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Article

Mitigation of gaseous emissions from swine manure with the surficial application of biochars

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Abstract: Environmental impact associated with odor and gaseous emissions from animal manure is one of the challenges for communities, farmers, and regulatory agencies. Microbe-based manure additives treatments are marketed and used by farmers for mitigation of emissions. However, their performance is difficult to assess objectively. Thus, a comprehensive, practical, and low-cost treatments are still in demand. We have been advancing such treatments based on physicochemical principles. The objective of this research was to test the effect of the surficial application of a thin layer (¼"; 6.3 mm) of biochar on the mitigation of gaseous emissions from swine manure. Two types of biochar were tested: highly alkaline and porous (HAP) biochar made from corn stover and red oak (RO), both with different pH and morphology. Three 30-day trials were conducted with a layer of HAP and RO (2.0 & 1.65 kg·m^{-2}, respectively) applied on manure surface, and emissions of ammonia (NH_3), hydrogen sulfide (H_2S), greenhouse gases (GHG), and odorous volatile organic compounds (VOCs) were measured. A significant reduction of NH_3 and phenol emissions was observed. In the case of H_2S, CH_4, CO_2, N_2O, and other odorous VOCs, the biochar treatment reduced the emissions during the first 1~2 weeks, followed by either no effect or even (in some cases) increase of emissions. Based on this initial lab-scale testing, biochar is promising to be an effective, practical, and economical treatment to reduce emissions from stored swine manure. However, larger-scale experiments are needed to understand how biochar properties and the dose and frequency of application can be optimized to mitigate odor and gaseous emissions from swine manure. The lessons learned can also be applicable to consider using biochar for surficial applications to mitigate gaseous emissions from other types of waste and area sources.

Keywords: air quality; air pollution; sustainable animal production; livestock and poultry; waste management; odor, ammonia; hydrogen sulfide; greenhouse gases; volatile organic compounds

1. Introduction

Animal production has a significant impact on local and regional air quality because of emissions of volatile organic compounds (VOC), ammonia (NH_3) and hydrogen sulfide (H_2S), greenhouse gases (GHG), and odor. These emissions have many adverse effects on the environment [1]. Manure management accounts for about 15% of the total GHG emissions from the agriculture sector in the United States [2]. The median emission rates from swine facilities were 2.08 and 0.20 kg·yr^{-1} pig for NH_3 and H_2S, respectively [3]. Iowa State University Extension and Outreach Air Management Practices Assessment Tool summarized twelve methods of gaseous emissions mitigation in livestock,

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manure storage, and handling [4]. Farmers use manure additives because of their ease in application and low-cost in comparison with other odor mitigation technologies that can be complex and require expensive equipment. The performance of manure additives is not well studied, especially on a farm-scale. It is estimated that only ~25% of technologies were tested at the farm scale while remaining mitigation methods and technologies have not emerged from the laboratory or pilot scale [5]. Microbe-based manure additives treatments are the most popular and are marketed and used by farmers for mitigation of emissions. However, their performance is difficult to assess objectively. Most research is concentrated on a particular type of gases that a proposed treatment reduces and sometimes ignore other emissions that can be negatively affected by the treatment [5]. Thus, a comprehensive, practical, and low-cost treatments to gaseous emissions are still in demand.

We have been advancing surficial treatments to livestock and poultry manure based on the physicochemical mode of action. These include various mineral sorbents (e.g., zeolites and bentonites), plant-based enzymes (e.g., soybean peroxidase), and urease inhibitors [6-10]. One of the manure additives that could potentially simultaneously reduce different types of gas emission is biochar. Biochar is the carbon-rich material (a.k.a. char, biocoal) obtained from pyrolysis, torrefaction, or gasification of various types of biomass and biowaste [11-16]. Biochar is proposed as a soil amendment and for its relatively low-cost and ease of application [17]. Biochar is obtained as the chemical structure of biomass changes when heated in the absence of oxygen, resulting in a loss of H, N, and O relative to C. The C atoms are firmly bound to one another that is difficult for microorganisms to break down [18]. A considerable number of studies show how biochar positively affects soil parameters [19,20]. The evidence of recent research on applications of biochar in crop and animal production agriculture is reviewed elsewhere [21].

To date, there are only a few research papers published that test biochar application on stored manure to mitigate gaseous emissions. A recent study by Maurer et al. (2017) showed that biochar has the potential for being an economical and effective treatment for odorous gaseous emissions from swine deep-pit barn [22]. In experiments conducted by Maurer et al. [22] and Dougherty et al. [23], biochar was applied surficially to swine and dairy manure, respectively. Maurer et al. stated that there was a statistical difference in Trial 2 (4.56 $kg \cdot m^{-2}$ biochar; ~ 6 mm thick layer) measured on days 6, 9, and the entire 30-day trial period, of 22.6%, 15.2%, and 12.7%, respectively, while, trials 1 and 3 with two times less amount of biochar have no significant difference in NH_3 reduction. Moreover, there were significant differences between H_2S and VOCs during all three trials, except for indole on trial 1 after 9 and 30 days of 11.6% and 8.7%, respectively. Only CH_4 showed a significant difference among GHGs studied, with 24.5% and a 22% increase on days 10 and 30 in Trial 2. Dougherty et al. (2017) reported that biochar made of Douglas fir bark mixed with wood fiber showed a 72-80% reduction of NH_3 while Douglas fir biochar showed a lower reduction of NH_3 of 1-22% [23] at a ~5 cm thick biochar layer application. A summary of current research on uses of biochar as a manure additive and its effect on gaseous emissions is presented in Table 1.

Biochar is known to affect GHGs emissions, particularly evidenced in the research related to soil. Feng et al. [24] reported that biochar application on the soil during the rice-growing season could reduce up to 91% of CH_4 emissions. Moreover, Brassard et al. [25] reported N_2O emission reduction after wood and switchgrass biochar application from 42% to 92% in a short-term incubation study. However, the mechanism of biochar activity in mitigation is complex, and while it can reduce some emissions, it can also increase emissions for other gases. According to Brassard et al. [25] and Rogovska et al. [26], biochar application on soil may increase CO_2 emission from 8 – 91%. The summary of the mitigation effects of gaseous emissions from the soil is presented in Table 2 [25-27].

Biochars have high sorption capacity that could be useful for gas filtration. Results from an experiment conducted by Komnitnas et al., 2016 [28], show that biochar can adsorb 77% of phenol and 26% of NH_3 emitted according to Li et al. [29]. A mini-review of research on uses of biochar as an adsorbent for different gases in laboratory-scale experiments is summarized in Table 3 [28-31].

Highly alkaline and porous biochar (HAP) is a result of the addition of 95% of N_2 and 5% of O_2 during a pyrolysis process [32]. HAP has a high pH, which potentially can be effective in mitigating emissions of H_2S and volatile fatty acids (VFAs). According to Zhu et al. [33], most of the bacteria

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producing malodor and H_2S have pH in the range of 6.5~7.5. Raising the pH of manure by adding HAP biochar could potentially cause a decrease in gaseous emissions, especially in VFAs that are considered significant malodor contributors. HAP has high porosity and large surface that provide improved sorption capacity compared with conventional process biochar (such as the red oak, RO) of lower pH. High porosity biochars could be explored for the sorption of NH_3, VOCs, and GHGs.

Most recently, we reported on the spatial and temporal effects on the pH in the liquid-air interface after the surficial application of HAP and RO biochars to water [34] and swine manure [35]. This research reports on the next logical step, i.e., evaluation of the mitigation effect of biochars on gaseous emissions from swine manure.

The objective of this research was the initial evaluation of HAP biochar and common RO biochar treatment of gaseous emissions from swine manure storages. Specifically, we evaluated:

- Mitigation of odor
- Reduction of H_2S, NH_3, GHG, and VOCs emissions
- Impact on manure properties (total solids, total volatile solids, total nitrogen, and pH)
- Evaluation of how long biochar floats on the manure surface assessment on how the pH of biochar effects manure properties and odorous compounds.

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Table 1. Review of research on uses of biochar as a manure additive and tests its effect on gaseous emissions.

Reference	Scale and Duration	Trial #	Treated source	Biochar source	Biochar dose	Biochar pH	Manure pH	Post-trial manure pH	Gaseous emissions reduction (%)					
									NH_3	H_2S	CH_4	CO_2	N_2O	Indole
Maurer et al. 2017 [22]	Pilot (118 L), 30 d	1	Swine manure	Pine	2.28 kg·m^{-2} 3.11 mm thick	7.28	7.97	7.28	NS	NS	NA	NS	NS	Day 9 – 11.6 Day 30 – 8.7
	Pilot (76.4 L), 30 d	2	Swine manure	Pine	4.56 kg·m^{-2} 6.35 mm thick	7.28	7.97	7.28	Day 6 – 22.6 Day 9 – 15.2 Day 30 – 12.7	NS	Day 10 – (-24.5) Day 30 – (-22)	NS	NS	
	Pilot (84.0 L), 30 d	3	Swine manure	Pine	1) 1.14 kg·m^{-2} 1.58 mm thick	7.28	7.97	7.28	NS	1) Day 9 – 30	NA	NS	NS	2) Day 30 – 26
					2) 2.28 kg·m^{-2} 3.11 mm thick	7.28	7.97	7.28	NS	2) Day 9 – 30 Day 30 - 12	NA	NS	NS	2) Day 30 – 26
Note: There is no significant reduction for any other VOCs monitored over three trials: n-butyric acid, valeric acid, isovaleric acid, p-cresol, skatole														
Dougherty et al., 2017 [23]	Pilot (26.5 L), 56 d Volume of manure	1	1) Fresh dairy manure mixed with flush water	Douglas fir	5 cm thick	9.32			< 1	NS	NA	NA	NA	NA
			2) Fresh scrapped dairy manure	Douglas fir	5 cm thick				22	NS	NA	NA	NA	NA

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Table 1. (continued)

Reference	Scale and Duration	Trials	Treated source	Biochar source	Biochar dose	Biochar pH	Manure pH	Post-trial manure pH	Gaseous emissions reduction (%)					
									NH_3	H_2S	CH_4	CO_2	N_2O	Indole
	Pilot (26.5 L), 56 d	1	1) Fresh dairy manure mixed with flush water	Douglas fir bark and wood fiber	5 cm thick	7.28			80	NS	NA	NA	NA	NA
			2) Fresh scrapped dairy manure	Douglas fir bark and wood fiber	5 cm thick				72	NS	NA	NA	NA	NA

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Table 2. Review of research on uses of biochar as a soil amendment and its effect on gaseous emissions.

Reference	Scale and Duration	Trials	Treated source	Biochar source	Biochar dose	Biochar pH	Soil pH	Post-trial soil pH	Gaseous emissions reduction (%)					
									NH_3	H_2S	CH_4	CO_2	N_2O	Indole
Rogovska et al., 2011 [26]	Pilot (0.0011 m^3 PVC column), 500d	1	Surface soil with swine manure	Mixed hardwood and hickory	1) 0 g/kg	7.6	6.4	7.5	NA	NA	NA	1) 0	NS	NA
					2) 5 g/kg	7.6	6.4	7.5	NA	NA	NA	2) -24	NS	NA
					3)10 g/kg	7.6	6.4	7.5	NA	NA	NA	3) -11	NS	NA
					4) 20 g/kg	7.6	6.4	7.5	NA	NA	NA	4) -8	NS	NA
Troy et al., 2013 [27]	Pilot (0.031 m^3 PVC column), 28 d	1		Swine manure mixed with Sitka spruce sawdust		9.6	6.9	7.24-7.39	NA	NA	NS	-87	NS	NA
				Sitka spruce wood		9.3	6.9	7.11-7.23	NA	NA	NS	-91	NS	NA
Brassard et al., 2018 [25]	Laboratory (747g of soil), 28 d	1	Soil surface	Wood 1 (black spruce and Jack pine)	2%(w/w) of soil	6.8	6.2	5.5	NA	NA	NA	NA	53	NA
				Wood 2 (black spruce and Jack pine)	2%(w/w) of soil	7.6	6.2	5.5	NA	NA	NA	NA	42	NA
				Switchgrass 1	2%(w/w) of soil	6.4	6.2	5.8	NA	NA	NA	NA	90	NA
				Switchgrass 2	2%(w/w) of soil	8.8	6.2	5.7	NA	NA	NA	NA	58	NA
				Pig manure 1	2%(w/w) of soil	8.6	6.2	6.5	NA	NA	NA	NA	-113227	NA
				Pig manure 2	2%(w/w) of soil	9.3	6.2	6.9	NA	NA	NA	NA	-15157	NA

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Table 2. (continued)

Reference	Scale and Duration	Trials	Treated source	Biochar source	Biochar dose	Biochar pH	Soil pH	Post-trial soil pH	Gaseous emissions reduction (%)					
									NH_3	H_2S	CH_4	CO_2	N_2O	Indole
Feng et al., 2011 [24]	Field-scale, Rice growing season	1	Rice field	Cornstalk		9.3-10.12	4.4	NA	NA	NA	91	NA	NA	NA

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Table 3. Review of research on uses of biochar as an adsorbent for different gases in laboratory-scale experiments.

