/m^2)		**45.7**		**22.8**		**4.57**		**2.28**		**2.28**		**2.28**	
SBP dose (lb/ft^2)		**9.36**		**4.67**		**0.936**		**0.467**		**0.467**		**0.467**	
SBP dose (g/L)		**50**		**25**		**5.0**		**2.5**		**12**		**12**	
Gas	**Before / After SBP Application**		p value		p value		p value		p value	**A**	p value	**N**	p value
NH_3	Before	-4.4	0.720	3.7	0.794	1.5	0.919	3.1	0.847	-28.3	0.340	-61.1	0.103
NH_3	After	**83.6**	**<.0001**	**66.8**	**<.0001**	**31.9**	**0.001**	15.3	0.110	**21.7**	**0.008**	12.0	0.187
H_2S	Before	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000	10.1	0.702	-69.0	0.165
H_2S	After	**-330.6**	**0.005**	**62.9**	**0.004**	-158.4	0.104	-14.3	0.680	**79.7**	**<.0001**	**71.6**	**<.0001**
CH_4	Before	10.5	0.942	6.7	0.943	1.7	0.982	9.5	0.893	-7.3	0.625	-17.2	0.294
CH_4	After	**-228.8**	**<.0001**	**-86.4**	**0.004**	**-59.4**	**0.012**	-32.2	0.161	6.2	0.404	-1.7	0.833
CO_2	Before	1.4	0.956	1.3	0.971	2.9	0.858	0.1	0.997	-1.7	0.877	-3.1	0.780
CO_2	After	**-128.8**	**<.0001**	**-88.7**	**<.0001**	**-31.1**	**0.001**	**-24.6**	**0.023**	3.0	0.545	1.9	0.706
N_2O	Before	-3.9	0.748	-2.3	0.852	-0.5	0.970	-2.7	0.830	-8.3	0.450	**-55.3**	**0.001**
N_2O	After	-1.4	0.916	0.2	0.990	0.1	0.997	-2.9	0.944	9.8	0.121	**-32.8**	**0.001**
DMDS	Before	-21.5	0.999	-5.6	0.997	-4.7	0.997	-3.3	0.999	-31.1	0.576	-15.0	0.758
DMDS	After	45.1	0.628	90.6	0.051	87.3	0.058	65.1	0.205	**-30.6**	**0.029**	-22.1	0.084
DMTS	Before	-77.5	0.992	-36.5	0.999	98.6	0.970	-150.7*	0.923	99.7*	0.121	**99.8***	**0.044**
DMTS	After	-5.4	0.610	-12.4	0.590	4.7	0.613	19.5	0.458	185.0*	0.084	-9385.9*	0.430
***n*-Butyric Acid**	Before	64.2	0.284	**77.5**	**0.015**	32.6	0.172	85.0	0.136	25.7	0.195	-56.5	0.176
***n*-Butyric Acid**	After	**-168.3**	**0.004**	38.4	0.169	36.5	0.156	17.7	0.922	**37.2**	**0.000**	-21.5	0.235
Valeric Acid	Before	**72.3**	**<.0001**	**77.8**	**<.0001**	-110.8	0.198	**80.3**	**0.002**	21.9	0.191	-62.5	0.076
Valeric Acid	After	-33.4	0.108	10.9	0.539	6.9	0.858	5.6	0.781	**47.7**	**<.0001**	-4.3	0.784
Isovaleric Acid	Before	60.1	0.580	88.9	0.137	77.5	0.174	90.8	0.290	26.2	0.248	-100.0	0.106
Isovaleric Acid	After	**-170.2**	**0.007**	70.1	0.059	65.5	0.059	46.9	0.485	**39.3**	**<.0001**	-22.3	0.233
***p*-Cresol**	Before	-6.6	0.956	-9.9	0.926	-9.3	0.929	5.9	0.997	7.7	0.849	-81.7	0.307
***p*-Cresol**	After	46.8	0.460	**92.0**	**<.0001**	**61.7**	**0.006**	**58.3**	**0.030**	14.4	0.222	-18.8	0.258
Indole	Before	0.0	0.999	0.0	0.998	-809.19*	0.958	0.0	1.000	13.0	0.684	-148.1	0.109
Indole	After	-75.0	0.450	98.2	0.169	49.0	0.767	82.9	0.267	**31.2**	**0.001**	-7.3	0.573
Skatole	Before	-17.0	0.959	-25.8	0.989	-12.0	0.938	-33.1	0.795	11.5	0.459	**-151.4**	**0.001**
Skatole	After	**78.0**	**<.0001**	**95.4**	**<.0001**	**75.4**	**<.0001**	**81.4**	**<.0001**	**43.5**	**<.0001**	-22.1	0.125

Bold: Statically significantly at a 95% confidence level. *gas was not detected consistently enough at high enough levels to achieve reproducible results. **A**: adjusted data from the farm scale trail for differences observed between control and treated rooms prior to SBP application (Eq. 15). **N**: non adjusted data from the farm scale trial.

Manure Analysis - Farm Scale

Table 15: Farm Scale –manure analysis results.

