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Mitigation of acute hydrogen sulfide and ammonia emissions from swine manure during 3-hour agitation using pelletized biochar

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Abstract

The risk of inhalation exposure to elevated concentrations of hydrogen sulfide (H_2S) and ammonia (NH_3) during the agitation of stored swine manure is high. Once or twice a year, farmers agitate manure before pump-out and application to fields. Agitation of the swine manure causes the short-term releases of highly toxic levels of H_2S and NH_3. In our previous pilot-scale studies, the biochar powder had shown significant mitigation of H_2S and NH_3 emissions when surficially applied to manure immediately before agitation. However, fine biochar powder application poses hazards by itself and may not be practical to apply on a farm scale, especially when livestock and workers are present. We hypothesized that applying pelletized biochar to manure surface is just as effective as applying powder to protect farmers and animals from excessive exposure to H_2S and NH_3. This work reports on the lab-scale proof-of-the-concept trials with biochar pellets on the lab-scale. The objective was to compare the biochar pellets and biochar powder on their effectiveness of mitigation on H_2S and NH_3 gases during 3-hour long swine manure agitation. Three scenarios were compared in (n=3) trials (i) control, (ii) 12.5 mm thick surficial application to manure surface of biochar powder, and (iii) an equivalent (by mass) dose of pelletized biochar applied to manure surface. The biochar powder was bound with 35% (wt) water into ~5 × 10 mm (dia × length) pellets. Biochar powder was significantly ($p<0.05$) more effective than the biochar pellets. Still, pellets reduced total H_2S and NH_3 emissions by ~72% and ~68%, respectively ($p=0.001$), compared with ~99% by powder ($p=0.001$). The maximum H_2S & NH_3 concentrations were reduced from 48.1±4.8 ppm & 1,810±850 ppm to 20.8±2.95 ppm & 775±182 ppm by pellets, and to 22.1±16.9 ppm & 40.3±57 ppm by powder, respectively. These reductions are equivalent to reducing the maximum concentrations of H_2S and NH_3 during the 3-h manure agitation by 57% and 57% (pellets) and 54% and 98% (powder), respectively. Treated manure properties hinted at improved nitrogen retention, yet not significant due to high variability. We recommend scaling-up and trials on the farm-scales using biochar pellets to assess the feasibility of application to large manure surfaces and techno-economic evaluation.

1. Introduction

Animal production provides an excellent source of fertilizer in the form of manure for crop production. The animal-production system's sustainability depends on the efficient carbon (C) and nitrogen (N) cycling between manure, crops, and animal feed. Swine manure is generated and stored year-round. However, manure can be utilized by crops seasonally, typically before seed planting and/or after the harvest.

Stored manure requires pump-out and emptying to make room for a continued farm operation. Short-term (hours) agitation of manure is required to stir up and incorporate settled solids into a slurry that pumps can handle. Manure agitation is facilitated by using a high-capacity pump with recirculation for a vigorous mechanical stirring of settled manure solids at the bottom of the storage pit.

Agitation breaks the entrapped gas bubbles and causes the acute release of toxic gases (hydrogen sulfide; H_2S) and nutrients (ammonia; NH_3) (Barker et al., 1986; Donham et al., 1988; Hoff et al., 2006) from swine manure. This routine procedure sometimes results in the loss of livestock and rare unfortunate incidents involving human life lost due to excessive inhalation of H_2S. The Occupational Safety and Health Administration (OSHA) recommends the permissible exposure limits (PELs) concentration for H_2S at 20 ppm (General Industrial Peak Limit) and an acceptable maximum peak above the acceptable ceiling concentration at 50 ppm (General Industry Ceiling Limit), with a maximum duration of 10 min (OSHA, 2017). Hoff et al. (2006) reported the maximum measured H_2S concentrations of 35 ppm during swine manure agitation at a deep-manure store farm in Iowa. But the release mechanism of H_2S causes the in-farm measurements to be unpredictable and irregular (Ni et al., 2018).

The NH_3 gas is one of the causes of odor and secondary particulate matter (PM2.5) aerosols affecting the surrounding communities' air quality. The U.S. NIOSH (National Institute for Occupational Safety and Health) recommends the time-weighted average (TWA) 10-h concentration for NH_3 at 25 ppm and a short-term exposure limit (STL) 15-min at 35 ppm (NIOSH, 1997). Hoff et al. (2006) reported the 4-5 times increase in maximum measured NH_3 emissions during swine manure agitation as compared to before agitation. Ni et al. (2018) reported that the NH_3 concentration inside a swine barn ranged from 0 to 40 ppm. CIGR (1992) and Busse (1993) reported that 20 to 40 ppm of NH_3 would increase respiratory diseases, 50 to 150 ppm causes a decrease of pig growth by 12-29%, and 100 to 200 ppm could cause irritation and anorexia to swine and workers.

There is no proven technology to mitigate the risk and gaseous emissions from agitated manure. Farmers take precautions by maximizing ventilation during agitation and generally avoiding being near the agitated manure storage. Animals can still be exposed to acute releases of uncontrolled emissions. The unfortunate loss of human and animal life continues to occur yearly. A recent evaluation of marketed manure additive products for controlling odor and nutrient emissions losses did not show statistically significant effects (Chen et al., 2020a). Thus, there is a need to mitigate the safety concerns and gaseous emissions representing the loss of nutrients and manure value as a fertilizer.

