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The Impact of Surficial Biochar Treatment on Acute H_2S Emissions during Swine Manure Agitation before Pump-Out: Proof-of-the-Concept

Baitong Chen [1], Jacek A. Koziel [1,*], Andrzej Białowiec [1,2], Myeongseong Lee [1,3], Hantian Ma [4], Peiyang Li [1], Zhanibek Meiirkhanuly [1] and Robert C. Brown [5]

[1] Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50010, USA; baitongc@iastate.edu (B.C.); andrzej.bialowiec@upwr.edu.pl (A.B.); leefame@iastate.edu (M.L.); peiyangl@iastate.edu (P.L.); zhanibek@iastate.edu (Z.M.)
[2] Faculty of Life Sciences and Technology, Wroclaw University of Environmental and Life Sciences, 37a Chelmonskiego Str., 51-630 Wroclaw, Poland
[3] Department of Animal Biosystems Sciences, Chungnam National University, Daejeon 34134, Korea
[4] Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA 50010, USA; hantian@iastate.edu
[5] Bioeconomy Institute and Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA; rcbrown3@iastate.edu
* Correspondence: koziel@iastate.edu; Tel.: +1-515-294-4206

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Abstract: Acute releases of hydrogen sulfide (H_2S) are of serious concern in agriculture, especially when farmers agitate manure to empty storage pits before land application. Agitation can cause the release of dangerously high H_2S concentrations, resulting in human and animal fatalities. To date, there is no proven technology to mitigate these short-term releases of toxic gas from manure. In our previous research, we have shown that biochar, a highly porous carbonaceous material, can float on manure and mitigate gaseous emissions over extended periods (days–weeks). In this research, we aim to test the hypothesis that biochar can mitigate H_2S emissions over short periods (minutes–hours) during and shortly after manure agitation. The objective was to conduct proof-of-the-concept experiments simulating the treatment of agitated manure. Two biochars, highly alkaline and porous (HAP, pH 9.2) made from corn stover and red oak (RO, pH 7.5), were tested. Three scenarios (setups): Control (no biochar), 6 mm, and 12 mm thick layers of biochar were surficially-applied to the manure. Each setup experienced 3 min of manure agitation. Real-time concentrations of H_2S were measured immediately before, during, and after agitation until the concentration returned to the initial state. The results were compared with those of the Control using the following three metrics: (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. The Gompertz's model for determination of the cumulative H_2S emission kinetics was developed. Here, 12 mm HAP biochar treatment reduced the peak (1) by 42.5% ($p = 0.125$), reduced overall total emission (2) by 17.9% ($p = 0.290$), and significantly reduced the total emission during 3 min agitation (3) by 70.4%. Further, 6 mm HAP treatment reduced the peak (1) by 60.6%, and significantly reduced overall (2) and 3 min agitation's (3) total emission by 64.4% and 66.6%, respectively. Moreover, 12 mm RO biochar treatment reduced the peak (1) by 23.6%, and significantly reduced overall (2) and 3 min total (3) emission by 39.3% and 62.4%, respectively. Finally, 6 mm RO treatment significantly reduced the peak (1) by 63%, overall total emission (2) by 84.7%, and total emission during 3 min agitation (3) by 67.4%. Biochar treatments have the potential to reduce the risk of inhalation exposure to H_2S. Both 6 and 12 mm biochar treatments reduced the peak H_2S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments reduced the H_2S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm). Research scaling up to larger manure volumes and longer agitation is warranted.

Keywords: hydrogen sulfide; biocoal; livestock manure; agricultural safety; fertilizer; waste management; air pollution; odor; kinetics; Gompertz model

1. Introduction

Hydrogen sulfide (H_2S) is a serious safety concern in agriculture and other industries. Inhalation of H_2S can be harmful to both humans and livestock, and sometimes deadly. The Occupational Safety and Health Administration (OSHA) recommends the permissible exposure limits (PELs) concentration for H_2S at 20 ppm and an acceptable maximum peak above the acceptable ceiling concentration at 50 ppm, with a maximum duration of 10 min [1].

The mid-western United States has a significant presence of pork production. Many large swine buildings use deep-pits to store manure under the slatted floor for up to 1 year. When a pit is full, farmers pump-out most of the manure to fertilize their fields in the fall. Agitating manure prior to pump-out is required to incorporate sediments and efficiently empty the pits. This routine seasonal operation generates a high risk of inhalation exposure to gases released from manure. Agitating the manure can break the entrapped gas bubbles, which causes an instantaneous increase in H_2S concentration (Figure 1) [2]. Fatal accidents have been recorded involving a high concentration of H_2S owing to the agitation of manure in the past several years [3–6].

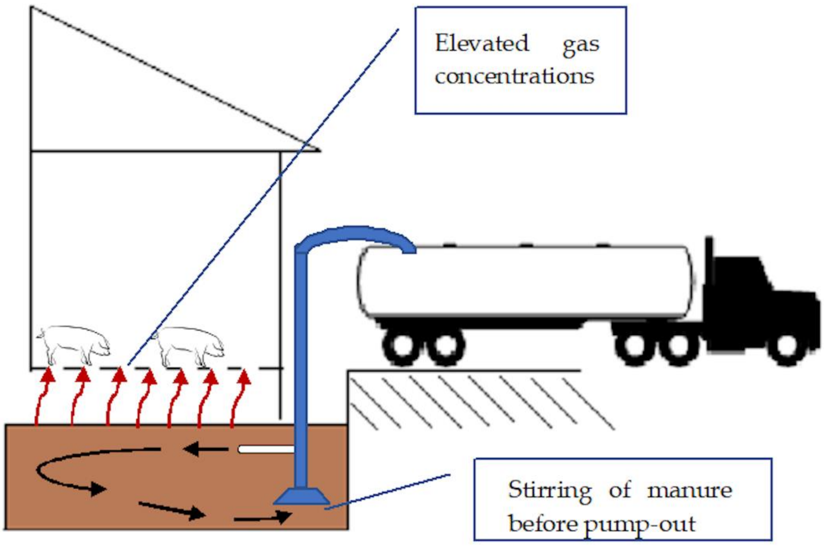

Figure 1. Schematic of the agitation process before seasonal manure pump-out from deep-pit storage under swine barn with a slatted floor. Fatal accidents are known to occur to people and livestock owing to the dangerous acute release of entrapped gases (e.g., H_2S) from stored manure during agitation.

To date, there is no proven technology to mitigate these short-term releases of toxic gas from manure. Commercial pit manure additives of the microbial mode of operation are used by some swine farmers to control gaseous emissions. Still, science-based guides, as well as more data, are needed to evaluate manure additive effect on the mitigation of gases emitted from storage [7]. Recent research on manure additives such as soybean peroxidase, zeolite, and biochar show the effectiveness of mitigating H_2S, NH_3, volatile organic compounds (VOCs), and greenhouse gas (GHG) emissions from swine manure over extended periods of time [8–13]. Additionally, we evaluated the performance of numerous commercial manure additives, but there was no overall statistically significant mitigation for gaseous emissions [14,15].

In our previous research, we have shown that 6 mm and 12 mm thick layer treatment of biochar, a highly porous carbonaceous material, can float on manure and mitigate gaseous emissions over extended periods (days–weeks). The mitigation effects on H_2S were typically the greatest on the first day of application and decreased over the duration of the trial [16]. This observation led us to explore the possibility of using surficial biochar treatment for *short-term* mitigation of H_2S emissions from swine manure. In this research, we aim to test the hypothesis that biochar can mitigate H_2S emissions over short periods (minutes–hours) during and shortly after manure agitation. The biochars tested had similar properties to those used for testing the spatial and temporal effects on pH near the liquid–gas interface owing to biochar addition to water [17] and manure surface [18].

