

Can Biochar Save Lives? The Impact of Surficial Biochar Treatment on Acute H₂S and NH₃ Emissions During Swine Manure Agitation Before Pump-out

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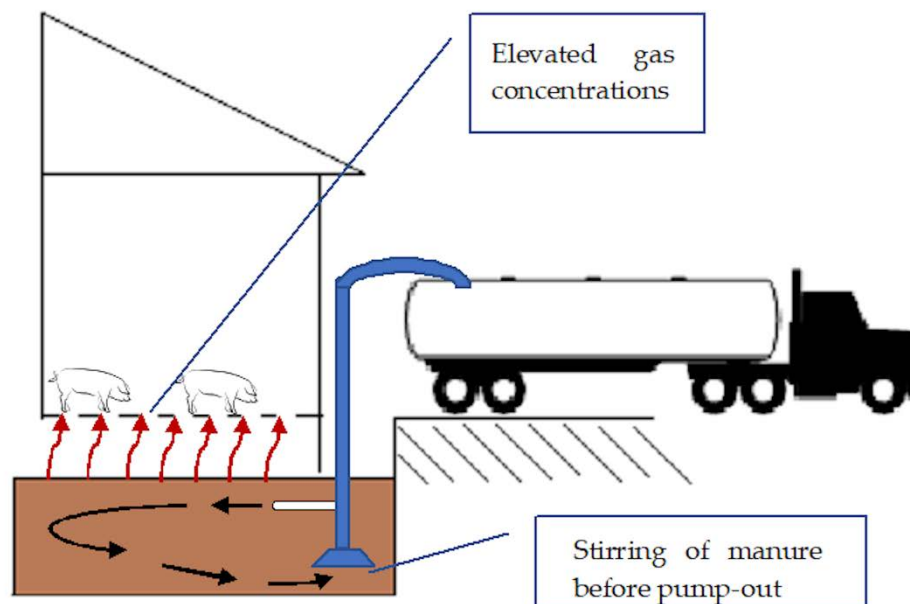
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Abstract: Hydrogen sulfide and ammonia are always a concern in the livestock industries, especially when farmers try to clear their manure storage pits. Agitation of manure can cause dangerously high concentrations of harmful agents such as H₂S and NH₃ 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 NH₃ and H₂S. 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 NH₃ and H₂S 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 NH₃, 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 H₂S, 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.

48 1. Introduction

49 Hydrogen sulfide (H_2S) and ammonia (NH_3) have always been a severe concern in livestock
50 industries. These gases can be harmful to both humans and livestock, sometimes deadly. The
51 Occupational Safety and Health Administration gives the acceptable ceiling concentration for H_2S as
52 20 ppm and an acceptable maximum peak above the acceptable ceiling concentration as 50 ppm, with
53 a maximum duration of 10 min [1]. Although there is no reliable quantitative exposure data available
54 for human fatality due to NH_3 , people feel unbearable irritation when exposed for 30 min to 2 h at
55 140 ppm [2]. In the mid-western United States, most swine buildings use deep-pits to store tons of
56 manure. When a pit is full, farmers pump out most of the manure to fertilize their fields. This routine
57 seasonal operation can sometimes be very dangerous. Agitating the manure can break the entrapped
58 gas bubbles, which cause a tremendous increase in the concentration of H_2S and NH_3 (Figure 1) [3].
59 Fatal accidents have been recorded involving a high concentration of H_2S due to the agitation of
60 manure in the past several years [4-7].



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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.

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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

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

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

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

91 2. Experiments

92 2.1. Materials

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

103 Red oak biochar used in this study was made from red oak and pyrolyzed at 500 to 550°C. It had
104 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%
105 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
106 biochar was made from corn stover and pyrolyzed at 500°C. This biochar had a pH of 9.2; 8.42 zero-
107 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
108 solids; 34.98% d.m. fixed C; 46.82% d.m. ash [16-18].