We have been advancing the use of carbon-rich adsorbent (biochar) as a manure treatment to mitigate gaseous emissions from stored manure (Chen et al., 2021). Biochar is a by-product of the thermal processing of biomass. Biobased-fuels production, waste-to-carbon, and waste-to-energy thermal processes result in a relatively low-value biocoal. Circular economy opportunities exist for the valorization of biochar and the improvement of sustainability in animal and crop production systems (Banik et al., 2021a; Banik et al., 2021b). The long-term goal is to test and scale up the treatments from laboratory-scale to farm-scale, keeping in mind the techno-economic constraints for many swine farmers.

Biochar powder has been proposed as a soil amendment, adsorbent with properties similar to activated charcoal, fertilizer, and alternative fuel (Bialowiec et al., 2018; Stepien et al., 2019a; Pulka et al., 2019). Biochar can be made via pyrolysis or torrefaction from biomass and waste, which with different feedstock and process conditions resulted in biochar with different physicochemical properties (Stepien et al., 2019a; Pulka et al., 2019; Swiechowski et al., 2019; Stepien et al., 2019b; Sygula et al., 2019; Kalus et al., 2019; Kalus et al., 2020a, Kalus et al., 2020b).

Biochar powder is the simplest form of biochar generated in typical pyrolysis. Biochar powder effectively mitigates emissions of H_2S and NH_3 for both long-term (weeks to months) (Meiirkhanuly et al., 2020; Chen et al., 2021) and short-term (few minutes) trials (Chen et al., 2020b; Chen et al., 2020c). Chen et al. reported up to 60% reduction in H_2S emissions and 70 to 80% reduction in NH_3 emissions by surficial biochar powder application immediately before 3-min manure agitation (Chen et al., 2020b; Chen et al., 2020c). Synergistic effects to biochar use could be achieved for the animal-crop production system. First, biochar can be used to mitigate gaseous emissions from manure, and then the biochar and manure mixture can be used as a better quality fertilizer, improve the soil nutrients content and minimize the nutrient losses from soil (Banik et al., 2021a; Banik et al., 2021b). Therefore, innovative biochar treatment could be a one-stop solution to solve the gaseous emissions challenge and improve agriculture's sustainability.

It is impractical to apply biochar powder to large manure surfaces on a farm-scale. Handling powder might be hazardous, especially when livestock and workers are present. Biochar is a fine and lightweight powder that can generate PM air pollution and potentially self-ignite (Dzonzi-undi et al., 2014), while methane (CH_4) is generated by swine manure.

Thus, we propose to use pelletized biochar for the treatment of gaseous emissions from agitated manure. The corn- and wood-derived biochars are difficult to pelletize; therefore, a low-cost 'additive' ('glue') to hold it together is needed. Socio-economic constraints also drive the selection of additives to make biochar pellets for this purpose. However, no data exists on how the pelletized biochar behaves when applied to manure and how effective it is in mitigating gaseous emissions, particularly H_2S and NH_3.

This research aimed to compare the biochar pellets and biochar powder on their effectiveness of mitigation on H_2S and NH_3 gases during swine manure agitation. A 3 h agitation was used to represent a realistic timeline for manure storage stirring immediately before the field application.

2. Material and Methods

The experiment evaluated three scenarios with n=3 replication during 3 h of manure agitation: (*i*) control, (*ii*) 12.5 mm (½ inch) thick surficial application to manure surface of biochar powder, and (*iii*) and an equivalent (in mass) dose of pelletized biochar applied to manure surface. The previous research showed that both 12.5 mm and 6 mm thick surficial application has a similar effect in reducing emissions (Chen et al., 2020b; Chen et al., 2020c). In this research, we selected the thicker powder dose (12.5 mm) to minimize surficial coverage bias due to pelletized biochar's corresponding dose. The pelletized biochar is densified and cannot cover the manure surface as efficiently as uniformly spread powder. This decision was also made to accommodate the proof-of-the concept that biochar pellets can still effectively mitigate emissions.

The reactor used in this experiment has a height of ~40 cm (15 inches) and a diameter of 14 cm (5.5 inches), as shown in Figure 1. The working volume of manure was 3 L, which was freshly collected from a local swine farm with a deep-pit and stored in the lab during the experiment. The Masterflex L/S pump (Masterflex, Gelsenkirchen, Germany) was recirculating the manure at a rate of 10 ml/s. The system was designed to simulate swine manure agitation. However, this lab-scale study's hydraulic retention time is much smaller than the swine manure agitation on a farm (Fullhage, 1994). At the end of this study, 18 samples (3 scenarios with n = 3 and before&after agitation) of manure samples were sent to Brookside Laboratories, Inc. (New Bremen, OH, USA) for analyses. The airflow rate was kept at 2 L/min to match the requirements of the gas measurement system. The feedstock of the HAP biochar was corn stover and was pyrolyzed at 500 °C. Corn stover was ground to 3 mm and treated with 8% (wt) iron sulfate resulted in a pH of 5.2.

