Can Biochar Save Lives? The Impact of Surficial Biochar Treatment on Acute H_2S and NH_3 Emissions During Swine Manure Agitation Before Pump-out

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Abstract: Hydrogen sulfide and ammonia are always a concern in the livestock industries, especially when farmers try to clear their manure storage pits. Agitation of manure can cause dangerously high concentrations of harmful agents such as H_2S and NH_3 to be emitted into the air. Biochar has the ability to sorb these gases. We hypothesized that applying biochar on top of manure can create an effective barrier to protect farmers and animals from exposure to NH_3 and H_2S. In this study, two kinds of biochar were tested, highly alkaline, and porous (HAP, pH 9.2) biochar made from corn stover and red oak biochar (RO, pH 7.5). Two scenarios of (6 mm) 0.25″ and (12 mm) 0.5″ thick layers of biochar treatments were topically applied to the manure and tested on a pilot-scale setup, simulating a deep pit storage. Each setup experienced 3-min of agitation using a transfer pump, and measurements of the concentrations of NH_3 and H_2S were taken in real-time and measured until the concentration stabilized after the sharp increase in concentration due to agitation. The results were compared with the control in the following 3 situations: 1. The maximum (peak) flux 2. Total emission from the start of agitation until the concentration stabilized, and 3. The total emission during the 3 min of agitation. For NH_3, 0.5″ HAP biochar treatment significantly ($p<0.05$) reduced maximum flux by 63.3%, overall total emission by 70%, and total emissions during the 3-min agitation by 85.2%; 0.25″ HAP biochar treatment significantly ($p<0.05$) reduced maximum flux by 75.7%, overall, total emission by 74.5%, and total emissions during the 3-min agitation by 77.8%. 0.5″ RO biochar treatment significantly reduced max by 8.8%, overall total emission by 52.9%, and total emission during 3-min agitation by 56.8%; 0.25″ RO biochar treatment significantly reduced max by 61.3%, overall total emission by 86.1%, and total emission during 3-min agitation by 62.7%. For H_2S, 0.5″ HAP biochar treatment reduced the max by 42.5% ($p=0.125$), overall total emission by 17.9% ($p=0.290$), and significantly reduced the total emission during 3-min agitation by 70.4%; 0.25″ HAP treatment reduced max by 60.6% ($p=0.058$), and significantly reduced overall and 3-min agitation's total emission by 64.4% and 66.6%, respectively. 0.5″ RO biochar treatment reduce the max flux by 23.6% ($p=0.145$), and significantly reduced overall and 3-min total emission by 39.3% and 62.4%, respectively; 0.25″ RO treatment significantly reduced the max flux by 63%, overall total emission by 84.7%, and total emission during 3-min agitation by 67.4%.

Keywords: biochar; hydrogen sulfide; ammonia; livestock manure; agricultural safety; deep pit storage; waste management; air pollution; odor.

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1. Introduction

Hydrogen sulfide (H_2S) and ammonia (NH_3) have always been a severe concern in livestock industries. These gases can be harmful to both humans and livestock, sometimes deadly. The Occupational Safety and Health Administration gives the acceptable ceiling concentration for H_2S as 20 ppm and an acceptable maximum peak above the acceptable ceiling concentration as 50 ppm, with a maximum duration of 10 min [1]. Although there is no reliable quantitative exposure data available for human fatality due to NH_3, people feel unbearable irritation when exposed for 30 min to 2 h at 140 ppm [2]. In the mid-western United States, most swine buildings use deep-pits to store tons of manure. When a pit is full, farmers pump out most of the manure to fertilize their fields. This routine seasonal operation can sometimes be very dangerous. Agitating the manure can break the entrapped gas bubbles, which cause a tremendous increase in the concentration of H_2S and NH_3 (Figure 1) [3]. Fatal accidents have been recorded involving a high concentration of H_2S due to the agitation of manure in the past several years [4-7].