109 OMS-300 analyzer (Smart Control & Sensing Inc., Daejeon, Rep. of Korea) was used to measure
110 the real-time concentration for both NH_3 and H_2S [26]. OMS-300 is the real-time monitoring system
111 equipped with electrochemical gas sensors ($\text{NH}_3/\text{CR}-1000$ and $\text{H}_2\text{S}/\text{C}-50$). OMS-300 was calibrated
112 with standard gases before using, and from which a calibration curve was created [27, 28].

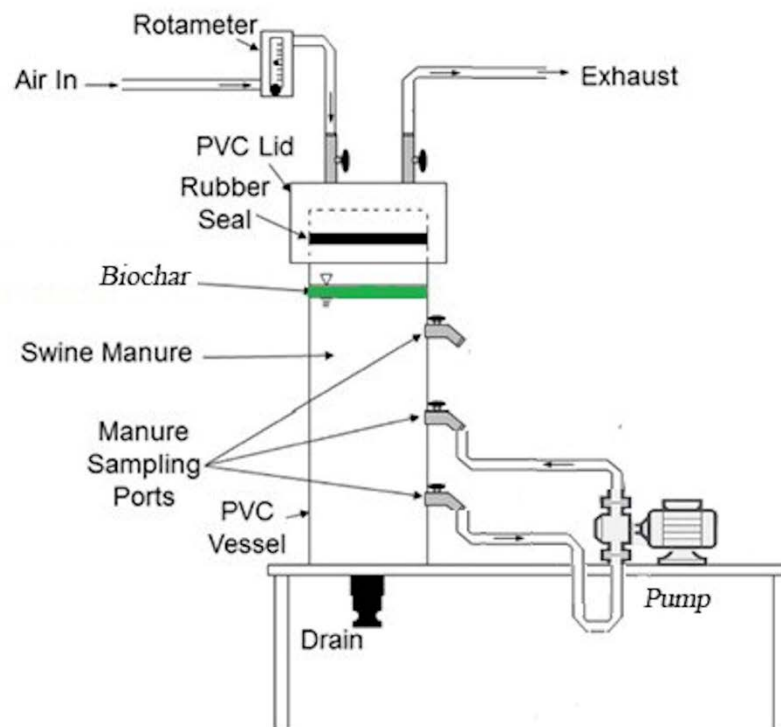
113 2.2. Methods

114 This pilot-scale setup was designed to simulate deep pit swine manure storage while manure is
115 being agitated, as shown in Figure 2. The inlet of the pump is connected to the bottom manure
116 sampling port; the outlet is connected to the middle manure sampling port, as shown in Figure 2. In
117 the process of agitation, the manure flowed from the bottom to the middle zone at a constant rate for
118 3 min. The air flowrate was controlled at 7.5 ACH via rotameters and valves. There were two types
119 of biochar with three scenarios per biochar and each with triplicate results:

- 120 • Manure not treated with biochar – control variant
- 121 • Manure treated with 0.25" (~ 6 mm) thick layer of biochar
- 122 • Manure treated with 0.5" (~ 12 mm) thick layer of biochar

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

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



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

138 H₂S and NH₃ concentrations were measured from the headspace before and immediately after
 139 applying biochar. When the concentrations of both gases were stable, the pump would begin to
 140 agitate the manure for 3 min at a constant rate of 360 GPH. Real-time concentration measurements
 141 stopped when the concentrations for both gases reset to their initial concentrations before the
 142 agitation process started.

143 3. Results

144 3.1. Post-application of the biochar and pre-agitation gaseous emissions

145 Immediately after applying RO biochar, both scenarios showed a significant reduction in
 146 emissions. The 0.5" biochar treatment reduced the concentration of H₂S by 68.3% and by 56.8% for
 147 NH₃; the 0.25" biochar treatment reduced about 65.1% of H₂S and 78.9% of NH₃ (Table 1).

