Biochar as a cover for dairy manure lagoons: reducing odor and gas emissions while capturing nutrients

By

Brian Dougherty

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Abstract

Liquid manure lagoons are known to be sources of odor and environmentally damaging gas emissions. Land application of the manure slurry after storage can lead to detrimental nutrient runoff and leaching. Floating lagoon covers (biocovers) are one option for reducing emissions, but to date they have only been used to address odors and emissions but not to address the problem of nutrient loss. This study evaluated the potential of floating biochar covers to reduce odor and gas emissions while simultaneously capturing nutrients from liquid dairy manure. The unique physical and chemical properties of biochars make them promising materials for odor, gas, and nutrient sorption. This new approach has the potential to mitigate multiple environmental problems.

Two biochars were used to test this approach: one made from Douglas-fir chips under a low oxygen combustion environment at 650°C (FC650), and the other made from Douglas-fir hog fuel pyrolyzed at 600°C (HF600). The HF600 biocover reduced mean headspace ammonia (NH_3) concentration by 7.5 to 13.6 μL/L. No significant reduction was found with the FC650 biocover. These biochars were able to sorb and hold nutrients while floating on the surface. Nutrient uptake by the two biochars ranged from 0.21 to 4.88 mg nitrogen g biochar^{-1} and 0.64 to 2.70 mg phosphorus g biochar^{-1}. Potassium ranged from a loss of 4.52 to a gain of 2.65 mg g biochar^{-1}. The biochars also sorbed calcium, magnesium, sodium, iron, aluminum, manganese, and silicon. In a separate experiment, a panel of judges evaluated the odor offensiveness (-10 to 10 scale) and odor threshold (1 to 10 scale) of five cover treatments including four biochars. Mean odor offensiveness ranged from -0.4 to -1.4 vs. -2.1 for the control. Mean odor threshold ranged from 1.6 to 2.1 vs. 2.6 for the control. These results show that biochar covers hold promise as an effective means for reducing odor and gas emissions while sorbing nutrients from liquid dairy manure. More research is needed to determine optimal biochar feedstock, production temperature, pH, and particle size distribution for use as a biocover material.

Introduction

The increasing prevalence of confined livestock production has led to an increase in the use of liquid manure (slurry) storage structures. These structures enable manure to be stored and subsequently spread when conditions are favorable or nutrients are needed for crop growth. However, these structures can be sources of odor (Blanes-Vidal et al., 2009) and greenhouse gasses (GHGs) including methane, carbon dioxide, and nitrous oxide (Leytem et al., 2011) during manure storage. The relationship between odor and specific gasses from livestock manure has proven difficult to quantify. However, strong odors from livestock operations are commonly associated with volatile compounds including ammonia (NH_3), sulfides, volatile fatty acids, phenols and indoles (Hobbs et al. 2000). Livestock manure is a particularly significant source of odorous NH_3 emissions (Vaddella et al., 2011). Animal agriculture accounts for an estimated 50 to 85 percent of total man-made NH_3 volatilization in the United States (Battye, 1994), and agricultural activities, including confined livestock, account for up to 80% of total NH_3 emissions worldwide (U.S. EPA, 2002). Ammonia and sulfide-containing compounds from livestock manure can contribute to ground-level air pollution (National Research Council (U.S.), 2003). Emissions of NH_3 can also contribute to eutrophication of water and have other detrimental impacts on ecosystems (Camargo and Alonso, 2006). Additionally, land application of the slurry after storage can lead to nutrient runoff and leaching when manure application exceeds the needs of crops (Carpenter et al., 1998). Regulations regarding odor emissions and field application of manure are likely to make it increasingly difficult to manage livestock manure in this manner in the future (NRC, 2003).

One practice that has proven effective in dealing with gas emissions is the application of a floating cover on the surface of the manure slurry. Various biologically-based materials (biocovers) have been tested for this purpose (Clanton et al., 1999), (Guarino et al., 2006), (Regmi et al., 2007), (Hudson et al., 2008). Straw, vegetable oil, corn stover, and wood chip biocovers have shown variable effectiveness for reducing odor, ammonia (NH_3) and hydrogen sulfide (H_2S) emissions (VanderZaag et al., 2008). While somewhat effective for reducing odor and gas emissions, biocovers have not been widely used. In many

cases their use is not justified due to the expense and difficulty of application and maintenance of the cover. Biocovers made from materials tested thus far may not offer additional benefits including nutrient capture or carbon sequestration. More efficient, multi-purpose cover materials are needed to address the problems associated with slurry storage.

One biocover material that has the potential to offer multiple benefits is biochar. Biochars are black carbon materials that are produced when biomass is heated to high temperatures without oxygen in a process known as pyrolysis. The process results in volatilization and loss of organic compounds leaving behind a carbon-rich material similar to charcoal. Biochars are resistant to decay in the environment and can persist for long periods of time, meaning that a portion of the carbon in biochars can be considered sequestered carbon (Lehmann, 2007) if returned to the soil. In addition to sequestering carbon, biochars can improve soil productivity, particularly for degraded and lower quality soils (Lehmann and Joseph, 2009). Biochars have unique chemical and physical properties including a highly porous structure at scales ranging from nanometers to millimeters and large surface area that can exceed 100 m^2 g^{-1}. This makes them suitable for a range of environmental applications including odor, gas, and nutrient sorption (Xie et al., 2015).

The application of biochar as a biocover on liquid manure storage structures has the potential to provide multiple environmental benefits. These include reduced odor and gas emissions along with sorption of valuable nutrients. When applied to soil, the nutrient-enriched biochar can serve as a fertilizer source for plants while improving soils and sequestering carbon. The high porosity, low density, and nutrient retention capabilities of biochars make them a good candidate for use as a biocover. Biochar has been shown to be effective in adsorbing and retaining nutrients from dairy lagoon effluent (Streubel et al., 2012), (Sarkhot et al., 2013). Research has further demonstrated that a biochar enriched with dairy manure effluent reduced GHG emissions and increased carbon (C) and nitrogen (N) storage when applied to soil (Sarkhot et al., 2012). It has also been proposed that biochars can be used to capture excess nutrients from dairy wastewater to create a sustainable nutrient recycling loop (Ghezzehei et al., 2014).

