2950 Niles Road, St. Joseph, MI 49085-9659, USA
269.429.0300 fax 269.429.3852 hq@asabe.org www.asabe.org

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Reduction of gaseous emissions from swine manure: effect of biochar dose and reapplication

Baitong Chen[1],Jacek A. Koziel[1,],Chumki Banik[1],Hantian Ma[2], Myeongseong Lee[1,3], Samuel C. O'Brien[1], Peiyang Li[1], Daniel S. Andersen[1], Andrzej Białowiec[4,1], and Robert C. Brown[5]*

[1] Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50011, USA;
[2] Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA 50010, USA;
[3] Department of Animal Biosystems Science, Chungnam National University, Daejon 34134, Republic of Korea
[4] Dept. of Applied Bioeconomy, Wroclaw University of Environmental and Life Sciences, 51-630 Wroclaw, Poland;
[5] Bioeconomy Institute and Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA;
*Correspondence: koziel@iastate.edu

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ABSTRACT. *The rural communities are affected by gaseous emissions from intensive livestock production. Practical mitigation technologies are needed to minimize emissions from stored manure and improve air quality inside barns. In our previous research, the one-time surficial application of biochar to swine manure significantly reduced emissions of NH_3 and phenol. We observed that the mitigation effect decreased with time during the 30-day trials. In this research, we hypothesized that bi-weekly reapplication of biochar could improve the mitigation effect on a wider range of odorous compounds using larger scale and longer trials. The objective was to evaluate the effectiveness of biochar dose and reapplication on mitigation of targeted gases (NH_3, odorous VOCs, odor, GHGs) from stored swine manure on a pilot-scale setup over 8-weeks. The bi-weekly reapplication of the lower biochar dose (2 kg/m^2) showed much higher significant percent reductions of emissions for NH_3 (33% without & 53% with reapplication) and skatole (42% without & 80% with reapplication), respectively. In addition, the reapplication resulted in the emergence of statistical significance to the mitigation effect for all other targeted VOCs. Specifically, for indole, the % reduction improved from 38% (p=0.47, without reapplication) to 78% (p=0.018, with reapplication). For phenol, the % reduction improved from 28% (p=0.71, without reapplication) to 89% (p=0.005, with reapplication). For p-cresol, the % reduction improved from 31% (p=0.86, without reapplication) to 74% (p=0.028, with reapplication). For 4-ethyl phenol, the percent emissions reduction improved from 66% (p=0.44, without reapplication) to 87% (p=0.007, with reapplication). The one-time 2 kg/m^2 and 4 kg/m^2 treatments showed similar effectiveness in mitigating all targeted gases, and no statistical difference was found between the dosages. The one-time treatments showed significant % reductions of 33% & 42% and 25% & 48% for NH_3 and skatole, respectively. The practical significance is that the higher (one-time) biochar dose may not necessarily result in improved performance over the 8-week manure storage, but the bi-weekly reapplication showed significant improvement in mitigating NH_3 and odorous VOCs. The lower dosages and the frequency of reapplication on the larger-scale should be explored to optimize biochar treatment and bring it closer to on-farm trials.*

Keywords. *livestock manure; waste management; air pollution; air quality; biocoal; odor emission*

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Introduction

Livestock production always plays a very important role in our daily life. This industry provides millions of people with jobs and food. However, along with all the benefits of livestock production, unwanted gas emissions such as ammonia (NH_3), greenhouse gases (GHG), volatile organic compounds (VOCs), and odor are rising worldwide concerns about their impact on the environment (Ni et al., 2009. NH_3 emissions are the major nitrogen (N) pollution and responsible for the formation of secondary particulate matter ($PM_{2.5}$) aerosols. GHGs such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) is related to the concerns about climate change (Maurer et al., 2017a). VOCs such as phenolics, fatty acids, sulfur-containing compounds are the major contributors to the odorous emissions from the swine barns (Koziel et al., 2006).

Research has been conducted to mitigate gas emissions from livestock agriculture. The user-friendly Air Management Practices Assessment Tool (AMPAT) organized 12 different mitigation technologies targeting gaseous emissions from stored manure (Maurer et al., 2016). Manure additives (i.e., proprietary mixtures of bacteria or chemicals) are popular low-cost products used by some U.S. farmers. Small doses of manure additives can be easily applied to manure without changes to the current waste management structures. However, in recent research, 12 commercial manure additives did not show significant impacts on the targeted gases in controlled side-by-side trials (Chen et al., 2020a, 2021b). Thus, there is still a need to develop and test manure additives that are adaptable to current animal farming systems.