	Control			SBP Treated		
	Day 2	Day 14*	Day 56	Day 2	Day 14*	Day 56
TS%	4.65 ± 0.37	8.07 ± 0.05	8.78 ± 0.02	3.01 ± 0.05	8.27 ± 0.05	8.49 ± 0.23
VS%	3.60 ± 0.36	6.59 ± 0.04	7.23 ± 0.10	2.21 ± 0.05	6.66 ± 0.15	6.69 ± 0.26
Volatility %	77.3 ± 1.70	81.6 ± 0.1	82.3 ± 0.9	73.5 ± 0.4	80.5 ± 1.3	78.8 ± 0.9
pH	7.64 ± 0.01	7.80 ± 0.03	7.92 ± 0.02	7.96 ± 0.03	8.16 ± 0.01	7.75 ± 0.01
COD mg/L	19161 ± 1319	22265 ± 1630	24358 ± 2469	19419 ± 2184	25381 ± 4703	23746 ± 3854
NH3-N mg/L	4431 ± 74	5315 ± 177	6129 ± 117	4027 ± 64	5524 ± 168	6590 ± 141
TKN mg/L	5123 ± 170	6378 ± 209	7485 ± 198	4364 ± 261	7391 ± 64	8853 ± 356
PO4-P mg/L	161 ± 11	130 ± 21	142 ± 24	98 ± 10	96 ± 4	107 ± 16
TP mg/L	376 ± 82	332 ± 37	461 ± 14	416 ± 82	607 ± 4	477 ± 22

*Day 14 is the day of SBP treatment, manure samples were taken after SBP treatment.

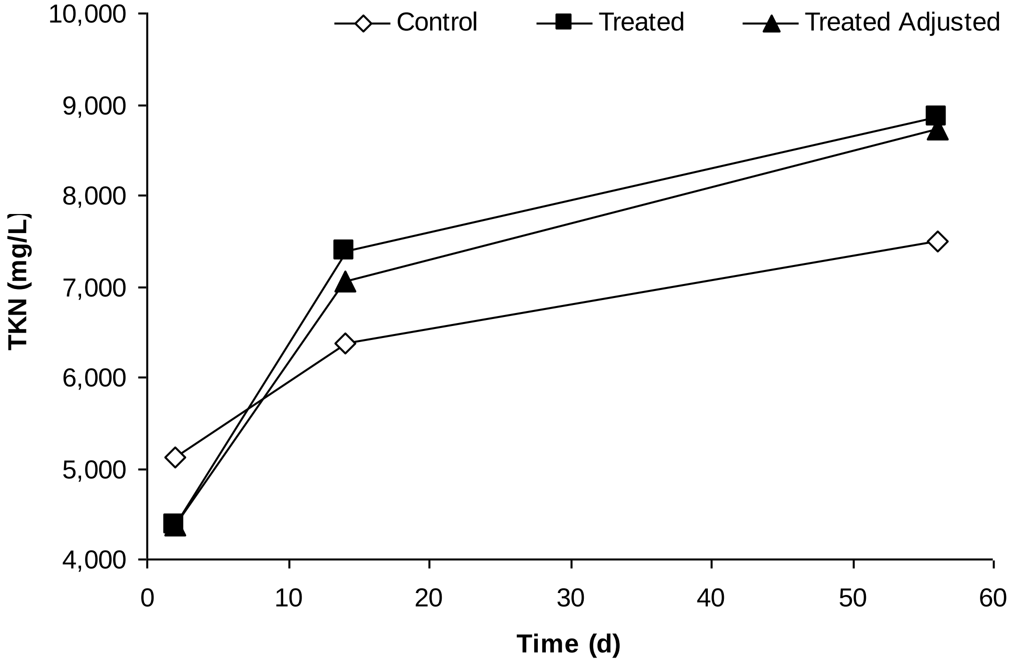

Figure 67: Farm Scale –total Kjeldahl nitrogen evolution at farm scale. Note: Treated adjusted has been adjusted by removing nitrogen that was introduced from the SBP.

The manure from the SBP treated room accumulated nitrogen at a faster rate compared to the control room, 34.8, 26.4 TKN (mg/L)/day respectively (**Figure 67**). The total loss of nitrogen in the form of NH_3 for the control and SBP treated rooms were, 30.4 and 27.6 kg of nitrogen respectively based on observed emissions. The total loss of nitrogen in the form of N_2O for the control and SBP treated rooms were, 0.843 and 1.17 kg of nitrogen respectively based on observed emissions.

Comparison with Previous Studies and Economic and Cost Analysis

Comparison of percent emissions reduction and cost of SBP treatment with other published research on farm-scale topical manure additives is presented in **Table 16**. This study was the most comprehensive, to date, assessment of a topical manure treatment for a suite of gases of concern for the swine industry. Previous studies focused on a smaller subset of target gases.

The cost of SBP treatment was based on the following assumptions:

a) SBP cost. Bulk purchase of soybean hulls from an (Midwest-based co-op market ($173/ton, February 06-2014 availability pricing, mean of 3 estimates from Iowa, Missouri and Minnesota. Reference – University of Missouri Extension, By-Product Feed Price Listing - http://agebb.missouri.edu/dairy/byprod/bplist.asp)
b) $CaCO_2$ cost. Bulk purchase of 900 kg, $6.48/kg (Supplier = American International Chemical, Inc., Framingham , MA)
c) Grinding of bulk soybeans. $5/ton (Dr. Kurt Rosentrater, ABE, ISU, Ames IA, personal communication, February 06, 2014).
d) Mixing and application time cost. Based on 8 men-hours and $13/h.

Resulting cost was $2.62 per marketed pig.

Heber et al., (2000) studied the effects of Alliance treatment developed by Monsanto during a 6 month study. Alliance treatment, a proprietary mix of surfactants, neodol, glyoxal, copper sulfate, and water was sprayed onto manure pit surface every 4 h for 4 min at a time, resulting in 20% dilution of fresh manure. Heber et al, (2000) reported 24% reduction in NH_3 emissions and no significant difference in H_2S emissions.