In order to justify the use of biochar as a lagoon cover, it must offer advantages over traditional cover materials. Floating biochar covers have the potential to be an effective approach for capturing nutrients while suppressing odor and gas emissions. However, to date no biochar research has documented simultaneous nutrient sorption, reduced gas emissions, and odor mitigation from livestock manure. Determining the efficacy of floating biochar covers is necessary for proof-of-concept of this technology. The objectives of this study were to determine the effectiveness of floating biochar covers for (i) reducing gas emissions, (ii) adsorbing nutrients, and (iii) mitigating odor from dairy manure slurry.

Materials and Methods

Two different experiments were carried out for this study. In Experiment 1, concentrations of NH_3 and H_2S emitted from floating biochar and straw covers were measured over an eight week period. The covers were then removed and analyzed to determine nutrient uptake. In Experiment 2, a panel of judges evaluated odor from floating biochar and straw covers over a 12 week period.

Manure Source and Analysis

Two different dairy manure slurries were used for Experiment 1. Manure 1(M1) was collected from the Oregon State University Dairy Research Center in Corvallis, OR on Aug. 14, 2014. The manure was flushed from the dairy barn with water and collected from a holding basin prior to solids separation. Manure 2 (M2) was collected from Jer-Osa Dairy near Gervais, OR on Aug. 15, 2014. The manure was gathered from an alleyway adjacent to a collection basin. It was not mixed with flush water. For Experiment 2, Manure 3 (M3) was collected from the Oregon State University Dairy Research Center on Oct. 12, 2015 in the same manner as M1. Manure samples were submitted to Dairyland Laboratories, Arcadia, WI for analysis. Solids content by mass was 0.64%, 5.39%, and 0.64% for Manures 1 through 3 respectively. Results from the elemental analysis are shown in Table 1.

Table 1. Elemental analysis of manures used in Experiment 1 (Manures 1 and 2) and Experiment 2 (Manure 3)

Element	Manure 1 (M1)†	Manure 2 (M2)†	Manure 3 (M3)†
	mg L^{-1} of manure		
N	300	1200	600
P	200	500	100
K	900	1200	1300
Ca	500	3700	600
Mg	200	600	200
S	100	300	100
Na	180	336	210
Fe	17	237	33
Al	7	183	24
Zn	4	18	22
Mn	5	16	5
Cu	3	14	1
B	1	3	1

† n = 1 for each manure

Biocover Source and Analysis

All biochars were acquired from Bio-Logical Carbon, LLC in Philomath, OR. Two biochars were used in Experiment 1. The first was a Douglas-fir chip biochar made via gasification at approximately 650°C (FC650). The second was a Douglas-fir hog fuel biochar made via slow pyrolysis at approximately 600°C (HF600). Four biochars were used in Experiment 2. Two were Douglas-fir hog fuel biochars made via slow pyrolysis at 550°C (HF550) and 350°C (HF350) respectively. The third was a pine chip biochar made via slow pyrolysis at 500°C (PC500). The fourth was a Douglas-fir hog fuel biochar produced via rapid (seconds to a few minutes) combustion in an industrial cogeneration facility at 1200°C (HF1200). The feedstock used for all hog fuel biochars was a mixture of Douglas-fir bark, cambium, center wood, and shavings. The wheat straw (Straw) for both experiments was acquired from the Oregon State University Dairy Research Center in Corvallis, Oregon.

Proximate analysis was done on 3 replicates of each biochar to determine ash, volatile matter, and fixed carbon content according to the American Society of Testing and Materials (ASTM) D1762-84 method (ASTM, 2007). Electrical conductivity (EC) and pH were determined by preparing suspensions of biochar particles (<250μm) in water (1% w/w). The suspensions were heated to 90°C and stirred for 20 min. then cooled to room temperature. Electrical conductivity was measured with an EC4083 meter (Amber Science Inc., Eugene, OR) and pH was measured with a PT-15 meter (Sartorius Corp., Bohemia, NY). The results are shown in Table 2.

Table 2. Characteristics of biochars used in Experiment 1 (FC650 and HF600) and Experiment 2 (HF1200, HF550, HF350, and PC500)

	Experiment 1		Experiment 2			
Property	**(FC650)**	**(HF600)**	**(HF1200)**	**(HF550)**	**(HF350)**	**(PC500)**
Moisture, mg g^{-1}	145.8 ± 7.38	81.9 ± 0.63	128.2 ± 1.42	91.7 ± 3.57	138.6 ± 3.85	163.7 ± 11.66
Volatile matter, mg g^{-1}	72.4 ± 1.45	113.3 ± 4.39	103.3 ± 10.77	86.9 ± 7.76	162.2 ± 7.95	112.6 ± 3.84
Ash, mg g^{-1}	86.9 ± 19.30	6.8 ± 4.01	71.5 ± 5.31	71.4 ± 5.91	119.7 ± 4.45	17.8 ± 1.90
Fixed C, mg g^{-1}	840.6 ± 20.74	879.9 ± 2.99	825.2 ± 7.33	841.8 ± 12.48	718.1 ± 11.35	869.6 ± 4.49
pH†	9.32 ± 0.04	7.28 ± 0.03	8.53 ± 0.02	8.65 ± 0.04	8.45 ± 0.02	8.19 ± 0.02
EC, μS cm^{-1}†	260.9 ±0.52	42.4 ±0.12	790 ± 10	111.2 ±0.50	107.5 ±0.86	58.7 ±0.09

All values are means (n=3) ± SE

† Reported values are for 1% w/w biochar/water solutions

Experiment 1 Design

Experiment 1 was conducted in a temperature-controlled greenhouse on the Oregon State University campus in Corvallis, OR. Three cover treatments (FC650, HF600, and Straw) were applied to both M1 and M2. Covers were applied on the manure surface to a depth of 5 cm. These were compared to a control (Control) with no cover. Each treatment was replicated three times. For each replicate, 17 L of slurry was placed in a 26.5 L polyethylene pail model S-16969 (Uline, Pleasant Prairie, WI). A gas sampling apparatus was constructed from a threadable airtight lid model S-17945W (Uline, Pleasant Prairie, WI). Holes were drilled on opposite sides of the lid and fitted with 4.75 mm I.D. PVC tubing. The tubing was joined with a tee to create a single gas sampling port.