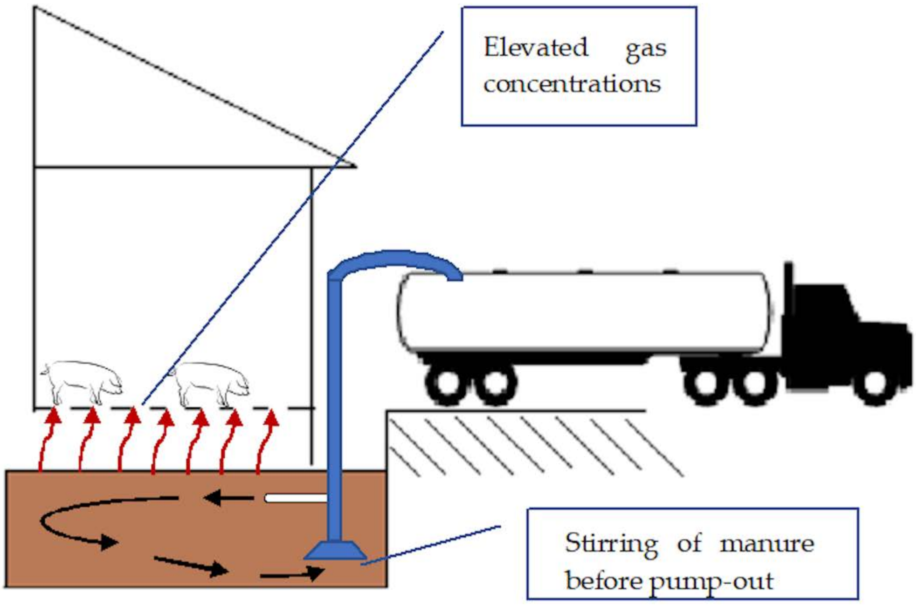

Figure 1. Schematic of the agitation process before seasonal manure pump-out from deep-pit storage under swine barn with a slatted floor. Fatal accidents are known to occur to people and livestock due to dangerous acute release of entrapped gases (e.g., H_2S) from stored manure during agitation.

Manure additives of microbial mode of operation are used by swine farmer to control gaseous emissions. Still, science-based guides as well as more data are needed to evaluate manure additive effectiveness on the mitigation of gases emitted from storage [8]. From recent studies, manure additives such as soybean peroxidase, zeolite, and biochar show the effectiveness of mitigating NH_3, H_2S, VOCs, and GHG emissions from swine manure [9-14]. Additionally, in our recent research, we evaluated numerous commercial manure additives for gaseous emissions mitigation, but there are no statistically significant findings [15].

In this study, non-active biochar was tested since we observed temporal effects of biochar addition to water [16] and manure surface [17, 18]. The mitigation effects on NH_3 and H_2S were

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typically the greatest on the first day of application and decreased over the duration of the trial [18]. This led us to explore the possibility of using surficial biochar treatment for *short-term* mitigation of NH_3 and especially H_2S emissions from swine manure.

Biochar is a very stable and lightweight solid, often used as a soil amendment or an alternative source of fuel, but can also be used as a suitable adsorbent [19-21]. It can be made from many kinds of inexpensive biomass and waste through pyrolysis with none or a low oxygen level [19-25]. With different temperature and time of the process, the resulting biochar will have different physical and chemical properties [20-24]. By using the desired chemical and physical properties, it has excellent research potential to benefit our society. Additionally, due to its low specific density, biochar can float on top of swine manure and create a physical barrier.

The first research question arose: what biochar barrier thickness should be applied. We hypothesized that the increase of the biochar cover barrier thickness would increase the H_2S and NH_3 emission rates. The next question which came from the typical technological procedure (Figure 1) is how the agitation of manure with biochar will influence the H_2S and NH_3 emission rates? We hypothesized that manure agitation with biochar would decrease the H_2S and NH_3 post-agitation emission rates in relation to pre-agitation.

2. Experiments

2.1. Materials

Fresh manure was collected from the local deep-pit swine farms in central Iowa. They have been stored for 3 months. The manure used with high alkaline porous (HAP) biochar and red oak (RO) biochar is from the same location, but manure for use in RO treatment was collected in summer, whereas manure used in HAP biochar collected in winter. Thus, the concentrations for control groups were different. For the simulation of deep pit performance, the manure storage simulators had a height of 4′ (1.22 m) and a diameter of 15″ (0.38 m). The working volume of the manure of each lysimeter was 103.1 L, while the headspace was ventilated with a 7.5 air exchanges per hour (ACH), which is the typically recommended value for deep-pit manure storage [12, 26]. A simple transfer pump with 1/10 horsepower (hp) and a maximum flowrate of 360 gal h^{-1} (~1.36 m^3 h^{-1}) (Little Giant, Mexico) was used to agitate the manure (Figure 2).