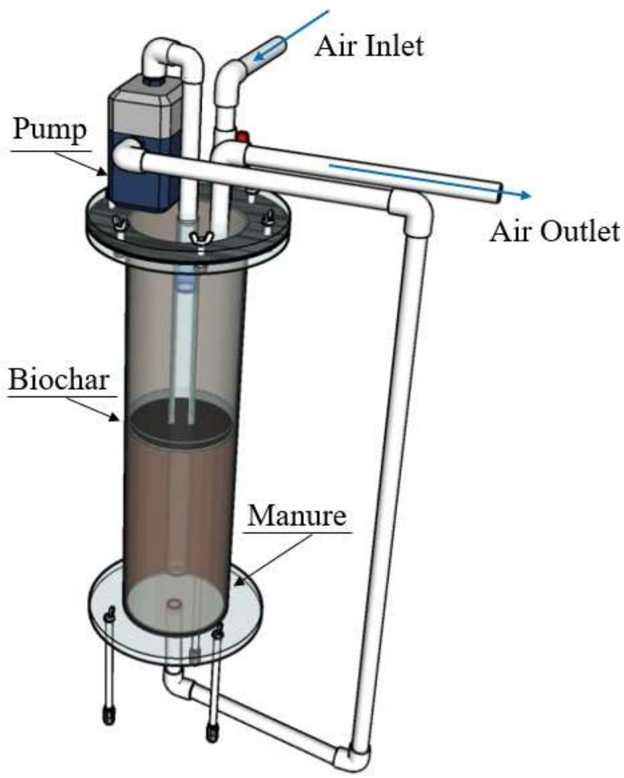

Figure 1. The schematic of the reactor to simulate the process of manure agitation before pump-out.

2.1 Pelletization of biochar

In this research, mild acidic (pH 5.2) Fe-treated porous autothermal (HAPE) biochar made from corn stover was bind with 35% (wt) water into ~5 × 10 mm (3/16 × 3/8 inch, dia × length) pellets. The biochar powder was mixed with 35% (wt) water, then feed into pellet mill PMCL5 (California Pellet Mill, Crawfordsville, IN, USA) with ~ 5 mm disks. The length of pellets varied, but the average was around ~10 mm. The effect of pelletization process on the biochar morphology were then visually compared using the scanning electron microscopy (SEM).

2.2 NH_3 & H_2S Measurements

OMS-300 (Smart Control & Sensing Inc., Daejeon, Rep. of Korea) real-time monitoring system equipped with electrochemical gas sensors H_2S/C-50 and NH_3/CR-5000 (Membrapor, Wallisellen, Switzerland) was used to measure the real-time H_2S and NH_3 concentration in units of parts per millions (ppm). The H_2S sensor can measure up to 100 ppm, and the NH_3 sensor can measure up to 5000 ppm. All sensors were calibrated with standard gases before the experiment (Chen et al., 2020; 2021).

2.3 Manure Properties

Changes in manure properties (Δ Control, Δ Pellets, and Δ Powder) were calculated using the following Equation 1.

$$\Delta\, manure\ property = manure\ property\ after - manure\ property\ before \quad (1)$$

Manure properties such as moisture, mineral matter, and various types of chemicals are all in the units of % wet basis. Then manure properties were compared using Δ Control, Δ Pellets, and Δ Powder.

The percent difference (%Diff) were calculated based on Δ Control vs. Δ Pellets and Δ Control vs. Δ Powder. The following Equation 2 was used:

$$\%Diff = \frac{\Delta\,\text{Treatment} - \quad \text{Control}}{\text{Abs}(\Delta\,\text{Control})} * 100\% \quad (2)$$

Where the Δ Treatment is either changes in manure properties of biochar powder or pellets (Δ Pellets or Δ Powder) and Abs(Δ Control) is the absolute values of the Δ Control. Thus, a negative %Diff indicates manure properties of Δ Treatment were %Diff less than the manure properties of Δ Control; a positive %Diff indicates otherwise.

2.4 Data Analysis

The H_2S and NH_3 concentrations (ppm) were converted into flux units of mg/min using the standard lab conditions. The percent reductions (%R) of biochar treatments were calculated with Equation 3.

$$\%R = \frac{E_{Control} - E_{biochar}}{E_{Control}} * 100\% \quad (3)$$

Whereas $E_{control}$ is the average total emissions or max concentration of H_2S or NH_3 from manure without any treatment during manure agitation, and $E_{biochar}$ is the average total emissions or max concentration of H_2S or NH_3 from manure treated with biochar powder or pellets during agitation.

The One-Way Analysis of Variances (ANOVA) and Tukey-Kraner method was used to analyzed the emissions and calculated the *p*-values of associated %R. The one-tailed T-test was used to calculate the p-values for the %R of the max concentrations. All data analyses were done in JMP (version Pro 15, SAS Institute, Inc., Cary, NC, USA). A *p*-value less than 0.05 was used to determine significance.

3. Results

For all treatments, a nearly immediate spike in the headspace NH_3 and H_2S concentrations was observed at the start of agitation. This spike was also the highest concentration throughout each trial. After the initial spike, the gas concentrations stabilized with a slightly decreasing trend for the pellet treatment (Figures 2 and 3) or returned to the pre-agitation concentrations (for the powder treatment).