Research shows that some experimental manure additives can have a positive impact on the targeted emissions. Zeolite applications to laying hen manure showed significant effectiveness in controlling the odorous VOCs; the average reduction of the total odor was reduced up to 67% (Cai., et al., 2007). The pilot-scale study of using soybean peroxidase with calcium peroxide to mitigate the emissions from stored swine manure showed significant reductions of NH_3 by up to 68%, dimethyl disulfide (DMDS) by up to 85%, p-cresol by up to 90%, and skatole by up to 93%; also significant generations were observed in CH_4 by up to ~200% and in CO_2 by up to ~124% (Maurer et al., 2017b). Furthermore, the farm-scale testing of soybean peroxidase and calcium peroxide in the deep-pit swine barns were observed significant reductions of NH_3 by 22%, H_2S by 80%, and some targeted VOCs by 30% to 40%; no significant changes to GHGs (Maurer et al., 2017c).

Surficial (one-time) application of biochar as a manure additive was proposed for the comprehensive mitigation of gas emissions from stored manure. Biochar (a carbonaceous material) can be made from various types of biomass and waste through pyrolysis or torrefaction. Different feedstock and process conditions will produce biochar with different physicochemical properties (Stępień et al., 2019a and 2019b; Świechowski et al., 2019; Syguła et al., 2019; Pulka et al., 2019; Kalus et al., 2019; Białowie et al., 2018). Thus, biochar with desired properties (e.g., pH, porosity, chemical moiety) could be explored and used to mitigate targeted gaseous emissions.

Recent research using biochar as a manure additive to mitigate gas emissions from livestock manure focused on one-time application. For example, Maurer et al. reported that a thin layer of biochar (pH: 7.28) resulted in a significant reduction of NH_3 and a significant generation of CH_4 as applied to stored swine manure in a pilot-scaled setup (Maurer et al., 2017c). Dougherty et al. showed that biochar (pH: 9.32) had a significant reduction of NH_3 up to 22% as applied to dairy manure (Dougherty et al., 2017). Meiirkhanuly et al. showed that the one-time surficial application of biochar to swine manure significantly reduced NH_3 and phenol (Meiirkhanuly et al., 2020). However, we observed that the mitigation effect *decreased* with time during the 30-day trials (Meiirkhanuly et al., 2020).

In this research, we hypothesize that bi-weekly reapplication of biochar can improve the mitigation effect on a wider range of compounds and their gaseous emissions using larger scale and longer trials. The objective of this study is to evaluate the effectiveness of highly alkaline and porous (HAP) biochar (pH 9.2) reapplication and dose on mitigation of targeted gases (NH_3, GHG, and odorous VOCs) from stored swine manure on a pilot-scale setup over eight weeks.

Materials and Methods

Four triplicated treatments were evaluated during 8-weeks long trials:

i. Control - Manure not treated with biochar.
ii. Treatment 1 - manure treated (one-time) with a ~2 kg/m^2 of HAP biochar.
iii. Treatment 2 - manure treated (one-time) with a ~ of 4 kg/m^2 of HAP biochar.
iv. Treatment 3 - manure treated with a ~2 kg/m^2 of HAP biochar and bi-weekly reapplications of ~2 kg/m^2 of HAP biochar after manure addition.

The pilot-scale experimental setup aimed to simulate the deep pit swine manure storage structure. A detailed description of the pilot-scale setup, manure properties, and collection, gas (NH_3, CO_2, CH_4, N_2O), 11 odorous VOCs) and odor concentration measurements are presented elsewhere (Chen et al., 2020a, 2020b). Briefly, fresh manure was collected from 3 different deep pit swine farms in Iowa. Twelve manure storage simulators were filled with 74.6 L of fresh swine manure. Bi-weekly, 9.5 L of the same type of manure (Control, Treatments 1-3) and the biochar for reapplication (Treatment 3 only) were added into the simulators from the top. The ranges of total solids, volatile solids, total Kjeldahl nitrogen, and total phosphorus in manure were 4.6-8.2%, 3.6-6.7%, 4,340-7,350 mg/L, 3,050-5,300 mg/L, and 940-2,450 mg/L, respectively. The highly alkaline (pH=9.2) and porous (HAP) biochar resulted from autothermal corn stover pyrolysis at 500 °C. Detailed properties of the biochar were presented elsewhere (Chen et al., 2020b).