Biochar has received considerable interest in the recent decade. It was proposed to be used as a soil amendment, an alternative source of fuel, and an adsorbent [19–21]. Biochar can be made from abundant biomass and waste through pyrolysis or torrefaction with no oxygen or a low-oxygen level [20–25]. Biochar's physicochemical properties vary as a result of differences in feedstock and its pretreatment, temperature, and time of the process [20–25]. The desired properties (e.g., pH, porosity, chemical moiety) could be explored to achieve environmental sustainability goals.

The first research question was, what biochar dose should be applied? The second research question was, how could a farm-scale system (Figure 1) be scaled down for a proof-of-the-concept experiment? The third research question was, how will the agitation of manure with added biochar influence the H_2S emission rates? Finally, will the mitigation effect be sufficient to meet the OSHA PELs recommendations, and will the results warrant scale-up research? We hypothesized that a greater biochar dose (thickness of the surficial layer applied to manure) would increase the H_2S mitigation effect; proof-of-the-concept experiments could use a shorter agitation time and a smaller amount of manure; and the mitigation effect would be significant and practical enough to warrant further scale-up research.

2. Results

2.1. Gaseous Emissions Post Biochar Application and Pre-Agitation (Stage 1)

Immediately after applying RO biochar, both scenarios showed a significant reduction in emissions. The 12 mm biochar treatment reduced the concentration of H_2S by 68.3%, and the 6 mm biochar treatment reduced 65.1% of H_2S (Table 1).

Table 1. H_2S emissions (expressed as flux) after applying red oak (RO) biochar (6 or 12 mm surficial dose) to manure surface and before manure agitation.

		RO Biochar	
Condition	**Control**	**12 mm Biochar**	**6 mm Biochar**
Pre-agitation H_2S ($mg{\cdot}m^{-2}{\cdot}s^{-1}$)	0.00181 ± 0.000503	0.000782 ± 0.000388	0.000632 ± 0.000154

Once the HAP biochar was applied, the 12 mm biochar treatment immediately reduced the concentration of H_2S by about 99%, and the 6 mm biochar treatment reduced emissions by nearly 100% for H_2S (Table 2).

Table 2. H_2S emissions (expressed as flux) after applying highly alkaline and porous (HAP) biochar (6 or 12 mm surficial dose) to manure and before manure agitation.

		HAP Biochar	
Condition	**Control**	**12 mm Biochar**	**6 mm Biochar**
Pre-agitation H_2S ($mg{\cdot}m^{-2}{\cdot}s^{-1}$)	0.0146 ± 0.0206	0.00014 ± 0.00011	0 *

* below detection limits.

2.2. Effect of the Dose on the Apparent Biochar Behavior Post-Agitation

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 2). The treatments with 12 mm biochar dose were visibly wetter and mixed more readily with manure than those treated with 6 mm biochar. Patches of open (not covered) manure were more prevalent to higher biochar dose. We observed similar dose-dependent behavior with surficially applied soybean peroxidase treatment to swine manure [11].

Figure 2. Swine manure surface: Control (left), highly alkaline and porous (HAP) biochar evenly spread on top of the swine manure (center left), 6 mm thick HAP biochar layer after agitation (center right), and 12 mm thick HAP biochar layer after agitation (right). Patches of open (uncovered) manure (red circles) were more apparent when higher biochar dose was used.

2.3. Gaseous Emissions during Agitation (Stage 2)

Both the 6 mm and 12 mm RO biochar treatment significantly ($p < 0.0001$) reduced the total emission of H_2S by 67.4% and 62.4%, respectively (Table 3, Figure A1). The 6 mm and 12 mm RO biochar treatment resulted in a 63.0% ($p = 0.0511$) and 23.6% ($p = 0.145$) reduction in the maximum peak flux of H_2S, respectively (Table 3).

Table 3. RO biochar treatment: the maximum peak flux and total H_2S emission *during* 3 min agitation (bold font signifies statistical significance).

	RO Biochar during the 3 min of Agitation		
	Control	**12 mm Biochar**	**6 mm Biochar**
Maximum peak flux while agitating, ($mg{\cdot}m^{-2}{\cdot}s^{-1}$)	0.0504 ± 0.00078	0.0385 ± 0.0138	0.0186 ± 0.00977
% Reduction of maximum peak flux while agitating	–	23.6 ($p = 0.145$)	63.0 ($p = 0.0511$)
Total emission during 3 min agitation, ($mg{\cdot}m^{-2}$)	7.18 ± 0.644	2.7 ± 0.698	2.34 ± 0.472
% Reduction of total emissions during 3 min agitation	–	**62.4** ($p < 0.0001$)	**67.4** ($p < 0.0001$)

Both the 6 mm and 12 mm HAP biochar treatment significantly ($p < 0.0001$) reduced the total emission of H_2S by 66.6% and 70.4%, respectively (Table 3, Figure A2). The 6 mm and 12 mm RO biochar treatment resulted in 60.6% ($p = 0.05804$) and 42.5% ($p = 0.1249$) reduction in the maximum peak flux of H_2S, respectively (Table 4).

Table 4. HAP biochar treatment: the maximum peak flux and total H_2S emission *during* 3 min agitation (bold font signifies statistical significance).

	HAP Biochar during the 3 min of Agitation		
	Control	**12 mm Biochar**	**6 mm Biochar**
Maximum peak flux while agitating, ($mg{\cdot}m^{-2}{\cdot}s^{-1}$)	0.0455 ± 0.0192	0.0261 ± 0.00665	0.0179 ± 0.00321
% Reduction of maximum peak flux while agitating	–	42.5 (p = 0.1249)	60.6 (p = 0.05804)
Total emission during 3 min agitation, ($mg{\cdot}m^{-2}$)	6.36 ± 1.23	1.88 ± 0.625	2.12 ± 0.433
% Reduction of total emissions during 3 min agitation	–	**70.4** ($p < 0.0001$)	**66.6** ($p < 0.0001$)

2.4. Gaseous Emissions Post-Agitation (Stage 3)

Once the agitation stopped, the concentrations of H_2S started to decrease for both HAP and RO biochar treatments (Figures A1 and A2). The H_2S concentrations were recorded until they reached the levels before agitation and were stable. Both the 6 mm and 12 mm RO biochar treatment significantly ($p < 0.0001$) reduced cumulative H_2S emissions by 84.7% and 39.3%, respectively (Table 5).

Table 5. RO biochar treatment: the average flux and cumulative H_2S emission after agitation (bold font signifies statistical significance).

	RO Biochar after the 3 min of Agitation		
	Control	**12 mm Biochar**	**6 mm Biochar**
Duration (min)	36	36	36
Average emissions [1] ($mg{\cdot}m^{-2}{\cdot}min^{-1}$)	1.37 ± 0.175	0.831 ± 0.0483	0.209 ± 0.00174
Cumulative emissions [2] ($mg{\cdot}m^{-2}$)	49.2 ± 2.63	29.9 ± 1.74	7.52 ± 0.627
% Reduction of cumulative emissions	–	**39.3** ($p < 0.0001$)	**84.7** ($p < 0.0001$)

[1] the average emissions were calculated using the cumulative emissions divided by the duration. [2] the cumulative emissions were calculated based on the same period (post-agitation) (Figure A1).

For HAP biochar treatments, the 6 mm biochar treatment significantly ($p < 0.0001$) reduced cumulative emissions of H_2S by 64.4%. The 12 mm biochar treatment reduced the cumulative H_2S emissions by 17.9%, yet the reduction was not significant ($p = 0.2897$) (Table 6).

Table 6. HAP biochar treatment: the average flux and cumulative H_2S emission after agitation (bold font signifies statistical significance).

	HAP Biochar after the 3 min of Agitation		
	Control	**12 mm Biochar**	**6 mm Biochar**
Duration (min)	14	14	14
Average emissions [1] ($mg{\cdot}m^{-2}{\cdot}min^{-1}$)	1.00 ± 0.134	0.821 ± 0.0936	0.356 ± 0.0379
Cumulative emissions [2] ($mg{\cdot}m^{-2}$)	14.0 ± 1.88	11.5 ± 1.31	4.99 ± 0.531
% Reduction of cumulative emissions	–	17.9 ($p = 0.2897$)	**64.4** ($p < 0.0001$)

[1] the average emissions were calculated using the cumulative emissions divided by the duration. [2] the cumulative emissions were calculated based on the same period (post-agitation) (Figure A2).