Moreno et al., (2010) studied the effect of molybdate treatment on H_2S, NH_3 and CO_2 emissions from swine manure due to microbial inhibition. These tests were conducted in two chamber rooms housing 8 pigs each. The sodium molybdate was sprayed and raked over to mix with manure. Gas concentrations were measured during manure agitation on day 28 and 48 post application at the pit, animal and human breathing zone level. Moreno et al., reported approximate 79 to 97% reduction in H_2S in pit headspace on Days 28, and 48 respectively. Mean percent reduction, 89% is reported in **Table 16**. No statistically significant difference in NH_3 and CO_2 concentrations was measured.

Balsari et al., 2006 reported 73 to 87% reduction of NH_3 emissions from open swine slurry storage tank (300 m^3, ~80,000 gal capacity) with the use of 0.1 m layer of Leca (extruded clay) floating balls. Four measurement trials, each lasting 6 days per season, were made over 1 year period. The mean of the lowest, wintertime (73%) to highest summertime (87%) NH_3 emissions reduction, i.e., 80% is reported in **Table 16**.

Heber et al., 2001 reported concentrations of NH_3 and H_2S in headspace of 35 manure additives. The tests were done on pilot scale over 42 days with three replications of each, with samples taken over 4 h period on a weekly bases. All additives were added with no pH adjustments or agitation. Concentrations of acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, phenol, *p*-cresol, indole and skatole in manure were also monitored. Statistically significant reductions in headspace concentrations were observed for 7 and 8 of the additives for H_2S and NH_3 respectively.

The estimated cost of treatment (including SBP and CaO_2 only) was estimated at $1.45 per marketed pig and $2.62 per marketed pig when the cost of labor was added. Similarly, the estimated cost was $2.19/pig space/year of the (including SBP and CaO_2 only) and $3.95 when the cost of labor was included. Similarly, the estimated cost was $2.96/m^2/year of the (including SBP and CaO_2 only) and $5.34 when the cost of labor was included (2014 price benchmarking). The cost estimate was at the lower range of comparable products tested for air quality mitigation with and mean cost of $4.28 ± $5.80 ($0.01 to $18.2 per marketed pig) (**Table 16**). The SBP treatment resulted in a more comprehensive mitigation of greater number of gases of concern for swine industry.

There are several publications reporting swine manure treatments discussed below however, no cost of treatment was reported.

Ye et al., 2009 reported 32 to 54% and 28 to 41% reduction in indolic compounds and volatile fatty acids (VFAs), respectively and nearly 100% reduction in *p*-cresol from 21 L bucket trials on swine manure treated with topically applied horseradish peroxidase and peroxides. Reductions in volatiles were determined by concentration in the manure over a 72 h period.

Portejoie et al., 2003 reported a 93% and 92% reduction in NH_3 emissions from 5 kg scale trails over 15 days with topical application of kitchen oil and peat, respectively on swine manure.

There were other additives reported in the literature but the effectiveness and general practicality of employing these additives was not to the point of real world use, and so were not included for comparison.

Table 16: Farm Scale – comparison of estimated % emissions reduction and cost of treatment.

Reference	Additive	Gaseous Emissions Reduction (%)														Additive Cost ($)			Total Treatment Cost[i] ($)		
		NH_3	H_2S	CH_4	CO_2	N_2O	DMDS	DMTS	n-Butyric Acid	Valeric Acid	Isovaleric Acid	*p*-Cresol	Phenol	Indole	Skatole	Per marketed pig	per m^2 per year	per pig space per year	Per marketed pig	per m^2 per year	per pig space per year
This Study, 2014	SBP/CaO_2	**21.7**	**79.7**	6.15	2.99	9.76	**-30.6**	185[g]	**37.2**	**47.7**	**39.3**	14.4	NM	**31.2**	**43.5**	1.45[h]	2.96	2.19[c]	2.62[h]	5.34	3.95[c]
Heber et al., 2000	Alliance	24	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	0.69	2.55[c]	1.89	0.85[f]	3.17[c]	2.35[d]
Moreno et al., 2010	Sodium Molybdate	NS	89	NM	NS	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	0.45[b]	1.98[c]	1.46[e]	0.98[b]	4.31[c]	3.18[e]
Balsari et al., 2006	Leca Balls	80	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	0.01[d]	0.06[a]	0.05[c]	NA	NA	NA
Heber et al., 2001[k]	AgriKlenz Plus	6	-34	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	0.57	2.14	1.59	NA	NA	NA
Heber et al., 2001[k]	Alken Clear-Flo	-4	47	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	18.18	67.51	50.18	NA	NA	NA
Heber et al., 2001[k]	AWL-80	10	NS	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	0.41	1.52	1.13	NA	NA	NA
Heber et al., 2001[k]	Biocharge Dry	7	37	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	0.94	3.48	2.59	NA	NA	NA
Heber et al., 2001[k]	BMT	5	-58	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	14.87	55.24	41.05	NA	NA	NA
Heber et al., 2001[k]	EM Waste Treatment	15	-70	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	8.27	30.72	22.84	NA	NA	NA
Heber et al., 2001[k]	GT-2000OC BC-2000AF	NS	34	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	12.15	45.12	33.53	NA	NA	NA
Heber et al., 2001[k]	Inhibodor	NS	36	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	1.78	6.61	4.91	NA	NA	NA
Heber et al., 2001[k]	Krystal Air	7	NS	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	1.11	4.13	3.07	NA	NA	NA
Heber et al., 2001[k]	Manure Management Plus	6	-47	NM	NM	NM	NM	NM	NS	NS	NS	-129	NS	NS	NS	2.95	10.94	8.13	NA	NA	NA
Heber et al., 2001[k]	Peroxy Odor Control	3	-27	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	0.16	0.59	0.44	NA	NA	NA
Heber et al., 2001[k]	ROE	-9	23	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	NA	NA	NA	NA	NA	NA
Heber et al., 2001[k]	SMOC	NS	37	NM	NM	NM	NM	NM	NS	-26	NS	NS	NS	NS	NS	7.96	29.56	21.97	NA	NA	NA
Heber et al., 2001[k]	ZymPlex	NS	27	NM	NM	NM	NM	NM	NS	NS	NS	NS	NS	NS	NS	0.82	3.05	2.27	NA	NA	NA
Ye et al., 2009	HRP/CaO_2	NM	NM	NM	NM	NM	NM	NM	38[j]			93[j]		46[j]		NA	NA	NA	NA	NA	NA
Portejoie et al., 2003	Oil	93	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NA	NA	NA	NA	NA	NA
Portejoie et al., 2003	Peat	92	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NA	NA	NA	NA	NA	NA