Ammonia

NH_3 concentrations were measured with the real-time analyzer OMS-300 equipped with an NH_3/CR-1000 electrochemical gas sensor (Wallisellen, Switzerland) (Chen et al., 2020a, 2020b).

Greenhouse Gases

GHG samples were analyzed with gas chromatography (GC) (SRI Instruments, Torrance, CA, USA) equipped with flame ionization detector (FID) and electron capture detector (ECD) (Chen et al., 2020a; Maurer et al., 2017b).

Volatile Organic Compounds

VOC samples were collected using 1 L gas sampling glass bulbs (Supelco). Then, a 2 cm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/Carboxen/PDMS) solid-phase microextraction (SPME) fiber (57384-U, Supelco, Bellefonte, PA, USA) was used to extract the VOCs from the sampling glass bulbs for 50 min at lab temperature (23-24 °C). Finally, the fiber with extracted VOCs was inserted into a 260 °C GC (Microanalytics, Round Rock, TX, USA) inlet; VOCs were thermally desorbed for 2 min and analyzed by a mass spectrometer (MS) (Agilent, model 5973N, Santa Clara, CA, USA) (Chen et al., 2020a).

Odor

Gas samples were collected in 10 L Tedlar sample bags using Vac-U-Chamber (SKC Inc., Eighty-Four, PA, USA). Then, the samples were analyzed with AC'SCENT International Olfactometer (St. Croix Sensory Inc., Stillwater, MN, USA) using dynamic triangular forced-choice methods. Each sample was evaluated twice by four panelists (Chen et al., 2020a).

Mitigation and Statistical Analyses

NH_3, CO_2, N_2O, and CH_4 were all measured in units of parts per million (ppm). The concentrations were converted to flux in units of ($mg/m^2/h$) using measured environmental conditions (Maurer et al., 2017a). For VOCs, all analyses of treatment effectiveness were completed in the units of peak area counts (PACs) as a MS detector response to compounds abundance in the gas sample. Although the PAC unit is arbitrary, it is sufficient for estimating the percent reduction due to each Treatment by comparing the PACs for Treatment with Control. The overall mean percent reduction was calculated with Equation 1:

$$\%\boldsymbol{R} = \frac{E_{Control} - E_{Treatment}}{E_{Control}} * \mathbf{100\%} \quad (1)$$

Where %R is the overall mean percent reduction, $E_{Control}$ & $E_{Treatment}$ are the means (n=3 replicates) of flux, odor concentrations, or PACs from Control & Treatment, respectively.

The one-way ANOVA and Tukey-Kramer Method were used to determine the *p-values* of the reduction. All statistical analyses were completed using JMP software (version Pro 15, SAS Institute, Inc., Cary, NC, USA). When a *p*-value was less than or equal to 0.05, the reduction was considered statistically significant.

Results

The 8-weeks of performance of biochar on mitigation of gaseous emissions (evaluated as the % reduction) were summarized in Table 1 for the one-time application (Treatments 1 & 2, 2 & 4 kg/m^2) and bi-weekly reapplication (Treatment 3, 2 kg/m^2). The one-time biochar treatment could significantly reduce NH_3 (up to 33%) and skatole (up to 48%) emissions. There were no significant impacts of biochar on the mitigation of odor and GHGs. However, there was a clear advantage to biochar reapplication. The % reduction of NH_3 and skatole emissions improved to 53% and 80%, respectively. Also, the emissions of all other targeted VOCs (indole, phenol, p-cresol, 4-ethyl phenol) were significantly reduced (78%, 89%, 74%, 87%). However, still, no statistically significant impacts were found on the mitigation of odor and GHGs.

Table 1: Mitigation of gaseous emissions with HAP biochar treatments. Effects of the dose (biochar mass/manure surface area) and bi-weekly reapplication. Statistically significant % reduction (Control vs. Treatment) of emissions are in **bold**. Negative % reduction signifies gas generation.