The H_2S in the headspace of RO treated manure needed longer to return to the initial state compared with the HAP treatment. The H_2S release was higher in the experiment testing the RO treatment (Figure A1) compared with the experiment testing the HAP treatment (Figure A2). The control concentrations exceeded the limitations of the H_2S sensor. The apparent difference in the control concentrations is the result of the differences in manure used in RO and HAP experiments, that is, collected at the same farm, yet at two different times for the RO and HAP trials.

2.5. Kinetics of the Post-Agitation Emissions of H_2S

The kinetics modeling allowed further evaluation of the effect of biochar type and the dose. The E_0 parameter shows the potential of H_2S emission during an 'infinite' time. The cumulative emission during the post-agitation showed that there was no ($p > 0.05$) significant influence of the HAP biochar treatment on the potential maximum cumulative flux (Figure 3). However, the lack of the significance of the differences may be caused by high variability, while still, the apparent potential for lower emission is visible. The RO application of biochar significantly ($p = 0.0086$) reduced the potential of the maximum cumulative emission in the case of the 6 mm dose; however, there were no differences between the biochar dose (Figure 3, Table A1—Appendix B). For both the RO and HAP biochar, the lowest values of E_0 were determined for 6 mm biochar thickness, implying that a low biochar dose could be just as effective.

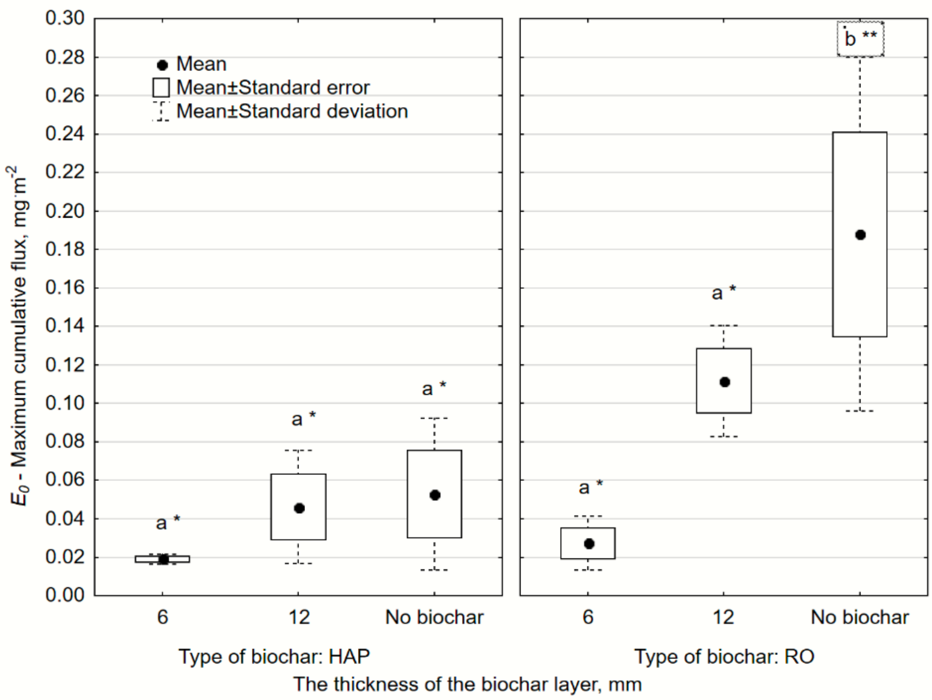

Figure 3. The differences between the maximum cumulative H_2S flux per biochar type and dose (thickness of the biochar layer). Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between biochar dose (Table A1). RO, red oak.

The k constant presents the rate of H_2S emission. The treatment by application of both types of biochar did not significantly influence ($p > 0.05$) the k constant (Figure 4, Table A2—Appendix B). The lack of significant differences could be caused by high values of the standard deviations. However, the influence of the biochar dose was observed only in the case of HAP, where the 12 mm biochar reduced the k value.

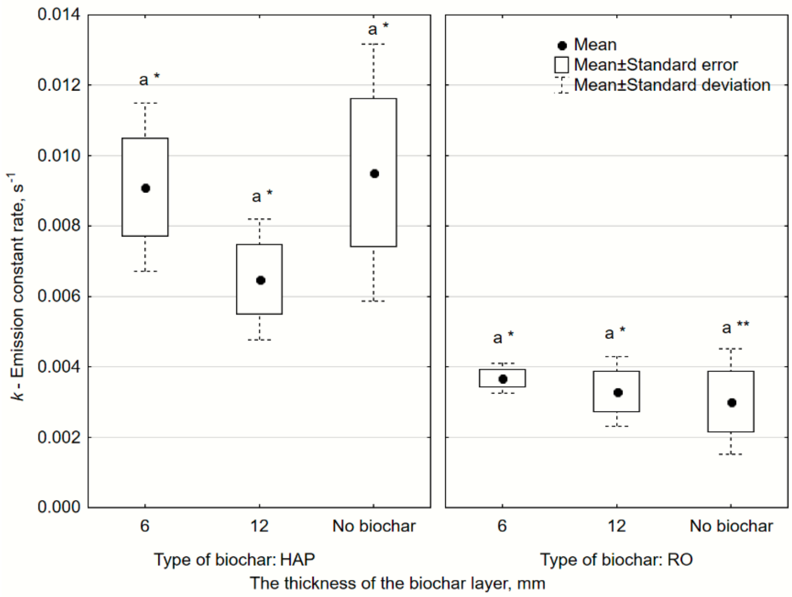

Figure 4. The differences between H_2S emission constant rates per the type and dose (thickness of the layer) of biochar. Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between thicknesses of the biochar layers (Table A2).

The a_1 parameter, the inflection time of the cumulative H_2S emission curve, represents the moment when the emission rate starts to 'slow' down. Similar to the k parameter, the treatment by the application of both types of biochar did not significantly influence ($p > 0.05$) the inflection time of the H_2S emission (Figure 5, Table A3). The lack of significant differences could be caused by high variability. However, in this case, the lowest a_1 values were observed for 6 mm for both biochar types.

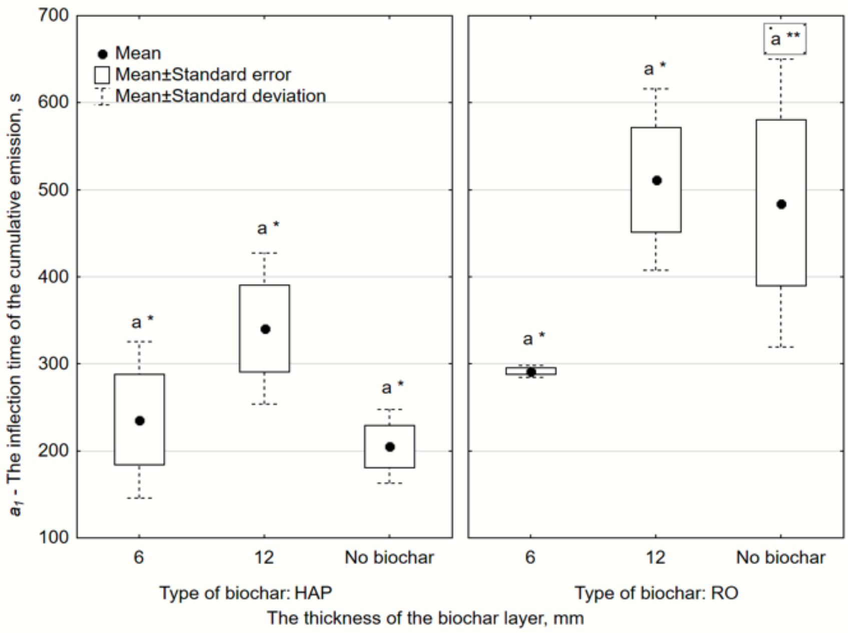

Figure 5. The differences between the inflection time of the cumulative H_2S emission per biochar type and the dose (thickness of the layer). Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between biochar dose (Table A3).