SBP/CaO_2: based on overall means of farm scale trial.
HRP: Horseradish peroxidase.
Bold: statistically significant differences compared to control at 95% confidence level for this study.
NS: No significant difference at 95% confidence level.
NM: Not measured.
NA: Not available.
a: calculated based on the average exchange rate (1.26 USD = 1 Euro) in 2006 (year of publication).
b: calculated based on the average exchange rate (0.8704 USD = 1 $CAD) in 2009 (year of publication).
c: calculated based on 0.74 m^2 (8 ft^2) per pig space.
d: calculated based on 2.76 swine finishing cycles per year.
e: calculated based on 3.25 swine finishing cycles per year (from publication).
f: calculated based on $1,500 equipment costs (equipment life time 5 years) for a 1,200 head finisher and $13.00 per hour per cycle labor of filling and maintaining equipment 3 h per grow cycle.
g: Reduction is skewed due to very few days of gas detection during trial.
h: The stocking density of 1.35 m^2/pig (14.6 ft^2/pig) was lower than industry standards, i.e., 0.74 m^2/pig (8 ft^2/pig).
i: Total cost estimated added expense of labor and equipment if applicable. Pricing was not adjusted for inflation. Prices are based on the original cost at the time of publication.
j: publication reductions were in categories: VFAs (isobutyric acid, isocaproic acid, and isovaleric acid), phenolics (phenol and *p*-cresol), and indolics (indole and skatole). Values are also determined in the manure not the headspace.
k: Concentrations were taken from the manure not the headspace for all but NH_3 and H_2S.
Cost for this study is based on SBP application once per cycle (2.76 swine finishing cycles per year).
All previously published results on cost have been adjusted for inflation using the US Inflation Calculator (http://www.usinflationcalculator.com/).
Cost for Heber et al., 2001 were based on supplier recommended application rates and frequencies and on a modern 2500 head finisher building with a half full 8 ft pit and a stocking density of 0.74 m^2.