Targeted Gases	% Reduction (*p*-value)		
	2 kg/m^2 One-time application (Treatment 1)	4 kg/m^2 One-time application (Treatment 2)	2 kg/m^2 Bi-weekly reapplication (Treatment 3)
NH_3	**33 (0.008)**	**25 (0.0152)**	**53 (0.0001)**
Skatole	**42 (0.0442)**	**48 (0.0119)**	**80 (0.0001)**
Indole	38 (0.4715)	36 (0.5153)	**78 (0.0184)**
Phenol	28 (0.7054)	49 (0.1686)	**89 (0.0049)**
P-cresol	31 (0.8619)	-40 (0.7653)	**74 (0.0282)**
4-Ethyl phenol	66 (0.4445)	53 (0.9664)	**87 (0.0074)**
Odor	11 (0.8806)	4.2 (0.9923)	22 (0.4733)
CO_2	-1.4% (0.9916)	1.7 (0.9842)	-0.3 (0.9999)
CH_4	-15 (0.9536)	-16 (0.9435)	-46 (0.3588)
N_2O	-2 (0.9963)	2.3 (0.9947)	4.4 (0.964)

In case of NH_3 (Table 1, Figure 1), both one-time biochar treatments (2 kg/m^2 & 4 kg/m^2) significantly ($p < 0.05$) reduced emissions by 33% and 25%, respectively; the 2 kg/m^2 with reapplication treatment showed significant ($p < 0.05$) reduction by 53%. In case of skatole (Table 1, Figure 2), both one-time biochar treatments (2 kg/m^2 & 4 kg/m^2) significantly ($p < 0.05$) reduced emissions by 25% & 48%; the 2 kg/m^2 with reapplication treatment showed significant ($p < 0.05$) reduction by 80%.

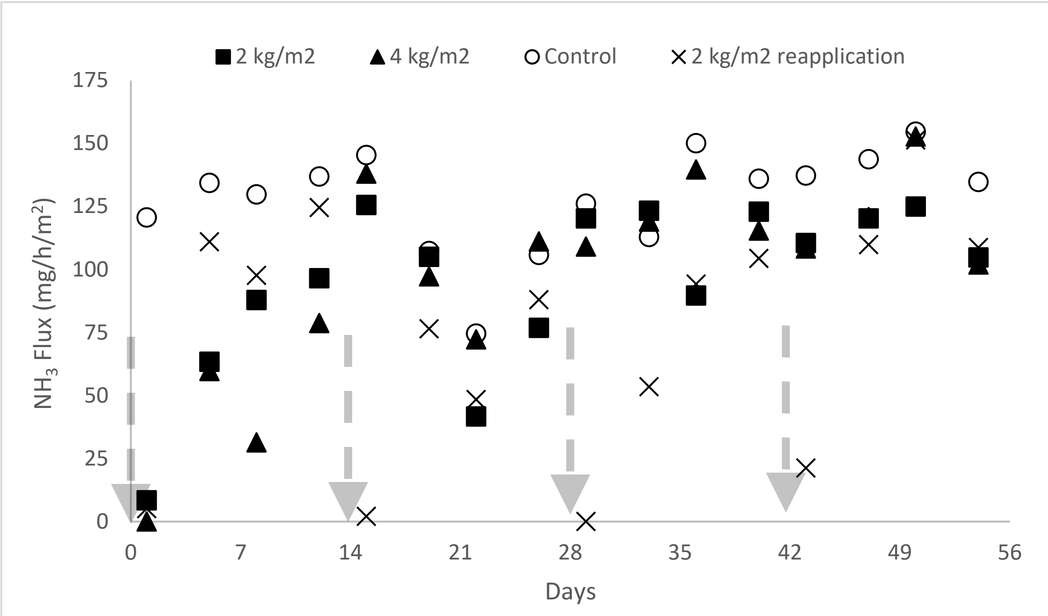

Figure 1. Mitigation of NH_3 emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. (Published as Figure 1 in Chen et al., 2021c under CC BY license).