Reference	Scale and Duration	Trials	Treated source	Biochar source	Biochar dose	Biochar pH	Treated source pH	Post-trial pH	Gaseous emissions reduction (%)					
									NH_3	H_2S	CH_4	CO_2	N_2O	Phenol
Komnitsas et al., 2016 [28]	Laboratory scale (100 mL of phenol solution)	1	Phenol solution	Pistachio shells	5 g·L^{-1}	6.1	NA	NA	NA	NA	NA	NA	NA	76.6
				Pecan shells	5 g·L^{-1}	5.8								61.7
				Pinewood sawdust	5 g·L^{-1}	4.6								46.2
Li et al., 2017 [29]	Laboratory scale (250 mL of wastewater) 2 d	1	Swine wastewater	Sugarcane harvest residue + 20% Mg	0.25 g	4 – 10 (adjusted)	7.86	8.49 – 9.92	25.77 (pH=8.5)	NA	NA	NA	NA	NA
Hervy et al., 2017 [30]	Laboratory scale (0.014 m id x 0.0235 m H) 0.14	1	Biogas	Leaf waste HTT* 200°C	4.8 x10^{-4} m^3	9.62	NA	LWB**200 7.91	NA	62.52	NA	NA	NA	NA
				Leaf waste HTT* 300°C		9.89		LWB**300 8.34		68.76				
				Leaf waste HTT* 400°C		10.23		LWB**400 8.12		84.22				
Shang et al., 2015 [31]	Laboratory scale	1	H_2S gas concentration	Camphor HTT 500°C	1 g	9.55	NA	NA	NA	10.9	NA	NA	NA	NA
				Bamboo HTT 500°C	1 g	10.21				38.2				
				Rice-hull HTT 500°C	1 g	10.56				36.6				

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2. Materials and Methods

2.1. Manure

Three types of manure were used; two of them were collected from deep pit manure storage barn of AG 450 farm of Iowa State University (trial 1), Iowa Select Farm (ISF) in North Central Iowa (trial 2), and outdoor storage in Prestage Farms (PF) in Mid-West Iowa (trial 3). The pH of manure samples was measured with the Accumet Refillable electrode [36] connected to Accumet AB 15 pH meter (Fisher Scientific, Kansas City, KS). Samples were weighed in a crucible and dried for 16 h in the temperature range from 105 to 110 °C and then weighed again to determine total solids [37]. The total volatile solids were derived by muffling samples for 2 h at 550 °C [38]. Dumas method of combustion was used to analyze total N. Samples were put in an induction furnace at 950 -1350 °C with He and O_2 carrier gases. O_2 was removed by Cu catalyst and converted to N_2, and magnesium perchlorate and ascarite removed moisture and CO_2. Total N was estimated by a thermal conductivity cell [37].

At the end of each trial, four containers of the same treatment were mixed and emptied into a 3 L jar, then kept in a refrigerator at 4 °C for manure analyses. After the end of the whole experiment, all 12 samples (n=3 pre-trial, n=3 control, n=3 RO, and n=3 HAP) were sent to Brookside Laboratories, Inc. (New Bremen, OH) for analyses of total solids, total volatile solids, and total N.

The properties of the manures are shown in Table 4:

Table 4. Properties of swine manure (pit- or outdoor stored) used in the experiments.

Properties	AG 450 (trial 1) (pit storage)	ISF (trial 2) (pit storage)	PF (trial 3) (outdoor storage)
pH	7.47	8.00	7.55
Total solids (%)	2.64	4.07	2.60
Total volatile solids (%)	66.67	71.01	66.54
Total Nitrogen (%)	16.10	13.37	11.88

2.2. Biochar properties

Biochar made of red (RO) oak and highly alkaline and porous biochar (HAP) made of corn stover were topically applied on manure. Both of the biochars were ground in a ball mill and analyzed for elemental content (C, H, N, and S) by a C/N combustion analyzer (Vario Microcube, Elementar Analysensysteme GmbH) [39]. Thermogravimetric analysis (TGA) on a Mettler-Toledo TGA/DSC STARe System was used with N flow at 100 $mL \cdot min^{-1}$ for the proximate analysis of biochar. The temperature increased from 25 to 105 °C with a rate of 10 $°C \cdot min^{-1}$ and held for 40 min to measure the moisture content of biochar. The volatile matter was estimated by increasing temperature to 900 °C and holding it for 20 min. N was replaced with 1000 $mL \cdot min^{-1}$ of air gas, and the sample was kept at 900 °C for 20 min for ash content analysis. Fixed C content was estimated by subtracting percentages of moisture, volatile matter, and ash content from the sample [41]. Results of the elemental analyses, moisture/fixed C, volatile matter, and pH are summarized elsewhere [34]. In addition, a solid addition method was used to analyze the zero point charge (ZPC) of biochars. The initial pH of 1M NaCl was adjusted between pH 2-11 by adding 1M HCl or NaOH and distributed into a 50 mL flask. After the addition of biochar into the flasks, they were sealed and stirred for 4 h, after which final pH was measured in the flasks, and the difference between the final and initial pH was assumed to be ZPC of biochar [40]. Pore images of biochars were taken using the scanning electron microscopy (SEM) method (FEI Quanta 250 FE-SEM) [39]. Results of SEM analyses are summarized elsewhere [34].

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Fourier transforms infrared (FTIR) analysis was conducted to analyze functional groups in the biochar by using Thermo Scientific Nicolet iS20 (Thermo Fisher Scientific Inc., Waltham, MA) with attached iTR accessory. The sample was measured 32 times at resolution 4 cm^{-1} with a wave range of 750~4000 cm^{-1} [42].

2.3. The experimental stand description

The study of two types of biochar on odor mitigation was completed in a lab-scale manure storage simulators ('containers', 'reactors'). Manure was put into twelve 1700 mL glass containers (19 cm x 14.5 cm x 7.5 cm). 800 mL of the volume was filled with manure, and 900 mL of the volume remained as a controlled headspace. Two types of biochar were added manually on the top of the manure. The headspace was continuously flushed with 100 $mL \cdot min^{-1}$ and controlled by rotameters (Dwyer, RMA-11-SSV, Michigan City, IN) with valves to adjust a ventilation rate of 7 headspace exchanges per hour to match farm-scale ventilation of pit manure storages. Air from the compressed air source was flowing through the air filter (Sigma-Aldrich, St. Louis, MO) in order to clean it from residuals and moisture and then flowed to the mass flow controller (MFC, Aalborg, range of 0-1000 $mL \cdot min^{-1}$, Orangeburg, NY) that controlled total flow. After passing the MFC, the air was flowing to a manifold that distributed the air equally to flush the headspace of manure (Figure 1).

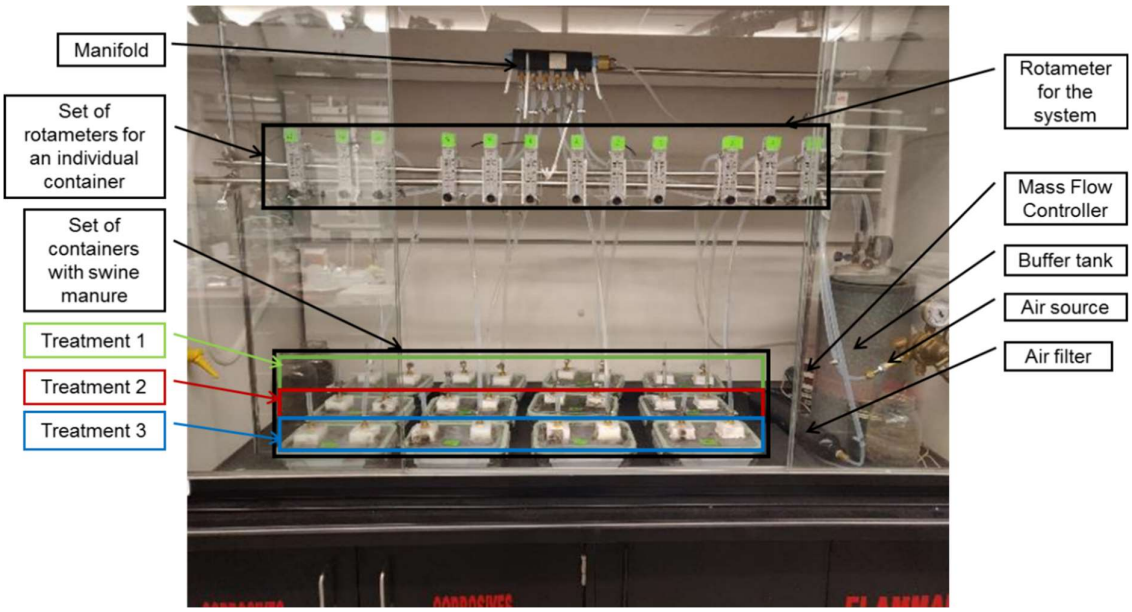


Figure 1. A laboratory-scale system to test the effects of surficial biochar application to swine manure on gaseous emissions.

2.3. Experimental design

The laboratory-scale experiment was designed to imitate manure in a deep pit swine manure storage. The experimental design was a completely randomized design for 3 trials with 30 days of duration and 1 week of stabilization before each trial (i.e., before application of biochars on Day 1). The dose of 1/4" (6.35 mm) of the biochar layer applied on manure was selected according to Maurer et al. [22]. Manures from AG 450, ISF, and PF were used in trials 1, 2, and 3, respectively. Each trial consisted of testing 4 reactors of fresh swine control manure, 4 reactors of fresh swine manure treated with RO biochar at a dosage of 1.65 $kg \cdot m^{-2,}$ and 4 reactors of fresh swine manure treated with HAP biochar at a dosage of 2 $kg \cdot m^{-2}$ (Table 5).

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Table 5. Matrix of the experiment.

Trial #	RO Biochar Dose ($kg \cdot m^{-2}$)	HAP Biochar Dose ($kg \cdot m^{-2}$)	Control	Manure Type	Trial Length (d)
1	1.65	2	0	AG 450	30
2	1.65	2	0	ISF	30
3	1.65	2	0	PF	30

2.4. Gas concentration measurements

2.4.1. Ammonia and hydrogen sulfide

To measure NH_3 and H_2S concentrations, the real-time system (OMS-200, Smart Control & Sensing Inc., Daejeon, Rep. of Korea) attached with electrochemical gas sensors from Membrapor Co. (Wallisellen, Switzerland) [43] was sampling the air for 5 min with the suction rate of 2 $L \cdot min^{-1}$. Due to the restrictions of the laboratory scale deep barn pit simulation system, gas samples were collected from 4 containers of the same treatment simultaneously into 1 Tedlar bag. A manifold with 4 ports, connected to 4 containers via Teflon tubes, was attached to a vacuum chamber with a suction rate of 350 $mL \cdot min^{-1}$. A Tedlar bag was put in the chamber for 35 min to collect ~12.25 L of the air sample. After the collection of the gas sample, the Tedlar bag was attached to the real-time analyzing system, which measured the concentration of NH_3 and H_2S in ppm. Gases from each treatment were collected in triplicates (Figure 2).



(a) **(b)** **(c)**

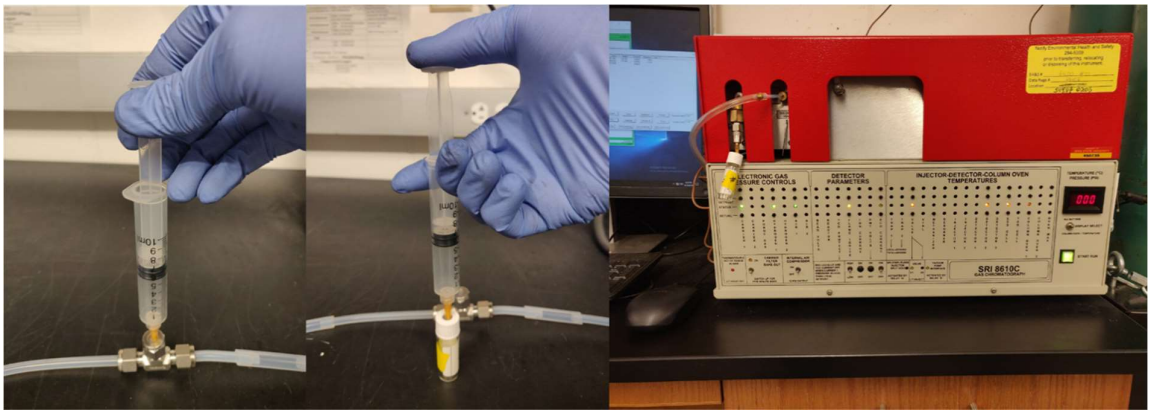
Figure 2. Process of collecting gas samples emitted from manure for analyses of NH_3 and H_2S: (a) The manifold is attached to a block of containers (i.e., replicated treatments of the same kind); (b) Tedlar bag filled with the gas sample in the vacuum chamber; (c) The Tedlar bag is attached to the real-time analyzer.

2.4.2. Greenhouse gases

A gas chromatograph (SRI Instruments, Torrance, CA, USA) with a flame ionization detector (FID) and electron capture detector (ECD) was used to measure GHG concentrations. The GHG analyses followed the processes used earlier [22]. The instrument was calibrated with standard gases in triplicates with 1,005 and 4,020 ppm CO_2, 0.1 and 1.0 ppm N_2O, and 10.5 and 20.5 ppm CH_4.

A four-port manifold with an attached sampling port was connected to 2 pocket pumps with a pumping rate of 175 $mL \cdot min^{-1}$ each. After connecting the manifold to a block of 4 same treatment containers via Teflon tubes, triplicates of samples were collected through a sampling port using a syringe and injected to the vacuum of 5.9 mL Exetainer (Labco Limited, UK) vials which were previously cleaned by 7 cycles of He flushing and vacuuming. Then, samples were analyzed with a GC (Figure 3). Results were plotted in a calibration curve against concentrations of standard gases.