3. Discussion

Biochar treatments have the potential to reduce the risk of inhalation exposure to H_2S. Both 6 and 12 mm biochar treatments reduced the peak H_2S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments, both HAP and RO, reduced the H_2S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm) (Figures A3 and A4).

This proof-of-the-concept study shows that biochar has the potential to be an effective treatment of short-term releases of H_2S during and post-agitation of swine manure. From the kinetics of the post-agitation H_2S emissions analysis, only RO biochar has shown the significant ($p = 0.0086$) reductions on the maximum cumulative emission (E_0). Further, the smaller dosage (6 mm) worked just as well as the 12 mm dosage. The pH value of HAP was 9.2, while the RO pH was 7.5 [17]. It has been expected that HAP (more alkalic) would have a greater influence on H_2S emissions mitigation, owing to H_2S transformation into S^{2-} ions. Previously, we have found that HAP had a stronger influence on the water pH increase than RO [17]. The apparent absence of the differences between RO and HAP in the present experiment, and even (numerically) better performance of RO biochar, could be caused by the different buffering capacity of the manure used for the experiment [18]. However, the comparison between these two types of biochars was not the aim of the study.

Biochar treatments did not have much impact on the constant emission rate (k) owing to the high standard deviations, except for the 12 mm HAP biochar treatment. The high variations could be caused by high heterogenicity of the stored manure properties (i.e., stratified, biologically-active, not a well-mixed solution, with local solids aggregates, and zones with different chemical properties). Therefore, one possible solution is to work with artificial surrogate manure (if a particular mechanism behind the mitigation needs to be isolated). The inflection time (a_1) of the cumulative emissions was not influenced much by either type of biochar; the lowest a_1 values were observed for 6 mm for both biochar types, where the emission rate started to slow down after 4–5 min. These findings still need to be proven on a larger scale and optimized. Still, this initial work has implications that could potentially save people and livestock lives and reduce inhalation risks during routine seasonal manure agitation, pump-out, and land application. With further research, the optimal biochar type, dose, and form of application (e.g., pellets instead of powder), it could become an effective adsorptive 'barrier' to protect farmers, neighbors, and livestock from harmful gases and odors emitted from manure.

Surprisingly, the 6 mm biochar treatment was a numerically more effective dosage because the % reduction was slightly higher while using less biochar. The smaller amount of biochar used has an immediate impact and economics and on the feasibility of technology adoption. When the biochar is wetted, it forms 'chunks'. When manure is being agitated, the bigger chunks of biochar in 12 mm treatments started to turn over, sink, and mix with manure much faster than with the 6 mm dose. Once the physical barrier on the surface was broken, the maximum concentration of the treatment began to rise and was closer to the Control.

In future research, other kinds of biochar could be tested for their efficacy to mitigate gaseous emissions from manure. The effects of the dose and frequency of application of commercial biochars, functionalized biochars, pelletized biochar, as well as the synergy between gaseous emissions and agronomic benefits to soil should be tested. Additionally, farm-scale research is also required for the proof-of-the-concept. With more extensive farm-scale trials, researchers should consider how and where the biochar could be practically applied in order to create an effective short-term barrier to maximize the benefit of biochar treatment. Application of powdery, light, and dusty material might be hazardous itself and not be feasible in farm conditions. Pelletized biochar could be a more practical and safer mode of application. Opportunities exist to mitigate other types of gases and other applications (e.g., industrial wastewater, compost, landfill leachate) with biochar.

4. Experiments

4.1. Manure, Biochars, H_2S Measurements

Fresh manure was collected twice from deep-pit storage at a local swine farm in central Iowa. The manure treated with the red oak (RO) biochar was collected in summer, whereas manure treated with the highly alkaline and porous (HAP) biochar was collected in winter. Thus, the experimental design was set up to compare the Treatment and Control of the same type of biochar. The manure properties and, therefore, baseline H_2S concentrations for control groups were different for HAP and RO trials. The proof-of-the-concept simulation of the deep pit and agitation was facilitated by 1.22 m (height) and 0.38 m (diameter) manure storage. The working volume of the manure was 103.1 L, while the headspace was ventilated with 7.5 air exchanges per hour (ACH), which is representative of the ventilation of deep-pit manure storage [11,26]. A 1/10 hp transfer pump (Little Giant, Fort Wayne, IN) was used to agitate the manure with a 1.36 m^3 h^{-1} flow rate.

Biochar physicochemical properties were described elsewhere [16–18]. Briefly, some key properties are listed below. RO biochar was pyrolyzed at 500–550 °C. It had a pH of 7.5 and a 6.75 zero-point charge, consisting of C (78.53% dry matter, d.m.), H (2.54% d.m.), N (0.62% d.m.), and volatile solids (VS, 26.38% d.m.). Fixed C and ash were 54.76% and 15.83% d.m., respectively [16–18]. The HAP biochar was made from corn stover pyrolyzed at 500 °C. The pH was 9.2 and 8.42 zero-point charge, consisting of C (61.37% d.m.), H (2.88% d.m.), N (1.21% d.m.), and VS (16.27% d.m.). Fixed C and ash were 34.98% and 46.82% d.m., respectively [16–18].

OMS-300 real-time monitoring system equipped with electrochemical gas sensors (H_2S/C-50) (Smart Control & Sensing Inc., Daejeon, Korea) was used to measure the real-time H_2S concentration [27,28]. The analyzer was calibrated with standard gas before use [27,28].

4.2. Experimental Design

The pilot-scale setup was simulating deep pit swine manure storage while manure was being agitated (Figure 6). The inlet of the pump was connected to the bottom manure sampling port; the outlet was connected to the middle manure sampling port. During agitation, the manure was pumped from the bottom to the middle zone for 3 min. Three variants per each biochar and each with triplicates experiments:

- Manure not treated with biochar—control variant.
- Manure treated with—6 mm thick layer of biochar.
- Manure treated with—12 mm thick layer of biochar.

The biochar dose was based on its volume spread over the manure surface, resulting in either 6 or 12 mm average thicknesses. The headspace H_2S concentrations were measured in the exhaust (Figure 6) continuously during the following stages:

- Stage 1: No agitation. Post biochar application and pre-agitation for all three variants.
- Stage 2: Agitation. All three variants during agitation.
- Stage 3: Post-agitation. All three variants after agitation until the headspace H_2S concentration reached its initial state.

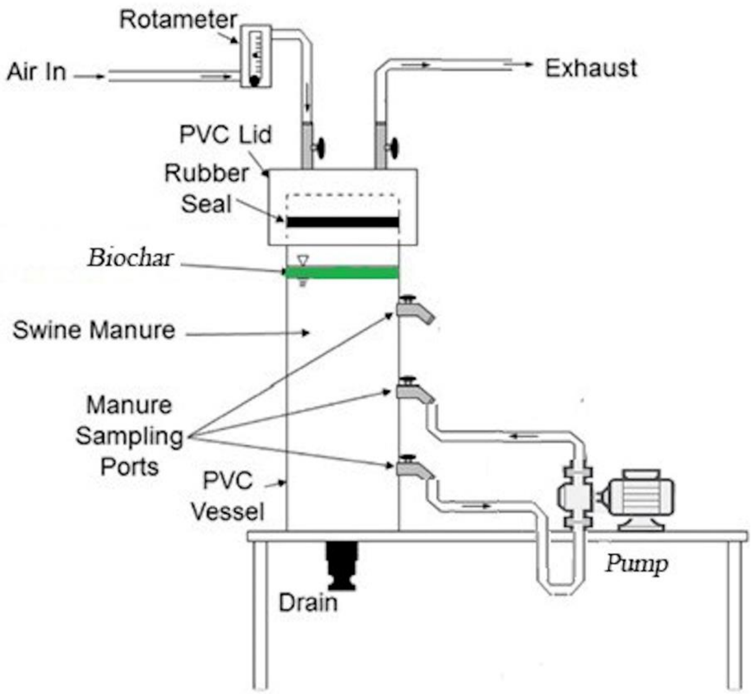

Figure 6. Pilot-scale design for simulating deep pit manure storage treated surficially with a thin layer of biochar prior to agitating.