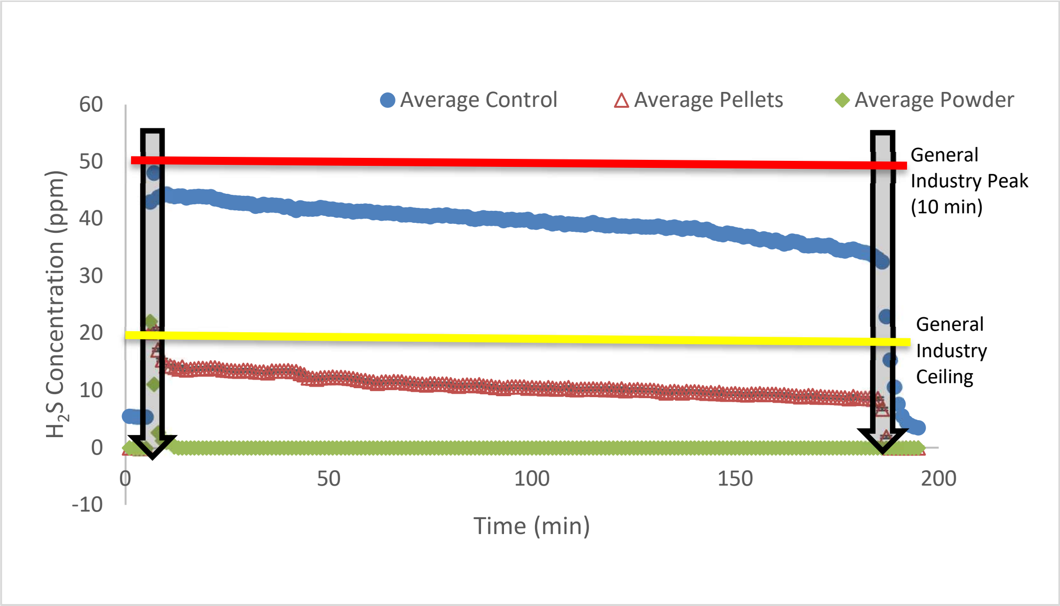

Figure 2. The average headspace concentrations of H_2S during the 3 h agitation of swine manure treated with biochar pellets and powder. The vertical arrows indicate the start and end of manure agitation. The red and yellow lines indicate the OSHA General Industry Peak (50 ppm) and the General Industry Ceiling (20 ppm) concentrations of H_2S.

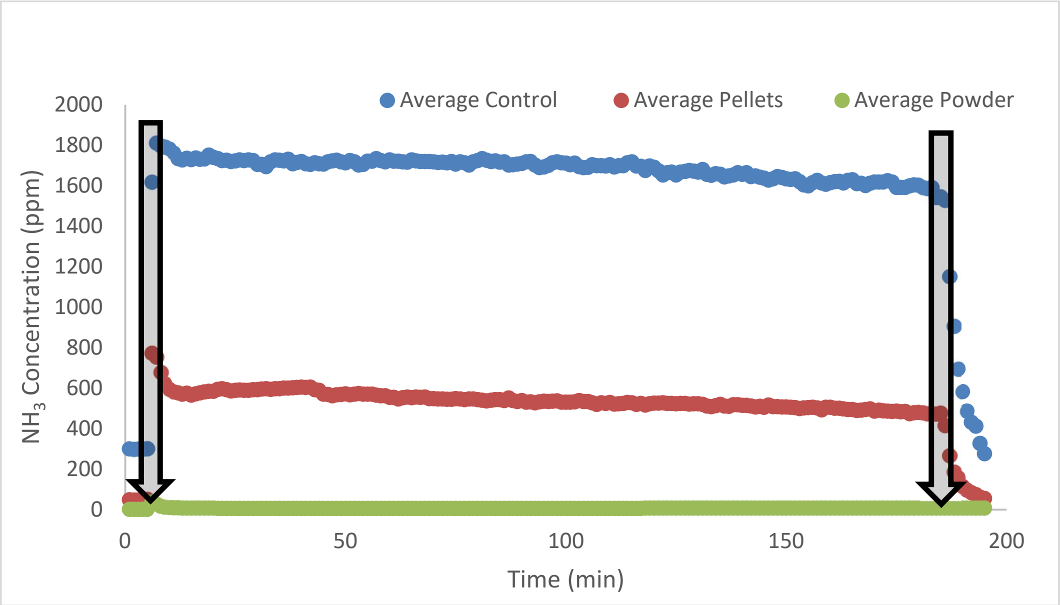

Figure 3. The average headspace concentrations of NH_3 during the 3 h agitation of swine manure treated with biochar pellets and powder. The vertical arrows indicate the start and end of manure agitation. The U.S. NIOSH (National Institute for Occupational Safety and Health) recommends the time-weighted average (TWA) 10-h concentration for NH_3 at 25 ppm and a short-term exposure limit (STL) 15-min at 35 ppm (not shown to retain figure legibility).

The biochar powder had a greater mitigation effect than biochar pellets for both H_2S and NH_3 emissions during manure agitation (Table 1). The biochar pellets treatment significantly reduced the maximum H_2S concentration by 57% ($p = 0.02$). The NH_3 maximum concentration was also reduced by the same percentage (57%), but it was not significant ($p = 0.08$). The biochar powder treatment significantly reduced the maximum NH_3 concentration by 98% ($p = 0.001$), while the percent reduction of the maximum H_2S concentration (54%) was not significant ($p = 0.052$).

Table 1. The maximum headspace concentrations of H_2S and NH_3 (± standard deviation), % reductions (%R) during the 3 h agitation of swine manure averaged for n=3 trials. Statistical significance is reported as (*p*-values) and bold font.

	Control	**Pellets**	**Powder**
Maximum H_2S Concentration, ppm	48.1 ± 4.84	20.8 ± 2.95	22.1 ± 16.9
%R (*p*-value)	-	**57%** (0.02)	54% (0.052)
Maximum NH_3 Concentration, ppm	1,811 ± 852	775 ± 182	40.3 ± 57.0
%R (*p*-value)	-	57% (0.08)	**98%** (0.001)

The total H_2S and NH_3 emissions were also significantly (p=0.001) mitigated by biochar pellets and powder (Table 2). Biochar pellets reduced the total H_2S and NH_3 emissions by 72% and 68%, whereas biochar powder reduced the H_2S and NH_3 by 99% during the 3 h of swine manure agitation.