Manure-Air Biochemical Cycles of Target Gases

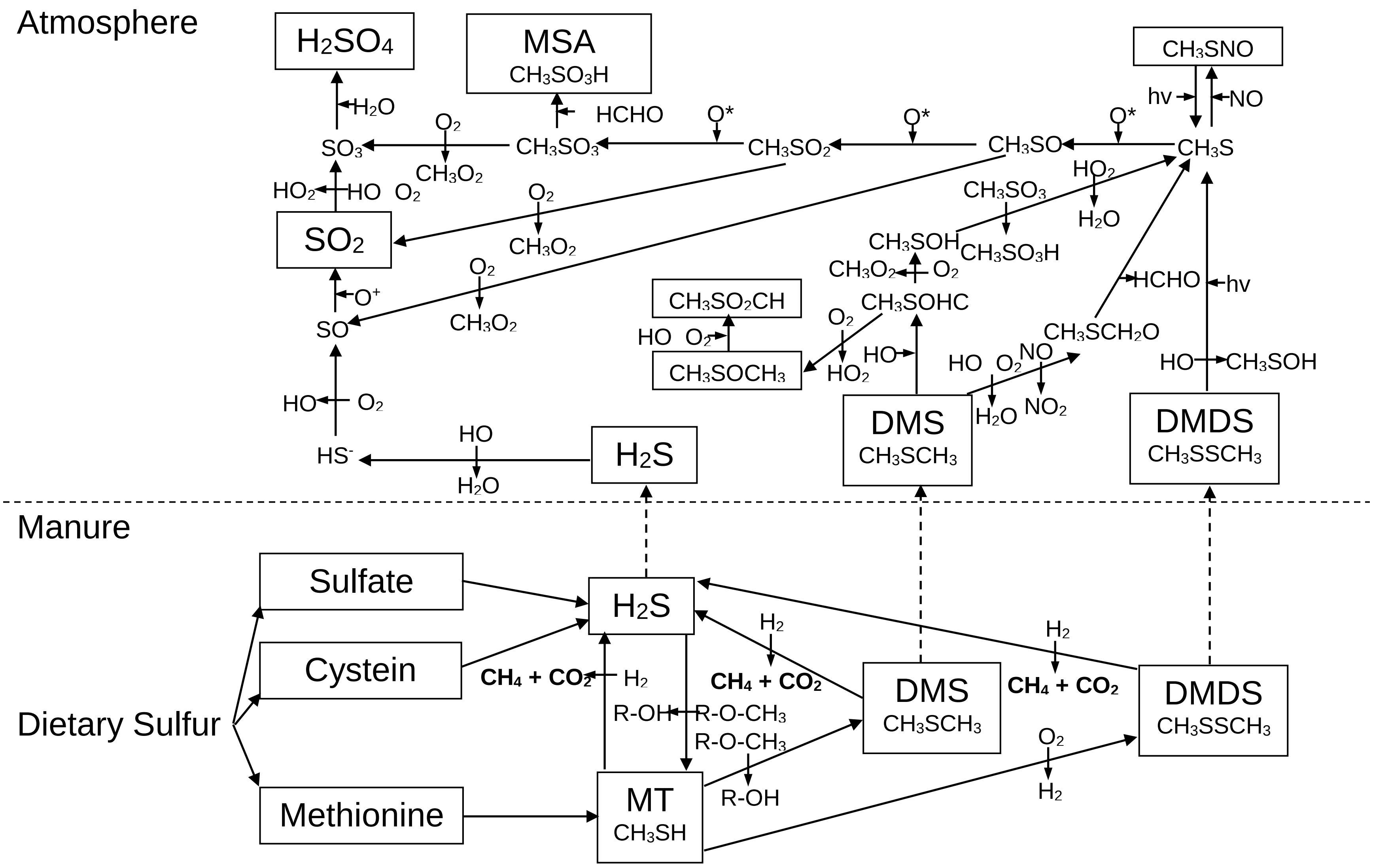

Figure 68: Sulfur Cycle. MT, methanethiol; DMS, dimethyl sulfide; MSA, methanesulfonic acid, * Oxygen from NO_2, O_3, HO_2 or O_2 to an intermediate which is then reduced by NO. $^+$ Oxygen from NO_2, O_2, O_3. (Eriksen 2010, Higgins 2006, Yin 1990, Gaedel 1977, Kennes 2013, Pitts 2000)

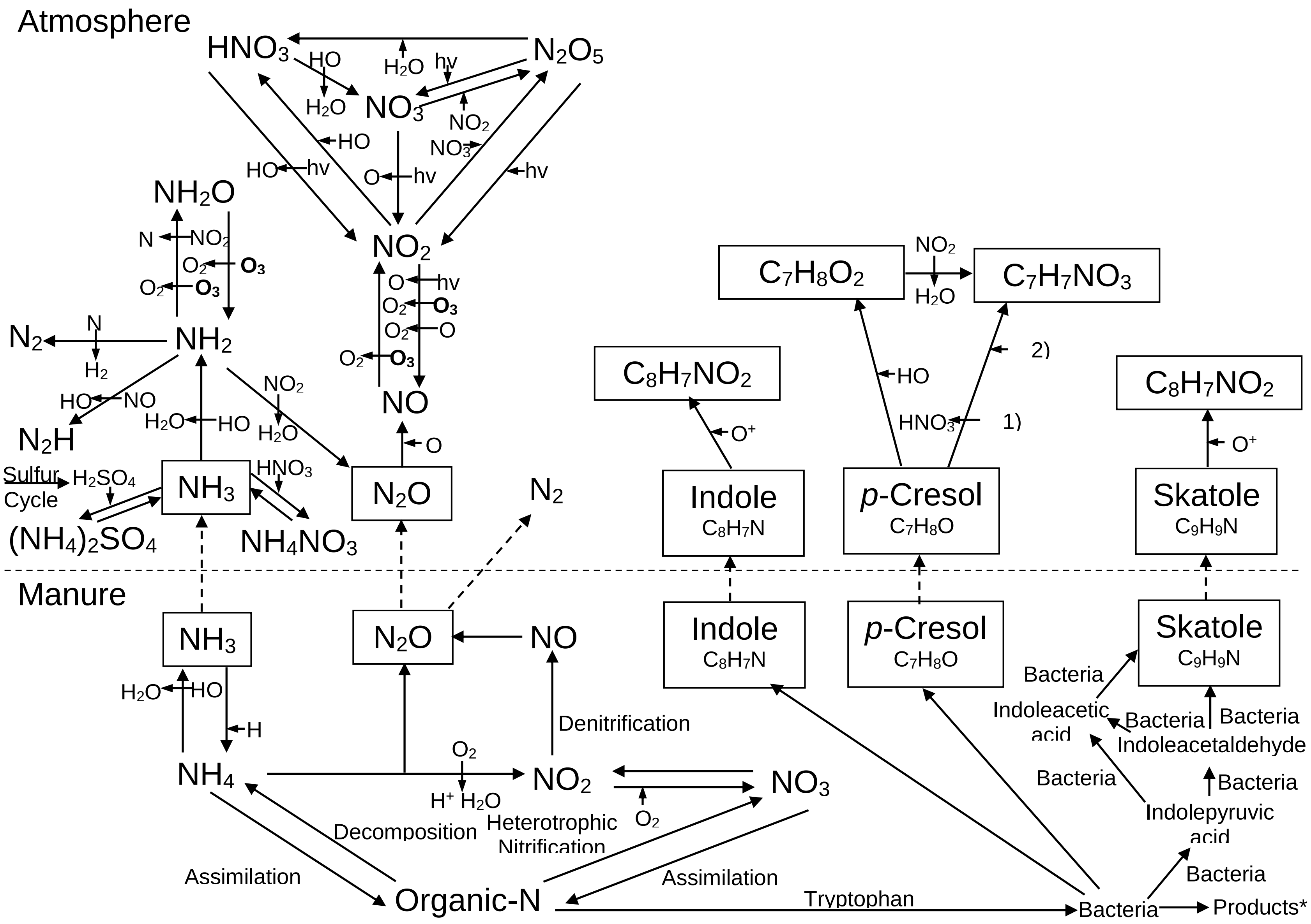

Figure 69: Nitrogen Cycle. * Other products from bacteria and tryptophan: Indolepropionic acid, Indolelactic acid, tryptophol. + Oxygen from O_3, OH, NO_2, NO_3. (Atkinson 1992, Atkinson 1995, Jacob 1999, Pitts 2000, Patrick 1984, Maeda 2011, Mohammed 2003, HSDB)