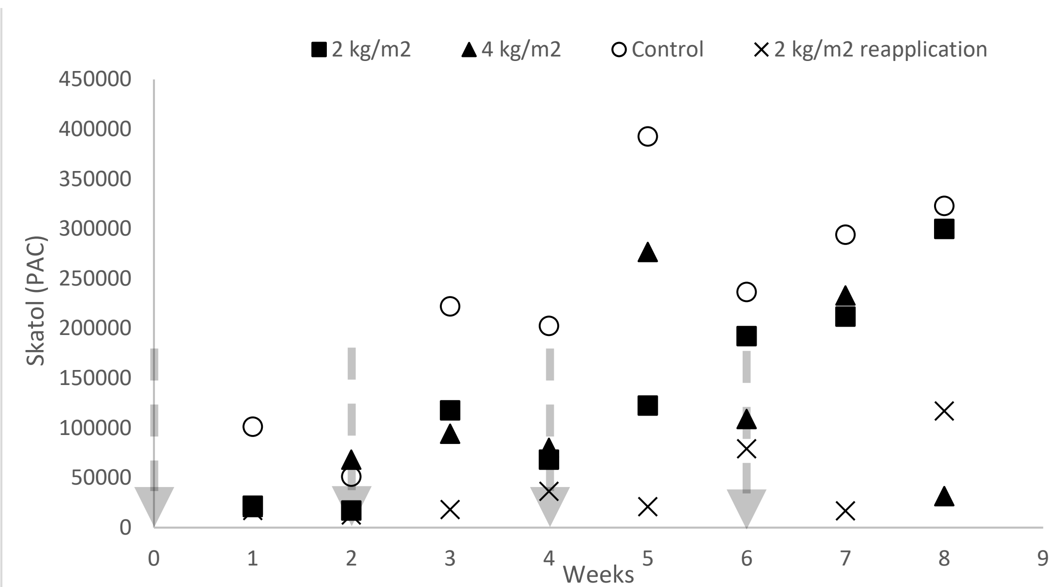

Figure 2. Mitigation of skatole emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. A surrogate abundance of indole is represented by (PAC), i.e., peak area counts for indole in the headspace above manure measured by SPME and analyzed by GC-MS. PACs are arbitrary units of M.S. detector response. (Published as Figure 2 in Chen et al., 2021c under CC BY license).

In case of other targeted odorous VOCs (Table 1), the one-time 2 kg/m^2 & 4 kg/m^2 biochar treatments showed ~36-38% reduction in indole (Figure 3), ~28-49% in phenol (Figure 4), ~-40-31% in p-cresol (Figure 5), ~53-66% in 4-ethyl phenol (Figure 6) without statistical significance. However, bi-weekly 2 kg/m^2 reapplication treatment showed significantly ($p < 0.05$) reduced phenol, p-cresol, and 4-ethyl phenol by 89%, 74%, and 87%, respectively (Table 1).

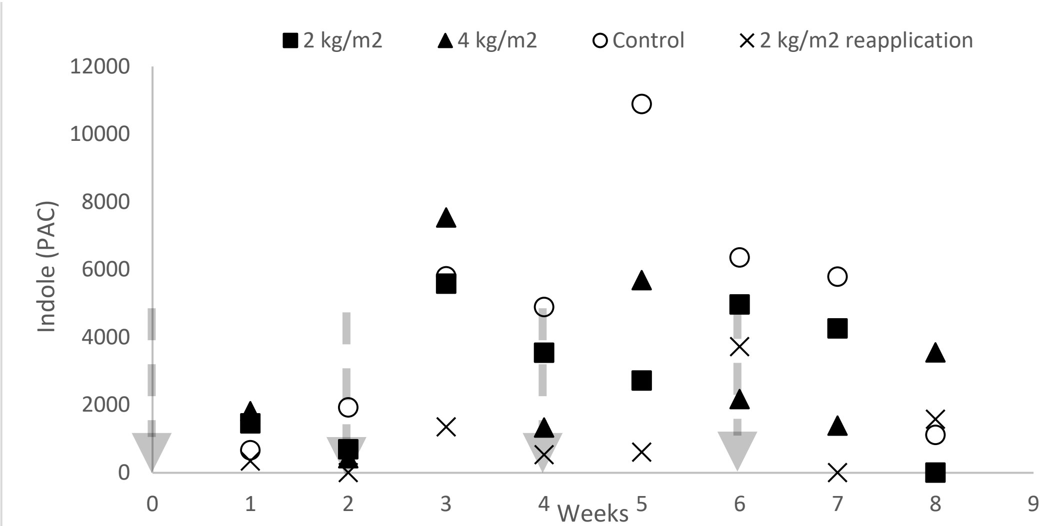

Figure 3. Mitigation of indole emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. A surrogate abundance of indole is represented by (PAC), i.e., peak area counts for indole in the headspace above manure measured by SPME and analyzed by GC-MS. PACs are arbitrary units of M.S. detector response. (Published as Figure 3 in Chen et al., 2021c under CC BY license).