Table 2. The total emissions of H_2S and NH_3 (± standard deviation), % reductions (%R) during the 3 h agitation of swine manure averaged for n=3 trials. Statistical significance is reported as (*p*-values) and bold font.

	Control	**Pellets**	**Powder**
Total Emission of H_2S, mg/m^2	1.31 ± 0.305	0.361 ± 0.0453	0.0071 ± 0.005
%R (*p*-value)	-	**72%** (0.001)	**99%** (0.001)
Total Emission of NH_3, mg/m^2	28.0 ± 12.3	8.93 ± 1.70	0.152 ± 0.216
%R (*p*-value)	-	**68%** (0.001)	**99%** (0.001)

The average H_2S concentrations of Control and both Treatments were lower than the General Industry Peak (50 ppm, 10 min), but the H_2S concentrations of the Control were above the General Industry Ceiling (20 ppm) during the 3-h agitation. Both biochar pellets and powder treatments kept the H_2S concentrations below the General Industry Ceiling except for the first two minutes of agitation (Figure 2).

The average NH_3 concentration for the biochar powder treatment was below both TWA and STL limits (25 and 35 ppm, respectively). In contrast, the average NH_3 concentrations of Control and biochar pellets treatment were above STL and TWA limits even before the manure agitation and throughout the experiments.

There was no statistical significance to the selected manure properties due to the high variability in manure properties changes among the Control, Pellets, and Powder (Table 3, Table A1) except for the mineral matter and Na content. It is worth noting that both biochar pellets and powder (-0.008) showed ~50% smaller decreases in total N (-0.008% & -0.007%, respectively) when compared with the Control (-0.016), indicating a potential to retain more N in manure with biochar treatments. Biochar pellets and powder showed a smaller decrease in ammonium-N (~75%, -0.005 & ~50%, -0.008, respectively) in comparison with the Control (-0.015). Both biochar treatments increased the carbon content in the manure, whereas the Control showed a decrease in carbon content, as shown Carbon % and C/N ratio (Table 3, Table A1). Additional work and scaleup trials are still needed to elucidate statistical significance to these initial observations hinting at the potentially improved manure quality treated with biochar.

Table 3. The average changes (Δ) in manure properties from '*before*' and '*after*' 3-h manure agitation. A negative Δ value indicates a decrease, and a positive value indicates an increase. Moisture, mineral matter, and targeted chemicals are in units of % wet basis. A negative %Diff indicates manure properties of Δ Treatment were %Diff less than the manure properties of Δ Control; a positive %Diff indicates otherwise. The **bold** font indicates statistical significance. *p*-Values are listed inside parentheses.

Manure Property	**Δ Control (% wet basis)**	**Δ Pellet (% wet basis)**	**Δ Powder (% wet basis)**
Moisture	0.073	0.043	-0.020
%Diff	-	-41 (0.41)	-127 (0.07)
Mineral Matter	-0.067	-0.053	0.010
%Diff	-	20 (0.43)	**115 (0.03)**
Total Nitrogen	-0.016	-0.008	-0.007
%Diff	-	49 (0.28)	55 (0.28)
Ammonium-N (NH_4-N)	-0.015	-0.005	-0.008
%Diff	-	64 (0.22)	45 (0.26)
Nitrate-N (NO_3-N)	0.000	0.000	0.000
%Diff	-	0	0
Organic-N	-0.001	-0.003	0.001
%Diff		-167 (0.33)	200 (0.38)
Phosphorus (P)	-0.006	-0.007	-0.002
%Diff		-22 (0.41)	61 (0.11)
Potassium (K)	0.002	-0.005	0.006
%Diff		-380 (0.15)	280 (0.12)
Calcium (Ca)	-0.004	-0.004	-0.004
%Diff		0	0
Magnesium (Mg)	-0.003	-0.005	0.000
%Diff		-60 (0.34)	100 (0.09)
Sodium (Na)	0.001	-0.003	-0.001
%Diff		**-550 (0.04)**	-200 (0.12)
Sulfur (S)	-0.003	-0.005	0.000
%Diff		-78 (0.09)	100 (0.22)
Carbon (C)	-0.003	0.093	0.013
%Diff		2,900 (0.15)	500 (0.35)
pH	0.003	-0.020	0.007
%Diff		-700 (0.06)	100 (0.47)
C/N ratio	-0.053	0.560	0.040
%Diff		1,150 (0.14)	175 (0.36)

4. Discussion

This proof-of-concept experiment showed biochar pellets have the potential in short-term (up to 3 h) mitigation of H_2S and NH_3 emissions during manure agitation but might not be as effective as biochar powder. Biochar pellets and powder treatments showed similar reductions on max H_2S concentrations, but biochar powder showed a much higher reduction on maximum NH_3 concentrations. For total emissions of both H_2S and NH_3, biochar powder showed significantly higher reductions than biochar pellets. The pH of the biochar was 5.2, which theoretically helps to retain nitrogen in liquid manure as ammonium.