Red oak biochar used in this study was made from red oak and pyrolyzed at 500 to 550°C. It had a pH of 7.5; 6.75 zero-point charge; contained 78.53% dry matter (d.m). of C; 2.54% d.m. of H; 0.62% d.m. of N; 26.38% d.m. of volatile solids; 54.76% d.m. fixed C; 15.83% d.m. ash [16-18]. The HAP biochar was made from corn stover and pyrolyzed at 500°C. This biochar had a pH of 9.2; 8.42 zero-point charge; contained 61.37% d.m. of C; 2.88% d.m. of H; 1.21% d.m. of N; 16.27% d.m. of volatile solids; 34.98% d.m. fixed C; 46.82% d.m. ash [16-18].

OMS-300 analyzer (Smart Control & Sensing Inc., Daejeon, Rep. of Korea) was used to measure the real-time concentration for both NH_3 and H_2S [26]. OMS-300 is the real-time monitoring system equipped with electrochemical gas sensors (NH_3/CR-1000 and H_2S/C-50). OMS-300 was calibrated with standard gases before using, and from which a calibration curve was created [27, 28].

2.2. Methods

This pilot-scale setup was designed to simulate deep pit swine manure storage while manure is being agitated, as shown in Figure 2. The inlet of the pump is connected to the bottom manure sampling port; the outlet is connected to the middle manure sampling port, as shown in Figure 2. In the process of agitation, the manure flowed from the bottom to the middle zone at a constant rate for 3 min. The air flowrate was controlled at 7.5 ACH via rotameters and valves. There were two types of biochar with three scenarios per biochar and each with triplicate results:

- Manure not treated with biochar – control variant
- Manure treated with 0.25″ (~6 mm) thick layer of biochar
- Manure treated with 0.5″ (~12 mm) thick layer of biochar

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Thus, two trials of experiments were conducted in the different days. In the first trial, both 0.5″ and 0.25″ treatments of RO biochar and the control were conducted on the same days. The HAP treatments and their control were also conducted on the same days. All analysis and reductions were done by comparing to the control done on the same days. All thicknesses were measured from the surface of the 103.1 L of manure. Biochar was spread evenly across the surface of the manure. The measurements were taken during the following stages of the procedure:

- Stage 1 - post-application of the biochar and pre-agitation emission, (it is represented by measurements in all 3 variants after biochar application but before the agitation; in case of the control variant the same values were used as in stage 1),
- Stage 2 - agitation (it is represented by measurements in all 3 variants during agitation),
- Stage 3 – post-agitation (it is represented by measurements in all 3 variants after agitation stopped).

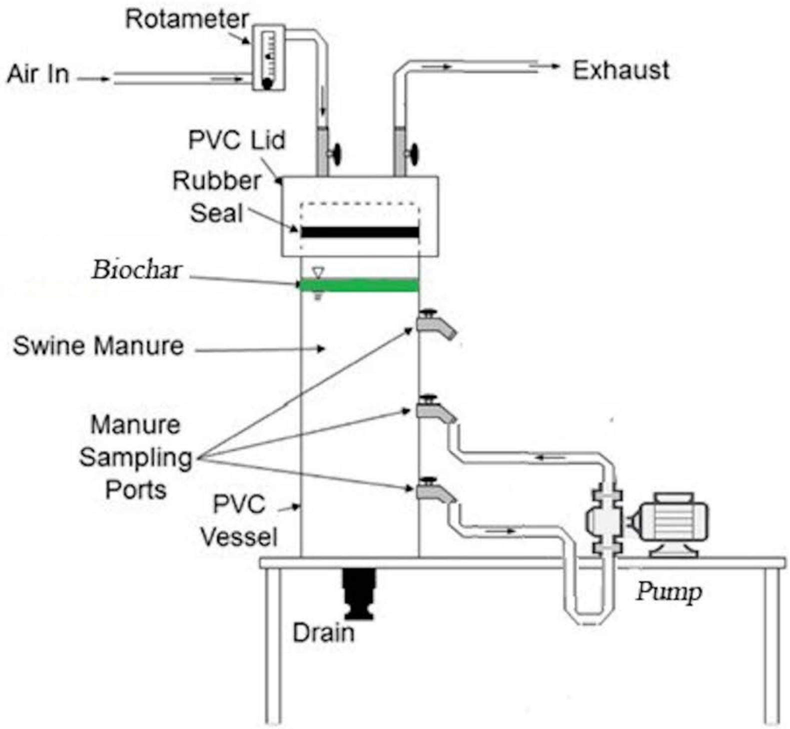

Figure 2. Pilot-scale design for simulating deep pit manure storage treated surficially with a thin layer of biochar prior to agitating.