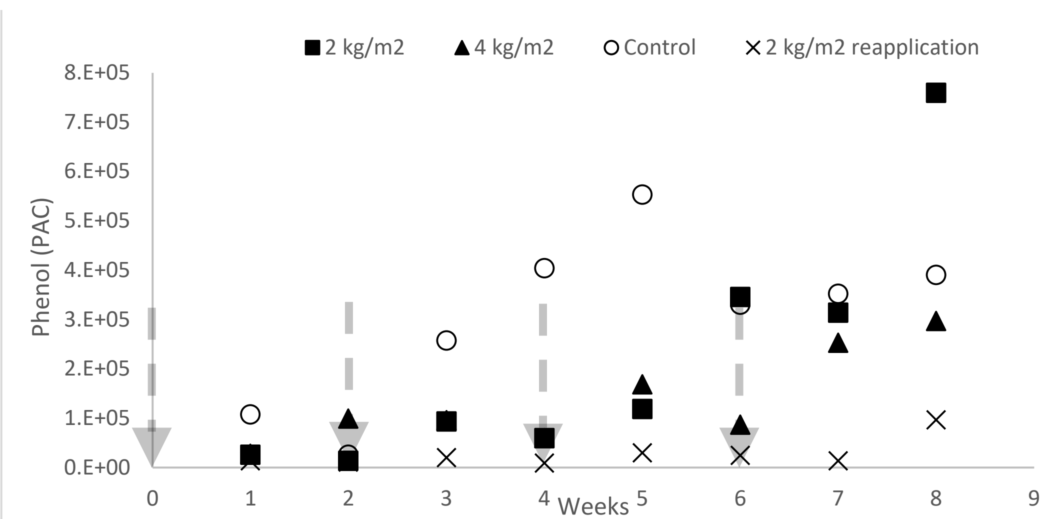

Figure 4. Mitigation of phenol emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. A surrogate abundance of indole is represented by (PAC), i.e., peak area counts for indole in the headspace above manure measured by SPME and analyzed by GC-MS. PACs are arbitrary units of M.S. detector response. (Published as Figure 4 in Chen et al., 2021c under CC BY license).

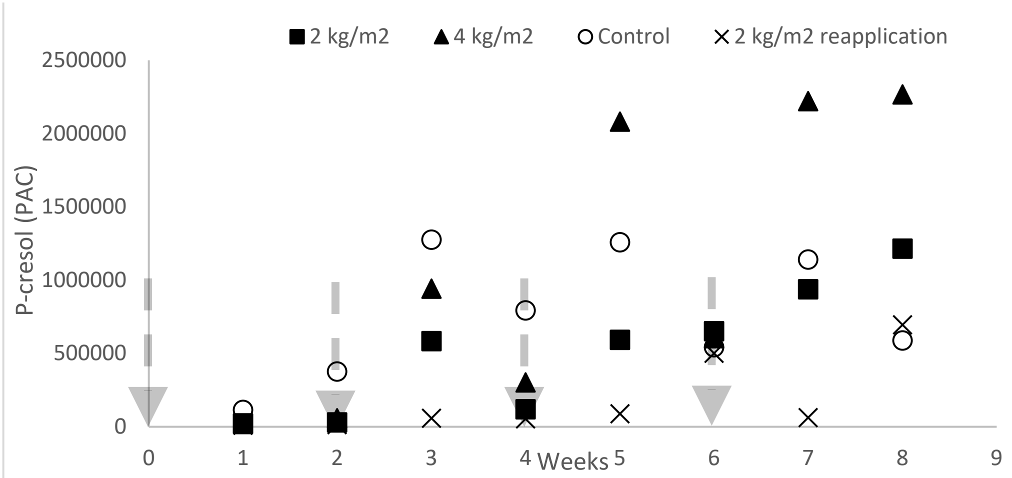

Figure 5. Mitigation of *p*-cresol (4-methyl phenol) emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. A surrogate abundance of indole is represented by (PAC), i.e., peak area counts for indole in the headspace above manure, sampled by SPME and analyzed by GC-MS. PACs are arbitrary units of M.S. detector response. (Published as Figure 5 in Chen et al., 2021c under CC BY license).