The containers were sealed with the lid once every 14 days to enable sampling of gasses in the headspace above the slurry. A 70 mm dia. battery powered fan was attached to the underside of the lid to homogenize the air in the headspace. The fan was run for 2 minutes prior to drawing gas samples. Concentrations of NH_3 and H_2S were measured with Colorimetric gas analysis tubes and pump (RAE Systems Inc., San Jose, CA). Analysis tubes had NH_3 detection ranges of 1 to 30 μL L^{-1} and 5 to 100 μL L^{-1} respectively. H_2S detection range was 0.2 to 3.0 μL L^{-1}. Gas samples were drawn on days 0, 14, 28, 42, and 56 to determine the changes in headspace gas concentration over time. Additional aged slurry was added weekly to compensate for evaporative losses and maintain a consistent headspace volume of 8 L. The slurry was slowly poured down the sidewall of the pail to minimize disturbance of the biocovers.

The floating covers were skimmed from the surface of each pail on day 56. The cover material was spread on a 1.5 mm mesh screen and allowed to drain for 30 minutes, then placed in frozen storage. For analysis, three samples from each replicate were thawed and oven dried at 105°C for 24 hours. For each sample, 3.0 g of material was placed in an Erlenmeyer flask with 100 mL of deionized water. The flasks were placed in an orbital shaker at 120 rpm for 60 minutes to leach the easily extractable nutrients. The mixture was then poured through a 630 μm screen. The solid portion remaining on the screen was collected and oven dried at 105°C for 24 hours. The dried material was ground and sieved with a 250 μm screen. The N content in three replicates of each dried cover material was determined with a CNS-2000 Macro Analyzer (Leco Corp., St. Joseph, MI). The remaining elements were determined via Inductively-Coupled Plasma (ICP) mass spectrometry using an Optima 2100DV (PerkinElmer, Waltham, MA). To release elements for subsequent ICP analysis, samples were digested using a mix of three mL each of HNO_3 (70%), HCl (37%), and HF (48%) added to 0.30 g of <250 μm dried sample. This mixture was heated for 25 min in a MDS2000 microwave digester (CEM Corp., Matthews, NC). Deionized water was used to dilute 2.0 mL of the digestate to 40 mL prior to analysis. This same procedure was used to analyze the unused cover materials for comparison.

Experiment 2 Design

Experiment 2 was conducted at the Oregon State University Dairy Research Center near Corvallis, OR. Six 210 L plastic barrels (Uline model s-9945, Pleasant Prairie, WI) were filled with 70 L of dairy manure slurry (M3) each on Oct. 14, 2015. Five barrels received 10 cm thick biocovers consisting of HF1200, HF550, HF350, PC500, and Straw respectively. The sixth barrel received no biocover and served as the control (Control). A seventh barrel was left empty (Empty) to serve as a standard for measuring background odor. Odor was judged by a panel of 5-10 judges once every two weeks over a twelve week period. Judges were recruited and selected according to Oregon State University Institutional Review Board rules and procedures. To prevent bias and ensure confidentiality, each judge was randomly assigned a unique ID number, known only to them. The judges evaluated the character of the odor using an odor wheel, which helps define the odors (Sheffield and Ndegwa, 2008). The offensiveness of the odor was ranked from -10 (extremely unpleasant) to +10 (extremely pleasant). Odor threshold was ranked from 1 to 10, with 10 being the worst smell the judges had ever experienced. Judges donned an odor blocking mask upon entering the site to prevent odor desensitization. The mask was only removed during evaluation of each barrel. The barrels were covered with muslin cloth one hour prior to each judging session. This eliminated bias from the judges based upon the visible appearance of the biocovers. The cloths were labeled and only used on their corresponding barrel. Cloths were aired out separately for 24 hours after each judging session and stored in Ziplock bags between sessions. Manure slurry was removed with a siphon pump as needed to compensate for rainfall and maintain a consistent slurry depth. The pump was inserted down the sidewall of the barrel to minimize disturbance of the biocovers.

Statistical Analyses

Unpaired two-sample t-tests (p = 0.05) were used to compare means for all experiments using OriginPro software version 9.3. For Experiment 1 mean headspace NH_3 concentrations from the Control were compared to the FC650, HF600, and Straw treatments respectively on both M1 and M2. Mean nutrient concentrations in the biocovers were compared pre vs. post experiment for each biocover

material on both M1 and M2. Experiment 2 compared mean odor offensiveness and mean odor threshold of the Control to the HF1200, HF550, HF350, PC500, Straw, and Empty treatments respectively on M3.

Results

Experiment 1

The FC650, HF600, and Straw covers all maintained surface coverage for the 8 week duration of the study. Green and white microbial growth on the surface of the biochar covers was evident as early as day 14. The species present were not identified. The greenhouse environment may have provided conditions favoring biological growth that would not have occurred in an outdoor setting. The effect of biological growth on gas emissions from the covers was not investigated.

