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Pilot-Scale Testing of Non-Activated Biochar for Swine Manure Treatment and Mitigation of Ammonia, Hydrogen Sulfide, Odorous Volatile Organic Compounds (VOCs), and Greenhouse Gas Emissions

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Abstract: Managing the environmental impacts associated with livestock production is a challenge for farmers, public and regulatory agencies. Sustainable solutions that take into account technical and socioeconomic factors are needed. For example, the comprehensive control of odors, ammonia (NH_3), hydrogen sulfide (H_2S), and greenhouse gas (GHG) emissions from swine production is a critical need. Stored manure is a major source of gaseous emissions. Mitigation technologies based on bio-based products such as biochar are of interest due to the potential benefits of nutrient cycling. The objective of this study was to test non-activated (non-functionalized) biochar for the mitigation of gaseous emissions from stored manure. Specifically, this included testing the effects of: (1) time; and (2) dosage of biochar application to the swine manure surface on gaseous emissions from deep-pit storage. The biochar surface application was tested with three treatments (1.14, 2.28 and 4.57 kg·m^{-2} manure) over a month. Significant reductions in emissions were observed for NH_3 (12.7–22.6% reduction as compared to the control). Concomitantly, significant increases in CH_4 emissions (22.1–24.5%) were measured. Changes to emissions of other target gases (including CO_2, N_2O, H_2S, dimethyl disulfide/methanethiol, dimethyl trisulfide, *n*-butyric-, valeric-, and isovaleric acids, *p*-cresol, indole, and skatole) were not statistically significant. Biochar treatment could be a promising and comparably-priced option for reducing NH_3 emissions from stored swine manure.

Keywords: biochar; swine manure; volatile organic compounds (VOCs); ammonia; greenhouse gases; mitigation

1. Introduction

Problematic by-products of pork production are emissions of odor, volatile organic compounds (VOCs), ammonia (NH_3), hydrogen sulfide (H_2S) and greenhouse gases (GHGs) (CH_4, N_2O, and CO_2) from stored manure to the atmosphere. Manure accounts for 14% of the total GHG emissions from agriculture in the United States and equated to 1.3% of the total GHG emissions produced in the United States' economic sectors in 2014 [1]. Local and regional air quality and potential contribution to climate change [2,3] due to these emissions results in the need for mitigation technologies that target multiple emissions and are cost-efficient for farmers to put into practice.

Twenty types of technologies to mitigate gaseous emissions from livestock housing, manure storage and handling have been reviewed and added to the Iowa State University Extension and Outreach Air Management Practices Assessment Tool [2]. Manure additives are one of the mitigation technologies that are appealing to producers due to the relative ease of adding the treatment to the manure compared to other technologies that require modifying existing livestock production infrastructure and/or purchasing expensive equipment. Manure additives, in general, are also well researched in comparison to other mitigation technologies, particularly at the farm scale. As much as ~63% of manure additives was evaluated and tested in the field (farm scale). This is compared to the mean of ~25% of all mitigation technologies that made it past the laboratory and pilot scales to be eventually tested in the field [3].

Manure additives added to a complex matrix such as manure may have many effects on emissions. Additives that reduce NH_3 emissions may also increase GHG emissions [3]. Most research has focused on a limited number of gases, mainly the target emissions that the treatment was designed to reduce, without monitoring other emissions that may be adversely affected due to the treatment [3]. Because of these limitations, it is difficult to evaluate mitigation technologies without comprehensive treatment data and an understanding of impact beyond those single or few target gases [3].

Biochar is the remaining solid fraction of charred biomass resulting from pyrolysis or gasification [4]. The Midwest (U.S.) has a large potential for production of second-generation of biofuels from corn stover or other forms of biomass. Thus, there is also a great need to improve the sustainability of this new industry by developing value-added and mass utilization plans for biochar. Biochar has a long history of being used as a soil amendment. Only recently has biochar been employed in wastewater and manure composting to absorb various compounds (Table 1) and it has been shown to adsorb NH_3 [5,6]. In these recent studies, biochar's ability to mitigate emissions from livestock has focused solely on the land application and composting of manures and on few target gases. To our knowledge, there are no published studies reporting on biochar as an emissions mitigation technology applied directly to the surface of stored manure in the context of deep pit or lagoon storage that is a common practice for swine production in the United States.

Table 1. Review of manure-related research on uses of biochar as compost or solid amendment and its effects on gaseous emissions.

Reference	Scale and Duration (d)	Treated Source	Gaseous Emissions Reduction (%)					
			NH_3	H_2S	CH_4	CO_2	N_2O	Phenol
Jindo, 2012 [7]	field, 150	poultry manure composting	NA	NA	NA	NA	NA	NA
Czekala, 2015 [8]	laboratory, 45	poultry manure composting	NA	NA	NA	−7	NA	NA
Zhang, 2015 [9]	laboratory, 105	swine manure composting	NA	NA	NA	NA	NA	NA
Steiner, 2010 [10]	pilot, 42	poultry litter composting	47–55	58–71	NA	NS	NA	NA
Jia, 2015 [11]	review	manure composting	reduced	NA	NA	NA	reduced	NA
Dias, 2010 [12]	field, 210	poultry manure composting	NA	NA	NA	NA	NA	NA
Jindo, 2012 [13]	field, 85	cattle or poultry manure composting	NA	NA	NA	NA	NA	NA
Mandal, 2016 [14]	laboratory, 30	poultry manure in soil	41–77	NA	NA	NA	NA	NA
Komnitsas, 2016 [15]	laboratory, 1	wastewater	NA	NA	NA	NA	NA	10-51
Rogovska, 2011 [16]	laboratory, 500	swine manure in soil	NA	NA	NA	33–78	NS	NA
Troy, 2013 [17]	laboratory, 28	swine manure in soil	NA	NA	NS	−45-NS	−79–68	NA
Wang, 2013 [18]	pilot, 82	swine manure composting	NA	NA	NA	NA	26	NA
Chowdhury, 2014 [19]	laboratory, 31	poultry manure composting	35–43	NA	NS	NS	NS	NA
Chen, 2015 [20]	field, 548	compost and urea in soil	NA	NA	NA	NS	−49-NS	NA
Brennan, 2015 [21]	laboratory, 15	cattle slurry in soil	77	NA	NS	84	63	NA

Note: NA = Not available, NS = Not significant.

This study aimed to address this need by investigating the feasibility of topical biochar application to swine manure for reducing gaseous emissions from stored pig manure. Comprehensive evaluation of odorous VOCs (sulfur-containing VOCs, volatile fatty acids, phenolics and indolics), NH_3, H_2S and greenhouse gas (CH_4, N_2O, and CO_2) emissions was completed at a pilot-scale system simulating a deep pit storage system. Storage of manure under slatted floors is typical in the Midwestern U.S. swine production systems. The objective of this study was to test non-activated (non-functionalized) biochar for mitigation of gaseous emissions from stored swine manure. Specifically, this included

testing the effects of: (1) time; and (2) dosage of biochar application to the swine manure surface on gaseous emissions from deep-pit storage. The key questions to answer were:

1. Can biochar float on top of swine manure for at least 1-month period?
2. Can a thin layer of biochar be effective at mitigating gaseous emissions?
3. Can biochar mitigate emissions of any key gases of concern (odorous VOCs such as sulfur-containing VOCs, volatile fatty acids, phenolics, and indolics), or NH_3, H_2S and greenhouse gases (CH_4, N_2O, and CO_2)?
4. Can non-activated, non-functionalized biochar be an economically-feasible option for controlling gaseous emissions from stored manure?