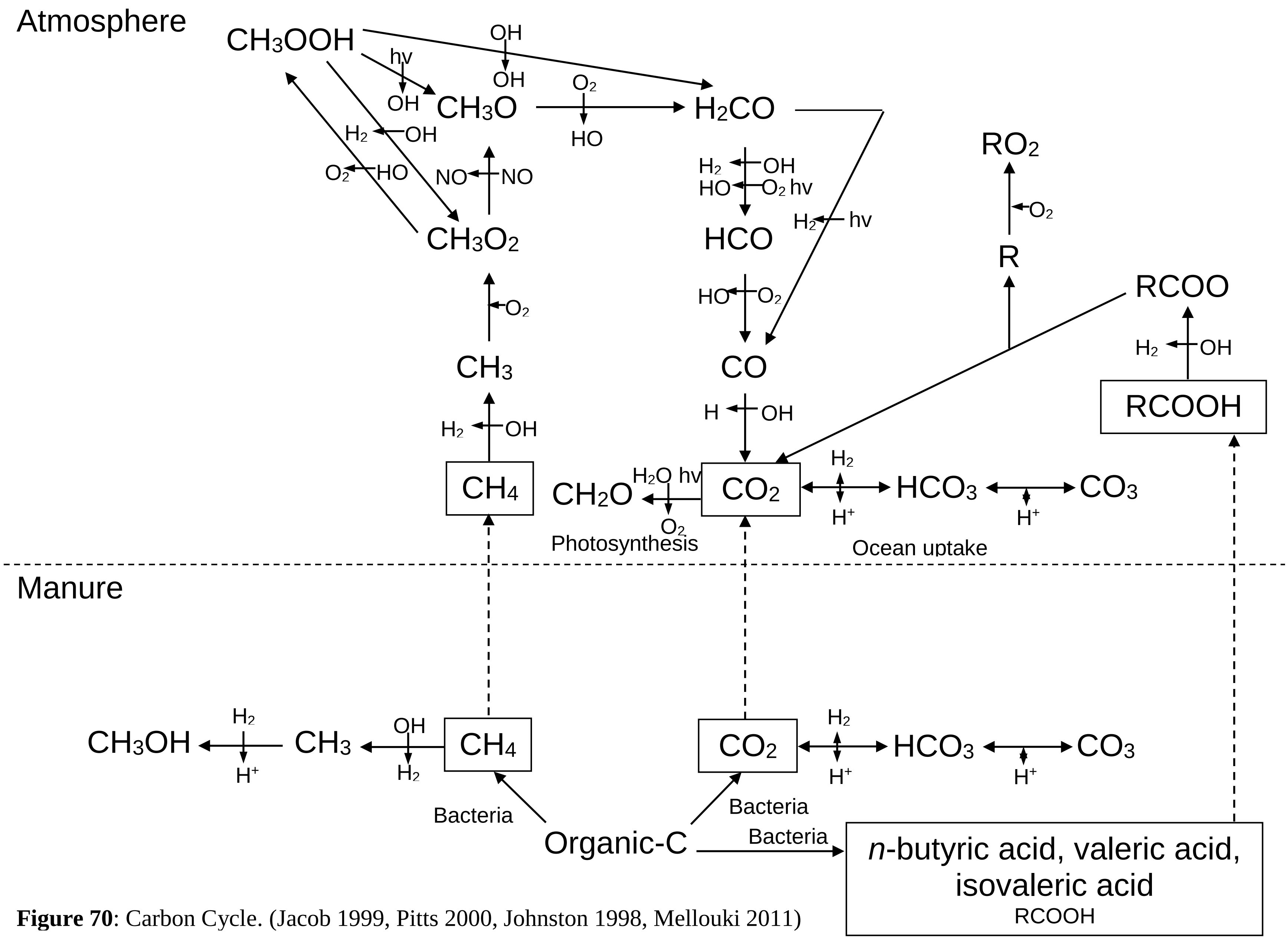

Figure 70: Carbon Cycle. (Jacob 1999, Pitts 2000, Johnston 1998, Mellouki 2011)

IX. Discussion

Pilot scale tests showed significant reductions in NH_3, *p*-cresol and skatole with NH_3 and *p*-cresol showing higher reductions with higher SBP dose that faded over time. Similar results were observed at the farm scale with the exception of significant reductions in indole, H_2S, *n*-butyric acid, valeric acid and isovaleric acid. In regards to indole and H_2S the fact that significant reductions were not observed at the pilot scale could be due to that these two compounds were not consistently measured/observed. Indole and H_2S at the pilot plant scale was observed only during the second and third months, during that time period reductions were observed for the treated manure. *p*-Cresol at the farm scale did not show significant reduction due to the treatment as was seen at the pilot scale, but it did result in a 14.4% non significant reduction overall. Significant reduction was seen in regards for *p*-cresol during the second and third week of the farm scale trial, but the SBP effect seemed to wear off after. Less variability in *n*-butyric acid, valeric acid and isovaleric acid flux estimates at the farm scale resulted in significant reductions while the reductions observed at the pilot scale were not significant.