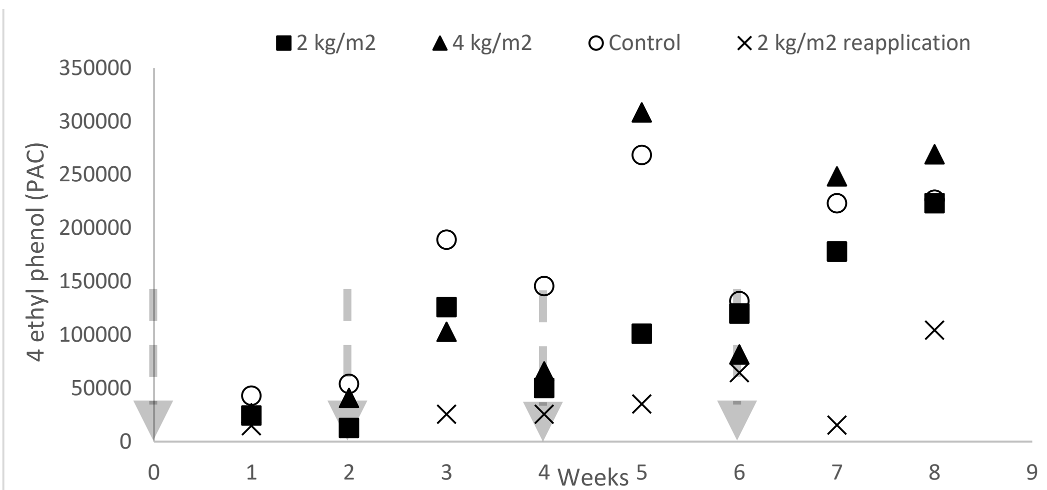

Figure 6. Mitigation of 4-ethyl phenol emissions from swine manure treated with biochar – effects of one-time dose (2 & 4 kg/m^2) and 2 kg/m^2 bi-weekly reapplication. Vertical arrows represent the application or reapplication of biochar and manure to storage simulators. Each data point represents the mean of (n=3) measurements. A surrogate abundance of indole is represented by (PAC), i.e., peak area counts for indole in the headspace above manure measured by SPME and analyzed by GC-MS. PACs are arbitrary units of M.S. detector response. (Published as Figure 6 in Chen et al., 2021c under CC BY license).

In the case of odor (Table 1), no significant mitigation impact was observed. The 2 kg/m^2 bi-weekly reapplication treatment reduced the odor concentration by 22%, whereas 2 kg/m^2 and 4 kg/m^2 showed 11% and 4.2% reductions, respectively (Table 1). All three treatments did not show statistical impacts on odor and GHGs. The treatments showed no significant impact of CO_2 (-1.4~1.7%) and N_2O (-2~4.4%). Interestingly, the HAP biochar showed the generation of CH_4 emission with the range of -46~-15%, without statistical significance. These findings are consistent with Meiirkhanuly et al. 2020 and Maurer et al. 2017a, i.e., HAP & red oak and pine biochar addition to swine manure resulted in the generation of CH_4 on lab- and pilot-scales, respectively. This finding should be developed as a potential application of HAP in biogas plants for increasing the biomethane yield.

Discussion

Effect of One-time Biochar Dose

There was no statistical significance to the mitigation effect between the two one-time biochar dosages. The 2 kg/m^2 (Treatment 1) and 4 kg/m^2 (Treatment 2) showed very similar % reduction of gaseous emissions from swine manure. Both treatments significantly (p<0.05) reduced NH_3 and skatole with very similar % reduction (33% and 25%; 42% and 48%, respectively). These results are consistent with Meiirkhanuly et al., where HAP biochar treatments in a lab-scale showed a significant (two out of three trials) % reduction of NH_3 emissions by 18-21% and a significant (all three trials) % reduction of skatole by 74%-95% (Meiirkhanuly et al. 2020).

For the rest of the targeted gases, no statistical significance was found (Table 1). The 2 kg/m^2 (Treatment 1) showed a 28% reduction of phenol, a 31% reduction of p-cresol, a 38% reduction of indole, and a 66% reduction of 4-ethyl phenol; the 4 kg/m^2 (Treatment 2) showed a 49% reduction of phenol, a 40% generation of p-cresol, a 36% reduction of indole, and a 53% reduction of 4-ethyl phenol. This lack of statistical significance to mitigation was observed in CO_2 and N_2O, whereas both dosages generated CH_4 emissions by 15% and 16%, respectively.

The practical significance of this finding is that a lower dose of HAP biochar treatment could be as effective as a higher dose. Lower than 2 kg/m^2 dosage could be evaluated in future experiments to explore the possibility of reducing the cost and improving the sustainability of this proposed treatment.