Gas concentrations were measured on days 0, 14, 28, 42, and 56. Concentrations of H_2S in the headspace were below the detectable level of 0.2 μL/L for most replicates on every sampling date. Due to lack of measurable H_2S concentrations no results are reported here. The concentration of NH_3 in the pail headspace declined over time with the control, straw, and FC650 covers. The HF600 cover showed an increase at day 14. The same trend was observed for all replicates on both manures. All replicates had higher NH_3 concentrations through day 28 on M2 compared to M1. Ammonia concentrations above the FC650 cover were higher than the control on day 0 for both manures. Figure 1 shows the pattern of NH_3 concentrations measured in the headspace above M1 and M2.

The initial spike in NH_3 concentration with the FC650 covers was unexpected. The mechanism leading to this initial increase is unknown. A possibility is that the high pH of the FC650 biochar (9.32 in a 1% w/w solution of biochar in water) caused a conversion of ammonium (NH_4^+) in the liquid to NH_3 gas near or on the surface of the biochar. The HF600 biochar had a lower pH (7.28 in 1% w/w solution) appeared to be more hydrophobic than the FC650 biochar. The FC650 covers saturated completely within four weeks, whereas the HF600 covers still had dry material on top. This may explain the delayed spike in

NH_3 concentrations seen in the HF600 covers. Delayed wetting of the biochar may have caused a delay in the conversion of NH_4^+ to NH_3.

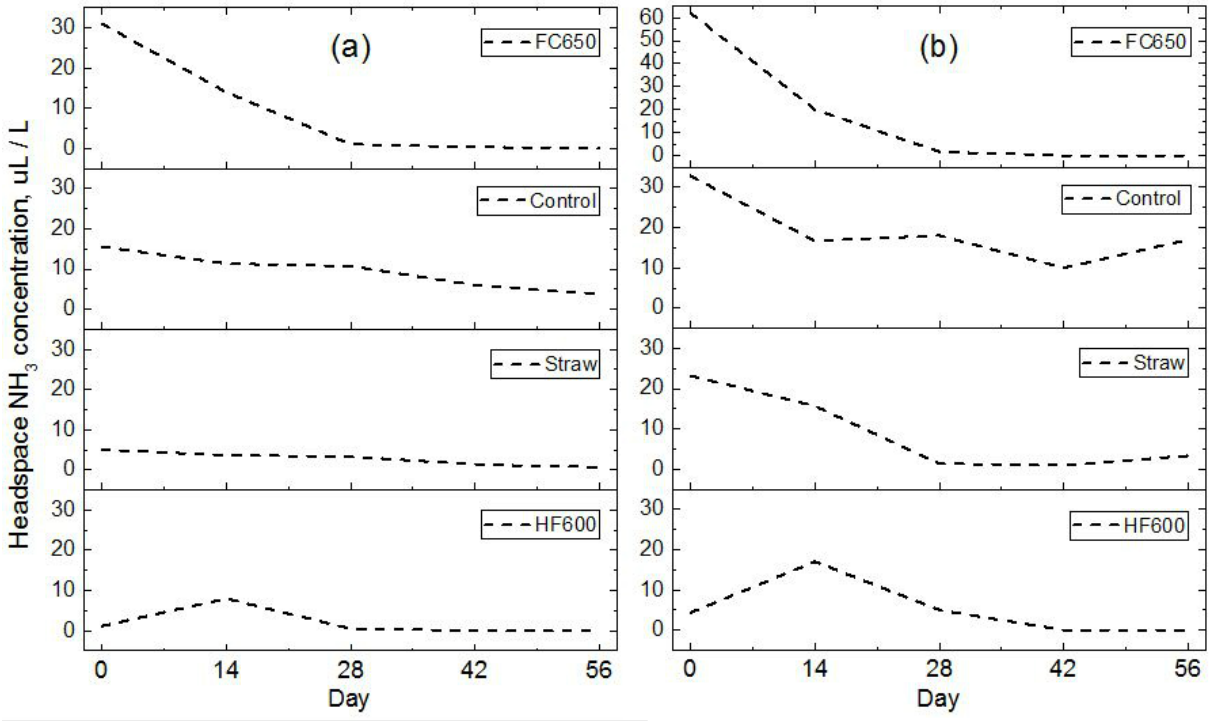

Figure 1. Change in ammonia concentration (µL/L) in the headspace above Manure 1 (a) and Manure 2 (b) over 56 days.

Figure 2 shows the mean headspace NH_3 concentration measured on days 0, 14, 28, 42, and 56. Mean concentrations were higher above all covers on M2 compared to M1. Mean concentrations above M1 were 9.4, 9.3, 2.8, and 1.9 µL/L above the Control, FC650, Straw, and HF600 replicates respectively. Mean concentrations above M2 were 18.9, 16.7, 8.9, and 5.3 µL/L above the Control, FC650, Straw, and HF600 replicates respectively. Unpaired two-sample t-tests were used to compare mean headspace NH_3 concentration above the control to the FC650, Straw, and HF600 replicates respectively. The Straw and HF600 covers showed statistically significant reductions ($p < 0.05$) on both manures. The FC650 cover reduced NH_3 concentrations compared to the control, but the difference was not statistically significant at $p < 0.05$.