2. Materials and Methods

2.1. Experimental Design

The pilot study was designed to simulate manure conditions in a deep pit swine manure storage system. 'Deep pit' storage is typical in the Midwestern U.S. region where swine manure is held under slatted barn floors for 6 to 12 months before land application. A slatted floor separates the animal space from the ventilated storage below. Biochar was obtained from 495 to 505 °C pyrolysis of 3-mm (1/8") pine; ash content: 1–25 wt %; carbon content: 60–75 wt %; mean particle diameter: 175 microns; pH: 7.28 ± 0.07.

The experimental design was a completely randomized design (CRD) for three trials. Trial 1 consisted of one biochar dosage of 2.28 kg·m^{-2} (n = 2) applied to (crusted and uncrusted) manure and a control (n = 1), with a total of six experimental units (Table 2). The manure types were: (1) from deep pit swine barn with a crust on manure surface; and (2) from outside storage lagoon with no crust. Development of crust can affect gaseous emissions by creating a semipermeable layer over the manure that impedes the mass transfer of volatiles from the manure to the vented headspace.

Trial 2 consisted of a 4.56 kg·m^{-2} surface-applied biochar dosage treatment (n = 3) and control (n = 3). Only manure type (1) from above was evaluated in Trial 2. Manure was added twice during Trial 2 for improved simulation of barn conditions (Table 2). Trial 3 consisted of two surface-applied biochar dosage treatments, 1.14 and 2.28 kg·m^{-2} (n = 3), and a control (n = 3). A fresh batch of manure (3) from a deep pit swine barn with a crust was evaluated for Trial 3. Manure was added four times during Trial 3 (Table 2).

Table 2. Experimental trial conditions.

	Biochar Dose (kg·m^2)	Manure Type	Manure Additions During Trial	Trial Length (d)	Replications
Trial 1	2.28	crusted	no	30	n = 2 treated; n = 1 control
Trial 1	2.28	uncrusted	no	30	n = 2 treated; n = 1 control
Trial 2	4.56	crusted	yes 2x	30	n = 3
Trial 3	1.14	fresh and crusted	yes 4x	35	n = 3
Trial 3	2.28	fresh and crusted	yes 4x	35	n = 3

Note: Crusted manure is from deep pit swine barn with a crust on manure surface, uncrusted manure is from outside storage lagoon with no crust. Trial length does not include time before treatment application.

2.2. Manure Storage Simulators

Observations of biochar layer on top of swine manure were completed in pilot-scale simulators. Deep pit swine manure from an Iowa State University swine finisher operation was pumped into six 1.22-m (4 ft) tall, 0.38-m (15 in) diameter sealed manure storage simulators previously described by Maurer et al. [22] (Figure 1). Each simulator initially received 118 L (31.2 gal) for Trial 1 and 68.8 L (18.2 gal) for Trial 2 and Trial 3 of swine manure, Trial 2 had 3.8 L (1 gal) of weekly manure additions

one week before and one week after biochar addition, resulting in a final volume of 76.4 L (20.2 gal). Trial 3 received four weekly 3.8 L (1 gal) manure additions resulting in final manure volumes of 84.0 L (22.2 gal). Manure additions were done by adding manure directly to the top of the manure to simulate farm conditions, where manure would drop down through the floor slats of the barn into the manure storage pit surface. The ventilation in each simulator was controlled via valves with rotameters to achieve a ventilation rate of 7.5 headspace exchanges per hour. The rate was adjusted when fresh manure was added to keep a constant exchange rate. Air exchange rates were consistent with recommended values for less than half-full manure pit storage (assuming cool season, minimum ventilation, growing (34 to 68 kg) pigs, in swine barn with the fully slatted floor) [23]. Storage temperature was kept between 10 and 16 °C (average = 12.5 ± 1.3 °C) to simulate the temperature of deep pit storage [24].

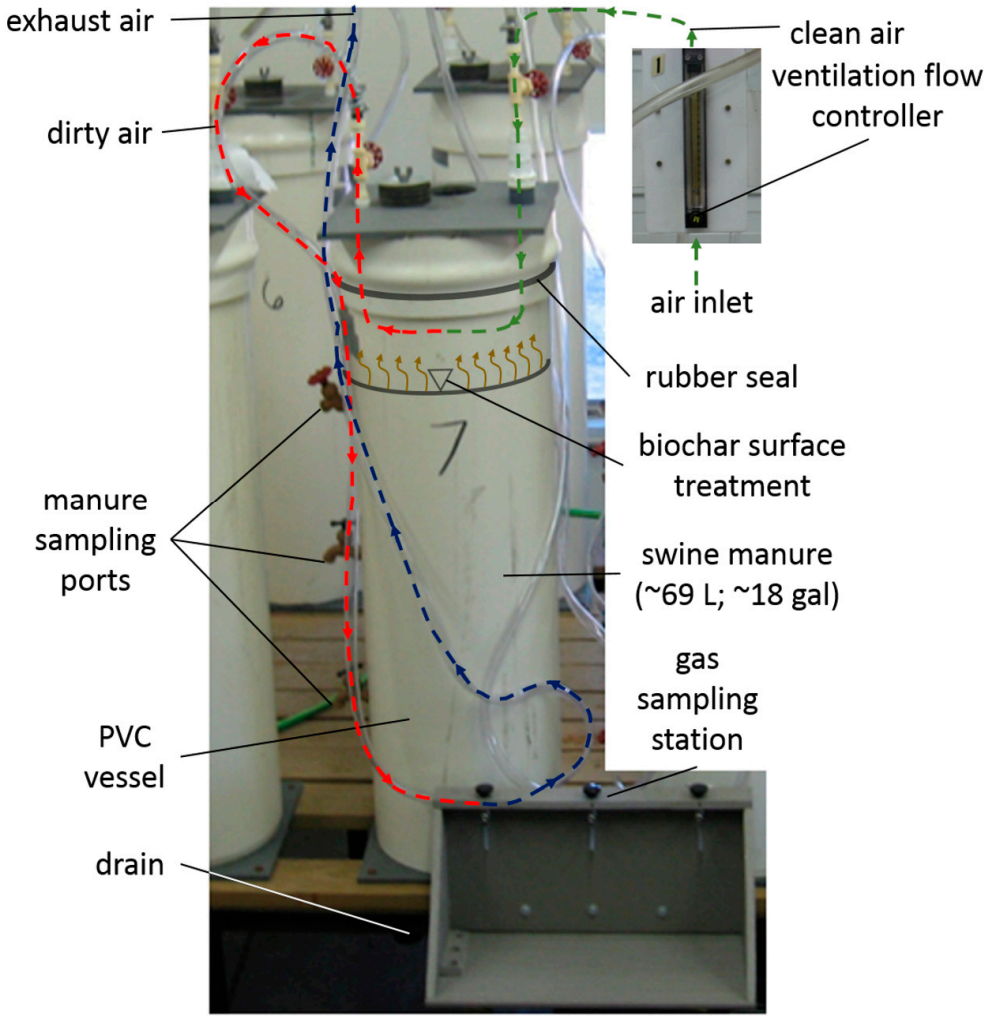

Figure 1. Pilot-scale manure storage simulator with capacity of ~100 L. Green: incoming clean air, Red: polluted (dirty) air before sampling, Blue: exhaust air (polluted air after sampling), PVC: polyvinyl chloride.