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

Condition	RO biochar		
	Control	0.5" biochar	0.25" biochar
Pre-agitation H ₂ S (mg/m ² /s)	0.00181 ± 0.000503	0.000782 ± 0.000388	0.000632 ± 0.000154
Pre-agitation NH ₃ (mg/m ² /s)	0.0867 ± 0.0128	0.0275 ± 0.00569	0.0183 ± 0.00659

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Once the HAP biochar was applied, the 0.5" biochar treatment immediately reduced the concentration of H₂S by about 99% and by 93% for NH₃; the 0.25" biochar treatment reduced emissions by nearly 100% for H₂S and by 90.6% for NH₃ (Table 2).

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

Condition	HAP biochar		
	Control	0.5" biochar	0.25" biochar
Pre-agitation H ₂ S (mg/m ² /s)	0.0146 ± 0.0206	0.00014 ± 0.00011	0
Pre-agitation NH ₃ (mg/m ² /s)	0.0597 ± 0.0248	0.00419 ± 0.00528	0.00563 ± 0.00787

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

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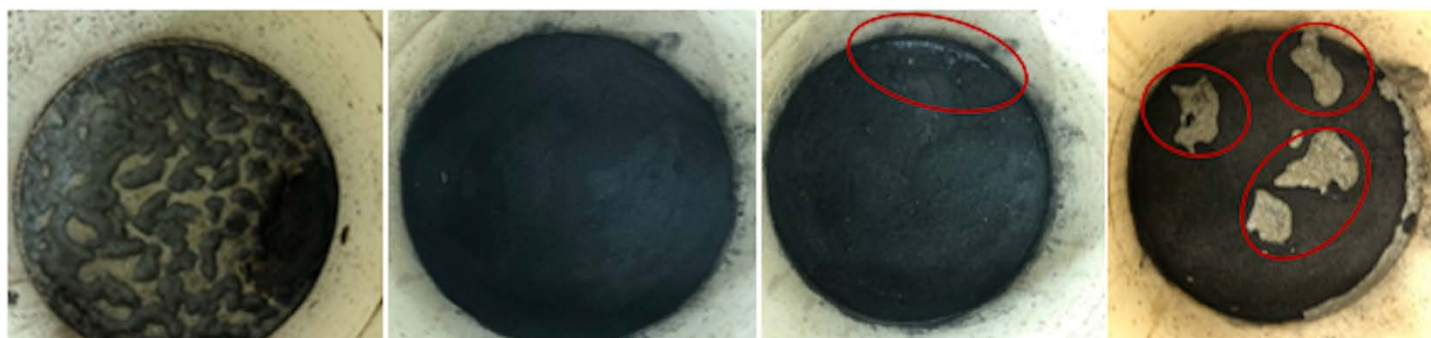
After the agitation process, most of the biochar was still floating on the top of the manure. Some of the biochar was wetted and mixed with manure (as circled in Figure 3). The treatments with 0.5" thickness of biochar were wetter and mixed more readily with manure than those treated with 0.25" biochar.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

Without biochar

Applied biochar evenly

0.25" biochar after agitation

0.5" biochar after agitation



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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 prevalent to higher biochar dose.

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3.3. Agitation emission

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During the 3-min agitation, the 0.5" RO biochar treatment showed a significant reduction in the maximum concentration of NH₃, but not for H₂S 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 NH₃ by 61.3%, and reducing H₂S by 63% ($p = 0.0511$). During the 3-min

169 agitation process, the 0.25" RO biochar treatment significantly reduced the total emission of NH₃
 170 concentration by 56.8% and reduced the total emission of H₂S by 62.4%; for the 0.5" RO biochar
 171 treatment, the total emission of NH₃ was reduced by 62.7%, and H₂S concentration was reduced by
 172 67.4% (Table 3).