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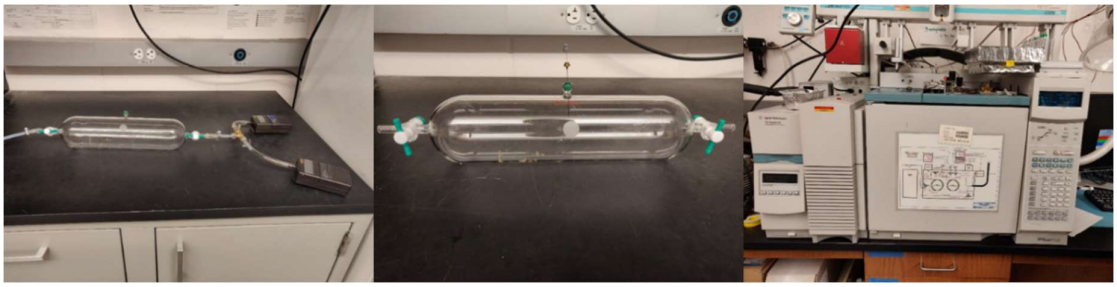


(a) **(b)** **(c)**

Figure 3. GHG sample collection: (a) extracting gas sample using a syringe; (b) injecting the gas sample in a vial; (c) measuring GHG concentration with a gas chromatograph.

2.4.3. Volatile organic compounds

Gas samples were also composited for the VOC analyses greatly reducing the variability inherent with gaseous emissions from manure. A four-port manifold was connected to a block of 4 (identical) treatment containers. A clean glass bulb with a volume of 1 L was connected to the manifold and on the other side to 2 pocket pumps with the suction rate of 175 mL·min^{-1} to flush air through the glass bulb. After 15 min of flushing, connections ports were closed, and the bulb was detached from the manifold and the pumps. Solid-phase microextraction (SPME) fiber assembly divinylbenzene/Carboxen/polydimethylsiloxane (DVB/Car/PDMS) with a length of 1 cm was inserted into the bulb through septa on it. After 10 min of passive sample collection, the SPME was injected into a thermal desorption-multidimensional GC-MS/olfactometry system (TD-MDGC-MS/O) by Microanalytics (Round Rock, TX, USA) for separation and analysis of VOCs. The details of the instrument are described in Zhang et al. [44]. Targeted compounds such as dimethyl disulfide, dimethyl trisulfide, propanoic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, phenol, *p*-cresol, indole, and skatole were scanned with selected ion monitoring (SIM) mode (Figure 4).



(a) **(b)** **(c)**

Figure 4. VOC sample collection process: (a) Flushing the glass bulb with sample air for 15 min; (b) SPME is injected in the bulb through septa to collect VOCs; (c) SPME is desorbed into a GC-MS for separation and identification of target odorous VOCs.

2.5. Statistical analysis

A simple linear regression model was used in the R program (R i386 3.6.0. Ink) to analyze the data and estimate the *p*-value. A level of significance of 0.05 was used to determine statistical significance.

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3. Results and Discussion

3.1. Observation of biochar layer interaction with swine manure

In trial 1, HAP biochar started sinking right after application. At the end of the trial, there was a thin layer of wet biochar floating near the surface; some biochar was in suspension, while most of it settled on the bottom. All RO was wet by day 4. RO had a thicker wet layer floating near the surface of the manure and settled fewer particles on the bottom in comparison with HAP.

During trial 2, RO biochar was floating for the first two weeks on top of the manure, and then it started to incorporate into manure after day ~15. On the last day of the trial, about half of RO biochar was wet and was floating near the top of the manure; another half settled on the bottom. HAP biochar absorbed liquid manure where it was interacting with it, then crusted and partially separated from manure. Thus, a headspace between the HAP layer and manure was created near the perimeter, and only ~30% of HAP biochar was still in contact with manure near the center of the storage container (Figure 5).

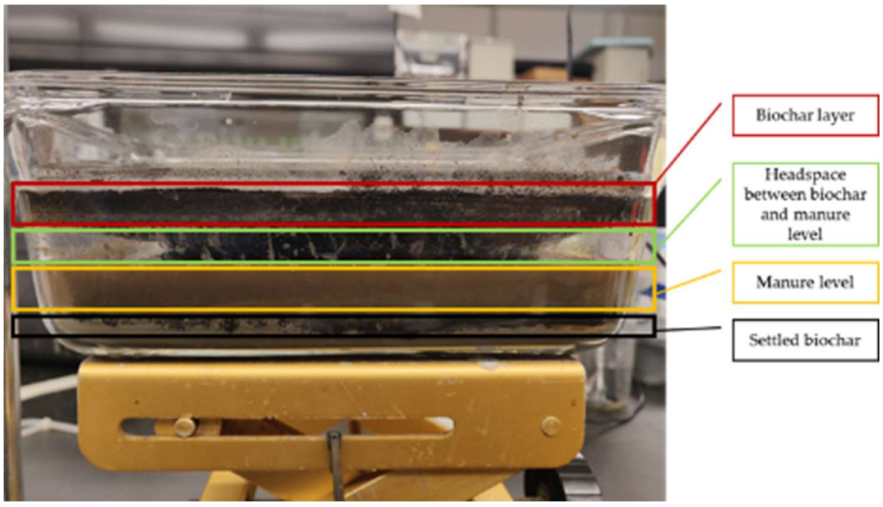


Figure 5. HAP biochar crusted, and headspace between biochar and manure surface was created.

In trial 3, HAP biochar started to incorporate into manure on day 3 and completely sank 8 days after application. At the end of the trial, all of the HAP biochar settled on the bottom of the container. A layer of RO biochar applied on the manure started getting wet after two weeks, and at the end of the trial, half of the RO biochar became wet and was floating on the manure surface while another half settled on the bottom of the container (Figure 6).



(a) **(b)** **(c)**

Figure 6. Overview photos of each treatment after the end of the trial 3: (a) HAP biochar completely sank and the manure surface crusted; (b) half of applied RO biochar became wet and floated on the manure surface; (c) some crust was observed on the surface of control manure.

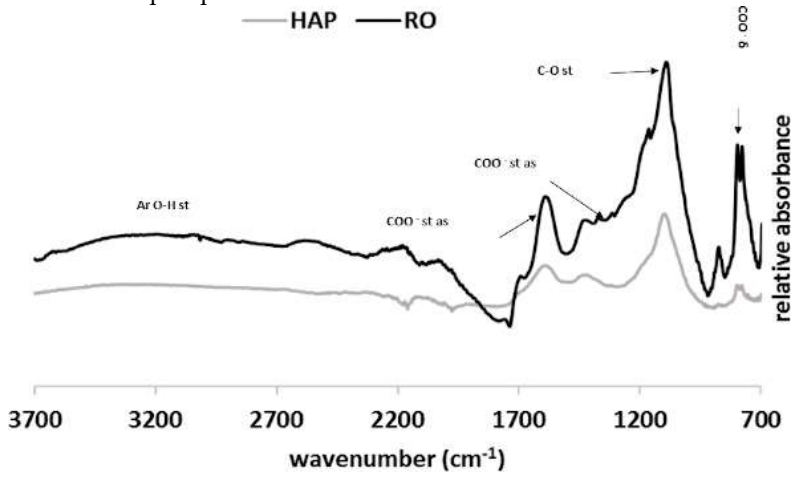
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Our working hypothesis was that the biochar layer influence manure pH, which could inhibit gas transfer from liquid to air. However, as it is shown in Table 6, because of the differences between pre-trial and other treatment manures as well as because there were no significant differences between control and biochar treated manures over all three trials, no effect of biochar on the manure pH can be assumed. Biochar-treated manure gained solids and volatile solids in comparison with the control manure. The total N content of dropped 1.5~2 times compared to control over all three trials, likely due to the high biochars porosity that might adsorb N (Table 6). The possibility of N adsorption and possible slow release to (e.g.) soil after biochar-treated manure is applied to the land should be further explored as the mitigation of gaseous emissions could be followed by agronomic benefits to the soils.

Table 6. Physical properties of manure before trials (pre-trial), control, RO, & HAP-treated manures.

Trial	Treatment	pH	Total solids (%)	Total volatile solids (%)	Total nitrogen (%)
	Pre-trial	7.47	2.64	66.67	16.10
	Control	9.16	2.17	48.85	10.65
1	RO	9.00	8.16	84.44	3.13
	HAP	9.03	4.87	60.78	4.78
	Pre-trial	8.00	4.07	71.01	13.37
	Control	9.07	4.08	66.18	7.57
2	RO	8.97	10.64	85.62	3.32
	HAP	8.99	8.81	68.56	4.43
	Pre-trial	7.55	3.60	66.54	11.88
	Control	9.07	2.41	59.75	7.47
3	RO	8.77	4.29	63.40	3.89
	HAP	8.75	8.33	86.19	2.61

One of the reasons for different biochars behavior in the meaning of sinking or floating on the manure surface could be a difference in hydrophobicity of biochars. Higher hydrophobicity decreases liquid absorption, which prevents biochar from sinking in manure [45]. Hydrophobicity of biochar is associated with residual alkyl functional groups, which can be decomposed by a higher temperature of charring. Thus, hydrophobicity depends on feedstock and temperature of charring. It is possible to compare the hydrophobicity of biochars by comparing the peak area in a range of 3000-2800 cm^{-1} on FTIR spectra [46]. As it can be seen in Figure 7, RO biochar has a small peak on that range, while the graph for HAP biochar is flat, which supports the above-mentioned hypothesis. Another property of HAP biochar that made it sink in manure could be high ash content in comparison with RO biochar. In addition, the differences in pore size associated with HAP and RO biochars (visible in SEM images, [34]) could also affect the liquid penetration.



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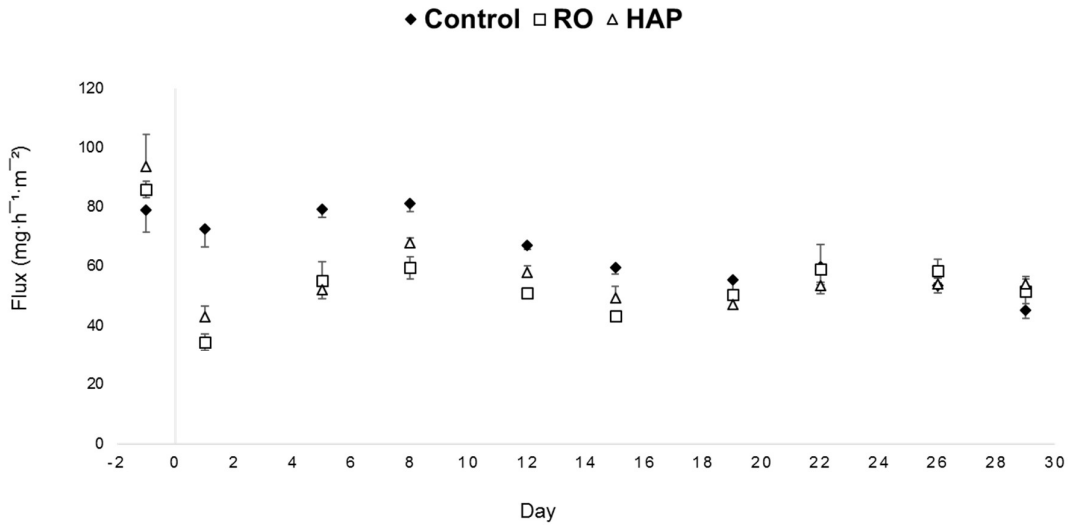
Figure 7. Results of FTIR analyses can explain the hydrophobicity and floating behavior when biochars are surficially applied to manure.

Another parameter that could affect biochar floating on top of manure is the solid content in manure. Trial 1 showed that HAP and RO started to incorporate with manure immediately after application and on day 2, respectively. Then, most of the particles of biochar with the lower solid content completely sank in manure. In trial 2, where manure with higher solid content was used, RO biochar became wet only after ~2 weeks, and there was a floating wet layer of biochar still near the manure surface. In trial 3, manure with total solids higher than in trial 1, RO behaved similarly to trial 2 and HAP settled on the bottom after ~1 week.

3.2. Effect of biochar treatment on ammonia and hydrogen sulfide

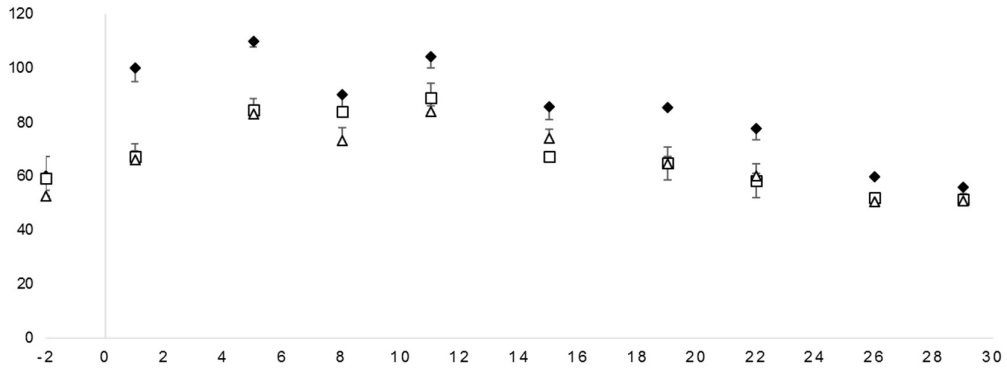
Biochar addition had a mitigating effect on NH_3 emissions. However, the effect was temporal, opening up the possibility of biochar reapplication in subsequent research. On the first day of trial 1, HAP and RO biochars showed as much as 40% ($p<0.0001$) and 52% ($p<0.0001$) reduction of NH_3, respectively. After that, the reduction rate started to decrease over time (Figure 8, Table A1). The last statistically significant reduction was measured on day 15 where it was 17% ($p=0.04$) and 27% ($p<0.0001$) for HAP and RO biochar, respectively. During the trial 2, HAP and RO started with 34% ($p<0.0001$) and 33% ($p<0.0001$) reduction of NH_3 emissions on day 1 and then gradually decreased to 15% ($p=0.01$) and 12% ($p=0.04$) on day 26. In trial 3, HAP biochar reduced 41.8% ($p<0.0001$) of NH_3 emission. However, from day 5, it showed no NH_3 reduction; in fact, it increased NH_3 emissions on some days. RO biochar started with 70.4% of NH_3 reduction ($p<0.0001$) on day 1, and then the reduction rate gradually decreased to 22.2% on day 29 ($p<0.0001$).