Measurements of gaseous emissions were estimated as a product of measured concentrations and the ventilation airflow rate. Baseline gas emissions measurements were taken for ~two weeks before biochar addition to evaluate emissions from each of the six manure storage simulators to make sure that there was no significant difference in emissions due to the system. The total duration of the pilot experiment was a month for all trials. Manure samples were collected at the end of each trial to determine effects on manure quality and the potential for nutrient retention. Percent relative humidity

in manure headspace was monitored via an 850071 Environmental Quality meter (Sper Scientific, Scottsdale, AZ, USA) each day that gas emission samples were collected.

2.3. Gas Concentration Measurements

Details of gas measurements and calibrations are presented elsewhere [22]. In short, gas samples were collected via syringe and vials and were analyzed for GHG concentrations using gas chromatography equipped with FID and ECD detectors, and a CO_2-to-CH_4 catalytic convertor. VOCs were collected in sorbent tubes filled with Tenax TA. Air samples were collected using a portable sampling pump. Chemical analyses of swine odorants were completed using the thermal desorption-multidimensional gas chromatography-mass spectrometer/olfactometry (TD-MDGC–MS/O) system using procedures previously described [25]. Challenges to proper sulfur-VOC speciation and quantification associated with sorbent tubes and thermal desorption (Andersen et al. [26]) were addressed by Cai et al. [27]. Thus, because it is not possible to determine the extent of methane thiol (MT) conversion, combined DMDS/MT, and DMTS/MT emissions are reported for dimethyl disulfide and dimethyl trisulfide, respectively. Ammonia and H_2S concentrations were measured via a portable gas analyzer with NH_3 and low-range H_2S XS sensors.

2.4. Swine Manure Analysis

Swine manure analysis was completed using standard methods. Total Kjeldahl nitrogen (TKN) was quantified by digestion followed by steam distillation and titrimetric analysis [28]. Ammonia (NH_3) was quantified by steam distillation followed by titrimetric analysis [29]. Dissolved reactive phosphorus (P) was quantified by the ascorbic acid method [29]. Total P was determined by sulfuric acid–nitric acid digestion followed by the ascorbic acid method, [29] while pH was determined using the electrode method [29]. Total solids/moisture content and volatile solids were determined by oven drying method [29]. Percent C, H, N, and S were acquired with a combustion analyzer (Perkin Elmer Inc., Waltham, MA) with a cysteine calibration standard.

2.5. Estimation of Time and Dose Effect on Gaseous Emissions

Measured gas concentrations were used for calculation of flux (E), i.e., emissions based on time and emitting surface area of manure (mass·time^{-1}·emitting area^{-1}). Gas concentrations were measured at field conditions and were converted to standard conditions (1 atm, 25 °C, dry air). Overall mean % reduction for each target gas was calculated using Equation (1).

$$\%R = \frac{E_{Con} - E_{Treat}}{E_{Con}} \times 100 \quad (1)$$

where: $\%R$ is the percent of reduction. E_{Con} is the average flux estimate of the desired time interval of the control. E_{Treat} is the average flux estimate of the desired time interval of the treatment.

Estimates of gas emissions for Trial 1 were adjusted to account for the differences observed during the baseline measurements conducted during the first two weeks before biochar treatment. This was completed by adding the average difference between the emissions before biochar application to the post-application emissions (Equation (2)).

$$E_{adj} = (E_{tb} - E_{cb}) + E_{ca} \quad (2)$$

where E_{adj} is the adjusted flux estimate, E_{tb} is the flux estimate for the treated manure before biochar surface application, E_{cb} is the flux estimate for the control manure before biochar surface application, and E_{ca} is the flux estimate for the control manure after biochar surface application.

2.6. Statistical Analysis

The First-Order Autoregression Model, in the JMP System (version Pro 12, SAS Institute, Inc., Cary, NC, USA) was used to analyze the data and determine the p values. A significance level of 0.05 was used as the cut-off for statistical significance. The data from the two manure types in Trial 1 were combined for the statistical analysis.

3. Results and Discussion

3.1. Visual Observations of the Biochar Surface Layer Over Time

Biochar floated on top of swine manure for at least one month. The biochar surface coverage of the swine manure in the simulators for the three biochar doses of 1.14, 2.28 and 4.57 kg·m^{-2} resulted in complete coverage of the manure at thicknesses of 0.375, 0.75 and 1.5 cm, respectively (dose 2.28 kg·m^{-2} is shown in Figure 2). After the month-long trials, it was observed that most of the biochar was still floating on the surface of the manure and appeared dry. Where manure addition was added in Trial 2 (largest dose) biochar had been incorporated into the manure (Figure 2). These visual observations of the topical biochar layer are important for two reasons: (1) they provide a better understanding of mechanisms responsible for the mitigation effect (e.g., chemical absorption of biochar, biofilm/biofilter layer interface between manure and air, or the combination of both); and (2) they affect the long-term implications for the manure management (e.g., settling of solids into the bottom of manure pit and potential issues with stirring and pumping out manure). No detrimental effects were observed in relation to concerns about (1) and (2).

Figure 2. Biochar 2.28 kg·m^{-2} surface application to swine manure. Swine manure before biochar application (**Left**), after biochar application (**Middle**), and one month after biochar application (**Right**).

3.2. Treatment Effects on Ammonia and Hydrogen Sulfide

The two types of manure, crusted and uncrusted, used in Trial 1 resulted in no statistical differences in measured gases. Therefore, the results for crusted and uncrusted manures were averaged and treated as additional repetitions for statistical analysis and comparisons with other trials. Trial 1 with a biochar application loading of 2.28 kg·m^{-2} showed no significant NH_3 reduction over the trial. Trial 2 with a biochar application loading of 4.56 kg·m^{-2} showed significant NH_3 reduction over the first 6 days, the first 9 days and over the total month post biochar application, of 22.6% (p = 0.0014), 15.2% (p = 0.0147) and 12.7% (p = 0.0257), respectively. Trial 3 with a biochar application loading of 2.28 kg·m^{-2} showed no significant NH_3 reduction (Figure 3) post biochar application. Trial 3 at the lowest biochar application loading of 1.14 kg·m^{-2} showed no significant NH_3 reduction. The average of Trial 1 and Trial 3 at a biochar application loading of 2.28 kg·m^{-2} showed no significant NH_3 reduction over the month post biochar application due to high variability between trials.