H_2S and NH_3 concentrations were measured from the headspace before and immediately after applying biochar. When the concentrations of both gases were stable, the pump would begin to agitate the manure for 3 min at a constant rate of 360 GPH. Real-time concentration measurements stopped when the concentrations for both gases reset to their initial concentrations before the agitation process started.

3. Results

3.1. Post-application of the biochar and pre-agitation gaseous emissions

Immediately after applying RO biochar, both scenarios showed a significant reduction in emissions. The 0.5″ biochar treatment reduced the concentration of H_2S by 68.3% and by 56.8% for NH_3; the 0.25″ biochar treatment reduced about 65.1% of H_2S and 78.9% of NH_3 (Table 1).

Table 1. Concentration after applying RO biochar to manure surface and before manure agitation.

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		RO biochar	
Condition	**Control**	**0.5" biochar**	**0.25" biochar**
Pre-agitation H_2S (mg/m²/s)	0.00181± 0.000503	0.000782 ± 0.000388	0.000632 ± 0.000154
Pre-agitation NH_3 (mg/m²/s)	0.0867 ± 0.0128	0.0275 ± 0.00569	0.0183 ± 0.00659

Once the HAP biochar was applied, the 0.5″ biochar treatment immediately reduced the concentration of H_2S by about 99% and by 93% for NH_3; the 0.25″ biochar treatment reduced emissions by nearly 100% for H_2S and by 90.6% for NH_3 (Table 2).

Table 2. Concentration after applying HAP biochar to manure and before manure agitation.

		HAP biochar	
Condition	**Control**	**0.5" biochar**	**0.25" biochar**
Pre-agitation H_2S (mg/m²/s)	0.0146 ± 0.0206	0.00014 ± 0.00011	0
Pre-agitation NH_3 (mg/m²/s)	0.0597 ± 0.0248	0.00419 ± 0.00528	0.00563 ± 0.00787

3.2. Influence of the agitation on the biochar applied surficially to manure

After the agitation process, most of the biochar was still floating on the top of the manure. Some of the biochar was wetted and mixed with manure (as circled in Figure 3). The treatments with 0.5″ thickness of biochar were wetter and mixed more readily with manure than those treated with 0.25″ biochar. Patches of open (uncovered) manure were more prelevant to higher biochar dose.