Even though manure pH changed for all treatments, there were no significant differences in pH between the control and biochar treated manures after each trial, so it cannot be stated that biochar inhibited NH_4^+ from transformation to NH_3 during the entire trial. ZPC of biochar could be a parameter that was responsible for NH_3 reduction. Because ZPC of biochars was below biochars pH, their surface was mostly negatively charged, which was favorable to attract NH_4 cations and keep them on the biochar surface.

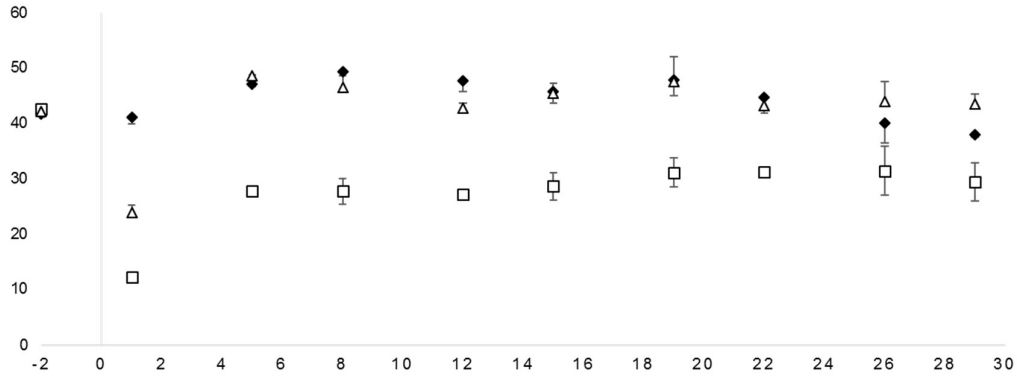


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(b)



(c)

Figure 8. Biochar effect on NH_3 emissions from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

During all three trials, manure pH changed from 7.47~8 to 8.75~9.07, and this increase in pH forced more NH_4^+ ions into gaseous NH_3 form. Thus, NH_3 emissions reduction gradually decreased from day 1 to day 29. Interestingly, Takaya et al. reported that the oak biochar has the NH_3 sorption capacity of 4~8 $mg \cdot g^{-1}$ of biochar [47]. Assuming this sorption capacity, the RO biochar would be fully saturated by day 7~14. Clearly, the RO biochar in this research was effective longer, e.g., still showing a significant reduction on day 29 in trial 3. Thus, the most probable explanation is that biochar created a semi-porous physical barrier that slowed mass transfer from manure to headspace.

Emissions of H_2S were more challenging to mitigate with biochars, with some interesting temporal effects (Figure A1, Table A2). Trial 1 showed no statistically significant reduction of H_2S due to the effect of RO. Similarly, HAP treatment was not significant, even though it had 100% ($p=0.07$)

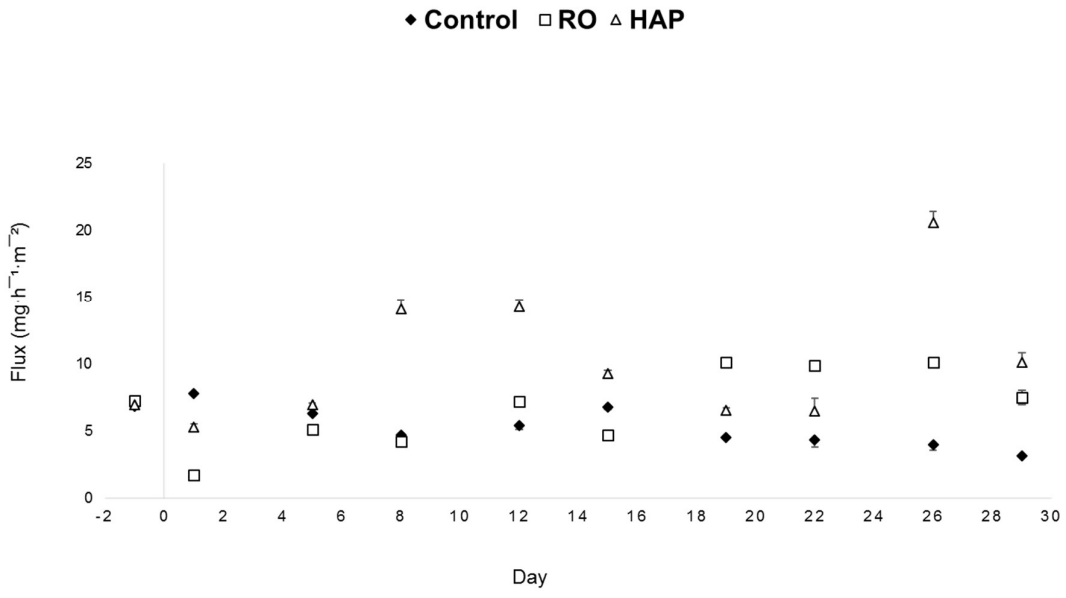
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of reduction starting on day 19 until the end of the trial. In trial 2, HAP biochar significantly reduced emissions by 24% (p=0.001) and 39% (p<0.0001) on day 1 and 8, respectively. RO biochar was reducing H_2S emission for the first ~12 days, where the highest reduction was 49% (p<0.0001) on day 5. During the trial 3, HAP biochar showed a significant reduction of 25.4% (p<0.0001) till day 8. RO biochar had a significant reduction of 26.2% (p<0.0001) until day 22. However, on day 15, even though RO reduced 43.7% of H_2S, it was not statistically significant (p=0.6221).

Shang et al. claimed that tested biochar had a range of sorption capacity from 1.2~121.4 $mg \cdot g^{-1,}$ and the most conducive pH for H_2S sorption was the pH higher than pKa of H_2S, which is 7. Shang also stated that FTIR peaks at 3420, and 1730 $cm^{-1,}$ which correlated to OH stretching and COO^- stretching respectively, were crucial for H_2S adsorption [48]. Ayiania et al. studied that the mechanism of H_2S sorption is driven by the size of biochar pores [49]. However, our experiments showed that HAP biochar with pH=9.2 and larger pores [34] performed less H_2S reduction in comparison with RO over all three trials. It should be mentioned that FTIR spectra (Figure 7) showed that RO had higher peaks in OH and COO^- stretching. Most likely, the complexity of swine manure content and competition between gases were not favorable for reducing H_2S emitted from the manure.

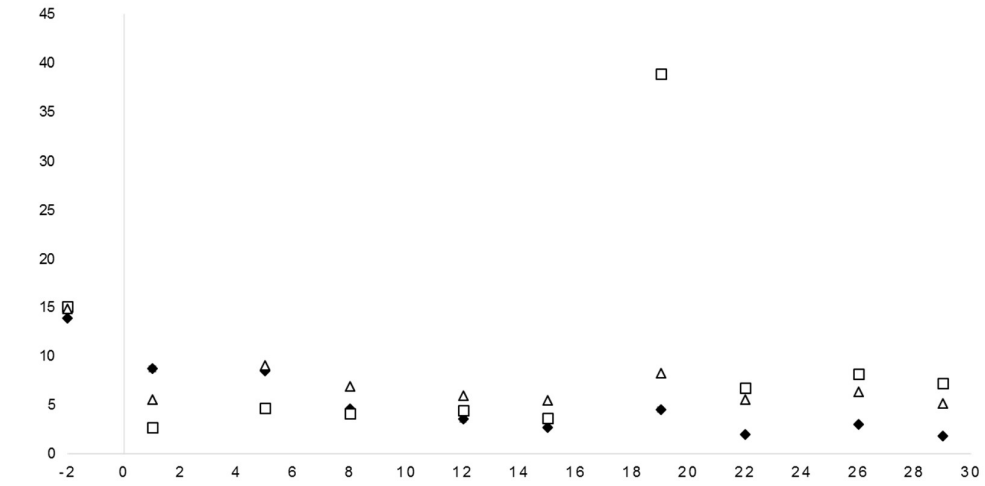
3.3. Effects of biochar treatment on greenhouse gas emissions

On day 1 of the trial 1, HAP and RO treatment had 31% (p=0.0001) and 77% (p=0.0001) of CH_4 reduction, respectively. However, after day 12, both started producing CH_4, and the highest production was observed on day 26, where HAP and RO treatment had 415% (p=0.0001) and 153% (p=0.0001) of increase of emissions. During the trial 2, on day 1, HAP and RO reduced CH_4 emission up to 35% (p<0.0001) and 65% (p<0.0001), respectively. However, from day 15 emissions increased up 101% (p<0.0001) and 35% (p<0.0001), respectively. The highest increase in the CH_4 emissions of 176% (p<0.0001) and 288% (p<0.0001) was measured on the last day of the trial for HAP and RO, respectively. On trial 3, CH_4 was reduced to 57.8% (p<0.0001) on day 1 due to RO biochar, and the reduction gradually decreased to 20.6% (p<0.0001) on day 11. On day 15, RO biochar started production of CH_4, where the highest production was 301.8% (p<0.0001) on day 19. HAP increased CH_4 emission during the whole trial, where the highest increase was 671% (p<0.0001) on day 19 (Figure 9, Table A3).

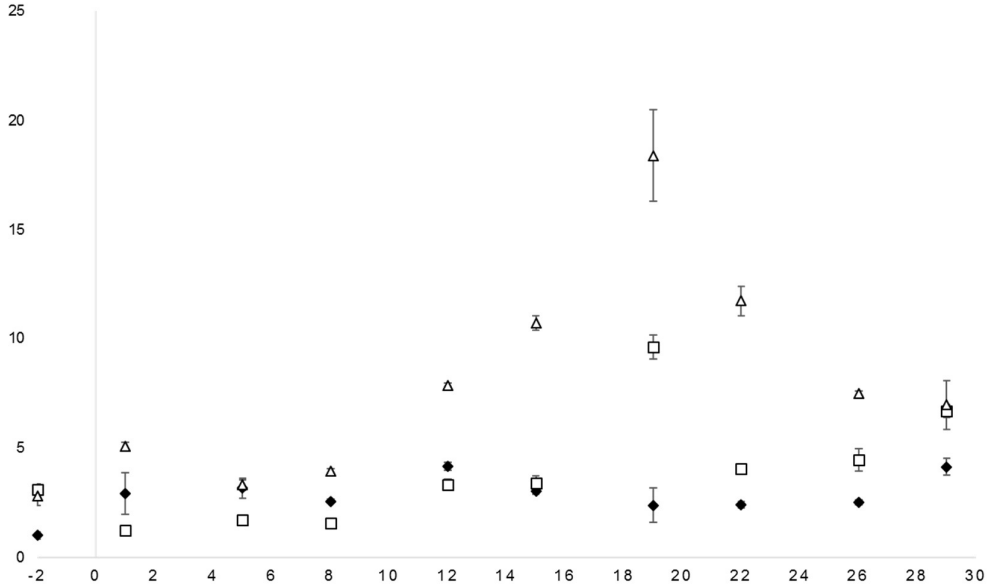


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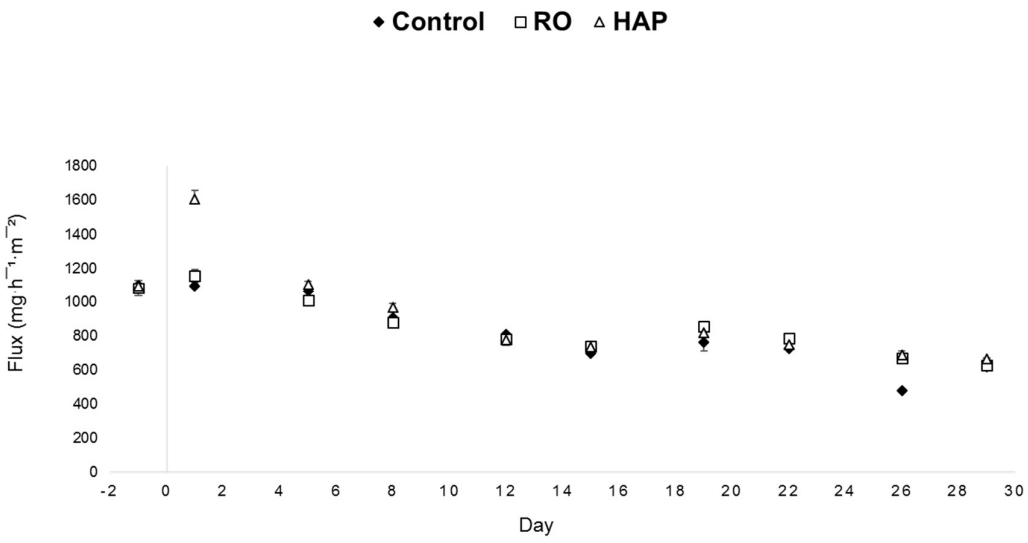


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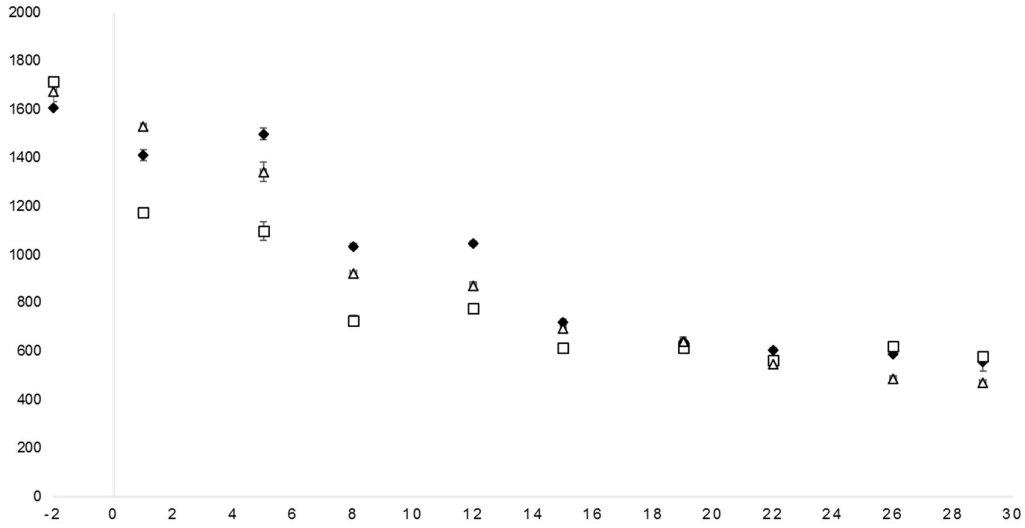
Figure 9. Biochar effect on CH_4 emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

On the first day of trial 1, HAP biochar increased CO_2 emission up to 46% ($p=0.0001$) (Figure 10, Table A4). Then again, on day 26, HAP and RO increased CO_2 emission up to 42% and 39%, respectively, but they were not statistically significant. Overall, the CO_2 reduction was not significant, and % reduction fluctuated between 2% and -9% (except for day 1 and 26). In trial 2, both HAP and RO reduced CO_2 emissions till day 11 where it was 17% ($p<0.0001$) and 26% ($p<0.0001$), respectively.