4.3. Data Analysis, the Kinetics of Emissions

The mitigation effect was estimated by comparing measured emissions associated with the Control (not treated) and treatment (treated with biochar) manure. The % reduction was calculated as the percent ratio of (control − treatment)/control.

The one-way analysis of variance (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 during 3 min. The maximum levels of concentrations were used for a pooled T-test to estimate the p-values. A p-value < 0.05 was used as a statistical significance threshold. The Gompertz model was used for the determination of the post-agitation cumulative H_2S emission kinetics [29]:

$$E = E_0 \cdot e^{\left(-e^{-k\cdot(t-a_1)}\right)} \quad (1)$$

where E—H_2S emission flux, mg.m^{-2}; E_0—H_2S maximum cumulative emission flux, mg m^{-2}; k—constant rate of the H_2S emission flux, s^{-1}; t—time, s; and a_1—the inflection time of the cumulative H_2S emission, s.

The non-linear regression was used for the determination of the cumulative emission kinetics with the application of the Statistical 13 software (TIBCO Software Inc., Palo Alto, CA, USA). The R^2 determination coefficient was estimated to indicate the fitting the model to data. The kinetic analysis was completed for each variant and each repetition. The result of the regression analysis for each variant is provided in Appendix A (Figures A5–A22) and used to estimate the average values of E_0, k, and a_1 (Equation (1)). The ANOVA test was applied with post-hoc Tukey's test to indicate the statistical significance ($p < 0.05$) of the differences between average values. The calculated probabilities of Tukey's test are given in Appendix B.

5. Conclusions

The highly alkaline and porous (HAP) and red oak (RO) biochar treatments have the potential to reduce the risk of inhalation exposure to H_2S. Both the 6 mm and 12 mm RO biochar treatment significantly ($p < 0.0001$) reduced the total emission of H_2S by 67.4% and 62.4%, respectively. The 6 mm and 12 mm RO biochar treatment resulted in a 63.0% ($p = 0.0511$) and 23.6% ($p = 0.145$) reduction in the maximum peak flux of H_2S, respectively. Both the 6 mm and 12 mm HAP biochar treatment significantly ($p < 0.0001$) reduced the total emission of H_2S by 66.6% and 70.4%, respectively. The 6 mm and 12 mm RO biochar treatment resulted in 60.6% ($p = 0.05804$) and 42.5% ($p = 0.1249$) reduction in the maximum peak flux of H_2S, respectively. Both 6 and 12 mm biochar treatments reduced the peak H_2S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments reduced the H_2S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm). Research scaling up to larger manure volumes and longer agitation is warranted.

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Appendix A

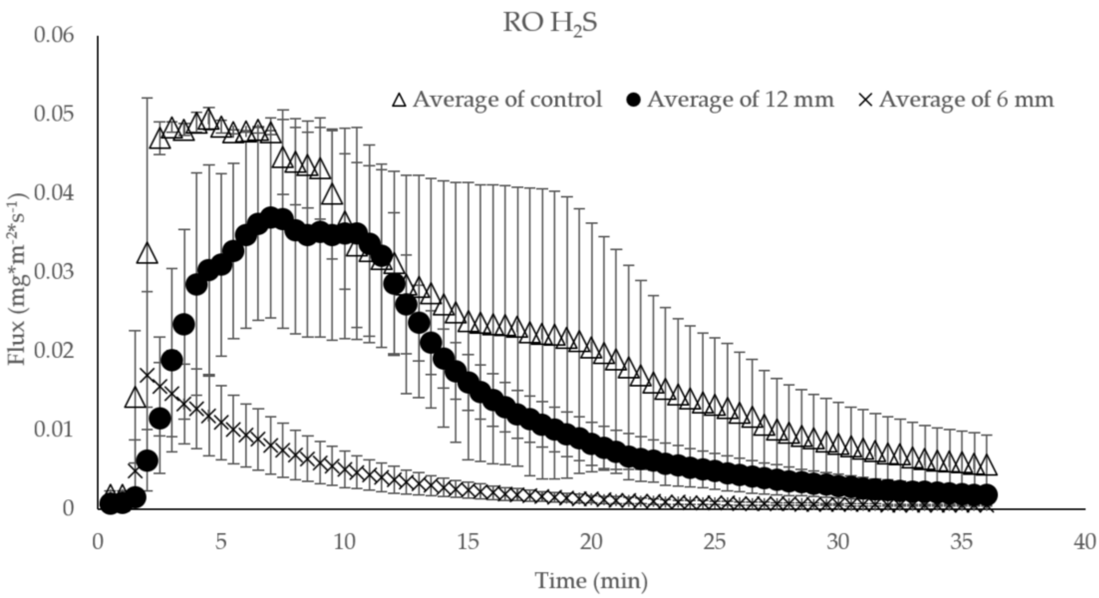

Figure A1. The short-term H_2S emissions when manure is treated surficially with RO biochar layer at two thicknesses (6 mm; 12 mm) immediately *prior to* 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

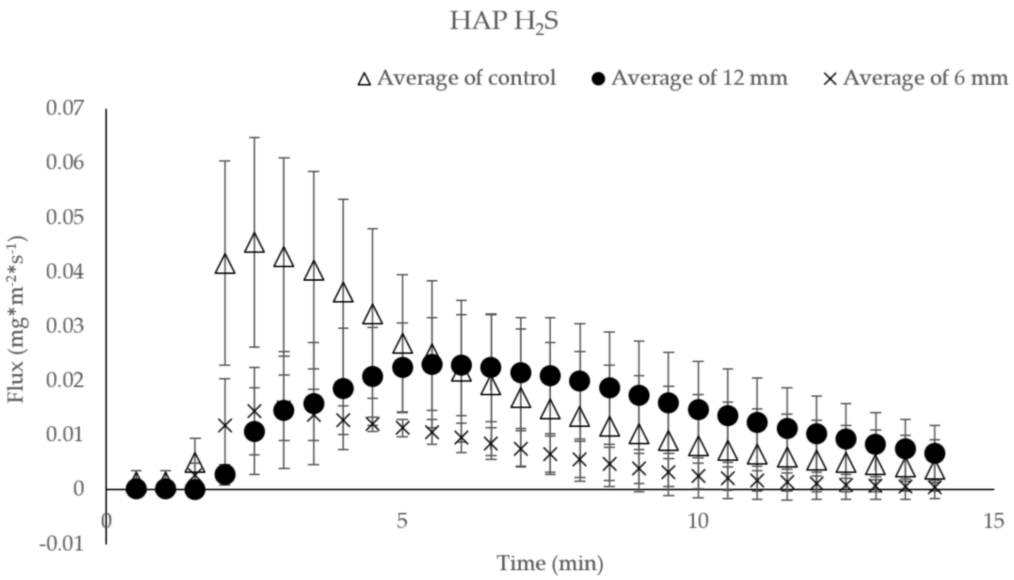

Figure A2. The short-term H_2S emissions when manure is treated surficially with HAP biochar layer at two thicknesses (6 mm; 12 mm) immediately *prior to* 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