173 **Table 3.** The mean of total emission and maximum concentration with its standard deviation for RO
 174 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 ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S
Maximum concentrations while agitating (mg/m ² /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/m ²)	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)

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 176 The 0.5" HAP biochar treatment showed a statistically significant reduction in the maximum
 177 concentration of NH₃ by 63.3%, but a not statistically significant reduction for H₂S at 42.5%. The 0.25"
 178 HAP biochar treatment also had higher maximum concentration reductions for both gases,
 179 significantly reducing NH₃ by 75.7%, and H₂S by 60.6% (p = 0.0580). During the 3 min of agitation,
 180 the 0.25" HAP biochar treatment significantly reduced the total emission of NH₃ concentration by
 181 85.2% and reduced the total emission of H₂S by 70.4%; for the 0.5" HAP biochar treatment, the total
 182 emission of NH₃ was reduced by 77.8%, and H₂S was reduced by 66.6% (Table 4).

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

HAP biochar during the 3 min of agitation						
	Control		0.5" Biochar		0.25" Biochar	
	NH ₃	H ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S
Maximum concentrations while agitating (mg/m ² /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/m ²)	44.6±7.32	6.36 ± 1.23	6.61±3.21	1.88 ± 0.625	6.01±3.18	2.12 ± 0.433

% Reduction of total emission	-	-	85.2 (P < 0.0001)	70.4 (P < 0.0001)	77.8 (P < 0.0001)	66.6 (P < 0.0001)
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187 3.4. Post-agitation gaseous emissions

188 For both scenarios treated by HAP and RO biochar, once the agitation stopped, the
 189 concentrations of H₂S and NH₃ started to decrease immediately. Comparatively, the control group
 190 tested alongside with RO biochar, had the concentration of H₂S reaching the maximum concentration
 191 for about 5 ~ 10 min before dropping, and NH₃ was elevated for about 20 to 30 min as shown in
 192 Figures A1 and A2. This is because the concentrations exceeded the limitations of sensors for both
 193 gases. After 3 min of agitation, the concentrations for both gases were recorded until the
 194 concentration was stable or close to the concentration before agitation. Within this period of time, the
 195 0.25" RO biochar treatment significantly reduced total emissions in H₂S by about 84.7% and NH₃ by
 196 about 86.1%; the 0.5" RO biochar treatment significantly reduced 52.9% of the total NH₃ emission and
 197 39.3% of the total H₂S emission (Table 5).

198 **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 ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S
Period of Time (min)	48	36	48	36	48	36
Average emission (mg/m ² /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/m ²)	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)

199 For HAP biochar treatments, the 0.25" biochar treatment significantly reduced total emissions
 200 of H₂S by about 64.4% and of NH₃ by about 74.5%; the 0.5" biochar treatment significantly reduced
 201 70% of total NH₃ emission, but statistically insignificantly reduced 17.9% of the total H₂S emissions
 202 (Table 6).
 203

204 **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 ₂ S	NH ₃	H ₂ S	NH ₃	H ₂ S
Period of Time (min)	29.5	14	29.5	14	29.5	14
Average emission (mg/m ² /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/m ²)	205 ± 9.88	14.0 ± 1.88	61.3 ± 5.76	11.5 ± 1.31	31.8 ± 5.01	4.99 ± 0.531

% Reduction of total emission	-	70.0 (P < 0.0001)	17.9 (P = 0.2897)	74.5 (P < 0.0001)	64.4 (P < 0.0001)
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206 3.5. Statistical Analysis

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

211 4. Discussion

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

219 Surprisingly, the 0.25" treatment was a more effective dosage since the percent reduction was
220 slightly higher while using less biochar. The smaller amount of biochar being used could be critical,
221 not only because it is more economical. When the biochar is wetted, it forms 'chunks.' With manure
222 is being agitated, the bigger chunks of biochar in 0.5" treatments started to sink and mix with manure.
223 Once the physical barrier on the surface was broken, the maximum concentration of the treatment
224 began to rise and be closer to the control. However, for both treatments, biochar was effective in
225 reducing the overall total emissions for both NH₃ and H₂S.

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

232 Comparing the two types of biochar, HAP biochar was more efficient in mitigating the NH₃
233 emissions, likely due to it being more porous, and the control group for RO treatment exceeded the
234 limitations of sensors. For H₂S, treatment with both types of biochar resulted in a considerable %
235 reduction. Although some of the reduction was statistically insignificant, it might be because the H₂S
236 concentrations in the control group in HAP biochar was not high.