Most of the biochar pellets dissolved and sunk nearly immediately after application. Some dissolved pellets fragments and powder were suspended in the manure after application (Figure A1). All biochar powder floated on top of the manure during manure agitation. Interestingly, biochar powder appeared to act as a physical barrier on the manure surface that kept most gas bubbles from being released from the liquid into the atmosphere. This behavior was confirmed (Figure A2) by applying biochar powder to the surface of DI water followed by agitation. We attempted to further elucidate the reasons for this difference in biochar behavior by taking SEM images. Pelletization of biochar powder 'crushed' the pores with a diameter of 2-3 um (Figure 4). Thus, the pelletization made the pellets denser and less porous.

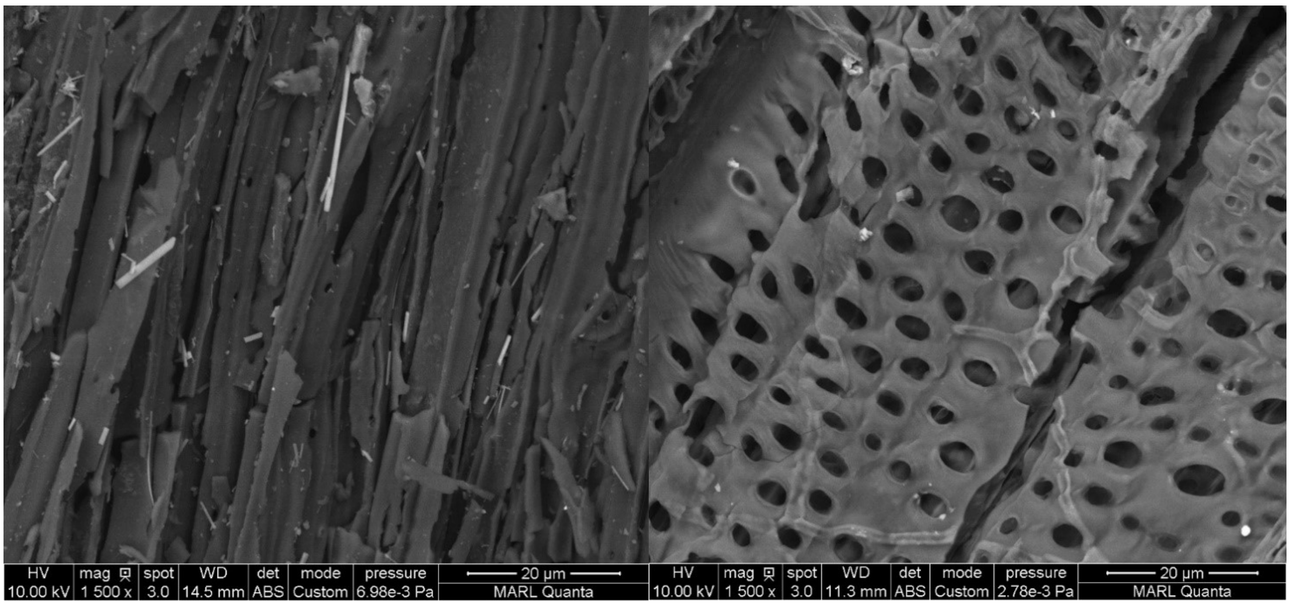

Figure 4. Comparison of the SEM images of biochar pellets (left) and biochar powder (right) shows morphological changes occur during pelletization.

Results comparing the changes in manure properties confirmed that acidic biochar could mitigate NH_3 emissions and likely prevent nitrogen loss in the manure. Manure treated with biochar powder showed benefits to soil health, lowered nutrient runoff risk, and the potential for agronomic benefits to corn and soybeans (Banik et al., 2021a, 2021b) shown on lab and greenhouse scales. In addition, more techno-economic analyses are warranted on the potential savings due to the nutrient retention in manure, as the average cost of anhydrous ammonia is $526/ton (USDA, 2021).

In future research, the different blinders that optimize biochar properties, including but not limited to floatability, porous, pH, need to be evaluated. The properties of biochar vary due to the pyrolysis or

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torrefaction process, feedstock, and pre-treatment. Thus, biochar properties can be made specially targeted to mitigate emissions of unwanted gases. The long-term effects of biochar pellets also need to be studied.

5. Conclusion

This research addresses the need to develop practical mitigation technologies for short-term release of highly toxic gases from agitated manure. Guided by the earlier success with using biochar powder to mitigate emissions, we addressed herein the concern about the hazardous nature of fine powder. This research tested the proof-of-the-concept pelletized biochar application to manure surface as intrinsically safer to use to easier to apply in farm conditions. The lab-scale results showed that while less effective than powder, the pelletized biochar can be recommended for continued research in scaled up applications. Specific results are summarized as follows:

1. Biochar powder was significantly ($p<0.05$) more effective than the biochar pellets.
2. Pellets reduced total H_2S and NH_3 emissions by ~72% and ~68%, respectively ($p=0.001$), compared with ~99% by powder ($p=0.001$).
3. The maximum H_2S & NH_3 concentrations were reduced from 48.1±4.8 ppm & 1,810±850 ppm to 20.8±2.95 ppm & 775±182 ppm by pellets, and to 22.1±16.9 ppm & 40.3±57 ppm by powder, respectively. These reductions are equivalent to reducing the maximum concentrations of H_2S and NH_3 during the 3-h manure agitation by 57% and 57% (pellets) and 54% and 98% (powder), respectively.
4. The changes in manure properties treated with biochar showed less loss of nitrogen and more carbon compared with the control, albeit not significant due to variability. This early observation should be further explored as the biochar treatment of manure hints on improved manure quality, and, therefore the potential for improved sustainability of on the nexus of animal and crop production.