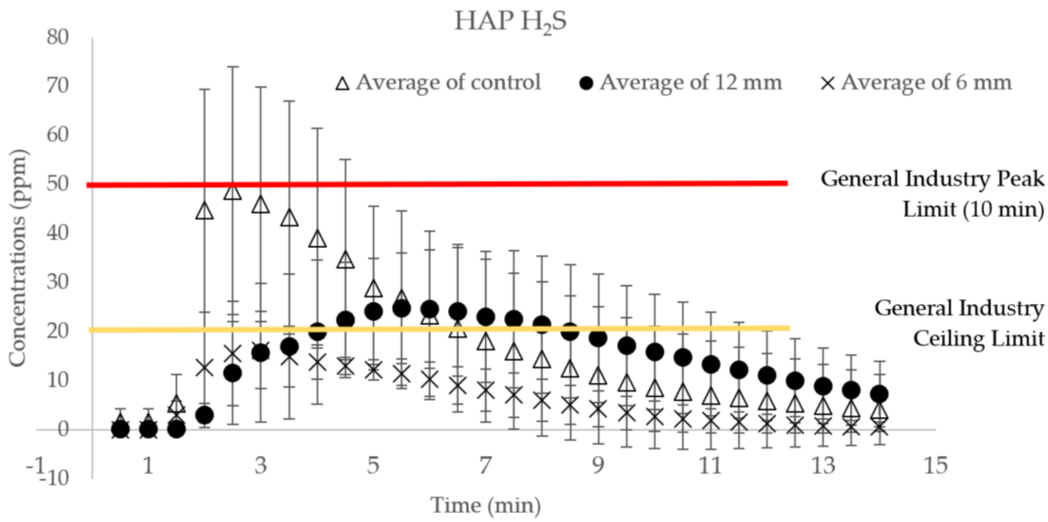

Figure A3. The short-term H_2S concentrations when manure is treated surficially with HAP biochar layer at two thicknesses (6 mm; 12 mm) immediately *prior to* 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation. Red line = the 'General Industry Peak Limit' (OSHA PEL = 50 ppm); yellow line = the 'General Industry Ceiling Limit' (OSHA PEL = 20 ppm) [1].

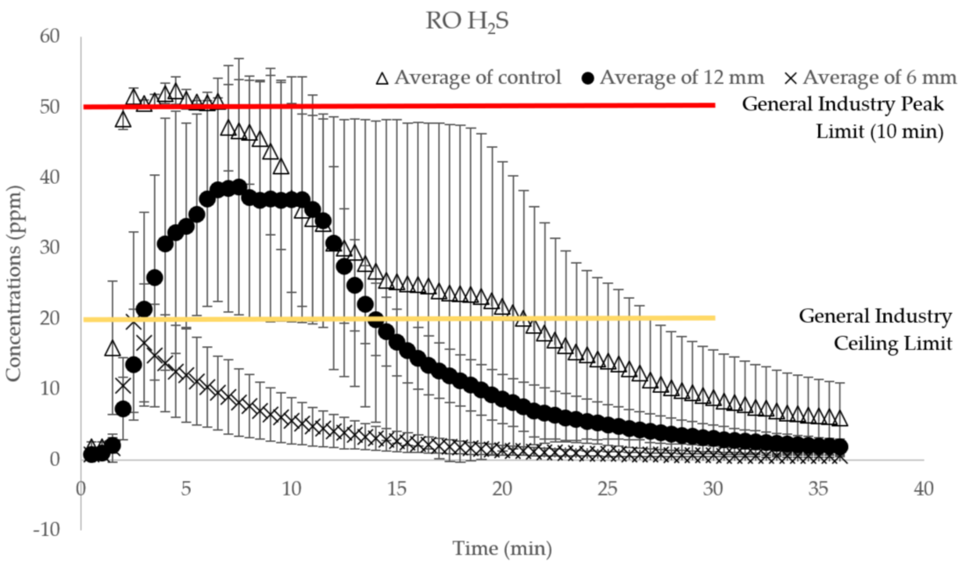

Figure A4. The short-term H_2S concentrations when manure is treated surficially with RO biochar layer at two thicknesses (6 mm; 12 mm) immediately *prior to* 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation. Red line = the 'General Industry Peak Limit' (OSHA PEL = 50 ppm); yellow line = the 'General Industry Ceiling Limit' (OSHA PEL = 20 ppm) [1].

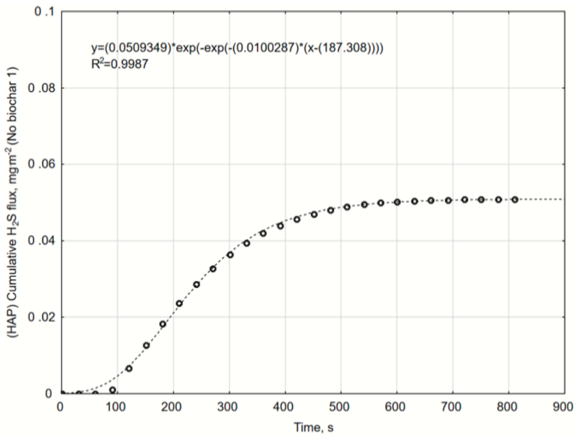

Figure A5. The cumulative H_2S flux. Variant with no HAP biochar, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

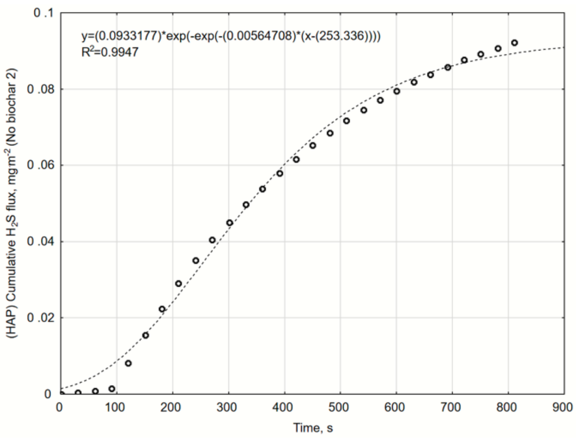

Figure A6. The cumulative H_2S flux. Variant with no HAP biochar, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

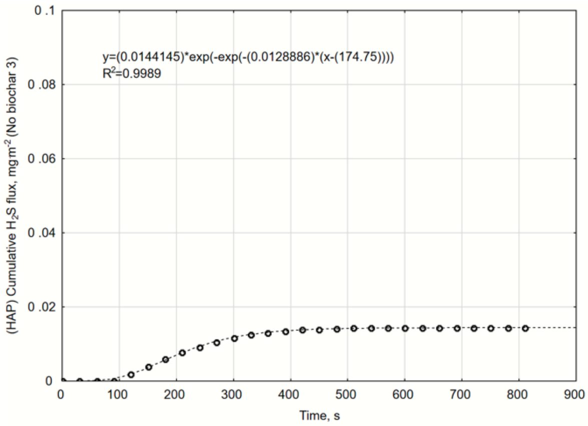

Figure A7. The cumulative H_2S flux. Variant with no HAP biochar, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

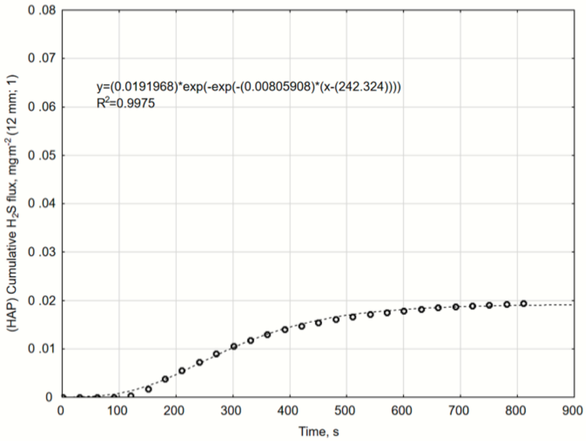

Figure A8. The cumulative H_2S flux. Variant with 12 mm HAP biochar layer, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

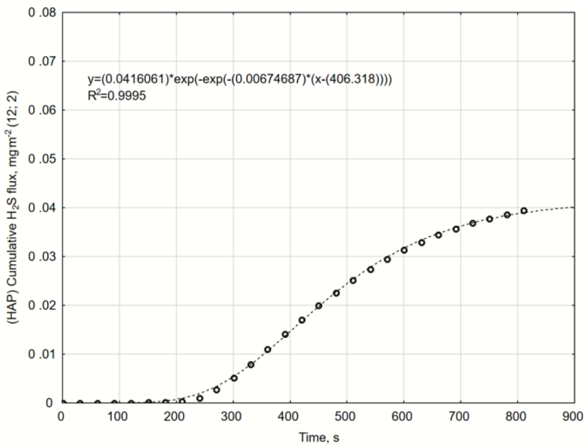

Figure A9. The cumulative H_2S flux. Variant with 12 mm HAP biochar layer, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