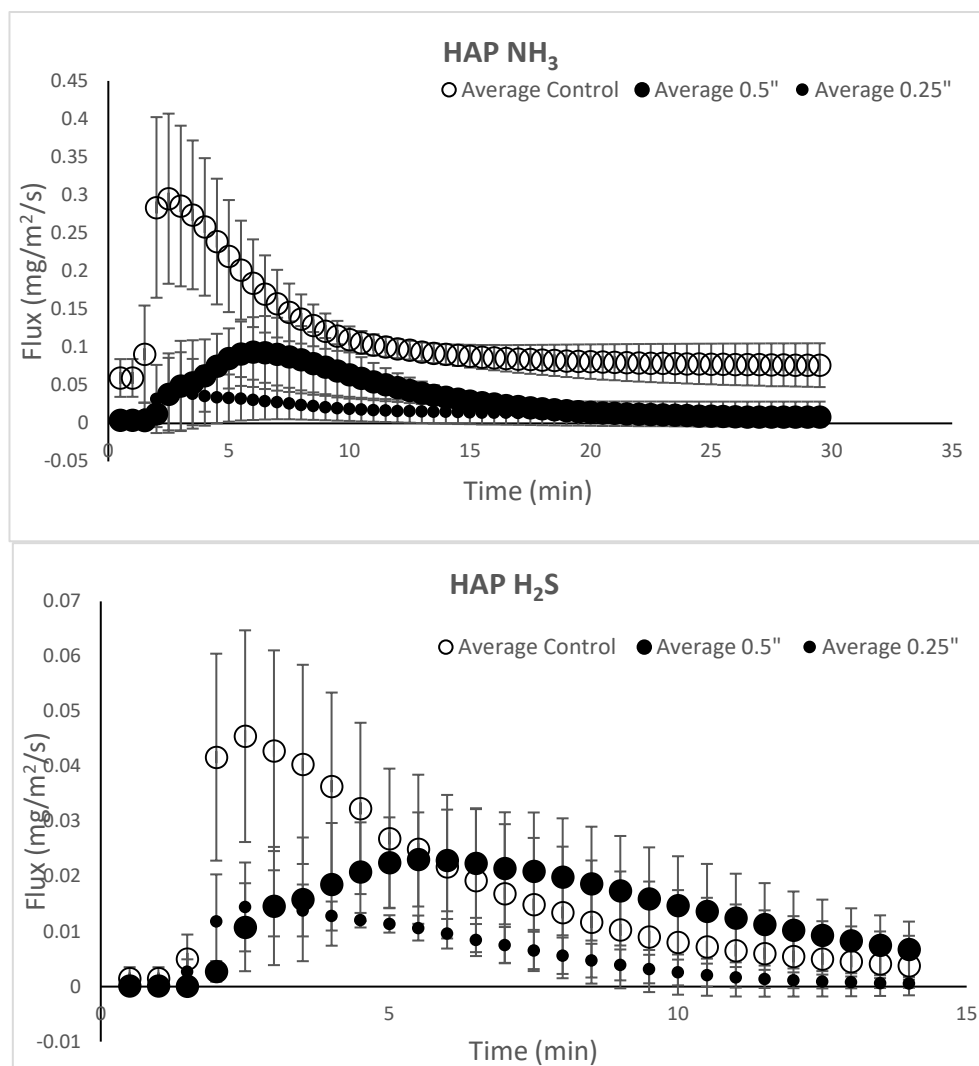
237 **Author Contributions:** conceptualization, J.K and B.C.; methodology, B.C. and J.K.; software, B.C.; validation,
238 J.K.; formal analysis, B.C.; investigation, B.C., M.L., H.M., P.L. and Z.M.; resources, J.K. and R.B.; data curation,
239 B.C., J.K.; writing—original draft preparation, B.C.; writing—review and editing, J.K. and A.B.; visualization,
240 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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253 publish the results.