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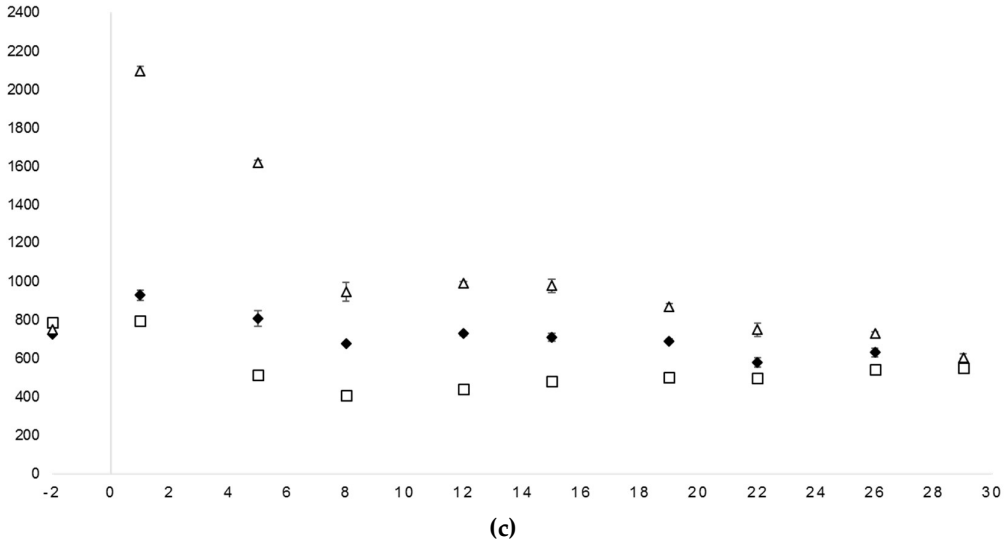


Figure 10. Biochar effect on CO_2 emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

No significant reduction of N_2O was measured during trial 1. The highest reduction was shown on day 11, where HAP and RO had 9% ($p=0.2$) and 11% ($p=0.3$) reduction, respectively. N_2O mitigation was statistically significant for the first two weeks and the highest reductions of 17% ($p<0.0001$) and 16% ($p<0.0001$) were observed on day 5 for HAP and RO, respectively on trial 2. In trial 3, both HAP and RO biochars increased N_2O emission up to 28.9% ($p<0.0001$) on day 8 and decreased the emission to 20.8% ($p<0.0001$) and 40.5% ($p<0.0001$), respectively, on day 22. No statistically significant reductions were observed on other days of the trial (Figure A2, Table A5).

Jiang et al. and Shen et al. studied that aeration during composting decreased CH_4 emission [37, 38], and in addition to that Agyarko-Mintah stated that biochar improved aeration and methanotrophy of compost [39]. Besides the fact that the headspace of the container with manure was continuously flushed with air, freshly applied biochars might enhance manure surface aeration and so decrease methanogenic activity. However, after biochar started to incorporate into manure, it could be a source of carbon for methanogens for CH_4 production. Moreover, according to, due to high porosity, biochar was not able to capture smaller CH_4 particles. In an agreement with the statement, HAP biochar with larger pores was less effective and increased methane emission after 1-2 weeks. Also, in the case of RO biochar, it started producing CH_4 after biochar incorporated into manure which can be seen in Figure 9 (part b) where biochar sank after day 15, and high CH_4 emission was observed on day 19. The theory was that biochar was adsorbing CH_4 and after incorporation into manure it released captured CH_4 out of its pores.

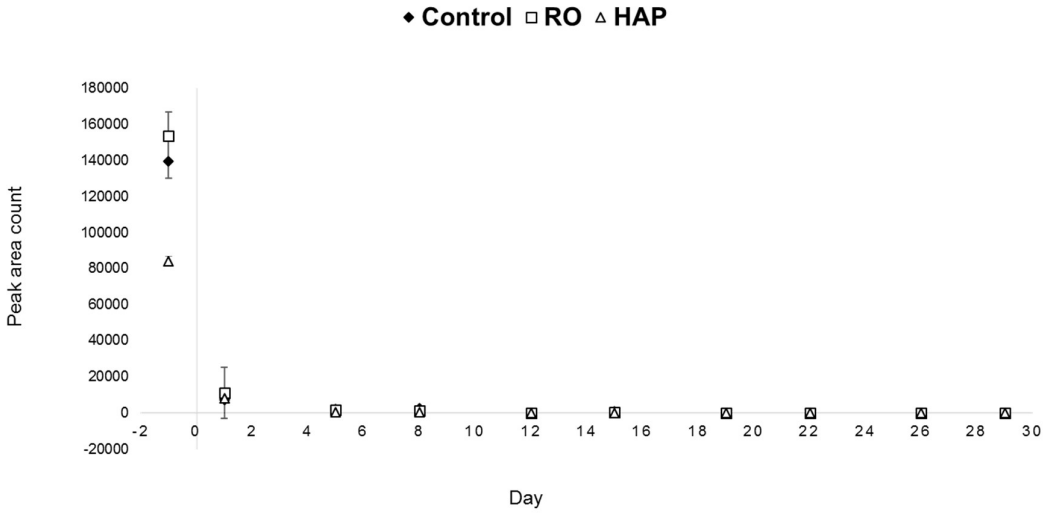
Sethupathi claimed that biochar with richer N content and larger pores adsorbed more CO_2. However, RO biochar with less N content (Table 6) and smaller pores showed better performance in CO_2 sorption in comparison with HAP biochar. Moreover, Zhang et al. revealed that micropores of <0.70 nm were responsible for CO_2 uptake [40]. Creamer found that sugarcane bagasse biochar had a CO_2 adsorption capacity of 73.55 mg $g^{-1,}$ which could be an explanation for biochars reducing CO_2 during the first 2 weeks and decrease of reduction rate after that. Results of biochar effect on N_2O differ from the decrease of emission to having no effect [41].

3.4. Effect on volatile organic compounds

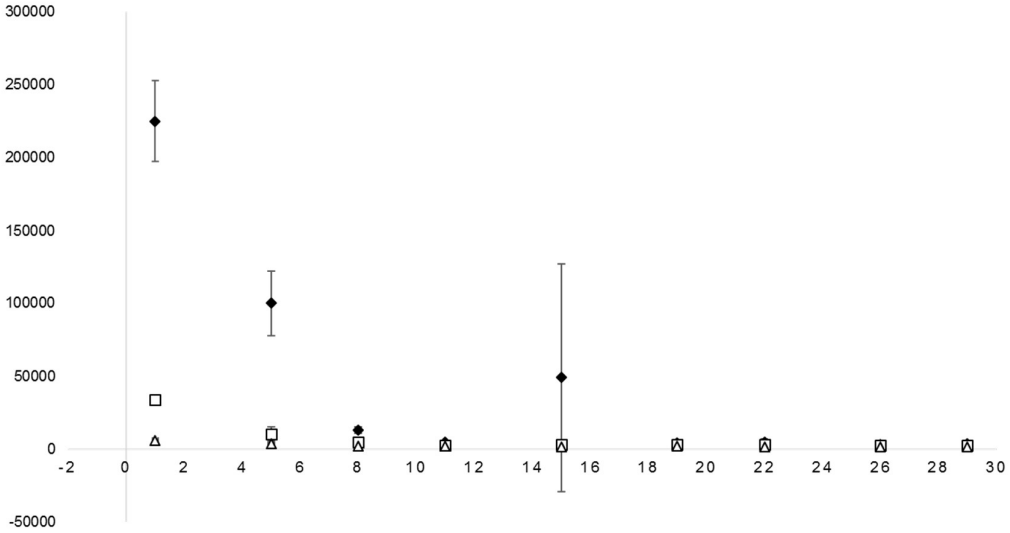
Emissions of almost all VOCs were reduced during the first week of the trial, and no reduction was measured after day 8 on trial 1. HAP reduced over 90% of dimethyl disulfide, acetic acid, propanoic acid, butyric acid, and skatole during trial 2. In trial 3, only phenol was reduced over 90% ($p<0.0001$) and 80% ($p<0.0001$) by HAP and RO biochars, respectively, over the trial (Figure 11, Table

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A6). Also, both biochars had a statistically significant reduction of p-cresol and skatole for the first two weeks and indole for the first week of the trial (Figure A3 & Table A7, Figure A4 & Table A8, Figure A5 & Table A9).

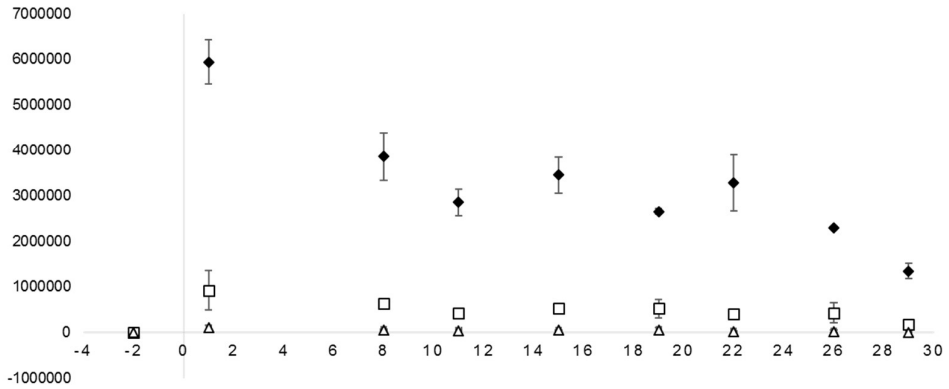


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(c)

Figure 11. Biochar effect on phenol emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

Zhang et al. reported that VOC sorption was mainly governed by surface area and non-carbonized organic matter; however, none of the VOCs from this experiment were tested [53]. In addition, Shen studied that surface area and pores volume were the main contributors in the sorption of gaseous phenol and toluene by activated char [56]. Moreover, according to Lee et al., phenol adsorption decreased with increasing pH of an aqueous solution [57]. In the case of trial 3, HAP biochar with larger pores showed a higher reduction rate of VOC, especially phenol. The presence of volatile fatty acids was significantly lower, and that could be a reason for a low reduction of them for all three trials.

For isobutyric acid, both types of biochar did not statistically reduce the emission from deep-pit manure (Trials 1 & 2, Table A10). However, RO biochar reduced the isobutyric acid emission by 26.2% (p = 0.0002), and HAP biochar reduced ~47% (p = 0.003) in Trial 3 (Table A10), which treated the manure from outdoor storage instead of a deep pit barn.

Finally, RO biochar showed ~22% reduction (p = 0.008) in the average odor concentration of the three trials throughout the one-month testing period (Table A11). HAP biochar showed an average reduction of 17.5% (p = 0.019) in the first week, decreased to 15% (p = 0.019) reduction in the second week, and showed generation (p > 0.05) of odor concentration in the last two weeks (Table A11).

The research is needed to develop and test practical technologies for the mitigation of gaseous emissions from stored swine manure. Clearly, the need is still there as the performance data for marketed products is nearly non-existent [4,5]. In a recent publication, Chen et al. (2020a) reported on a comprehensive study to evaluate gas emissions data from swine manure treated with different commercial additive products [58].

Most recently, Chen et al. (2020b) reported on the use of HAP and RO biochar as being very effective in mitigating acute releases of H_2S from agitated manure on a pilot-scale [59]. Up to ~80% reduction of short-term H_2S emissions were reported, showing a novel biochar application pathway for potential practical application immediately prior to manure pump-out and seasonal application to the land. However, more testing and scaling up research for both long- & short-term biochar application to manure should be planned, and different types of biochar and effects on targeted gases should be examined.