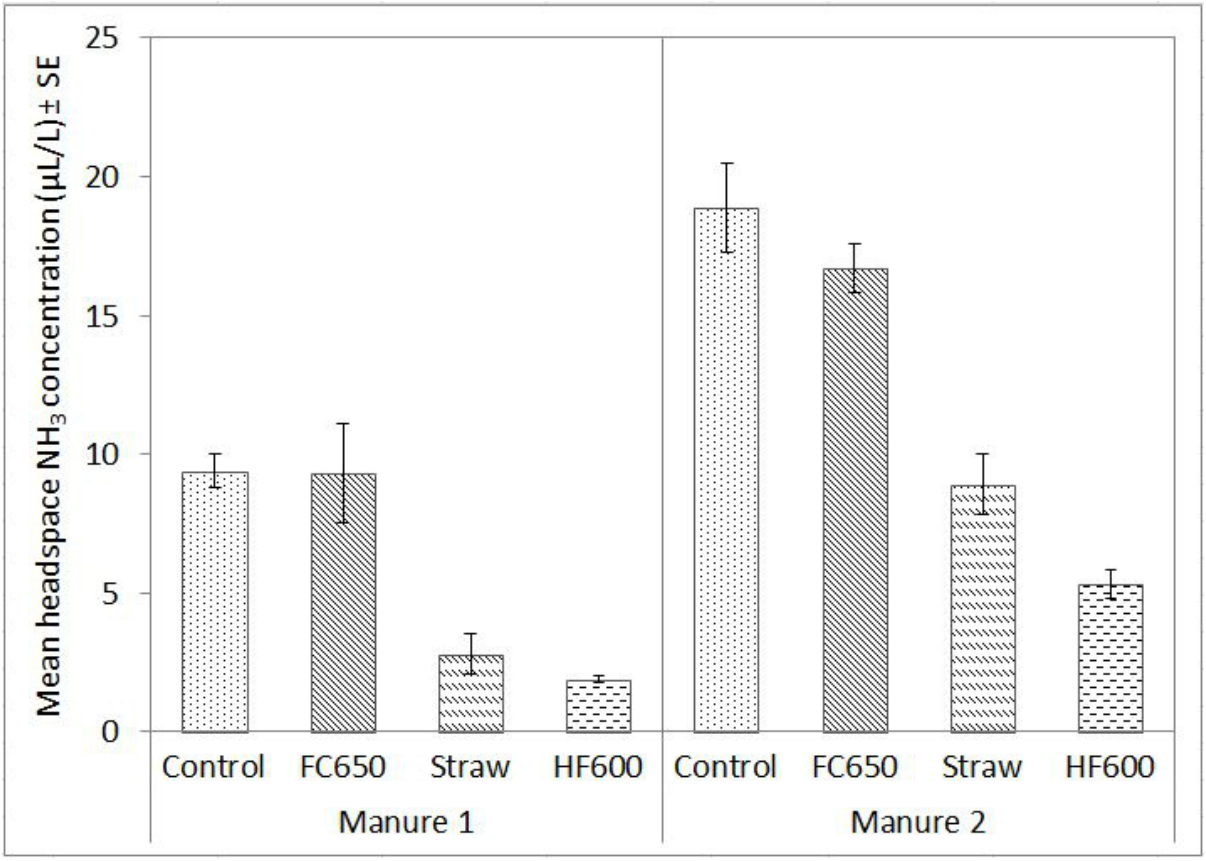

Figure 2. Comparison of mean headspace NH_3 concentration above the Control, FC650, Straw, and HF600 treatments. Error bars show ±SE.

The minimal reduction in mean NH_3 concentration with the FC650 cover is due to the increase in NH_3 observed at the onset of the study. The HF600 reduced mean NH_3 concentration in comparison to Straw on both manures, but the difference was not significant at $p < 0.05$. It is assumed that NH_3 would be escaping to the atmosphere if the gas sampling lid was not in place. Results indicate that the HF600 and Straw covers were effective for reducing NH_3 emissions over the 56 day experiment, whereas the FC650 cover was not.

Elemental analysis indicates that the FC650, HF600, and Straw biocovers all sorbed nutrients to some degree while floating on the manure surface. To determine nutrient sorption, the elemental concentrations of the covers pre vs. post experiment were compared. Table 3 shows the concentrations pre-experiment. The FC650 covers had a significantly greater concentration of potassium (K) than either HF600 or Straw. Silicon (Si) concentration was significantly higher in the Straw covers.

Table 3. Elemental analysis of fir chip (FC650), hog fuel (HF600), and straw (S) biocovers prior to application on the manure surface.

Element	FC650	HF600	Straw
	——————— mg g^{-1} of biochar ———————		
N	2.16	3.30	2.36
P	0.57 ± 0.03	0.05 ± 0.04	0.32 ± 0.03
K	9.74 ± 0.30	0.02 ± 0.02	1.64 ± 0.30
Ca	4.04 ± 0.08	0.87 ± 0.25	2.33 ± 0.14
Mg	0.56 ± 0.03	0.03 ± 0.02	0.39 ± 0.03
Na	0.41 ± 0.01	0.33 ± 0.01	0.36 ± 0.01
Fe	1.00 ± 0.03	0.60 ± 0.06	‡
Al	0.10 ± 0.01	0.04 ± 0.01	‡
Mn	0.15 ± 0.01	‡	‡
Si	3.95 ± 0.07	3.01 ± 0.37	54.01 ± 3.06

Values are means (n=6) ± SE, except for N (n=1)
‡Concentration is below the detection limit

The values in Table 4 reflect the mean concentrations at the end of Experiment 1 minus the pre-experiment means. It appears that the initial concentration may affect the ability of the covers to sorb nutrients. The FC650 covers had a lower K content at the end of Experiment 1 for replicates floating on both M1 and M2. The Straw had a lower Si content for replicates on M1. The initial concentration of nutrients in the manure also appears to be a factor. At the beginning of the study, M2 had a greater concentration of all nutrients than M1. Subsequently, all covers floating on M2 sorbed more of every nutrient than those same covers floating on M1. This is in agreement with research showing increased sorption of ammonium and phosphate onto biochar with increasing concentration of those ions in solution (Sarkhot et al., 2013).

Table 4. Biocover nutrient uptake, expressed as post minus pre-Experiment 1 nutrient concentration. Cases of nutrient release are underlined for greater clarity.