254 **Appendix A**

255



258 **Figure A1.** The short-term NH₃ and H₂S emissions when manure is treated surficially with HAP
259 biochar layer at two thicknesses (0.25 inches, ~6 mm; 0.5 inches, ~12 mm) immediately prior to 3-min
260 agitation. Each data point is the average of triplicate, and the error bar signifies a standard
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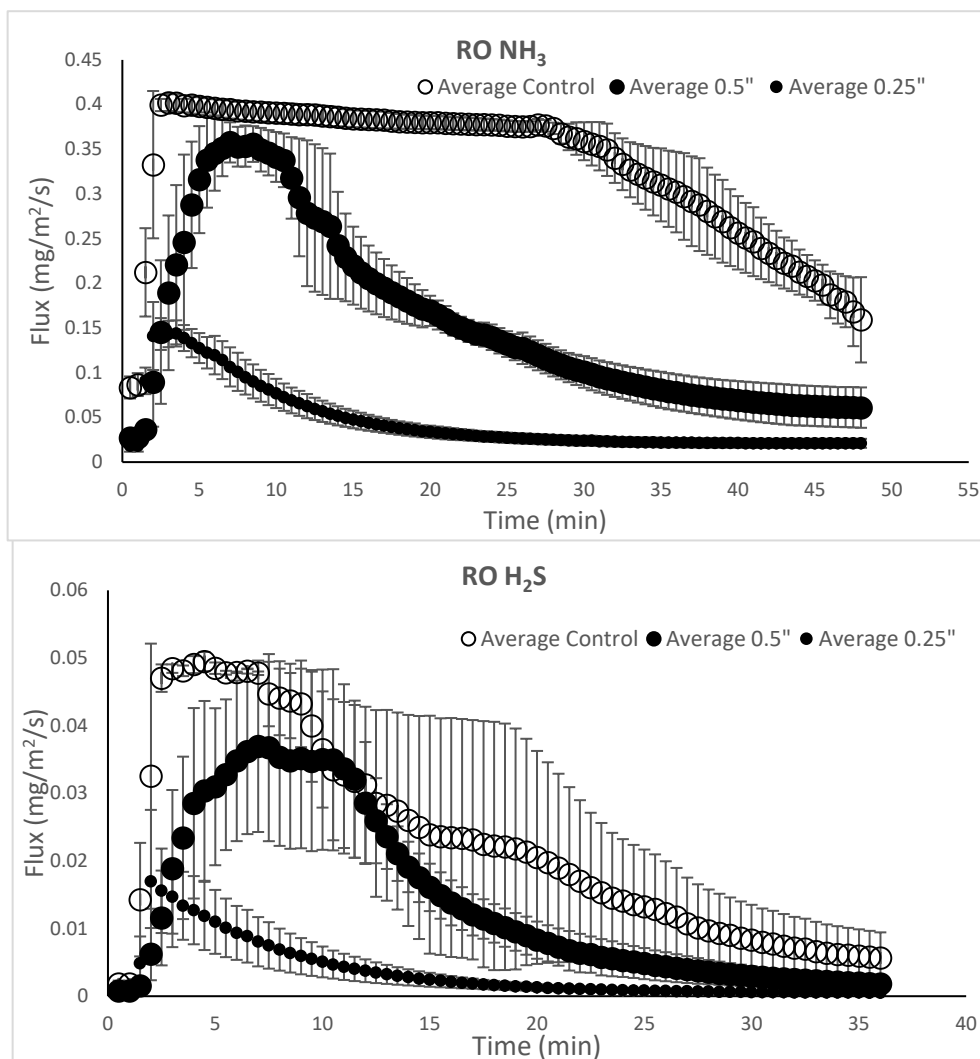
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Figure A2. The short-term NH_3 and H_2S emissions when manure is treated surficially with RO biochar layer at two thicknesses (0.25 inches, ~6 mm; 0.5 inches, ~12 mm) immediately prior to 3-min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

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