The pH of the manure (pH = 7.97) was not affected by the biochar (pH = 7.28), so the NH_3-NH_4^+ equilibrium in the manure slurry was not altered in a way to reduce NH_3 emissions. Ro et al. [6] performed ammonia adsorption capacity experiments on various biochar samples, one of which was

produced from wood shavings at a similar temperature (500 °C) to the biochar used in this study and was determined to have an ammonia adsorption capacity of 0.84 mg [NH_3-N]·g biochar^{-1}. This reported ammonia adsorption capacity equates to the capacity of the biochar to adsorb only the amount of NH_3 emitted in ~one day under the conditions studied for a biochar dose of 4.56·kg·m^{-2}, i.e., much shorter than observed to be effective in this research. This suggests that the biochar's major mode of mitigating NH_3 is likely due to creating a semi-porous crust layer over the surface of the manure affecting mass transfer to the headspace. Additional experiments aiming at confirming the actual mechanism of the mitigation effects including microbial flora capable of utilizing ammonia are warranted.

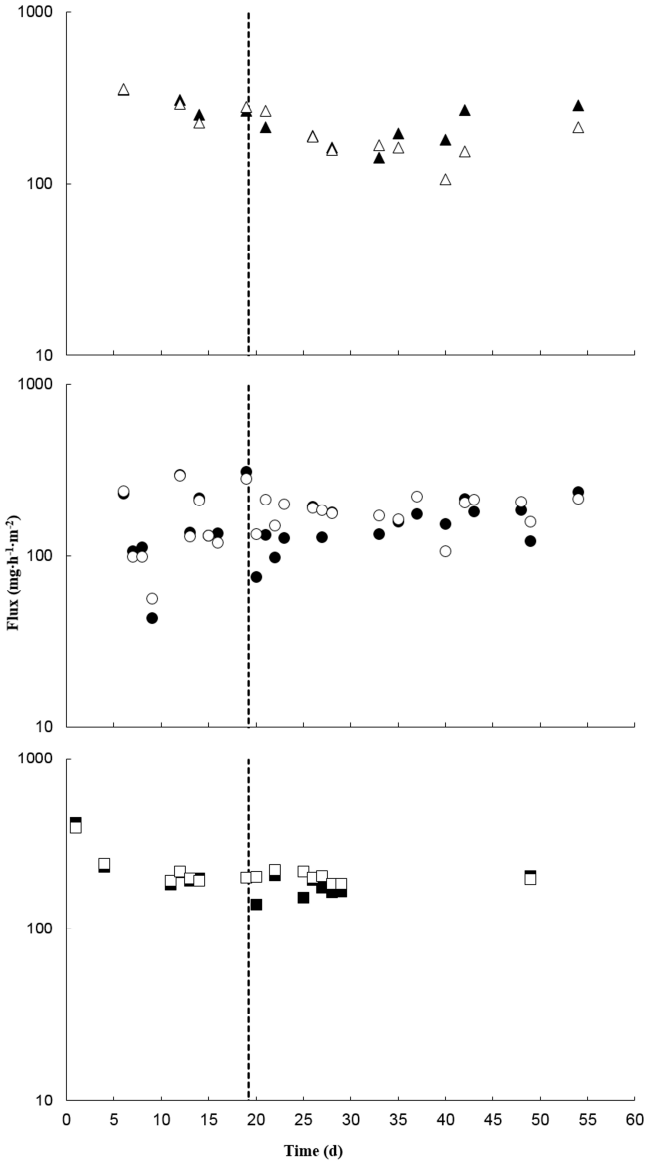

Figure 3. Biochar treatment of manure effect on NH_3 emissions. Δ: Control 1.14 kg·m^{-2}, ○: Control 2.28 kg·m^{-2}, □: Control 4.56 kg·m^{-2}, ▲: Treated 1.14 kg·m^{-2}, ●: Treated 2.28 kg·m^{-2}, ■: Treated 4.56 kg·m^{-2} biochar doses, -----: biochar application, NH_3: ammonia.

The biochar treatment in all of the trials did not have a significant effect on the emissions of H_2S. Reduction of H_2S was observed during Trial 3 at a biochar dose of 2.28 kg·m^{-2} over 9 days and the total trial period, of 30% and 12%, respectively, but this was not significant. Reduction of H_2S was also

observed during Trial 3 at a biochar dose of 1.14 kg·m^{-2} over 9 days (30%), but this was not significant. Sethupathi et al. [30] determined adsorption capacities for H_2S on various biochars such as Japanese oak biochar produced at ~500 °C (the closest biochar to this study). Sethupathi et al. [30] reported adsorptions of 5.69 mg H_2S·g biochar^{-1} when H_2S was tested alone and 0.613 mg H_2S·g biochar^{-1} when H_2S was tested in a gas mixture with CO_2 and CH_4. The reported biochar adsorption capacity for H_2S when mixed with CO_2 and CH_4 equates to ~311 days, at a biochar dose of 4.56 kg·m^{-2}, of H_2S emissions observed in this study. The reason for the insignificant effect of the biochar observed in this study is not known and still warrants investigation considering large theoretical adsorption capacity reported in the literature. Likely causes of apparent no effect can be due to the inconsistent nature of H_2S emissions from swine manure and the complex mixture of emissions from swine manure interfering with H_2S adsorption on the biochar.

3.3. Treatment Effects on Volatile Organic Compounds

Trials 2, 3 at a biochar application loading of, 4.56 kg·m^{-2} and 1.14 kg·m^{-2}, respectively, showed no significant indole reduction. However, Trial 1 at a biochar application loading of 2.28 kg·m^{-2} showed significant indole reduction of 11.6% (p = 0.0462) and 8.7% (p = 0.0462) after 9 days and the total month, respectively. Trial 3 with fresh, crusted manure and frequent manure additions at a biochar application loading of 2.28 kg·m^{-2} also showed significant indole reduction of 26.9% over the total month (p = 0.0292) (Figure 4). The average of Trial 1 (aged crusted and uncrusted manures) and Trial 3 (fresh manure) at a biochar application loading of 2.28 kg·m^{-2} showed no significant indole reduction over the month post biochar application due to high variability between trials. There was no significant reduction for any of the other VOCs that were monitored; DMDS, DMTS, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, or skatole, over the three 30-day post biochar application trials.

Reported DMDS emission reduction from soil resulting from surface applied biochar (mixed hardwood chips produced at ~500 °C) was 53% of maximum DMDS concentration in the air [31]. Reductions of DMDS were observed in this study, especially early in the study, but were not significant likely due to high variability over a longer exposure time, 30 d compared to the reported 1 d in [31]. Pinecone biochar produced at 600 °C was reported to have a 74% removal efficiency of DMTS (4 μg·L^{-1}) in aqueous solution after 4 h and reached equilibrium within 6 h [32]. Under average conditions observed in this study, the biochar tested in [32] would reach adsorption capacity in ~20 min for a 4.56 kg·m^{-2} dose, i.e., not practical for stored manure. Reductions of DMTS, similar to DMDS, were observed in this study but were not significant likely due to longer treatment time where the biochar's adsorption capacity was reached very quickly.

Several reports were found on *p*-cresol adsorption on biochars [33–35] with adsorption capacities for *p*-cresol ranging from 0.33, 6.97 and 7.63 mg·g^{-1} for bamboo, pinewood, and swine manure biochars, respectively. The two higher reported adsorption capacities equated to 3–4 h until the biochars reached their capacity under the conditions observed in this study at a biochar dosage of 4.56 kg·m^{-2}, i.e., not practical for stored manure. Literature reports could not be found with regards to biochar adsorption information of organic acids, skatole, and indole.