	N	P	K	Ca	Mg	Na	Fe	Al	Mn	Si
	mg g^{-1} of biochar									
Manure 1										
FC650§	3.66	2.53	-4.52	1.54^	1.57	0.61	33.24	0.54	0.34	17.02
		(0.10)	(0.33)	(0.53)	(022)	(0.07)	(4.10)	(0.11)	(0.05)	(1.83)
HF600§	0.21	0.64	2.57	1.48	0.96	0.39	1.21	0.03^	‡	2.54
		(0.06)	(0.14)	(0.20)	(0.05)	(0.02)	(0.15)	(0.01)		(0.36)
Straw#	5.45	2.40	0.19^	3.03	1.53	0.23	‡	0.01	‡	-3.55^
		(0.14)	(0.30)	(0.39)	(0.24)	(0.04)		(0.01)		(3.03)
Manure 2										
FC650#	4.88	2.70	-0.81^	3.34	2.43	1.40	74.46	1.46	0.62	32.96
		(0.22)	(0.71)	(0.71)	(0.44)	(0.07)	(12.80)	(0.33)	(0.07)	(3.14)
HF600#	1.40	0.82	2.65	2.23	1.10	0.69	5.20	0.15	‡	3.54
		(0.05)	(0.16)	(0.30)	(0.07)	(0.04)	(1.34)	(0.03)		(0.61)
Straw#	11.29	4.39	1.82	3.32	2.24	0.91	0.56	0.53	‡	3.19^
		(0.24)	(0.32)	(0.17)	(0.08)	(0.04)	(0.07)	(0.02)		(2.44)

Upper values are means, lower values (in parentheses) are pooled SE
§ n = 8 except N
# n = 9 except N
‡Concentration is below the detection limit
^ No statistically significant difference pre vs post Experiment 1 (t-test with $p < 0.05$)

The Straw cover was most effective at sorbing N, P, and Ca. The FC650 cover was most effective at sorbing Mg, Na, Fe, Al, Mn, and Si. The HF600 cover was most effective at sorbing K. The biochar covers (FC650 and HF600) exhibited differing sorption behavior. This agrees with other research showing that biochars with differing properties exhibit different sorption behaviors in the environment (Lehmann and Joseph, 2009), (Mukherjee and Zimmerman, 2013), (Zhang et al., 2013). Pre-experiment Si levels were high (>50 mg/g) in the Straw replicates and did not change significantly. Levels of K in M1 Straw and M2 FC650 replicates also did not change significantly. No significant change was measured in Ca levels in M1 FC650 or aluminum (Al) levels in M1 HF600 replicates. All other replicates had statistically significant increases in mean nutrient concentration using a two-sample t-test with $p < 0.05$.

Experiment 2

All biocovers reduced odor offensiveness and odor threshold in comparison to the control. Mean reductions over 12 weeks were not statistically significant (unpaired two sample t-test comparing treatments to the control with p <0.05) for the HF1200 or Straw covers. The HF1200 cover sank completely by week 6. The PC500 biochar started sinking at week 6 but never sank entirely. Data collection continued after the covers sank. The HF350 and HF550 covers cracked and broke into chunks, leading to inconsistent surface coverage. Straw maintained consistent surface coverage throughout the study. The covers were frozen during odor judging on week 6. It rained during judging on weeks 2, 8, and 10. These events likely affected odor perception. Rainfall totaled 460 mm over the 12 week period. The manure became significantly more diluted over time due to rainfall. This may have affected odor intensity. Descriptions of the character of the odor using the odor wheel were variable. No clear descriptive patterns emerged for the biocover treatments. The control was described as having a fecal or manure odor more frequently than the biocovers. Figures 3 and 4 show mean odor offensiveness and mean odor threshold over 12 weeks respectively.

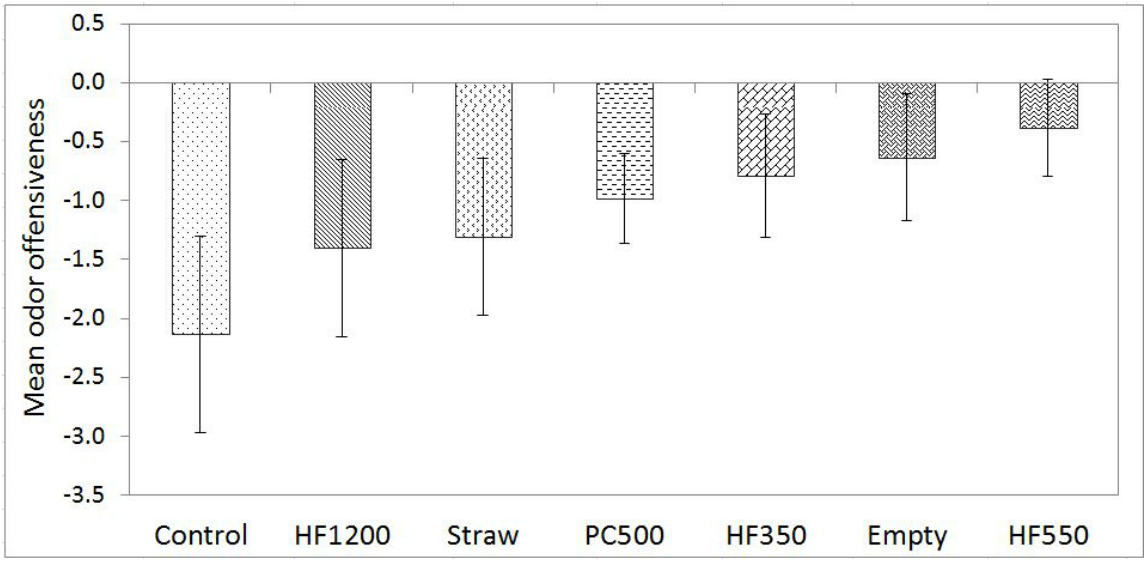

Figure 3. Mean odor offensiveness from each treatment over 12 weeks. Error bars show ± average SE.