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5. Conclusions

Effective and economical treatment that would comprehensively mitigate ammonia, hydrogen sulfide, volatile organic compounds, and greenhouse gases from swine production is in demand. This laboratory-scale experiment was designed to evaluate the effect of highly alkaline and porous (HAP) biochar made of corn stover and red oak (RO) biochar on the mitigation above-mentioned gaseous compounds with a topical application on swine manure surface. Three trials were conducted using manure from three different sources for each trial, and ¼" (6.35 mm) thick layer of biochars was applied on top of manure (58 and 48 g per 1 kg of manure). Most of the HAP biochar sank in manure except during trial 2, where it absorbed liquid from manure and crusted, and by that created headspace between the biochar layer and manure. Some parts of the RO biochar sank in manure, and another part became wet and was floating on the manure surface. Both biochars showed the highest NH_3 reduction on the day after application; then the treatments became less effective. HAP showed the highest efficiency when it crusted on top of the manure, while the highest reduction due to RO treatment was observed when outdoor-stored manure was used (trial 3). Both biochars reduced CH_4 emission for the first two weeks, then, methane emission increased due to biochars. Carbon dioxide emission was different from trial to trial, where both treatments had no significant reduction in trial 1, then reduced CO_2 emission for the first two weeks of the second trial, and RO reduced CO_2 emission while HAP increased it. Both biochars showed a reduction of VOCs for the first week of a trial, however, they showed phenol reduction for the whole period of trial 3, and it was statistically different. The experiment demonstrated that biochar has the potential to mitigate hazardous and odorous emissions such as ammonia, methane, carbon dioxide, and phenol, associated with swine production.

Author Contributions: Conceptualization and supervision J.A.K., R.C.B., A.B., and Z.M.; methodology, Z.M., B.C., M.L., J.W., C.B. and S.B.; formal analysis and investigation, Z.M., and C.B.; writing—original draft preparation, Z.M.; writing—review and editing, Z.M., J.A.K., B.C., and A.B. supervision, J.A.K. and A.B.; project administration, J.A.K. and R.C.B.; funding acquisition, J.A.K. and R.C.B. All authors read and approved the final manuscript.

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Appendix A

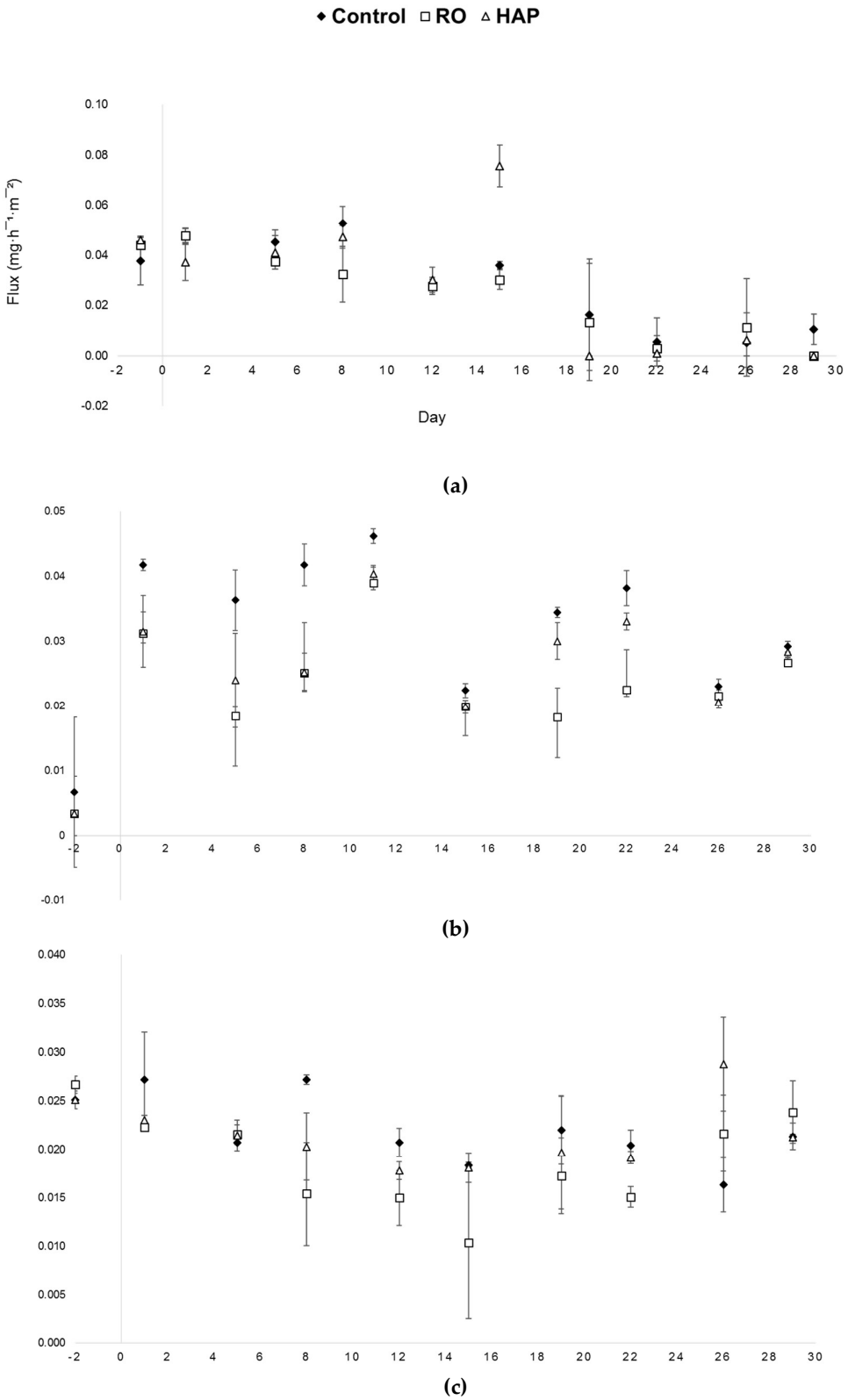
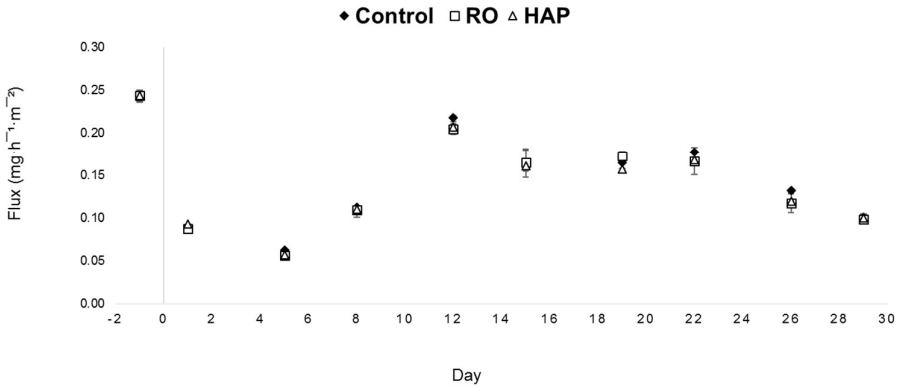
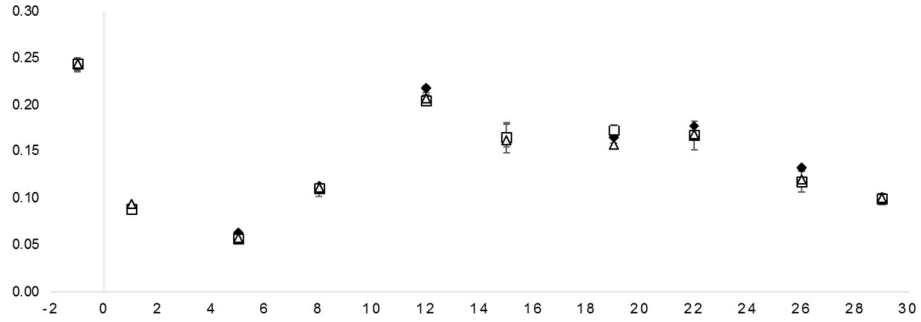


Figure A1. Biochar effect on H_2S emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

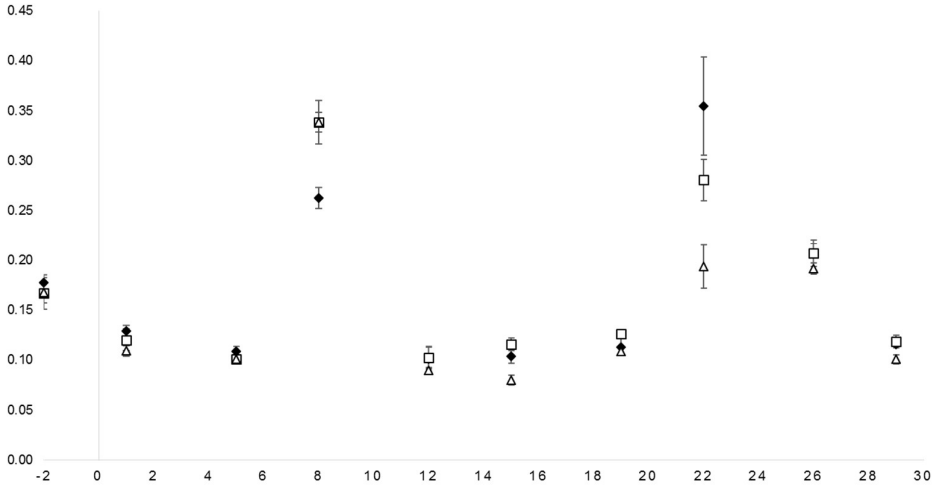
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(a)



(b)



(c)

Figure A2. Biochar effect on N_2O emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

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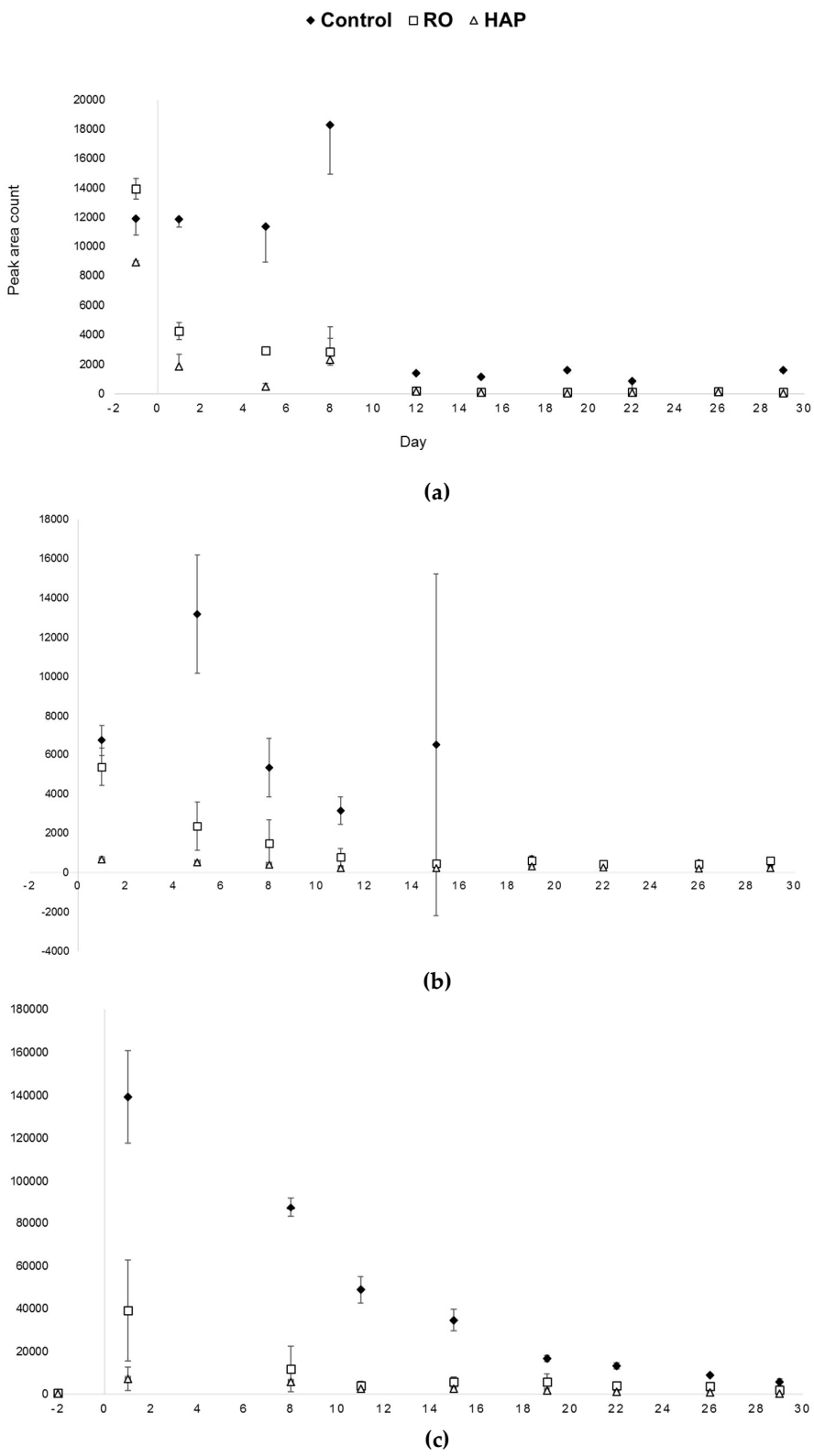


Figure A3. Biochar effect on p-cresol emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