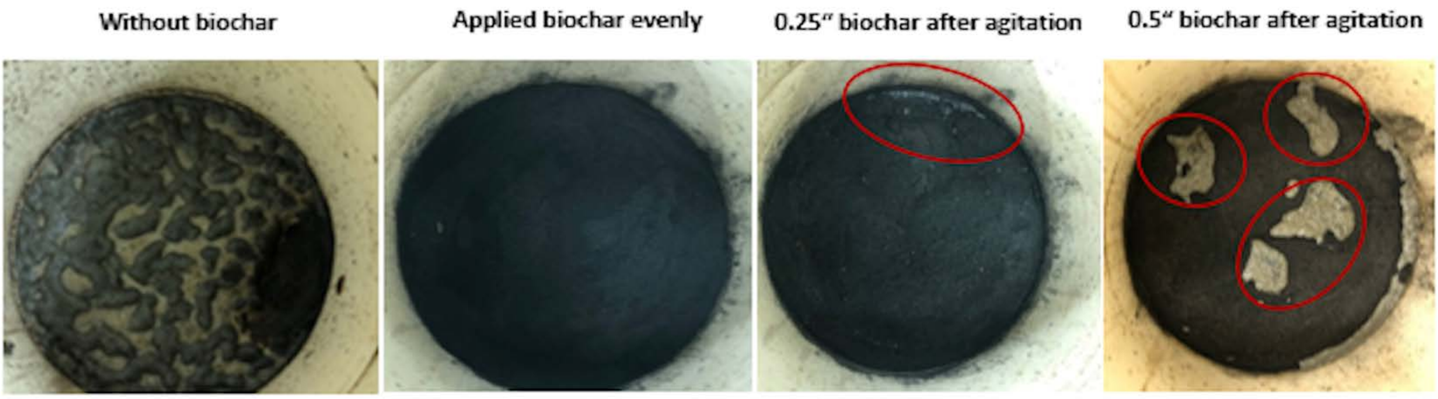

Figure 3. Swine manure without any treatment (left), HAP biochar evenly spread on top of the swine manure (center left), 0.25″ thick HAP biochar layer after agitation (center right), and 0.5″ thick HAP biochar layer after agitation (right). Patches of open (uncovered) manure (red circles) were more prelevant to higher biochar dose.

3.3. Agitation emission

During the 3-min agitation, the 0.5″ RO biochar treatment showed a significant reduction in the maximum concentration of NH_3, but not for H_2S with 8.8% and 23.6% reduction, respectively. The 0.25″ RO biochar treatment had much higher % reductions for maximum concentrations of both gases, significantly reducing NH_3 by 61.3%, and reducing H_2S by 63% ($p = 0.0511$). During the 3-min agitation process, the 0.25″ RO biochar treatment significantly reduced the total emission of NH_3 concentration by 56.8% and reduced the total emission of H_2S by 62.4%; for the 0.5″ RO biochar treatment, the total emission of NH_3 was reduced by 62.7%, and H_2S concentration was reduced by 67.4% (Table 3).

Table 3. The mean of total emission and maximum concentration with its standard deviation for RO biochar treatment during the 3 min of agitation process. Percent reduction is significant when P < 0.05.

	RO biochar during the 3 min of agitation					
	Control		**0.5" Biochar**		**0.25" Biochar**	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Maximum concentrations while agitating (mg/m²/s)	0.402±0.00956	0.0504 ± 0.00078	0.367±0.0141	0.0385 ± 0.0138	0.156±0.0287	0.0186 ± 0.00977
%Reduction of max	-	-	8.8 (P = 0.02137)	23.6 (P = 0.145)	61.3 (P = 0.00016)	63.0 (P = 0.0511)
Total emission of 3 min, (mg/m²)	64.4±2.93	7.18 ± 0.644	27.8±5.53	2.7 ± 0.698	24.0±1.54	2.34 ± 0.472
% Reduction of total emission	-	-	56.8 (P < 0.0001)	62.4 (P < 0.0001)	62.7 (P < 0.0001)	67.4 (P < 0.0001)

The 0.5″ HAP biochar treatment showed a statistically significant reduction in the maximum concentration of NH_3 by 63.3%, but a not statistically significant reduction for H_2S at 42.5%. The 0.25″ HAP biochar treatment also had higher maximum concentration reductions for both gases, significantly reducing NH_3 by 75.7%, and H_2S by 60.6% (p = 0.0580). During the 3 min of agitation, the 0.25″ HAP biochar treatment significantly reduced the total emission of NH_3 concentration by 85.2% and reduced the total emission of H_2S by 70.4%; for the 0.5″ HAP biochar treatment, the total emission of NH_3 was reduced by 77.8%, and H_2S was reduced by 66.6% (Table 4).

Table 4. The mean of total emission and maximum concentration for HAP biochar treatments with its standard deviation during the 3 min of agitation process. Percent reduction is statistically significant when P < 0.05.

	HAP biochar during the 3 min of agitation					
	Control		**0.5" Biochar**		**0.25" Biochar**	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Maximum concentrations while agitating (mg/m²/s)	0.297±0.110	0.455 ± 0.0192	0.109±0.0494	0.0261 ± 0.00665	0.0476±0.0485	0.0179 ± 0.00321
%Reduction of max	-	-	63.3 (P = 0.04642)	42.5 (P = 0.1249)	75.7 (P = 0.02154)	60.6 (P = 0.05804)
Total emission of 3 min, (mg/m²)	44.6±7.32	6.36 ± 1.23	6.61±3.21	1.88 ± 0.625	6.01±3.18	2.12 ± 0.433

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% Reduction of total emission	-	-	85.2 ($P < 0.0001$)	70.4 ($P < 0.0001$)	77.8 ($P < 0.0001$)	66.6 ($P < 0.0001$)