Effect of Bi-weekly Biochar Reapplication

Overall, the bi-weekly biochar reapplication resulted in much higher % reductions and a greater number of odorous VOCs with statistically significant % reductions. The % reductions for NH_3 and all the targeted VOCs (phenol, p-cresol, indole, skatole, and 4-ethyl phenol) were statistically significant. In the case of skatole, the biochar reapplication increased the % reduction from 42% to 80%. The 2 kg/m^2 bi-weekly reapplication showed an 89% reduction of phenol, a 74% reduction of p-cresol, a 78% reduction of indole, an 80% reduction of skatole, and an 87% reduction of 4-ethyl phenol.

Considering NH_3, the reapplication doubled the % reduction from 33% to 53% when compared to the one-time 2 kg/m^2 treatment. As shown in Figure 1, NH_3 emissions were significantly reduced immediately after each addition of biochar. The biochar reapplication was clearly solving the main motivation for this research, i.e., addressing the decreasing over time effectiveness reported for the 30-day trials with one-time biochar application (Maurer et al., 2017a).

The reapplication nearly doubled the % reduction of odor (from 11% to 22%), and almost tripled generation of CH_4 (from -15% to -46%) were also observed, yet without statistical significance. HAP biochar had no significant impact on CO_2 and N_2O emissions regardless of the treatment.

Several recommendations could be made for future research directions. There is an opportunity to further explore short-term biochar application to stored manure immediately prior to agitation and pumpout. We already showed significant % reductions of NH_3 and H_2S emissions during the swine manure agitation (Chen et al., 2021b; Banik et al., 2021). Testing of biochar addition on mitigating of odor and odorous VOCs emissions during agitation, pumpout, and land application is warranted. Treatment of gaseous emissions from open sources such as manure lagoons, open dirt feedlots could also be explored. Biochars with different physicochemical properties should be explored to target the mitigation of specific gases. Since biochar is a very fine powder, the pelletization of biochar along with different application and reapplication methods, should be explored before testing at the farm-scale. Enhanced generation of biogas (and its main component, CH_4) from biochar-treated manure could provide additional options for biorenewable energy production on a farm biogas plant. Furthermore, the biochar and manure mixture has shown the potential to be better fertilizers and helping to stop leaching (Banik et al., 2021). In addition, biochar treatment of manure from other types of livestock & poultry and other gaseous emissions sources such as municipal and industrial wastewater and landfills could be explored.

Thus, biochars can still be considered for a comprehensive solution on the food-energy-water nexus that could improve the sustainability of animal and crop agriculture. Specifically, mitigating gaseous emissions with biochar, a byproduct of biorenewable energy production, followed by the benefits stemming from the application of manure & biochar mixture on soil, minimizing risks to runoff and water quality, and enhancing crop production.

Conclusions

This pilot-scale experiment evaluated the effectiveness of different one-time biochar dose and bi-weekly reapplication on the mitigation of gaseous emissions from stored swine manure. The bi-weekly reapplication of the lower biochar dose (2 kg/m^2) showed much higher significant percent reductions of emissions for NH_3 (33% without & 53% with reapplication) and skatole (42% without & 80% with reapplication), respectively. In addition, the reapplication resulted in the emergence of statistical significance to the mitigation effect for all other targeted VOCs. Specifically, for indole, the % reduction improved from 38% ($p=0.47$, without reapplication) to 78% ($p=0.018$, with reapplication). For phenol, the % reduction improved from 28% ($p=0.71$, without reapplication) to 89% ($p=0.005$, with reapplication). For p-cresol, the % reduction improved from 31% ($p=0.86$, without reapplication) to 74% ($p=0.028$, with reapplication). For 4-ethyl phenol, the percent emissions reduction improved from 66% ($p=0.44$, without reapplication) to 87% ($p=0.007$, with reapplication). The one-time 2 kg/m^2 and 4 kg/m^2 treatments showed similar effectiveness in mitigating all targeted gases, and no statistical difference was found between the dosages. The one-time treatments showed significant % reductions of 33% & 42% and 25% & 48% for NH_3 and skatole, respectively. The practical significance is that the higher (one-time) biochar dose may not necessarily result in improved performance over the 8-week manure storage, but the bi-weekly reapplication showed significant improvement in mitigating NH_3 and odorous VOCs. The lower dosages and the frequency of reapplication on the larger-scale should be explored to optimize biochar treatment and bring it closer to on-farm trials.

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