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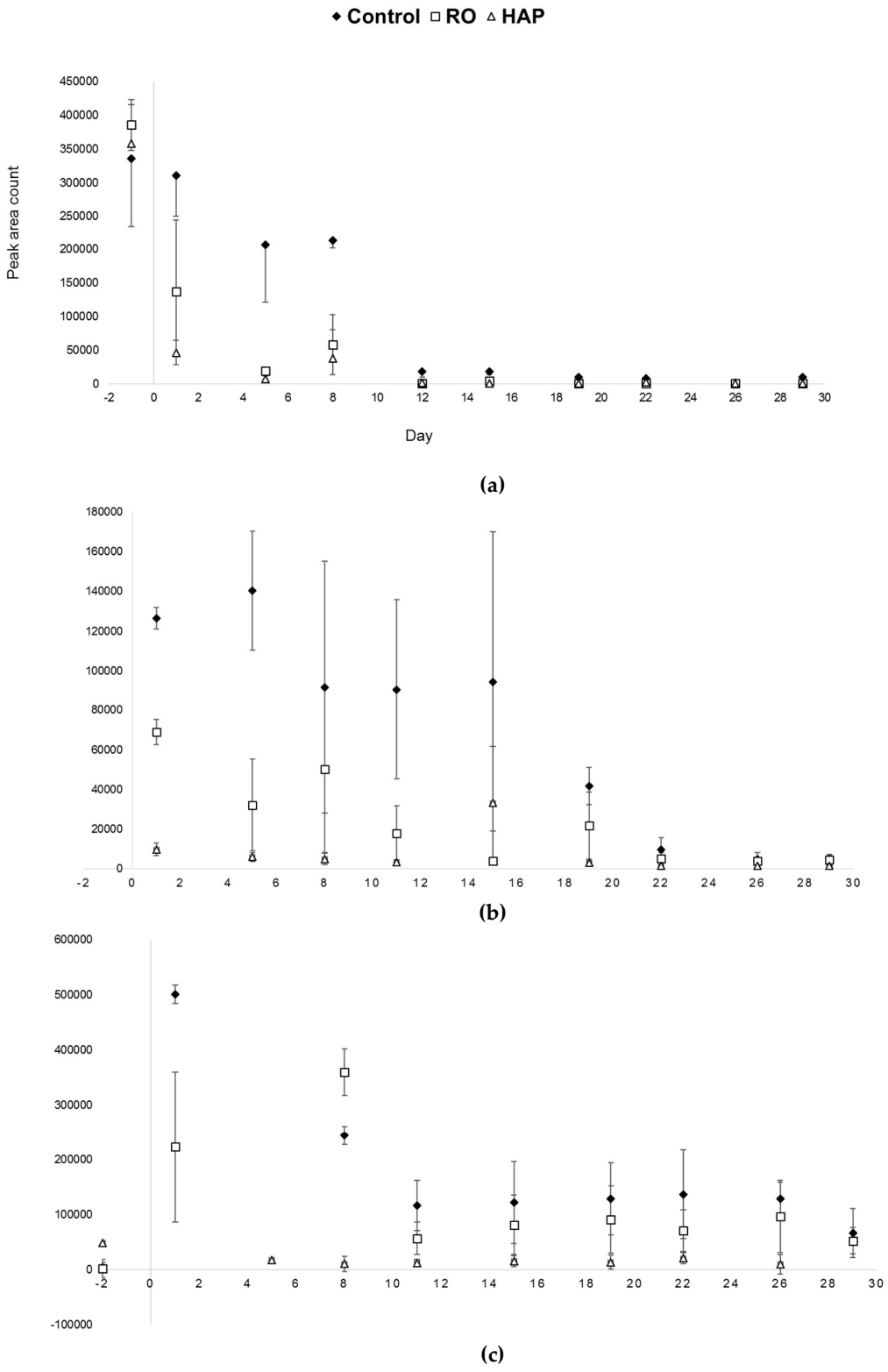


Figure A4. Biochar effect on skatole emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

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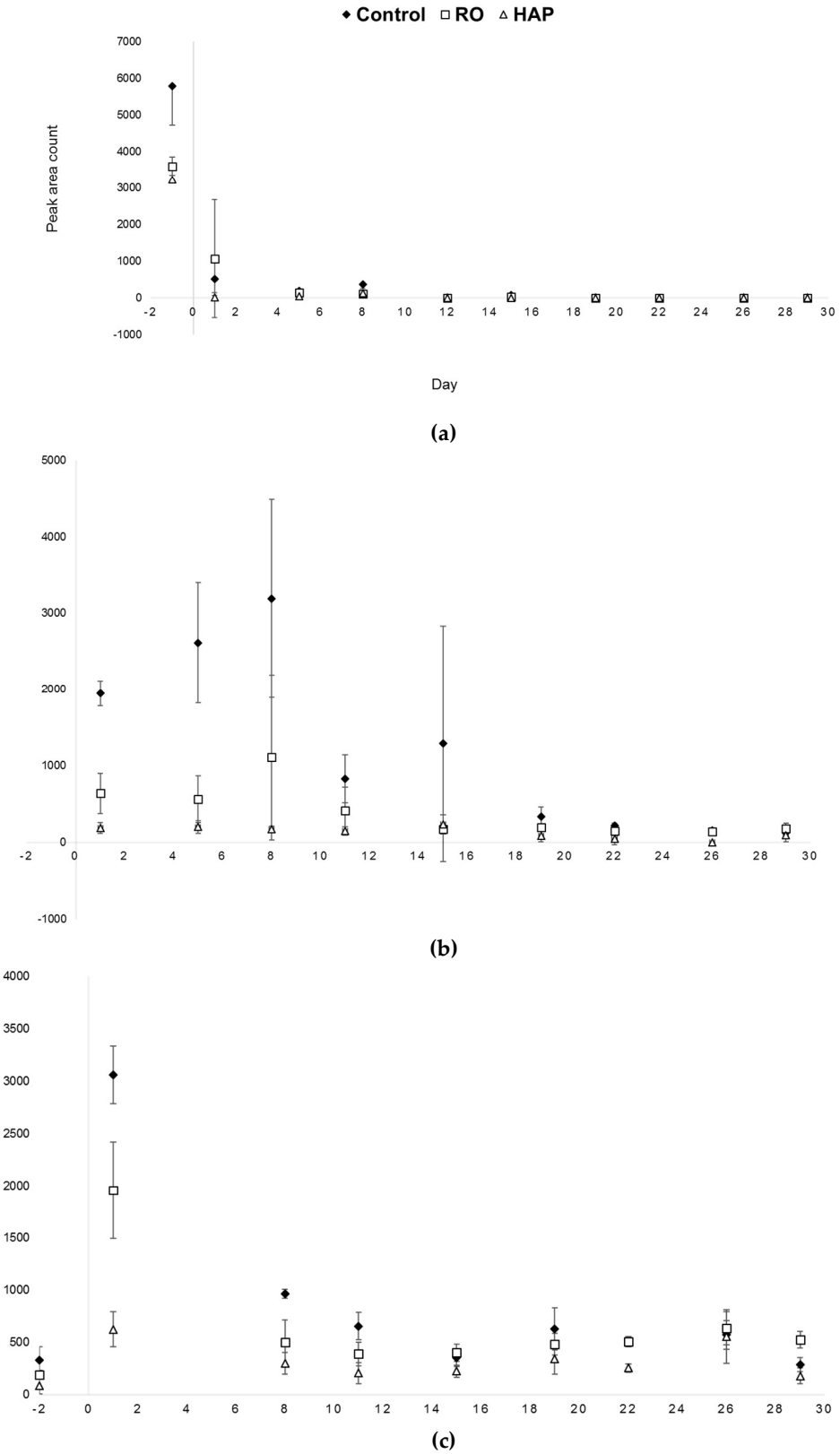


Figure A5. Biochar effect on indole emission from swine manure: (a) Trial 1; (b) Trial 2; (c) Trial 3.

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Table A1. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of NH_3 emission by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

NH_3	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	483±36	285.±77.5	**41.0**	<0.0001	477±42.7	318±66.7	**33.3**	<0.0001	431±65.3	320±59.1	**25.7**	<0.0001	405±77.4	327±55.1	**19.3**	<0.0001
2	669±40.8	483±62.5	**27.8**	0.0002	644±54.9	517±58.3	**19.8**	<0.0001	595±74.0	468±76.0	**21.3**	<0.0001	544±116	429±89.1	**21.2**	<0.0001
3	280±265	127±54.7	**54.7**	0.0013	294±21.6	151±45.0	**48.7**	<0.0001	293±19.2	169±40.6	**42.5**	<0.0001	283±26.6	174±38.5	**38.5**	<0.0001
Average	477±194	298±178	37.5	0.444	472±174	328±183	30.3	0.548	440±150	319±149	27.5	0.548	411±130	310±128	24.5	0.561

NH_3	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	483±36	302±37.6	**37.5**	<0.0001	477±42.7	351±62.2	**26.4**	<0.0001	431±65.3	337±52.2	**22.0**	<0.0001	405±77.4	334±47.1	**17.5**	0.0002
2	669±40.8	474±69.3	**29.1**	<0.0001	644±54.9	472±56.9	**26.7**	<0.0001	595±74.0	459±60.2	**22.8**	<0.0001	544±116	429±78.5	**21.2**	0.0003
3	280±265	230±85.8	**17.9**	<0.0001	294±21.6	252±65.3	14.4	0.144	293±19.2	270±52.5	7.9	0.149	283±26.6	272±46.7	4.1	0.510
Average	477±194	335±125	29.7	0.585	472±174	358±110	24.0	0.675	440±150	355±95.8	19.2	0.733	411±130	345±79.0	16.0	0.927

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Table A2. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of H_2S emission by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

H_2S	**First week**				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	148±12	119±7	**19.9**	0.071	139±32	107±21	**23.0**	0.048	106±59	82±47	22.1	0.449	88±62	68±53	22.5	0.512
2	124±13	79±23	**36.5**	0.004	132±14	91±28	**31.5**	0.0003	119±24	80±9	**32.6**	<0.0001	111±26	89±24	**19.4**	<0.0001
3	76±15	70±2	8.5	0.456	76±13	59±14	**22.6**	0.0036	71±12	53±17	**25.4**	0.0001	69±13	57±17	**16.4**	0.014
Average	120±40	90±30	23.3	0.590	120±90	90±20	26.1	0.493	100±20	70±20	27.1	0.275	90±7	70±20	19.6	0.447
H_2S	**First week**				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	148±12	133±20	10.4	0.357	139±32	128±26	8.0	0.622	106±59	84±61	20.1	0.435	88±62	67±63	22.4	0.436
2	124±13	88±23	**29.0**	0.02	132±14	86±25	**35.2**	0.0018	119±24	93±23	**21.8**	0.003	111±26	89±22	**19.3**	0.0049
3	76±15	71±4	7.2	0.565	76±13	66±8	13.9	0.093	71±12	63±9	10.9	0.14	69±13	67±13	2.4	0.906
Average	120±40	100±30	16.3	0.763	120±90	90±30	19.6	0.661	100±20	80±20	18.6	0.502	90±7	70±10	16.0	0.559

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Table A3. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of CH_4 emission by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

CH_4	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	47.4±5.6	23.1±12.5	**51.4**	0.0006	43.6±6.2	32.4±13	26.2	0.239	40±8	42.3±19	-5.7	0.894	36.5±9.8	46.2±18	-26.4	0.254
2	58.2±1.5	25.1±7.5	**56.8**	<0.0001	43±16.1	27.1±5.5	**36.7**	0.004	33.±17.1	63.1±84	-88.4	0.139	29.7±16	60.7±73	**-104.0**	0.03
3	20.5±1.9	9.9±1.7	**51.6**	0.001	21.6±4.3	13.2±5.6	**38.8**	0.044	19.9±4.1	24±18.4	-20.3	0.831	20.5±4.6	27±17.5	-31.7	0.476
Average	42.1±19.4	19.4±8.2	**53.9**	0.0001	36.1±12	24.2±9.8	**32.7**	0.004	31.1±10	43.1±19	-38.4	0.124	28.9±8	44±16.9	**-54.2**	0.005

CH_4	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	47.4±5.6	41.6±6.2	12.8	0.463	43.6±6.2	56.7±24	-30.0	0.146	40±8	53.9±19	**-34.6**	0.022	36.5±9.8	65±32.1	**-54.6**	<0.0001
2	58.2±1.5	49.6±12.8	14.7	0.227	43±16.1	46.5±9.5	-8.12	0.733	33.±17.1	45.2±9.3	-34.9	0.7275	29.7±16	43.8±8.8	-40.6	0.47
3	20.5±1.9	28.3±6.5	**-37.7**	0.012	21.6±4.3	34±12.3	**-57.3**	0.002	19.9±4.1	58±34.4	**-194**	<0.0001	20.5±4.6	56±30.5	**-221**	<0.0001
Average	42.1±19.4	39.8±10.7	5.4	0.866	36.1±12	45±11.3	**-26.8**	0.023	31.1±10	52.7±6.9	**-68.9**	0.001	28.9±8	55.2±10	**-82.2**	<0.0001

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Table A4. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of CO_2 emission by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

CO_2	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	2656±51	2662±211	-0.2	0.333	2382±304	2353±368	1.2	0.239	2149±366	2150±367	0.0	1.000	2031±395	2026±400	0.2	0.999
2	3578±129	2794±120	**21.9**	<0.0001	3069±538	2319±505	**24.4**	0.004	2443±845	1953±574	20.0	0.876	1845±544	1845±544	**16.5**	0.030
3	2135±179	1612±375	24.5	0.133	1931±250	1327±391	**31.2**	0.044	1799±261	1279±296	**28.8**	0.050	1295±262	1295±262	25.1	0.060
Average	2790±730	2356±647	15.5	0.106	2461±573	2000±582	**18.7**	0.029	2130±322	1794±456	**15.7**	0.028	1722±381	1722±381	**13.5**	0.045