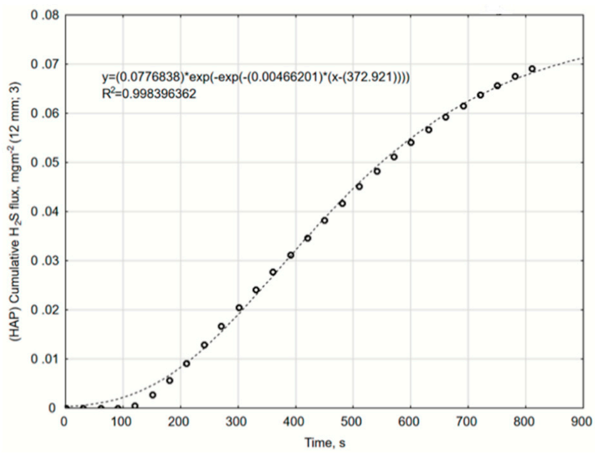

Figure A10. The cumulative H_2S flux. Variant with 12 mm HAP biochar layer, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

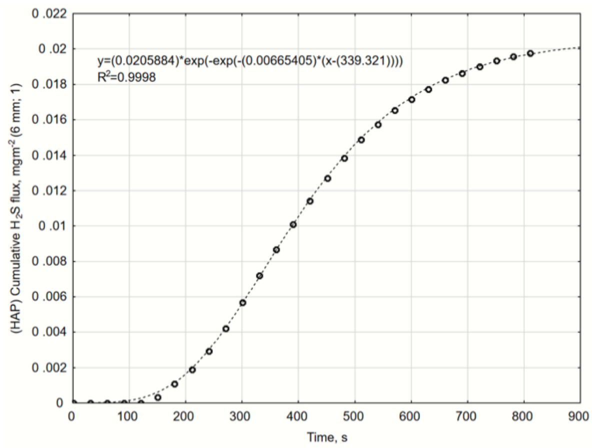

Figure A11. The cumulative H_2S flux. Variant with 6 mm HAP biochar layer, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

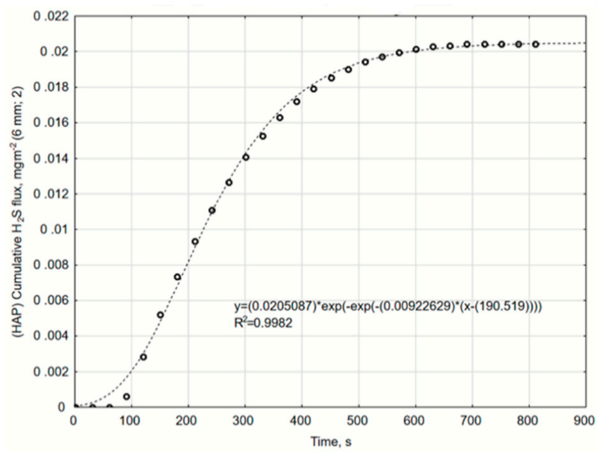

Figure A12. The cumulative H_2S flux. Variant with 6 mm HAP biochar layer, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

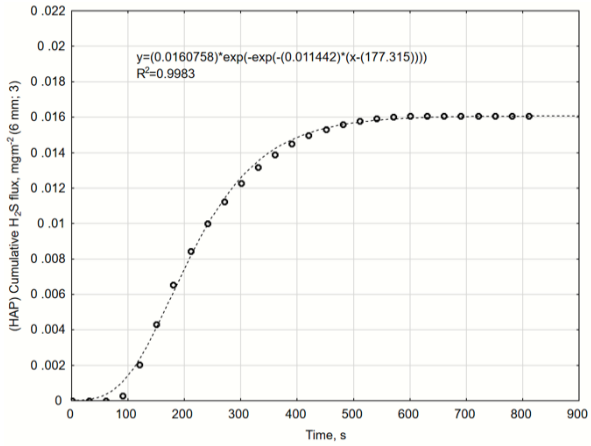

Figure A13. The cumulative H_2S flux. Variant with 6 mm HAP biochar layer, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

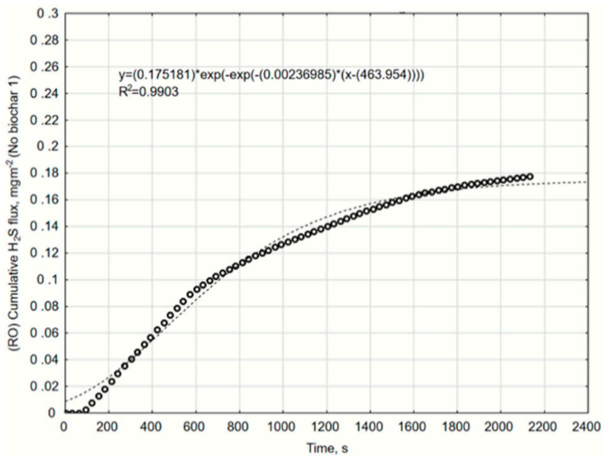

Figure A14. The cumulative H_2S flux. Variant with no RO biochar, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

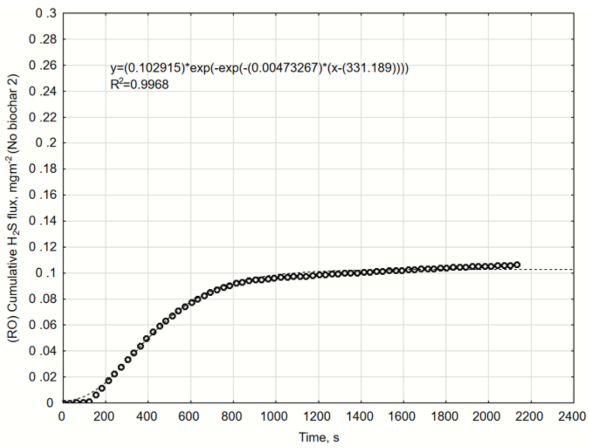

Figure A15. The cumulative H_2S flux. Variant with no RO biochar, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

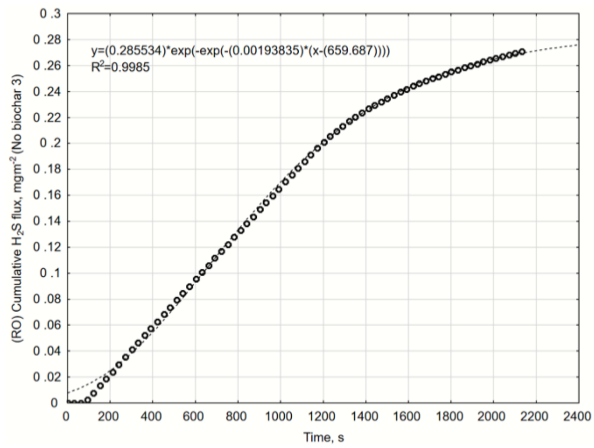

Figure A16. The cumulative H_2S flux. Variant with no RO biochar, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

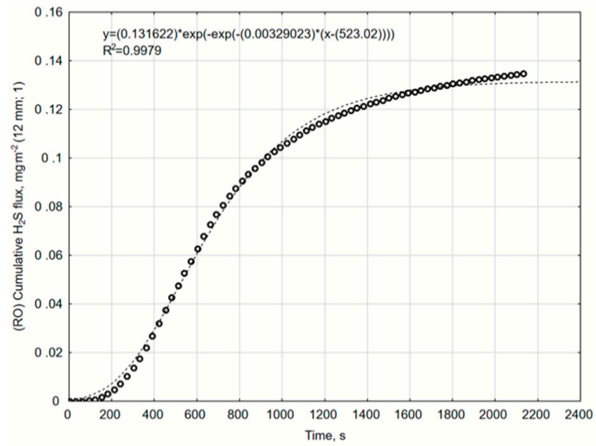

Figure A17. The cumulative H_2S flux. Variant with 12 mm RO biochar layer, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