Ammonia reduction was observed for all pilot scale and farm scale weekly averages for SBP treated manure, with more significant reductions observed for the higher SBP dose at the pilot plant scale. Skatole reduction was observed for all pilot scale and farm scale weekly averages for SBP treated manure, with the exception of a few weeks in the last 3 months of the pilot scale trials. *p*-Cresol estimated flux reduction was observed through out all weeks until the last weeks of the pilot scale trials, with significant reduction weeks not being effected by SBP dose. Significant H_2S reductions were observed every day that was monitored at the farm scale for the duration of the trial after SBP application. Indole reduction was observed over all weeks during the farm scale trial with significant reduction in the middle of the trail for the SBP treated room. Weekly significant reductions were observed for *n*-butyric acid, valeric acid and isovaleric acid during the first half of the farm scale trial with non significant reductions observed during the second half of the trial for the SBP treated room.

The SBP effect on CO_2 and CH_4 flux estimates at the pilot scale resulted in significant increases that were not observed at the farm scale, this could be explained by the contributions of these gases by the pigs themselves at the farm scale making the levels of CO_2 and CH_4 emitted from the manure minimal in comparison. Nitrous oxide flux estimates observed at the pilot scale and farm scale were not significantly different.

The significant increase in flux estimates for DMDS that was observed at the farm scale could be due to the oxidation of methanethiol (Higgins, 2006), which is product of protein degradation, by the SBP and CaO_2 treatment.

It was observed at the pilot scale that the relative humidity was also affected by the SBP treatment. The SBP layer seemed to provide a barrier contain the moisture in the manure. The effect of this was greater with higher SBP dose, and faded over time as the SBP became more incorporated into the manure.

The highest SBP dose of 45.7 kg/m^2 at the pilot scale incorporated itself into the manure faster than the next lowest dose 22.8 kg/m^2. This was due to the observed inability of the thick SBP layer to float on the surface of the manure when fresh manure was added, it would crack and roll as the fresh manure would raise the manure level under the SBP layer.

The peroxidase activity assay also showed that as the SBP was incorporated into the manure it would lose activity faster than that of the 22.8 kg/m^2 treatment that was thick enough to not have all soaked into the manure but thin enough to float on the surface when fresh manure was added at the pilot scale at 87 after application.

At the pilot scale there were significantly higher TKN levels in the manure after the 136 day trail which correlate to the higher SBP doses. These differences were not due to the SBP conserving the nitrogen that was in the manure but that the SBP was contributing nitrogen to the manure. If the TKN levels are adjusted for the amount of nitrogen contributed by the level of SBP there was no difference between the SBP treatments. The observed reduction in NH_3 does not makeup a high enough percentage to have an effect on the TKN levels in the manure. The farm scale, due to the increase in scale, showed a higher rate of TKN accumulation in the SBP treated room.

Practicality and cost of the SBP treatment was part of the reasoning for scaling up the SBP treatment to farm scale using the lowest topical dose of 2.28 kg/m^2. The estimated cost of \$2.19/pig space/year (additive only cost) of the SBP treatment was below average cost (\$11.72 ± \$16.05) to those in the literature, which ranged from \$0.05 to \$50.18/pig space/year. The SBP treatment resulted in a more comprehensive mitigation of problem compounds being emitted. According to Balsari the Leca Balls reduced NH_3 but no other gases were measured. Mereno measured NH_3, H_2S and CO_2 with only significant reductions seen for H_2S. Heber et al., (2000) measured only NH_3 and H_2S with only NH_3 showing significant reduction using Alliance additive sprayed into the manure pit. Heber et al., (2001) measured NH_3 and H_2S in the headspace for the 35 additives that were tested with only 14 of which that resulted in statistically significant reduction in NH_3 or H_2S. Almost all 14 cases of manure additive use resulted in one gas (NH_3 or H_2S) was significantly reduced while the other gas was significantly increased. This was likely due to the manure pH change. In this research, the SBP treatment resulted in significant reduction in not only NH_3 and H_2S but also a variety of odorous VOCs with no significant change in GHGs emissions on farm scale.

X. Summary

The control of odor, odorous volatile organic compounds (VOCs), hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gases (GHGs) emissions associated with commercial swine production is a critical need. Manure storage is the major source of gaseous emissions. This study aimed for the most comprehensive, to date, assessment of a manure additive for mitigation of gaseous emissions of all major compounds of interest from swine manure. This study tested *topical* application of manure additive treatment in controlled pilot and farm scales (soybean peroxidase (SBP); product code 516-IND; Bio-Research Products, Inc.). This research builds on the previous published study where SBP product was *mixed* into manure and resulted in significant mitigation of odorous VOCs in lab scale. In this research both pilot and farm scale testing of topical SBP treatment (and ~23.5:1 weight/weight mix of SBP:CaO_2 catalyst) was conducted over ~5 month and ~1.5 month, respectively. This work aimed at providing a comprehensive assessment of SBP treatment efficacy to mitigate emissions of odorous VOCs, odor, H_2S, NH_3, and GHGs, i.e., a set of target gases of concern to swine industry.