CO_2	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	2656±51	3334±638	**-25.5**	0.031	2382±304	2737±795	-14.9	0.146	2149±366	2385±727	-11.0	0.304	2031±395	2225±707	1.7	0.361
2	3578±129	3079±721	13.9	0.899	3069±538	2561±748	16.5	0.873	2443±845	2282±654	**6.5**	0.003	1845±544	2161±637	0.0	0.470
3	2135±179	4575±641	**-114.2**	<0.0001	1931±250	3478±122	**-80.0**	0.002	1799±261	2899±114	**-61.1**	<0.0001	1295±262	2619±114	**-57.3**	<0.0001
Average	2790±730	3662±800	**-31.2**	0.001	2461±573	2926±486	**-18.9**	0.005	2130±322	2522±330	**-18.3**	0.007	1722±381	2335±247	**-14.9**	0.019

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Table A5. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of N_2O emission by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

N_2O	**First week**				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	0.18±0.03	0.17±0.04	5.5	0.913	0.29±0.29	0.28±0.14	4.9	0.966	0.34±0.12	0.33±0.12	2.7	0.967	0.33±0.11	0.31±0.11	3.6	0.919
2	0.25±0.03	0.22±0.04	11.1	0.457	0.457±0.24	0.21±0.03	11.2	0.244	0.29±0.09	0.27±0.09	7.8	0.699	0.31±0.09	0.29±0.09	6.9	0.669
3	0.29±0.02	0.27±0.03	6.9	0.394	0.39±0.37	0.40±0.25	-10.1	0.920	0.41±0.28	0.41±0.23	-1.0	0.998	0.40±0.21	0.41±0.20	-0.9	0.997
Average	0.24±0.05	0.22±0.04	8.0	0.506	0.50±0.30	0.3±0.09	0.4	0.999	0.35±0.05	0.34±0.07	2.7	0.942	0.94±0.35	0.34±0.06	2.8	0.906
N_2O	**First week**				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	0.18±0.03	0.18±0.04	0.9	0.997	0.29±0.29	0.28±0.14	3.0	0.987	0.34±0.12	0.34±0.12	1.2	0.990	0.33±0.11	0.32±0.11	-6.3	0.972
2	0.25±0.03	0.22±0.04	12.0	0.401	0.457±0.24	0.22±0.03	8.4	0.419	0.29±0.09	0.27±0.08	8.5	0.657	0.31±0.09	0.28±0.08	2.5	0.604
3	0.29±0.02	0.25±0.01	11.6	0.090	0.39±0.37	0.39±0.26	-6.2	0.969	0.41±0.28	0.35±0.21	12.9	0.730	0.40±0.21	0.35±0.19	45.7	0.653
Average	0.24±0.05	0.22±0.03	9.0	0.421	0.50±0.30	0.30±0.08	0.7	0.998	0.35±0.05	0.32±0.04	7.8	0.613	0.94±0.35	0.32±0.03	23.0	0.491

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Table A6. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of phenol peak area count (PAC) by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	4802±2687	6577±10188	-36.9	0.8958	3096±2704	3038±67	7.8	0.963	1931±2449	2187±5851	-13.2	0.978	1529±228	1726±5206	-12.8	0.979
2	225048±27790	22273±13357	**90.7**	0.0001	85878±93798	13028±13224	**84.8**	0.007	57453±82350	9729±11670	**83.0**	0.004	45522±75724	7471±9982	**93.5**	0.006
3	5945627±484360	924841±426999	**84.4**	<0.0001	4816035±1422588	659473±309769	**84.3**	<0.0001	3671990±1179829	574075±244483	**84.3**	<0.0001	3208962±1327083	506526±258627	**84.2**	<0.0001
Average	1985077±3429937	317897±52687	84.5	0.1164	1435003±2408800	225180±376142	**84.3**	0.002	1243792±2103065	195330±328024	**84.2**	<0.0001	1085338±189244	171908±289802	**84.1**	<0.0001
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	4802±2687	4262±5472	11.2	0.9898	3096±2704	2316±4219	25.2	0.929	1931±2449	1431±3300	25.9	0.9185	1529±228	1163±2940	59.9	0.9294
2	225048±27790	4930±1115	**97.2**	<0.0001	85878±93798	3557±1626	**95.8**	0.0023	57453±82350	2829±1505	**95.0**	0.0014	45522±75724	2615±1383	**83.1**	0.0017
3	5945627±484360	101725±58136	**98.2**	<0.0001	4816035±1422588	63835±42062	**98.4**	<0.0001	3671990±1179829	52269±38705	**98.5**	<0.0001	3208962±1327083	43198±37664	**99.0**	<0.0001
Average	1985077±3429937	36972±56078	**98.2**	0.0577	1435003±2408800	23236±35165	**98.3**	0.0004	1243792±2103065	18843±28956	**98.4**	<0.0001	1085338±189244	15658±23860	**98.9**	<0.0001

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Table A7. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of p-cresol peak area count (PAC) by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	11639±1612	3589±818	**69.1**	<0.0001	10734±6551	2081±1732	**20.6**	<0.0001	6652±6857	1526±1705	**77.0**	0.0005	5368±6502	1221±1605	**77.2**	0.0006
2	6727±789	3866±1923	**42.5**	0.002	7098±4179	2506±2013	**64.6**	0.0006	5149±5105	1848±1882	**64.0**	0.001	4110±4896	1399±1654	**65.9**	0.037
3	139281±21614	39257±12594	**71.8**	0.001	91941±40904	18369±20631	**80.0**	<0.0001	56768±46335	11792±15769	**79.2**	0.0001	4497±4562	9574±14132	**78.4**	0.0001
Average	52549±11793	15571±12842	**70.9**	0.021	36591±20552	7652±10830	**79.0**	0.001	22856±23314	5055±8069	**77.8**	0.0001	17958±22971	4065±7218	**77.9**	0.0001
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	11639±1612	1184±917	**89.8**	<0.0001	10734±6551	1210±1388	**88.7**	<0.0001	6652±6857	722±1180	**89.1**	0.0001	5368±6502	582±1069	**97.3**	0.0001
2	6727±789	599±125	**91.0**	<0.0001	7098±4179	462±181	**91.4**	<0.0001	5149±5105	379±171	**92.6**	<0.0001	4110±4896	344±169	**90.7**	<0.0001
3	139281±21614	7354±5506	**94.7**	0.0003	91941±40904	5324±3456	**94.2**	<0.0001	56768±46335	3603±3004	**93.6**	<0.0001	4497±4562	2871±2895	**96.7**	<0.0001
Average	52549±11793	3046±2905	94.2	0.665	36591±20552	2332±1656	**93.6**	0.0001	22856±23314	1568±14437	**93.1**	<0.0001	17958±22971	1266±1388	**96.6**	<0.0001

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Table A8. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of skatole peak area count (PAC) by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance (p<0.05). A negative value of '% reduction' signifies generation.

	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	**Control**	**RO**	% R	**p-value**	**Control**	**RO**	% R	**p-value**	**Control**	**RO**	% R	**p-value**	**Control**	**RO**	% R	**p-value**
1	258691±87296	77776±94049	**69.9**	0.002	187296±119432	43818±68637	**76.6**	0.001	112145±125568	31449±60821	**71.9**	0.006	88461±119052	24577±54929	**72.2**	0.0084
2	126649±5394	50591±25213	**60.0**	<0.0001	112371±42247	42260±29318	**62.3**	<0.0001	85076±56173	32466±28654	**61.8**	<0.0001	67227±59889	23192±26774	**65.5**	0.0002
3	501842±16610	223403±136913	**55.4**	0.012	289655±171858	213507±259337	26.7	0.6617	208461±149958	147290±193064	29.3	0.403	180701±139763	129039±170721	28.5	0.345
Average	295701±190314	117257±92924	**60.3**	0.0004	195774±87949	99862±98422	**48.9**	0.0009	135227±64850	70402±66588	**47.9**	0.001	112130±60326	58936±60715	**47.3**	0.0376
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	258691±87296	26806±24166	**89.6**	0.0002	187296±119432	23150±28264	**87.6**	0.0001	112145±125568	13750±23751	**87.7**	0.0007	88461±119052	10793±21581	**94.8**	0.001
2	126649±5394	7972±3226	**93.7**	<0.0001	112371±42247	6102±3269	**94.5**	<0.0001	85076±56173	8939±13887	**89.4**	<0.0001	67227±59889	7321±12567	**74.4**	<0.0001
3	501842±16610	48571±16772	**90.3**	0.001	289655±171858	25657±20954	**91.0**	0.0135	208461±149958	19556±17013	**90.6**	0.0006	180701±139763	18409±16070	**93.0**	0.0001
Average	295701±190314	27783±20317	**90.6**	<0.0001	195774±87949	18303±10640	**90.6**	<0.0001	135227±64850	14082±5319	**89.5**	<0.0001	112130±60326	12174±5671	**92.7**	<0.0001

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Table A9. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of indole peak area count (PAC) by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance (p<0.05). A negative value of '% reduction' signifies generation.

	First week				First 2 weeks				First 3 weeks				Over the trial			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	365±307	613±1134	-68.0	0.804	282±262	277±736	1.9	0.959	177±232	200±628	-12.7	0.980	142±214	158±556	-11.2	0.984
2	1946±166	599±257	**69.1**	<0.0001	2143±1133	681±574	**68.2**	0.0001	1972±514	514±522	**73.9**	0.0003	1188±1263	394±457	**66.8**	0.001
3	3064±275	1958±462	**36.0**	0.014	17644±23663	2164±1851	87.7	0.062	9070±18475	1314±1543	85.5	0.086	6946±16323	1145±1361	83.5	0.092
Average	191±1356	1057±780	**40.9**	0.045	6690±9532	1041±993	84.4	0.052	4702±676	676±574	**81.9**	0.0495	2758±3663	565±515	79.4	0.052
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	4802±2687	41±45	88.7	0.692	3096±2704	54±56	80.9	0.054	1931±2449	34±47	80.5	0.460	1529±228	29±43	94.1	0.455
2	225048±27790	192±69	**90.0**	<0.0001	85878±93798	175±59	**91.7**	<0.0001	57453±82350	152±91	**92.2**	<0.0001	45522±75724	129±97	**92.4**	<0.0001
3	5945627±484360	625±168	**79.5**	0.0002	4816035±1422588	1211±1142	**93.7**	0.045	3671990±1179829	742±922	91.8	0.060	3208962±1327083	696±804	28.5	0.064
Average	1985077±3429937	286±303	**84.0**	0.0002	1435003±2408800	480±635	**92.8**	0.026	1243792±2103065	310±379	**91.7**	0.022	1085338±189244	284±359	**73.2**	0.023

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Table A10. Biochar (top table: RO; bottom table: HAP) effect on mitigation of isobutyric acid peak area count (PAC) by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). Negative value of '% reduction' signifies generation.

	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	526±265	846±571	-60.8	0.350	559±475	425±507	23.8	0.981	338±439	311±463	8.1	0.972	272±405	248±424	8.5	0.969
2	429±42	589±167	-37.2	0.171	7411±76	461±179	-12.0	0.852	443±145	394±184	11.1	0.571	432±139	355±165	17.8	0.328
3	639±207	519±187	18.8	0.683	613±129	409±129	**33.3**	0.002	563±127	405±101	**28.0**	0.0001	522±142	385±102	**26.2**	0.0002
Average	531±105	651±172	-22.5	0.262	104±432	432±26	18.1	0.788	448±112	370±51	17.4	0.267	409±126	329±71	19.3	0.171
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	526±265	359±230	31.7	0.739	559±475	334±268	40.1	0.426	338±439	205±251	39.1	0.527	272±405	171±230	87.5	0.569
2	429±42	396±95	7.50	0.586	7411±76	592±338	-44.0	0.136	443±145	472±291	-6.4	0.902	432±139	436±266	8.0	0.997
3	639±207	338±99	47.0	0.160	613±129	416±83	**32.1**	0.003	563±127	432±77	**23.1**	0.001	522±142	413±80	**46.9**	0.003
Average	531±105	364±29	31.3	0.266	104±432	447±131	15.1	0.627	448±112	370±143	17.4	0.310	409±126	340±146	61.2	0.263

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Table A11. Biochar (top table: RO; bottom table: HAP) effect on the mitigation of odor concentration by weeks. The mitigation effect is expressed as the % reduction (% R) defined the relative difference between control & treatment. **Bold** signifies statistical significance ($p<0.05$). A negative value of '% reduction' signifies generation.

	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value	Control	RO	% R	p-value
1	265±225	300±47	-13.2	0.216	357±118	296±38	17.1	0.151	385±113	311±46	**19.1**	0.008	386±112	320±50	**17.1**	0.025
2	286±50	213±22	25.3	0.096	418±201	357±174	14.6	0.645	375±166	301±162	19.8	0.507	365±157	287±142	21.3	0.287
3	327±66	257±28	**21.5**	0.042	270±76	219±47	18.8	0.148	312±165	212±78	31.9	0.188	314±155	218±76	30.2	0.139
Average	293±31	257±43	12.3	0.121	348±74	290±69	16.6	0.121	357±39	275±54	23.1	0.565	355±37	275±51	**22.4**	0.008
	First week				**First 2 weeks**				**First 3 weeks**				**Over the trial**			
Trial #	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value	Control	HAP	% R	p-value
1	265±225	268±26	-1.3	0.983	357±118	304±68	14.9	0.259	385±113	328±78	**14.6**	0.037	320±50	338±83	-31.1	0.143
2	286±50	270±28	5.6	0.798	418±201	345±113	17.3	0.543	375±166	421±235	-12.1	0.613	287±142	412±221	-11.6	0.633
3	327±66	186±31	**43.1**	0.0002	270±76	239±67	11.4	0.480	312±165	349±255	-11.8	0.732	218±76	336±241	-59.3	0.895
Average	293±31	241±47	**17.5**	0.019	348±74	296±53	**15.0**	0.019	357±39	366±48	-2.4	0.919	275±51	362±43	-29.6	0.799

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