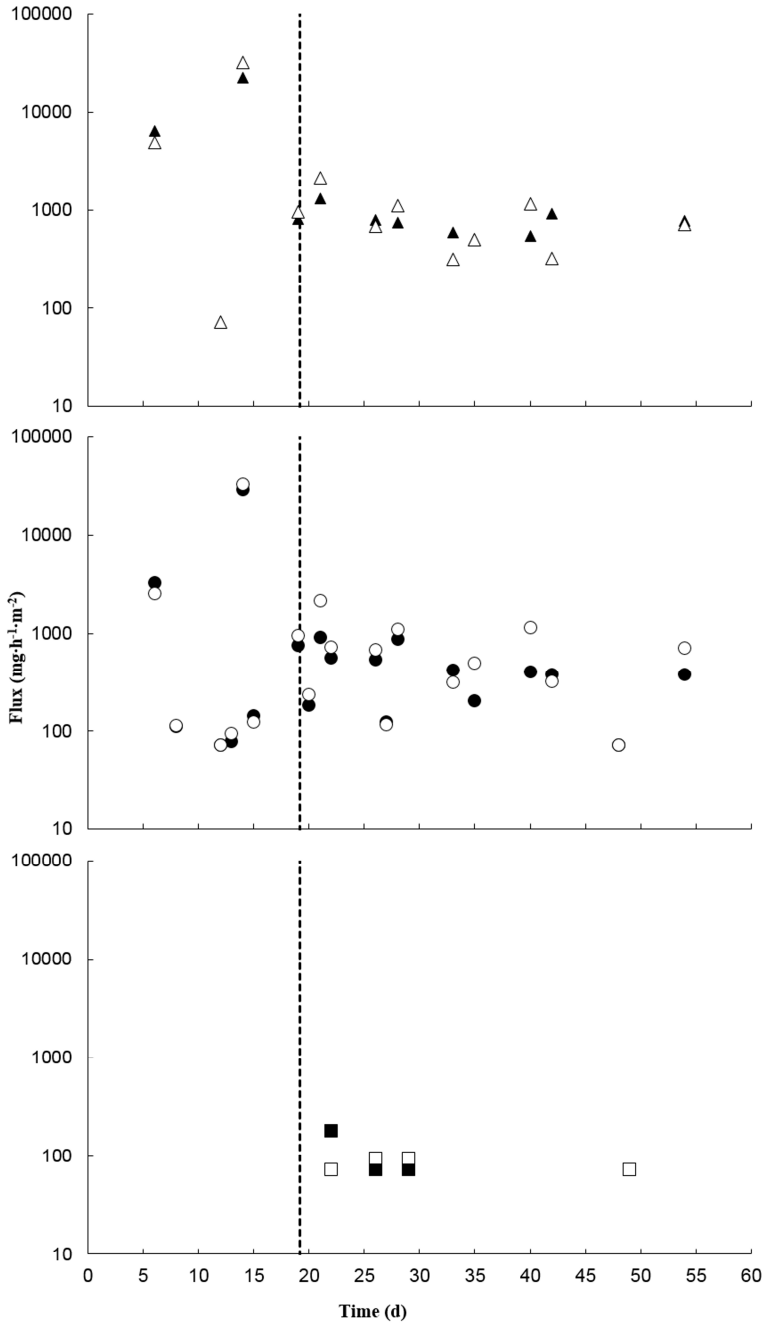

Figure 4. Biochar treatment of manure effect on indole emissions. Δ: Control 1.14 kg·m^{-2}, ○: Control 2.28 kg·m^{-2}, □: Control 4.56 kg·m^{-2}, ▲: Treated 1.14 kg·m^{-2}, ●: Treated 2.28 kg·m^{-2}, ■: Treated 4.56 kg·m^{-2} biochar doses, -----: biochar application.

3.4. Treatment Effects on Greenhouse Gases

Trial 2 at a biochar application loading of 4.56 kg·m^{-2} showed a significant CH_4 increase after 10 days and the total month post biochar application, of 24.5% (p = 0.0322) and 22.0% (p = 0.022), respectively (Figure 5). The increase of CH_4 emissions is likely due to the addition of nutrients and labile carbon in the biochar stimulating CH_4-producing microbes in the manure [36]. There was no significant increase of CH_4 over the other trials. Carbon dioxide and N_2O emissions resulted in no significant difference over any of the trials. The lack of reduction in emissions of CH_4 is in agreement with Sethupathi et al. [30], where it was reported that tested biochar capacities to adsorb CH_4 were

little to none. Sethupathi et al. [30] also reported the CO_2 adsorption capacity for the same biochar discussed earlier in regards to H_2S adsorption, with a low capacity when tested as a mix of gases. This low CO_2 adsorption capacity in the presence of other gases equates to <1 h before the biochar's capacity is reached under conditions observed in this study at all biochar doses. Biochar's effect on N_2O emissions varies greatly in the literature from reducing emissions, increasing emissions, or having no effect [37].