3.4. Post-agitation gaseous emissions

For both scenarios treated by HAP and RO biochar, once the agitation stopped, the concentrations of H_2S and NH_3 started to decrease immediately. Comparatively, the control group tested alongside with RO biochar, had the concentration of H_2S reaching the maximum concentration for about 5 ~ 10 min before dropping, and NH_3 was elevated for about 20 to 30 min as shown in Figures A1 and A2. This is because the concentrations exceeded the limitations of sensors for both gases. After 3 min of agitation, the concentrations for both gases were recorded until the concentration was stable or close to the concentration before agitation. Within this period of time, the 0.25″ RO biochar treatment significantly reduced total emissions in H_2S by about 84.7% and NH_3 by about 86.1%; the 0.5″ RO biochar treatment significantly reduced 52.9% of the total NH_3 emission and 39.3% of the total H_2S emission (Table 5).

Table 5. Total emissions and percent reduction treated with RO biochar after the agitation.

	Post-agitation using RO biochar					
	Control		**0.5" Biochar**		**0.25" Biochar**	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Period of Time (min)	48	36	48	36	48	36
Average emission (mg/m²/min)	19.8 ± 0.157	1.37 ± 0.175	9.35 ± 0.221	0.831 ± 0.0483	1123 ± 210	0.209 ± 0.00174
Total emission for the time spend (mg/m²)	952 ± 7.52	49.2 ± 2.63	449 ± 10.6	29.9 ± 1.74	132 ± 3.13	7.52 ± 0.627
% Reduction of total emission	-	-	52.9 ($P < 0.0001$)	39.3 ($P < 0.0001$)	86.1 ($P < 0.0001$)	84.7 ($P < 0.0001$)

For HAP biochar treatments, the 0.25″ biochar treatment significantly reduced total emissions of H_2S by about 64.4% and of NH_3 by about 74.5%; the 0.5″ biochar treatment significantly reduced 70% of total NH_3 emission, but statistically insignificantly reduced 17.9% of the total H_2S emissions (Table 6).

Table 6. Total emissions and percent reduction of using HAP biochar after the agitation.

	Post-agitation using HAP biochar					
	Control		**0.5" Biochar**		**0.25" Biochar**	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Period of Time (min)	29.5	14	29.5	14	29.5	14
Average emission (mg/m²/min)	6.95 ± 0.335	1.00 ± 0.134	2.08 ± 0.195	0.821 ± 0.0936	1.08 ± 0.170	0.356 ± 0.0379
Total emission for the time spend (mg/m²)	205 ± 9.88	14.0 ± 1.88	61.3 ± 5.76	11.5 ± 1.31	31.8 ± 5.01	4.99 ± 0.531

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% Reduction of total emission	-	-	70.0 ($P < 0.0001$)	17.9 ($P = 0.2897$)	74.5 ($P < 0.0001$)	64.4 ($P < 0.0001$)

3.5. Statistical Analysis

The One-way ANOVA and Tukey-Kramer Method in JMP software (version Pro 14, SAS Institute, Inc., Cary, NC, USA) were used to analyze the data to determine the P-values of total emissions for both overall and 3-min. The maximum levels of concentrations were used for a pooled T-test to calculate the p values. A P-value of less than 0.05 determines statistically significant.

4. Discussion

This study is a proof of concept these treatments with biochar has a possible potential to save people and livestock lives during routine seasonal manure stirring, pump-out, and land application. In this study, we showed that biochar applied surficially to manure can be effective for short-term mitigation of toxic gaseous emissions released during and shortly after agitation. Biochar could float on top of the manure, helping to stop or absorb the gaseous emissions being released. With the optimal amount of biochar, it could become an effective adsorbent 'barrier' to protect farmers and livestock from these harmful gases emitted from manure.

Surprisingly, the 0.25" treatment was a more effective dosage since the percent reduction was slightly higher while using less biochar. The smaller amount of biochar being used could be critical, not only because it is more economical. When the biochar is wetted, it forms 'chunks.' With manure is being agitated, the bigger chunks of biochar in 0.5" treatments started to sink and mix with manure. Once the physical barrier on the surface was broken, the maximum concentration of the treatment began to rise and be closer to the control. However, for both treatments, biochar was effective in reducing the overall total emissions for both NH_3 and H_2S.