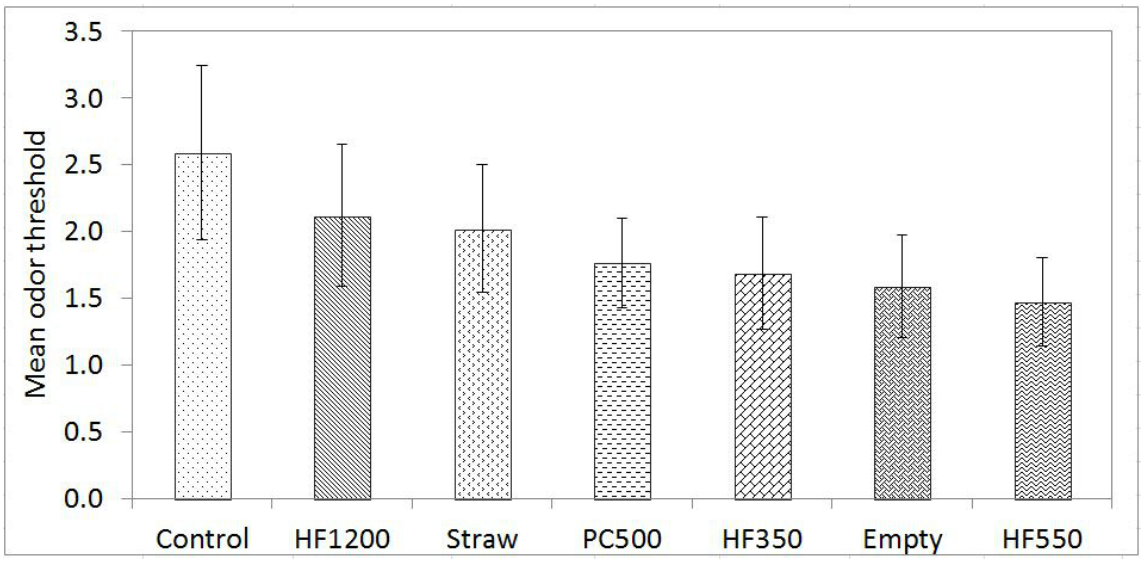

Figure 4. Mean odor threshold from each treatment over 12 weeks. Error bars show ± average SE.

A significant portion of the HF550 and HF350 biochars consisted of fine particles, which tended to clump together. Both covers showed considerable adhesion to the sides of the barrels. Bulging in the center of the covers became evident as rainwater infiltrated through the surface. This caused the HF550 and HF350 covers to crack and break up over time due to fluctuating effluent levels during rainfall and effluent removal events. Rainfall readily penetrated the HF1200, PC500, and Straw biocovers. They were able to fluctuate up and down with no adhesion to the barrel sides. Figure 5 shows a comparison of the Straw and HF350 covers after 12 weeks. Surface cracking is evident in the HF350 cover. Little adhesion of manure particles to the biochar itself was noted during Experiment 3. The biocovers were removed and examined at the end of the experiment. The HF350 biochar was visibly drier in the interior portion of the cover compared to the HF550 biochar. Biochars produced at a lower temperature tend to be more hydrophobic (Gray et al., 2014). This may explain the lower moisture uptake by the HF350 cover. Biochars that repel water and maintain air-filled voids would be expected to float for longer periods compared to hydrophilic biochars.

Figure 5: Straw (left) and HF350 (right) biocovers after 12 weeks on the manure surface.

Discussion

The reductions in NH_3 emissions associated with biocovers observed in Experiment 1 are in line with results from other studies (VanderZaag et al., 2008). However, the spike in NH_3 emissions from the FC650 covers at the beginning of the experiment was unexpected. More research is needed to investigate the cause of this temporary increase. One potential explanation is that the high pH of the FC650 biochar caused a temporary rise in pH of the surrounding manure, thus creating favorable conditions for NH_3 formation. Research suggests that the presence of oxygen or acidic functional groups in biochar are important factors affecting biochar pH (Li et al. 2013). Electron donors and acceptors on the surface of biochar particles will interact with H^+ ions, thus affecting solution pH. Streubel et al. found that adding biochar (pH 9.3) to anaerobic digester effluent caused an increase in solution pH (Streubel et al., 2012). It may be necessary to avoid high pH biochars for biocover applications where reducing NH_3 emissions is a primary goal.

There was no clear advantage to using biochar rather than straw in this experiment. However, the short duration of the study may have advantaged the straw covers. Biologically-based cover materials tend to decay and lose effectiveness over time (Meyer and Converse, 1982), (Clanton et al., 1999),

(Bicudo et al., 2004). Biochars, being more inert materials, should be less susceptible to decay and could provide cover function for a longer time period. It should be noted that the indoor setting for Experiment 1 did not allow for observation of cover durability under normal weather conditions. There also appeared to be edge effects from the small diameter pails used in the study. The biochar covers tended to adhere to the sides and bridging was noticeable in comparison to the straw covers. Longer duration experiments under outdoor conditions need to be carried out to determine whether biochars would maintain their effectiveness for reducing gas emissions in actual field conditions. Measuring gas concentrations once every two weeks, as was done in this study, limits the inferences that can be made from the data. More frequent sampling would reduce the uncertainty of the results and provide a better picture of actual gas emissions. A sampling methodology such as the dynamic flux chamber method used by Blaines-Vidal et al. would provide a more realistic estimate of gas concentrations in the headspace (Blanes-Vidal et al., 2009).

The mechanisms behind control of odor and gas emissions with biocovers have been discussed in other studies (VanderZaag et al. 2008), (Blanes-Vidal et al., 2009). A reduction in mass transport of gasses from the lagoon surface is generally considered to be the dominant mechanism. Microbial consumption of gasses may also be a factor in cases where covers provide a substrate for aerobic bacterial growth at the surface. Mechanisms for odor and gas reduction via biochar covers were not investigated in this study. It is possible that the porous structure of biochars would provide for enhanced microbial growth on the lagoon surface. Further research is needed to determine if microbial consumption could be a contributing factor for control of odor and gas emissions with biochar covers.