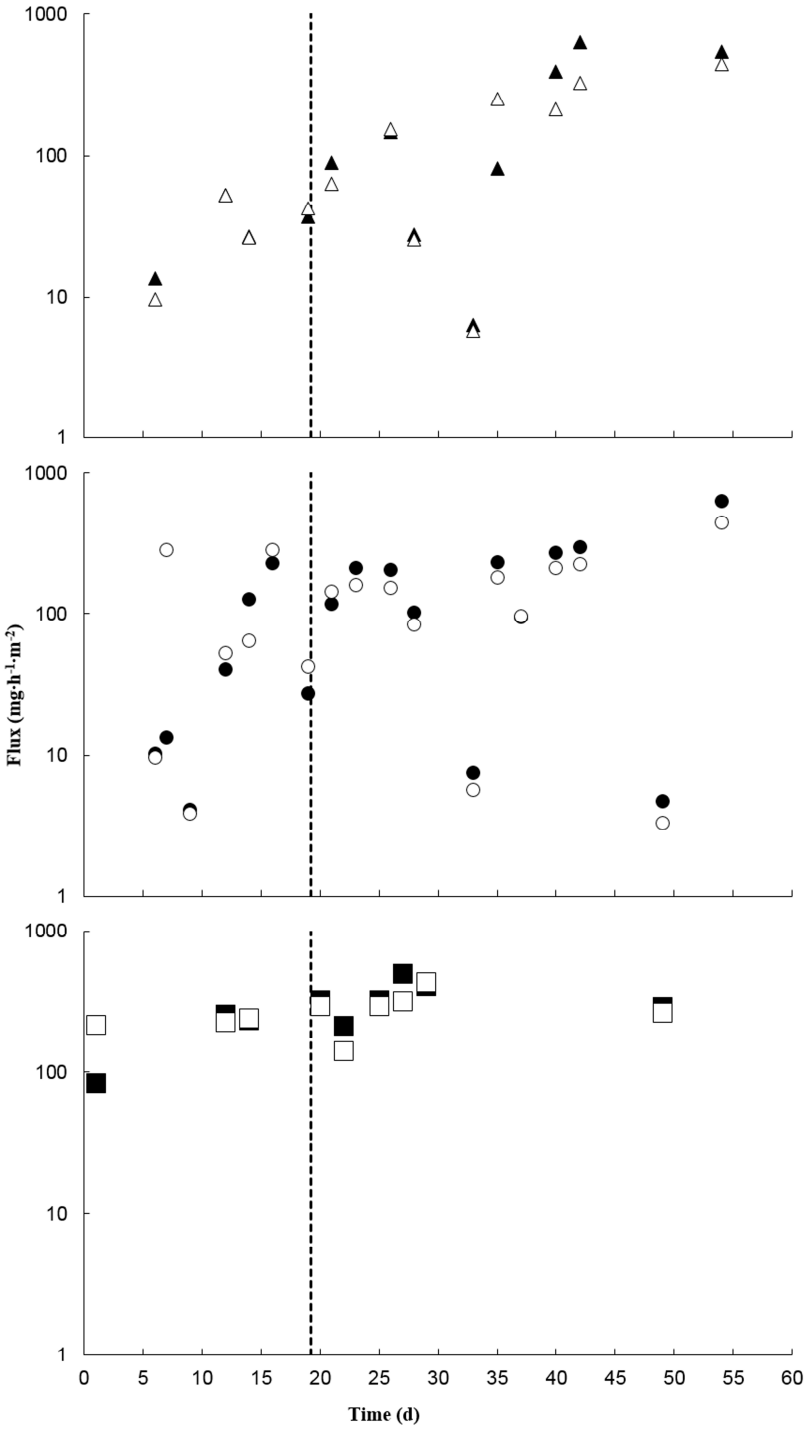

Figure 5. Biochar treatment of manure effect on methane emissions. Δ: Control 1.14 kg·m^{-2}, ○: Control 2.28 kg·m^{-2}, □: Control 4.56 kg·m^{-2}, ▲: Treated 1.14 kg·m^{-2}, ●: Treated 2.28 kg·m^{-2}, ■: Treated 4.56 kg·m^{-2} biochar doses, -----: biochar application.

3.5. Treatment Effects on Environmental and Physicochemical Parameters

The atmospheric pressure (Figure 6A) showed a drop and a rise in pressure at about 1 week after biochar addition for Trial 2 and Trial 1, respectively. Trial 2 showed the lowest storage temperatures (Figure 6B) and the highest temperatures were observed for Trial 1. Biochar treatment at any dosage did not have a significant effect on the relative humidity of the outlet air (Figure 7).

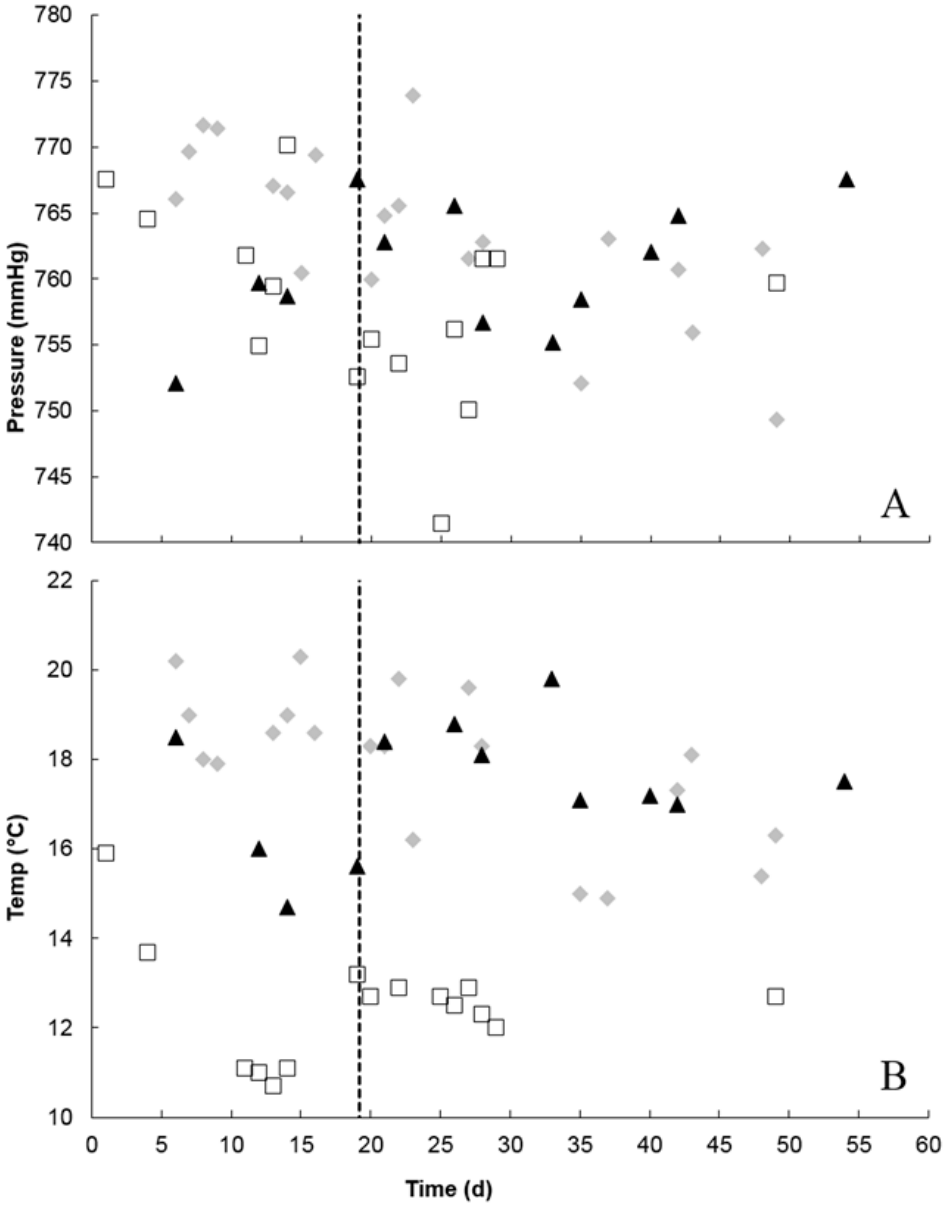

Figure 6. Pressure (**A**) and temperature (**B**). ♦: Trial 1, □: Trial 2, ▲: Trial 3, -----: biochar application.