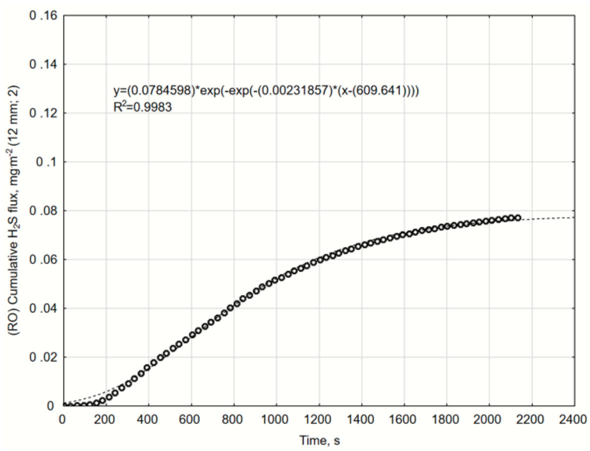

Figure A18. The cumulative H_2S flux. Variant with 12 mm RO biochar layer, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

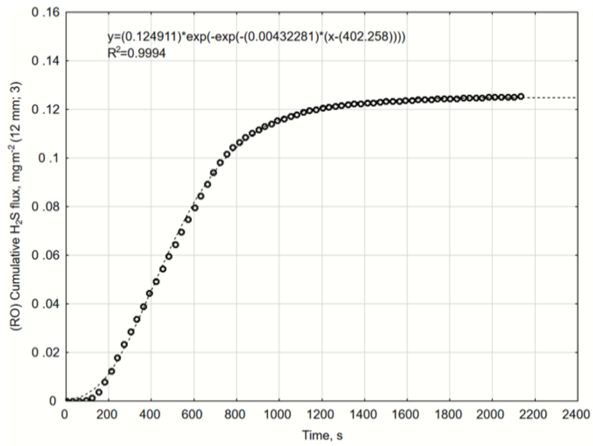

Figure A19. The cumulative H_2S flux. Variant with 12 mm RO biochar layer, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

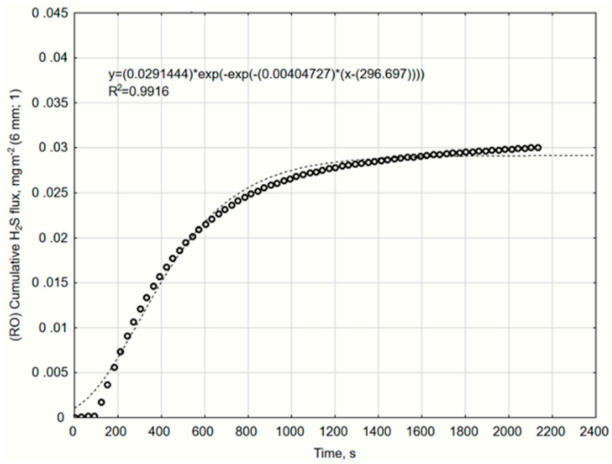

Figure A20. The cumulative H_2S flux. Variant with 6 mm RO biochar layer, repetition 1. Gompertz equation parameters and R^2 determination coefficient.

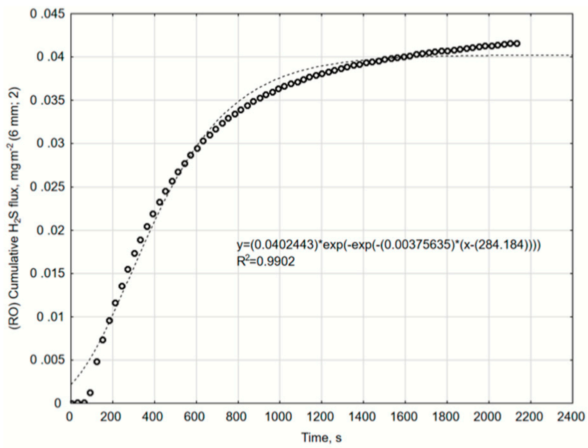

Figure A21. The cumulative H_2S flux. Variant with 6 mm RO biochar layer, repetition 2. Gompertz equation parameters and R^2 determination coefficient.

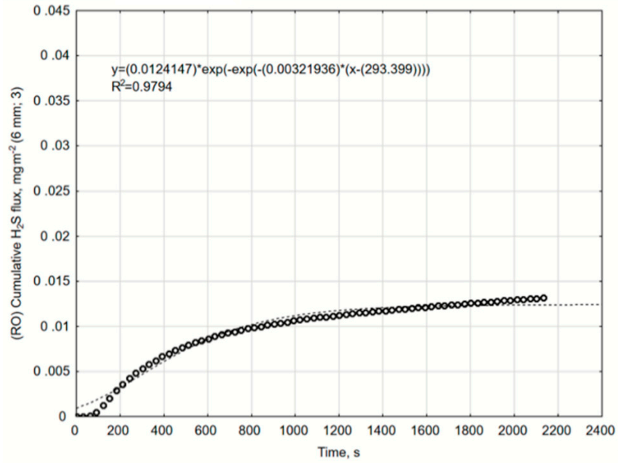

Figure A22. The cumulative H_2S flux. Variant with 6 mm RO biochar layer, repetition 3. Gompertz equation parameters and R^2 determination coefficient.

Appendix B

Table A1. Tukey's HSD test; variable: maximum cumulative H_2S flux ($mg \cdot m^{-2}$). Differences marked with red font are significant ($p < 0.05$).

Biochar		HAP	HAP	HAP	RO	RO	RO
	The Thickness of the Biochar Layer	6	12	No Biochar	6	12	No Biochar
HAP	6		0.971979	0.931431	0.999902	0.186020	0.005935
HAP	12	0.971979		0.999963	0.994297	0.500670	0.020403
HAP	No biochar	0.931431	0.999963		0.977866	0.604926	0.027845
RO	6	0.999902	0.994297	0.977866		0.258371	0.008562
RO	12	0.186020	0.500670	0.604926	0.258371		0.351435
RO	No biochar	0.005935	0.020403	0.027845	0.008562	0.351435	

Table A2. Tukey's HSD test; variable: H_2S emission constant rate (s^{-1}). Differences marked with red font are significant ($p < 0.05$).

Biochar		HAP	HAP	HAP	RO	RO	RO
	The Thickness of the Biochar Layer	6	12	No Biochar	6	12	No Biochar
HAP	6		0.637682	0.999840	0.061820	0.042644	0.031894
HAP	12	0.637682		0.496960	0.570706	0.448007	0.362320
HAP	No biochar	0.999840	0.496960		0.040832	0.028090	0.020990
RO	6	0.061820	0.570706	0.040832		0.999907	0.998455
RO	12	0.042644	0.448007	0.028090	0.999907		0.999973
RO	No biochar	0.031894	0.362320	0.020990	0.998455	0.999973	

Table A3. Tukey's HSD test; variable: The inflection time of the cumulative H_2S emission (s). Differences marked with red font are significant ($p < 0.05$).

Biochar		HAP	HAP	HAP	RO	RO	RO
	The Thickness of the Biochar Layer	6	12	No Biochar	6	12	No Biochar
HAP	6		0.762503	0.998558	0.977229	0.038806	0.068427
HAP	12	0.762503		0.543358	0.986894	0.314408	0.479691
HAP	No biochar	0.998558	0.543358		0.873116	0.020139	0.035707
RO	6	0.977229	0.986894	0.873116		0.124583	0.209978
RO	12	0.038806	0.314408	0.020139	0.124583		0.999261
RO	No biochar	0.068427	0.479691	0.035707	0.209978	0.999261	

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