The soybean based additive was first tested in **pilot scale** (Objective 1). Effects of SBP dose and time were tested. The following topical doses (mass per manure surface area) with three replicates of each: 0, 2.28, 4.57, 22.8 and 45.7 kg/m^2 (equivalent of 0, 0.467, 0.936, 4.67 and 9.36 lbs/ft^2; and equivalent of 0, 2.5, 5.0, 25 and 50 g/L of swine manure) were evaluated. Emissions of VOCs, H_2S, NH_3, and GHGs were monitored over the course of 21 days pre-application and 136 days post SBP application. Pilot scale tests resulted in reduction of gaseous emissions for some compounds, while no difference or increase in emissions for others for the entire SBP testing period of 136 days. Specifically:

7. **Ammonia** emissions were reduced by 14.6% to 67.6% and were statistically significant except for the lowest SBP dose. The percent reduction was correlated with the SBP dose. The apparent effectiveness of SBP treatment was decreasing over time.
8. **H_2S** emissions were highly variable and not correlated with the SBP dose.
9. **GHGs** emissions were not significantly changed for nitrous oxide (N_2O). Methane (CH_4) and CO_2 emissions increased by 32.7% to 232% and 20.8% to 124%, respectively. The percent increase was statistically significant (except for CH_4 and the lowest dose) and was correlated with the SBP dose. The increase of CO_2 and CH_4 emissions may be inferred considering biochemical breakdown of VOCs as a result of SBP treatment.
10. **Sulfur VOC** emissions were generally reduced by 36.2% to 84.7% (DMDS) and 10.7% to 16.9% (DMTS). However, the only statistically significant reduction was for DMDS at the mid-range SBP doses.
11. **Volatile fatty acids** emissions were reduced by 8.5% to 19.5% (butyric acid), 79.2% to 88.5% (valeric acid) and 42.7% to 59.2% (isovaleric acid) except for the highest SBP dose for butyric and isovaleric acids. However, none of the reductions were statistically significant.
12. **Phenolics** emissions were reduced by 53.1% to 89.5% (*p*-cresol), 52.6% to 81.8% (indole, except for the highest SBP dose), and 63.2% to 92.5% (skatole) and were statistically significant for *p*-cresol and skatole. Indole emission's reductions were not statistically significant. The apparent effectiveness of SBP treatment on phenolics was decreasing over time.

The soybean based additive was then tested at **farm scale** (Objective 2). Effects of time were tested using one (the lowest) SBP dose selected from the pilot study. A topical dose of 2.28 kg/m^2 (equivalent of 0.467 lbs/ft^2, equivalent of 12 g/L of swine manure was used. VOCs, H_2S, NH_3, and GHGs emissions were monitored over the course of 42 days post SBP application. In general, mitigating effects of SBP treatment were similar at the farm and the pilot scales (especially, when the similar, 42 day treatment periods at the pilot and farm scales were compared). Overall, the SBP treatment was effective in mitigating major gases of concern on the farm scale. NH_3 showed a significant 22% overall reduction in emissions in the treated room compared to the untreated room. Hydrogen sulfide emissions in the treated room resulted in a significant 80% overall reduction compared to the untreated room. Greenhouse gas emissions in the treated room showed an insignificant reduction compared to the untreated room. Non sulfur VOCs emissions from the treated room showed an average reduction of 36% based on the average overall means. Specifically:

4. **Ammonia** emissions were reduced by 21.7% and were statistically significant. The reduction at the farm scale was slightly higher than that observed at the pilot scale (15.3%) over the same treatment time at the same SBP dose.
5. **H_2S** emissions were reduced by 79.7% and were statistically significant. However, it was only the 22.8 kg/m^2 SBP dose at pilot scale that resulted in H_2S emissions reduction (62.9%). Effects of other pilot scale doses were highly variable.
6. **GHGs** emissions were reduced for N_2O at 9.8%. However, the reduction was not statistically significant. Similarly, a statistically insignificant change was also observed at the pilot scale for N_2O (2.9% increase) at the same SBP dose. Both methane and CO_2 emissions were reduced by 6.2% and 3.0%, respectively. However, the reduction was not statistically significant. Significant increase in CO_2 (24.6%) was observed at the same SBP dose at the pilot scale. This apparent discrepancy could be explained by contribution of exhaled CO_2 at the farm scale and its effect on significant increase in measured concentrations. Increased levels of CO_2 made it more challenging to measure the changes in CO_2 emissions from the manure. Methane also increased at the pilot scale for the same SBP dose (32.2%), however it was not significant.
7. **Sulfur VOC** emissions were significantly increased by 30.6% for DMDS. The pilot scale flux estimates resulted in a reduction of DMDS (65.1%) at the same SBP dose. DMTS was only present in high enough concentrations to be measured for one day in one room during the trial so the effect of the SBP could not be assessed.
8. **Volatile fatty acids** emissions were significantly reduced by 37.2% (butyric acid), 47.7% (valeric acid) and 39.3% (isovaleric acid). Similar reductions were observed (17.7%, 5.6% and 46.9%, respectively) at the pilot scale for the same SBP dose, however they were not significant.
9. **Phenolics** emissions were reduced by 14.4% (*p*-cresol), 31.2% (indole) and 43.5% (skatole) and were statistically significant for indole and skatole. The pilot scale resulted in reductions of 58.3% (*p*-cresol), 82.9% (indole) and 81.4% (skatole) at the same SBP dose, with significant reductions in *p*-cresol and skatole.

The estimated cost of treatment (additives only) was estimated at $1.45 per marketed pig and $2.62 per marketed pig when the cost of labor was added. Similarly, the estimated cost was $2.19/pig space/year of the (additives only) and $3.95 when the cost of labor was included (2014 price benchmarking). The cost estimate was at the lower range of comparable products tested for air quality mitigation ($0.01 to $18.2 per marketed pig). The SBP treatment with similar cost resulted in a more comprehensive mitigation of greater number of gases of concern for swine industry. It also may have a potential benefit to U.S. soybean farmers as the active ingredient is derived from soybean hulls, a low value by-product of soybean utilization.

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