Biochars have been shown to be capable of sorbing and releasing many elements and compounds from manures (Streubel et al., 2012), (Sarkhot et al., 2013) and soils, (Uchimiya et al., 2010), (Sun et al., 2011). The results reported here suggest that sorption and release of nutrients can also occur when biochar is used as a biocover. When biochar covers are blended with manure and soil-applied this dynamic nutrient exchange may continue. Other work suggests that biochar may reduce nutrient leaching from soils when combined with manure (Laird et al., 2010), (Troy et al., 2014), (Bradley et al., 2015). To date

we are unaware of any studies where biochar has been used as a lagoon cover and then field-applied. This concept needs further research to determine the potential benefits and drawbacks of the practice.

In this study the straw covers provided greater capture of N and P per gram than either of the biochars. The possibility remains that the biochars would retain sorbed N and P for longer periods in the environment, but this was not evaluated. As with Experiment 1, the biochars did not appear to provide an overall advantage over the straw covers for nutrient sorption. From an agronomic standpoint, sorption of N, P, and K would likely be desirable characteristics of a biocover material intended for soil application. However, the procedures used to collect and leach nutrients from the covers in Experiment 2 were not reflective of what would happen under field conditions. Many of the small (< 2mm) biochar particles sank to the bottom of the pails during Experiment 1. These smaller particles would have considerable surface area for nutrient sorption, but only the particles that remained floating were included in the elemental analysis. It is also difficult to distinguish between nutrients contained within residual manure particles loosely adhered to the surface vs. nutrients sorbed to the internal structure of the cover materials. Additionally, nutrients may be entrained in liquid trapped in pore spaces of the cover materials vs. actually sorbed to the surface. The FC650 biochar had noticeably more organic material stuck to the surface at the end of Experiment 1 than did the HF600 biochar. The reason for this remains unclear, but likely is related to the differing sorption characteristics of the biochars. The more hydrophobic nature of the HF600 biochar may have prevented attraction of slurry material to its surface. This may partially explain why the FC650 biochar appeared to be considerably more effective than HF600 at sorbing nutrients. Conversely, the HF600 biochar was more effective at reducing NH_3 emissions.

Surface area (SA) and cation exchange capacity (CEC) of biochars are an important factor in their ability to sorb organic and inorganic compounds. Feedstock type, production temperature, and post-production processing will all affect SA and CEC (Gaskin et al., 2008), (Keiluweit et al., 2010), (Zhao et al., 2013). Previous research has shown that the surface of biochars is typically negatively charged due the presence of oxygenated surface functional groups on biochar surfaces. This can enhance sorption of positively charged ions such as ammonium, but inhibit sorption of negatively charged ions including

nitrate and phosphate (Yao et al., 2011) (Hollister et al., 2013), (Gai et al., 2014). Biochar pH will also affect sorption characteristics because much of biochar CEC is pH dependent and can become protonated at lower pH and thus ineffective for cation sorption (Wang et al. 2015).

Experiment 2 posed several challenges with collecting data. There was significant variability among the judges' responses, and odor is known to be very subjective and this was reflected in the judges' responses. Even the empty barrel was ranked as having odor. This could be background odor, odor from rainwater in the bottom of the barrel, or odor from the barrel itself. It is also possible there was a placebo effect, where the judges perceived odor because they thought the barrel contained something. The muslin cloth used to prevent the judges from seeing the contents of the barrel appeared to cause significant problems for odor detection, especially during rain events. The outdoor setting posed a challenge due to the wind, rain, and cold weather during weeks 2, 8 and 10. At the conclusion of the study on week 12, the judges were asked to re-evaluate the odor without the cloth covers in place. Some barrels were rated as more offensive and others as less offensive. The change in odor offensiveness without the covers in place was not statistically significant at $p < 0.05$. There was a noticeable hesitation amongst the judges to sniff the contents of the barrel when the cloth was removed and they could see the contents.

Durability of the biochar biocovers is likely related to their density and hydrophobicity. Biochars with a skeletal density greater than 1g cm^{-3} would be expected to sink if the pore spaces become fully saturated. Density of most biochars exceeds this value. Brewer et al. reported skeletal density values ranging from 1.34 to 1.96 g cm^{-3} for biochars (Brewer et al. 2014). Adhesion of manure particles to the biochar surface could affect the buoyancy of biochar covers. In addition to low skeletal density, hydrophobicity would be desirable for flotation over long periods of time. The tradeoff with greater hydrophobicity of a biocover is likely to be lesser nutrient sorption. This was not evaluated in this study and needs further research.

Conclusions

Experiment 1 demonstrated that a biochar cover can reduce NH_3 emissions while sorbing nutrients from livestock manure. Experiment 2 showed that biochar covers can reduce odor. However, outdoor conditions led to cover degradation over time, as has been documented with other biocover types. The considerable variation in performance seen in these experiments underscores the difficulty in selecting a biochar that will sorb nutrients while effectively reducing odor and gas emissions. Whether biochars can be engineered to outperform traditional biocover materials remains an open question. High cost and availability of suitable biochars is a significant hurdle to overcome. Blending biochar with other biocover materials to enhance overall cover performance may be a more economical and effective approach. Despite the challenges, using biochar as a biocover material holds promise, particularly if biochar becomes more available as a by-product of bioenergy production. Many livestock operations struggle with excess nutrient loading and leaching from farm fields. Biochar covers could be blended with the manure and field applied, or collected and sold as a means for exporting excess nutrients off the farm. Practical methods for applying and collecting biochar from the surface of a lagoon or other manure storage are yet to be developed, but this method has the potential to serve as a nutrient capture mechanism while simultaneously reducing odor and gas emissions.

This preliminary investigation of biochar biocovers provides a basis for future research. We have shown that some biochar covers can sorb nutrients and provide reductions in odor and gas emissions. Hydrophobicity and pH have been identified as important characteristics of biochars for this application. More research is needed to determine the optimal hydrophobicity and particle size distribution for improved cover durability and nutrient sorption. The effects of biochar pH on odor and gas emissions needs further investigation in order to determine which biochars are best suited for use as a biocover material. The potential for improving cover performance by blending biochar with other cover materials should also be explored.

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