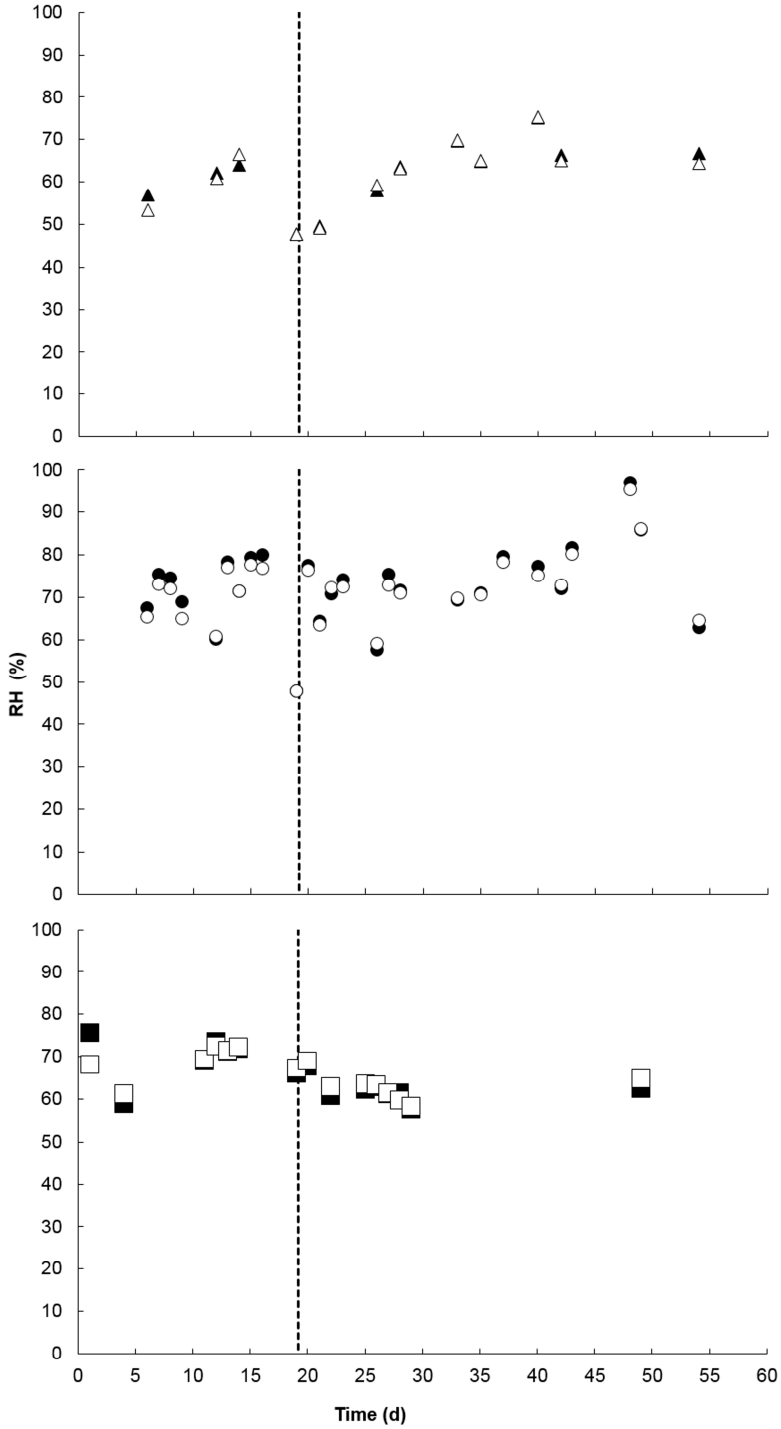

Figure 7. Relative humidity. Δ: Control 1.14 kg·m^{-2}, ○: Control 2.28 kg·m^{-2}, □: Control 4.56 kg·m^{-2}, ▲: Treated 1.14 kg·m^{-2}, ●: Treated 2.28 kg·m^{-2}, ■: Treated 4.56 kg·m^{-2} biochar doses, -----: biochar application.

3.6. Manure Analysis

A summary of swine manure and its physicochemical properties is summarized in Table 3. Manure properties were consistent with those of typical to the Midwestern U.S. swine industry and storage systems. Manure properties were not significantly affected by the biochar treatment. The manure from the outdoor lagoon had lower values for many of the manure properties as expected due to dilution caused by rain water entering the open outdoor lagoon.

Table 3. Swine manure properties.

Manure Type		TS	VS	Volatility *	COD	pH	NH_4-N	TKN	PO_4-P	TP
		(%)	(%)	(%)	($mg \cdot L^{-1}$)		($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)
(1) Deep Pit	Control	8.7	6.4	73.6	40,400	7.9	8300	10,400	173	400
	Treatment	8.5	6.3	74.1	37,000	8	8500	10,600	187	360
(2) Outdoor Lagoon	Control	4.4	3.5	79.5	26,800	8.2	7600	8450	241	294
	Treatment	4.6	3.7	80.4	26,000	8.2	7600	8650	259	326
(3) Deep Pit	Control	7.9	5.9	74.7	37,000	7.8	7700	9700	150	353
	Treatment	7.7	5.7	74	37,800	7.8	7900	9900	130	387

Note: TS = total solids. VS = volatile solids. * volatility = VS/TS × 100%. COD = chemical oxygen demand, TP = total phosphorus. TKN = total Kjeldahl nitrogen.

3.7. Effects of Biochar Dose and Time

Doubling the biochar dose improved the longevity of significant reduction of NH_3 emissions but also resulted in a significant increase in CH_4 emissions. The effect of increasing the dose was detrimental to reducing emissions of all other gases except for *p*-cresol and skatole (not significantly, though) for all overall time periods. Significantly affected compounds are shown in Figure 8. The biochar dosage must, therefore, be optimized to balance between reducing NH_3 and indole and not overly increasing CH_4. The biochar dosage of 2.28 $kg \cdot m^{-2}$ found the balance between effectiveness of reducing NH_3 for each of the individual 2.28 $kg \cdot m^{-2}$ trials, the average of the two 2.28 $kg \cdot m^{-2}$ trials due to trial variability was not significant. Indole was only significant during Trial 3, while not significantly increasing CH_4 emissions.

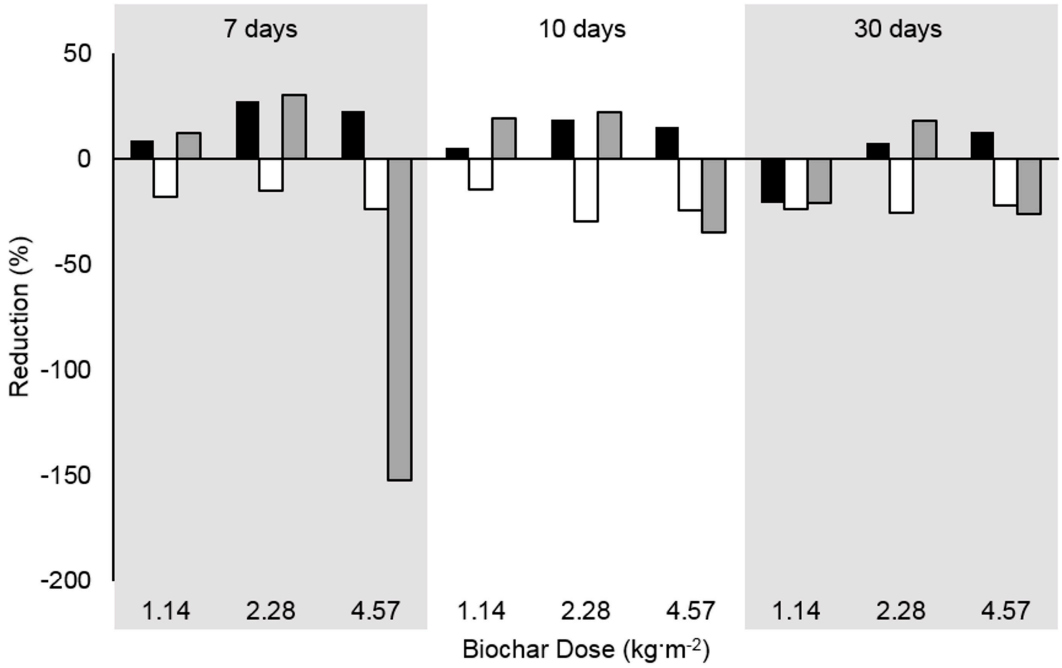

Figure 8. Effect of dose and time of biochar treatment for compounds that were significantly affected during the trials. Black: ammonia, White: methane, Gray: indole.