6. Appendix

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Figure A1. The visualization of biochar pellets dissolution during agitation demonstrated using DI water.

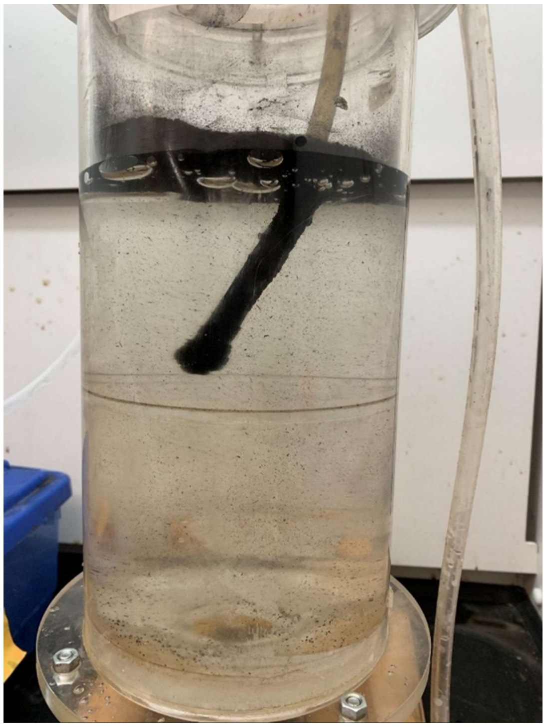

Figure A2. The visualization of the floating biochar powder layer that keeps the air bubbles from being released from DI water into the headspace.

Table A1. The average changes (Δ) in manure properties from 'before' and 'after' 3-h manure agitation. A negative Δ value indicates a decrease, and a positive value indicates an increase. Moisture, mineral matter, and targeted chemicals are in units of g/L. A negative %Diff indicates manure properties of Δ Treatment were %Diff less than the manure properties of Δ Control; a positive %Diff indicates otherwise. The **bold** font stated statistical significance.

Manure Property (g/L)	**Δ Control**	**Δ Pellet**	**Δ Powder**
Moisture	7.112	-10.79	3.95
%Diff		-252 (0.11)	-44 (0.35)
Mineral Matter	-0.619	-0.614	0.123
%Diff		1 (0.50)	**120 (0.03)**
Total Nitrogen	-0.143	-0.101	-0.062
%Diff		29 (0.39)	57 (0.31)
Ammonium-N (NH_4-N)	-0.135	-0.075	-0.072
%Diff		45 (0.33)	47 (0.30)
Organic-N	-0.008	-0.027	0.010
%Diff		-219 (0.31)	214 (0.39)
Phosphorus (P)	-0.038	-0.076	-0.023

%Diff		-99 (0.29)	41 (0.32)
Potassium (K)	0.028	-0.065	0.071
%Diff		-338 (0.14)	158 (0.16)
Calcium (Ca)	-0.036	-0.038	-0.037
%Diff		-6 (0.48)	-2 (0.49)
Sodium (Na)	0.010	-0.036	-0.004
%Diff		**-446 (0.047)**	-142 (0.12)
Sulfur (S)	-0.028	-0.058	0.001
%Diff		-109 (0.106)	104 (0.23)
Carbon (C)	-0.010	0.886	0.149
%Diff		9,346 (0.166)	1,650 (0.36)

7. Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

8. Funding

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9. References

Barker, J.; Curtis, S.; Hogsett, O.; Humenik, F. (1986). Safety in swine production systems. Raleigh: N.C. Cooperative Extension Service.

Banik, C.; Koziel, J.; De, M.; Bonds, D.; Chen, B.; Singh, A.; Licht, M. (2021a) Soil nutrients and carbon dynamics in the presence of biochar-swine manure mixture under controlled leaching experiment using a Midwestern Mollisols. *Front. Environ. Sci.*, 9, 66. doi: 10.3389/fenvs.2021.609621.

Banik, C.; Koziel, J.; Bonds, D.; Singh, A.; Licht, M. (2021b) Comparing biochar-swine manure mixture to conventional manure impact on soil nutrient availability and plant uptake – A greenhouse study, *Land* 10(4), 372. doi: 10.3390/land10040372.

Białowiec, A.; Micuda, M.; Koziel, J.A. (2018).Waste to Carbon: Densification of Torrefied Refuse-Derived Fuel. *Energies*, *11*, 3233, doi:10.3390/en11113233.

Busse, F.W. (1993) Comparison measurements of the house climate in swine stables with and without respiratory diseases or cannibalism. In: E. Collins & C. Boon (eds): Livestock Environment. Fourth International Symposium, pp. 904-908.

Chen, B.; Koziel, J.A.; Banik, C.; Ma, H.; Lee, M.; Wi, J.; Meiirkhanuly, Z.; O'Brien, S.C.; Li, P.; Andersen, D.S.; Białowiec, A.; Parker, D.B. (2020a) Mitigation of Odor, NH_3, H_2S, GHG, and VOC Emissions With Current Products for Use in Deep-Pit Swine Manure Storage Structures. *Front. Environ. Sci.* 8:613646. doi: 10.3389/fenvs.2020.613646

Chen, B.; Koziel, J.A.; Białowiec, A.; Lee, M.; Ma, H.; Li, P.; Meiirkhanuly, Z.; Brown, R.C. (2020b). The Impact of Surficial Biochar Treatment on Acute H_2S Emissions during Swine Manure Agitation before Pump- Out: Proof- of- the- Concept. *Catalysts*, 10, 940. https://doi.org/10.3390/catal10080940.