In future research, other kinds of biochar could be tested for their efficacy to mitigate gaseous emissions from manure. Additionally, farm-scale research is also required for the proof-of-the-concept. With larger farm-scale trials, researchers should be thinking about how and where the biochar should be practically applied in order to create an effective short-term barrier so as to maximize the benefit of biochar treatment. Application of powdery, light material might not be feasible in farm conditions. Pelletized biochar could be a more practical and safe mode of application.

Comparing the two types of biochar, HAP biochar was more efficient in mitigating the NH_3 emissions, likely due to it being more porous, and the control group for RO treatment exceeded the limitations of sensors. For H_2S, treatment with both types of biochar resulted in a considerable % reduction. Although some of the reduction was statistically insignificant, it might be because the H_2S concentrations in the control group in HAP biochar was not high.

Author Contributions: conceptualization, J.K and B.C.; methodology, B.C. and J.K.; software, B.C.; validation, J.K.; formal analysis, B.C.; investigation, B.C., M.L., H.M., P.L. and Z.M.; resources, J.K. and R.B.; data curation, B.C., J.K.; writing—original draft preparation, B.C.; writing—review and editing, J.K. and A.B.; visualization, B.C., H.M.; supervision, J.K.; project administration, J.K. and R.B.; funding acquisition, J.K. and R.B.

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Appendix A

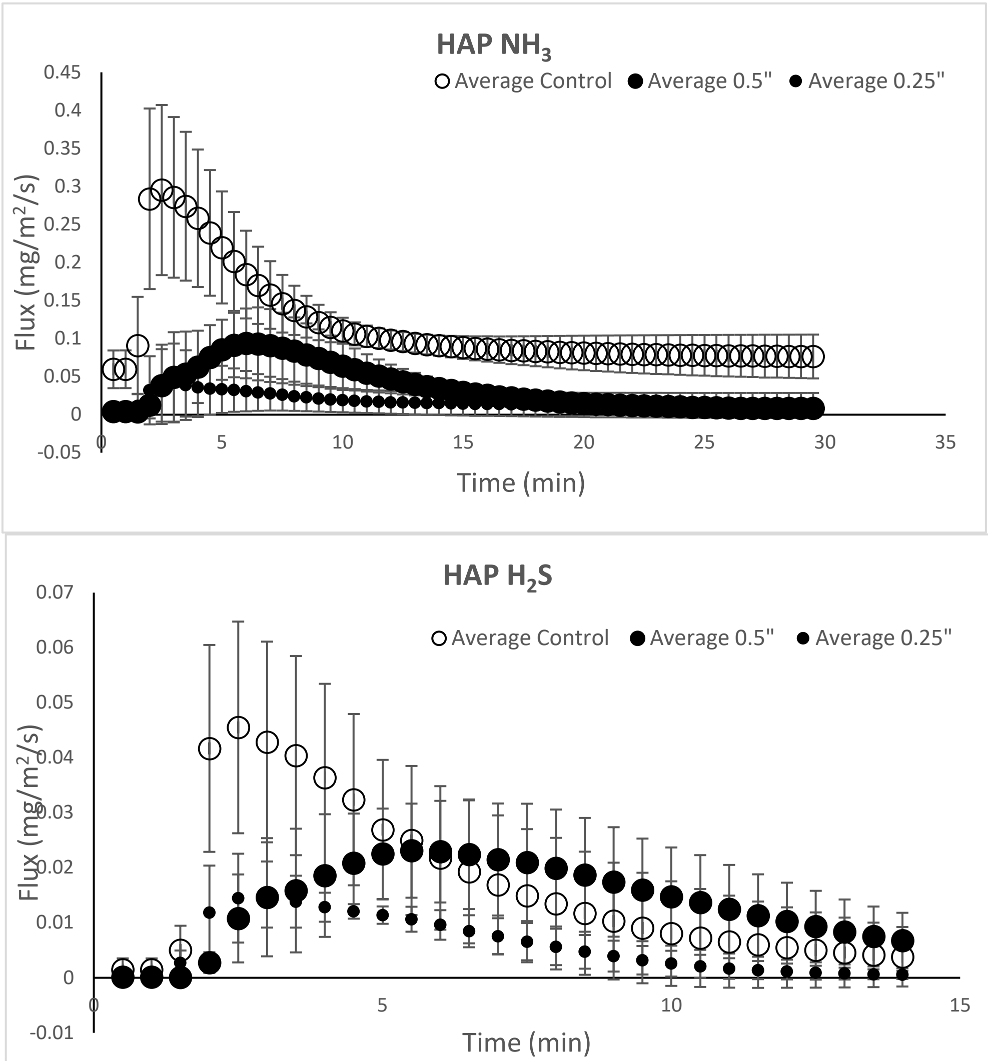

Figure A1. The short-term NH_3 and H_2S emissions when manure is treated surficially with HAP biochar layer at two thicknesses (0.25 inches, ~6 mm; 0.5 inches, ~12 mm) immediately prior to 3-min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