3.8. Economics of Biochar Treatment

It was determined that a non-activated, non-functionalized biochar can be an economically-feasible option for controlling gaseous emissions from stored manure. The resulting treatment costs ranged from 0.15 to 8.57 USD·marketed pig^{-1} for the 2.28 $kg \cdot m^{-2}$ biochar application rate with the low- and high-market values of biochar, respectively (Table 4). These costs are based on 90 to 5060 USD·metric ton^{-1} [38] for biochar with an application to a typical Midwestern U.S. 2500-head

swine barn. The following assumptions were made: 1858 m^2 of manure surface to cover, marketing 6900 pigs·$year^{-1}$·$barn^{-1}$, and 2.76 grow-out cycles·$year^{-1}$ using an industry standard stocking density of 0.74. Biochar treatment is assumed to be applied at the beginning of each grow-out cycle. The wide range of biochar pricing is based on the low-end (bulk) pricing and high-end (marketed as 'soil amendment') estimate. These costs do not include labor required to apply the treatments, which could vary greatly depending on the method of application. Cost estimates for mitigation additives are relatively few and often limited to one or few target gases reported. The biochar treatment cost of 0.15 to 8.57 USD·marketed pig^{-1} price estimates is within the range of 0.01 to 18.18 USD·marketed pig^{-1} price estimates reported in the literature, with an average additive cost of 4.28 ± 5.80 USD·marketed pig^{-1} for manure additive treatment for targeting one or more of the following: odor, VOCs, NH_3, and H_2S [39–42].

Table 4. Manure additive cost comparison.

Reference	Additive	Additive Cost (USD)		
		Marketed Pig^{-1}	m^{-2}·$Year^{-1}$	Pig $Space^{-1}$·$Year^{-1}$
This Study	1.14 kg·m^{-2} Biochar	0.08–4.29	0.29–15.92	0.21–11.84
This Study	2.28 kg·m^{-2} Biochar	0.15–8.57	0.57–31.84	0.42–23.67
This Study	4.56 kg·m^{-2} Biochar	0.30–17.14	1.14–63.68	0.84–47.34
Maurer et al. [22]	2.28 kg·m^{-2} SBP/CaO_2	1.45 [a]	2.96	2.19 [b]
Maurer et al. [22]	4.57 kg·m^{-2} SBP/CaO_2	2.90 [a]	5.93	4.39 [b]
Maurer et al. [22]	22.8 kg·m^{-2} SBP/CaO_2	14.53 [a]	29.62	21.95 [b]
Maurer et al. [22]	45.7 kg·m^{-2} SBP/CaO_2	29.06 [a]	59.33	43.90 [b]
Heber et al. [40]	Alliance	0.69	2.55 [b]	1.89
Moreno et al. [42]	Sodium Molybdate	0.45 [c]	1.98 [b]	1.46 [d]
Balsari et al. [39]	Leca Balls	0.01 [e]	0.06 [f]	0.05 [b]
Heber et al. [41] [g]	AgriKlenz Plus	0.57	2.14	1.59
Heber et al. [41] [g]	Alken Clear-Flo	18.18	67.51	50.18
Heber et al. [41] [g]	AWL-80	0.41	1.52	1.13
Heber et al. [41] [g]	Biocharge Dry	0.94	3.48	2.59
Heber et al. [41] [g]	BMT	14.87	55.24	41.05
Heber et al. [41] [g]	EM Waste Treatment	8.27	30.72	22.84
Heber et al. [41] [g]	GT-2000OC BC-2000AF	12.15	45.12	33.53
Heber et al. [41] [g]	Inhibodor	1.78	6.61	4.91
Heber et al. [41] [g]	Krystal Air	1.11	4.13	3.07
Heber et al. [41] [g]	Manure Management Plus	2.95	10.94	8.13
Heber et al. [41] [g]	Peroxy Odor Control	0.16	0.59	0.44
Heber et al. [41] [g]	SMOC	7.96	29.56	21.97
Heber et al. [41] [g]	ZymPlex	0.82	3.05	2.27

Notes: [a] The stocking density of 1.35 m^2·pig^{-1} (14.6 ft^2·pig^{-1}) was lower than industry standards, i.e., 0.74 m^2·pig^{-1} (8 ft^2·pig^{-1}), [b] calculated based on 0.74 m^2 (8 ft^2)·pig $space^{-1}$, [c] calculated based on the average exchange rate (0.8704 USD = 1 CAD) in 2009 (year of publication), [d] calculated based on 3.25 swine finishing cycles·$year^{-1}$ (from publication), [e] calculated based on 2.76 swine finishing cycles·$year^{-1}$, [f] calculated based on the average exchange rate (1.26 USD = 1 EUR) in 2006 (year of publication), [g] concentrations were taken from the manure not the headspace for all but NH_3 (ammonia) and H_2S (hydrogen sulfide) and costs were based on supplier recommended application rates and frequencies and on a modern 2500 head finisher building with a half-full 2.44 m (8 ft) pit and a stocking density of 0.74 m^2. All previously published results on cost have been adjusted for inflation using the U.S. Inflation Calculator [43]. SBP: soybean peroxidase, CaO_2: calcium dioxide.

4. Conclusions

Comprehensive control of odors, hydrogen sulfide (H_2S), ammonia (NH_3), and greenhouse gas (GHG) emissions associated with swine production is a critical need. A pilot-scale experiment was conducted to evaluate the surface application of biochar as a manure additive to mitigate emissions of NH_3, H_2S, dimethyl disulfide/methanethiol (DMDS/MT), dimethyl trisulfide, *n*-butyric acid, valeric acid, isovaleric acid, *p*-cresol, indole, skatole, and GHGs. The biochar was tested with three treatments (1.14, 2.28 and 4.56 kg·m^{-2} manure) over a month. Biochar floated on top of swine manure for at least a 1-month period. It was determined that a thin layer of biochar can be effective at mitigating gaseous emissions for selected types of gases. Based on the preliminary three trials, significant reductions in emissions were observed for NH_3 (13 to 23%) with concomitant significant increases in CH_4 (22–25%). The remaining emissions (including N_2O) were not statistically different. It was determined that non-activated, non-functionalized biochar can be an economically feasible option for

controlling gaseous emissions from stored manure. The resulting treatment costs ranged from 0.15 to 8.57 USD·marketed pig^{-1} for the 2.28 kg·m^{-2} biochar application rate at the low- and high-market values of biochar, respectively. Biochar treatment could be a promising option for reducing gaseous NH_3 emissions in swine operations.

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