Chen, B.; Koziel, J.A.; Lee, M.; Ma, H.; Meiirkhanuly, Z.; Li, P.; Białowiec, A.; Brown, R.C. (2020c). Mitigation of Acute Ammonia Emissions with Biochar during Swine Manure Agitation before Pump-Out: Proof-of-the-Concept. *Front. Environ. Sci.*, 9, 98. doi: 10.3389/fenvs.2021.613614.

Chen, B; Koziel, J. A.; Banik, C; Ma, H; Lee, M; O'Brien, S. C.; Li, P; Andersen, D. S.; Białowiec, A; Brown, R. C. (2021). Mitigation of Gaseous Emissions from Stored Swine Manure with Biochar: Effect of Dose and Reapplication on a Pilot-Scale. *Atmosphere*, 12(1), 96. doi: 10.3390/atmos12010096.

CIGR. (1992). *Climatization of Animal Houses*. 2nd ed. Commission Internationale du Génie Rurale, Faculty of Agricultural Sciences, State University of Gent, Gent, Belgium.

Donham, J. K; Yeggy, J; and Dague, R. R. (1988) Production Rates of Toxic Gases from Liquid Swine Manure: Health Implications for Workers and Animals in Swine Confinement Buildings. *Biological Wastes* 24, 3: 161–173. https://doi.org/10.1016/0269-7483(88)90059-6.

Dzonzi-undi, J.; Masek, O.; & Abass, O. (2014). Determination of spontaneous ignition behavior of biochar accumulations. *International Journal of Science and Research*, 3, 656–661.

Fulhage, D. C. (1994). "Solids Removal From Livestock Manure Lagoons." University of Missouri Extension. Accessed February 17, 2021. https://extension.missouri.edu/publications/wq324.

Hoff, S.J.; Bundy, D.S.; Nelson, M.A.; Zelle, B.C.; Jacobson, L.D.; Heber, A.J.; Ni, J.Q.; Zhang, Y.; Koziel, J.A.; Beasley D.B. (2006). Emissions of ammonia, hydrogen sulfide, and odor before, during and after slurry removal from a deep-pit swine finisher. *Journal of the Air & Waste Management Association*, *56*, 581-590, doi: 10.1080/10473289.2006.10464472.

USDA. (2021). Iowa production costs report. Washington, D.C.: USDA Agricultural Marketing Service. Retrieved from www.ams.usda.gov/mnreports/nw_gr210.txt.

Kalus, K.; Koziel, J.A.; Opaliński, S. (2019). A Review of Biochar Properties and Their Utilization in Crop Agriculture and Livestock Production. *Appl. Sci. 9*, 3494, doi:10.3390/app9173494.

Kalus, K.; Konkol, D.; Korczyński, M.; Koziel, J.A.; Opaliński, S. (2020a). Effect of Biochar Diet Supplementation on Chicken Broilers Performance, NH_3 and Odor Emissions and Meat Consumer Acceptance. *Animals*, 10, 1539, doi: 10.3390/ani10091539.

Kalus, K.; Konkol, D.; Korczyński, M.; Koziel, J.A.; Opaliński, S. (2020b). Laying Hens Biochar Diet Supplementation—Effect on Performance, Excreta N Content, NH3 and VOCs Emissions, Egg Traits and Egg Consumers Acceptance. *Agriculture*, 10, 237, doi: 10.3390/agriculture10060237.

Meiirkhanuly, Z; Koziel, J .A.; Chen, B; Białowiec, A; Lee, M; Wi, J; Banik, C; Brown, R. C.; Bakshi, S. (2020). "Mitigation of Gaseous Emissions from Swine Manure with the Surficial Application of Biochars" *Atmosphere,* 11(11), 1179. doi: 10.3390/atmos11111179.

NIOSH Pocket Guide to Chemical Hazards. (1997) Cincinnati, Ohio: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.

Ni, J. Q.; Heber; A. J. and Lim, T. T. (2018). Ammonia and hydrogen sulfide in swine production. In: Air Quality and Livestock Farming, pp. 69–88. *CRC Press*, London, UK.

OSHA. (2017). 29 CFR 1910.1000, Table Z-2: Toxic and Hazardous Substances; Occupational Safety and Health Administration: Washington, DC, USA.

Pulka, J.; Manczarski, P.; Koziel, J.A.; Białowiec, A. (2019). Torrefaction of Sewage Sludge: Kinetics and Fuel Properties of Biochars. *Energies 12*, 565, doi:10.3390/en12030565.

Stępień, P.; Świechowski, K.; Hnat, M.; Kugler, S.; Stegenta-Dąbrowska, S.; Koziel, J.A.; Manczarski, P.; Białowiec, A. (2019a). Waste to Carbon: Biocoal from Elephant Dung as New Cooking Fuel. *Energies 12*, 4344, doi:10.3390/en12224344.

Stępień, P.; Serowik, M.; Koziel, J.A.; Białowiec, A. (2019b). Waste to carbon: estimating the demand for production of carbonized refuse-derived fuel. *Sustainability 11*, 5685, doi:10.3390/su11205685.

Świechowski, K.; Stegenta-Dąbrowska, S.; Liszewski, M.; Bąbelewski, P.; Koziel, J.A.; Białowiec, A. (2019). Oxytree Pruned Biomass Torrefaction: Process Kinetics. *Materials 12*, 3334, doi:10.3390/ma12203334.