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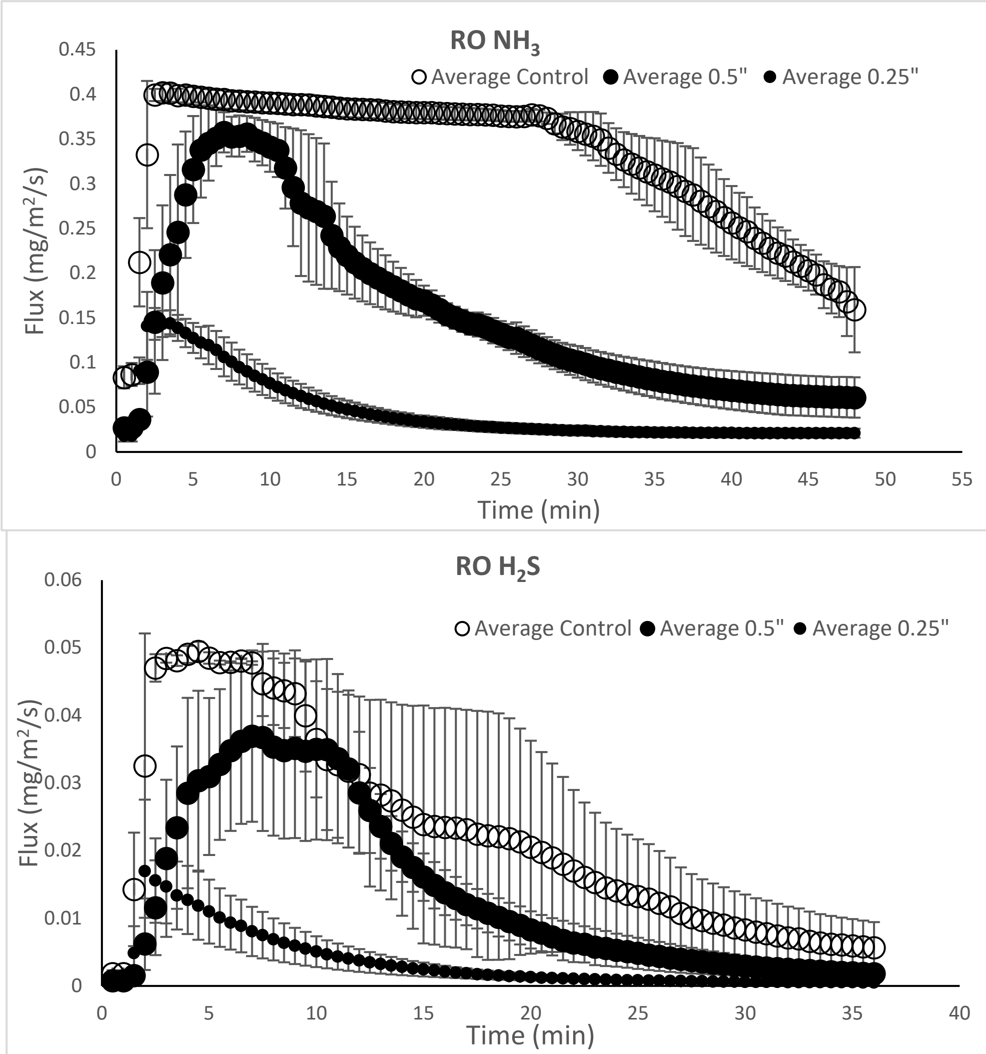

Figure A2. The short-term NH_3 and H_2S emissions when manure is treated surficially with RO biochar layer at two thicknesses (0.25 inches, ~6 mm; 0.5 inches, ~12 mm) immediately prior to 3-min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

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