

Thermochemical Conversion of Biomass Storage Covers to Reduce Ammonia Emissions from Dairy Manure

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Abstract Manure storages, and in particular those storing digested manure, are a source of ammonia (NH₃) emissions. Installing floating manure covers provide resistance to gas transfer from manure storage surface to air and reduces NH₃ emissions; however, performance can be limited to durability. Biochar and steam-treated wood have strong potential as manure storage covers as they are capable of repelling water, resistant to microbial degradation, and could be applied to crop acreage. An additional benefit of biochars as a cover is their capability of NH₃ sorption trapping TAN (total ammoniacal N) before it is volatilized resulting in further abatement. Installation of permeable manure storage covers is difficult and adding covers with agitators could facilitate implementation. This study measured NH₃ emissions from laboratory scale storages of digested manure with raw wood (white birch, *Betula papyrifera*), steam-treated wood, wood biochar, and corncob biochar covers. Additional treatments included mixing biomass treatments into manure storages to

measure the reduction potential of incorporated biomass. All treatments reduced emissions of NH₃ from the control by 40 to 96%. The highest NH₃ emissions reductions of 96% were achieved with the wood biochar cover. The primary mechanism for treatment was resistance to gas transfer provided by the physical barrier of covers as NH₃ sorption did not correspond to reductions. Covering digested manure storages with any of the treatments can reduce NH₃ emissions; biochar covers are a more effective barrier to NH₃ emissions and are recommended to minimize NH₃ manure storage losses.

Keywords Dairy manure · Ammonia · Storage cover · Biochar · Steam treatment

1 Introduction

Manure storages are a significant source of methane (CH₄) and ammonia (NH₃) emissions (Hou et al. 2015). Digesting manure reduces CH₄ emissions from manure during subsequent storage (Amon et al. 2006; Holly et al. 2017). However, these reductions come with a tradeoff, as digestion also increases ammonia (NH₃) emissions from storage (Amon et al. 2006; Clemens et al. 2006; Holly et al. 2017). An increase in NH₃ emissions from anaerobic digestion (AD) can result in formation as fine particulate matter (PM_{2.5}), further impacting air quality. PM_{2.5} is considered a major environmental risk to human health as it impacts human respiratory function when inhaled (WHO 2005). The

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process of AD increases manure pH while also increasing nitrogen mineralization, which increases total ammoniacal nitrogen (TAN), both of which lead to greater losses of NH_3 during storage (Christensen et al. 2013; Clemens et al. 2006; Uludag-Demirer et al. 2008). Storage of manure, and particularly digested manure, would benefit from additional treatment to abate losses of NH_3 and maintain nitrogen fertilizer value. The presence of a physical barrier on the surface of a manure storage is an inexpensive method used to reduce NH_3 emissions, thereby retaining ammoniacal nitrogen in the manure. The natural formation of a surface crust on dairy manure storages has measured NH_3 emissions reductions of around 60% (Smith et al. 2007). However, only cattle manures with dry matter content $> 7\%$ will normally result in natural crust formation (Webb et al. 2005). Many dairy manure storages contain manure with a dry matter content which is $< 7\%$, particularly separated liquid manures, and are therefore unlikely to form a crust.

Permeable covers are the placement of synthetic or natural material on top of manure storages and are intended to provide resistance to the transfer of gas from the manure storage surface to the air. Permeable covers are less expensive than impermeable covers and allow precipitation to infiltrate, eliminating the need to remove water from the cover (Nicolai et al. 2004; VanderZaag et al. 2009). Both synthetic and natural permeable covers have potential to reduce NH_3 emissions from manure storages by 17 to 90% (Amon et al. 2006; Berg et al. 2006; Guarino et al. 2006; Sommer et al. 1993). Natural permeable covers have additional adoption potential as they could be incorporated with manure and applied to crops with manure, unlike synthetic cover that requires removal. Adding straw to manure storages is an example of a natural permeable cover and is simple, inexpensive, and readily available method to prevent NH_3 emissions from manure storages.

Natural covers such as straw were also found to increase emissions of carbon dioxide (CO_2) and nitrous oxide (N_2O) due to the addition of aerobic conditions at the surface and the increased organic material (VanderZaag et al., 2009). Straw covers have a limited life span as a result of rainfall and degradation. In a study by Guarino et al. (2006), straw covers in a manure storage trial completely sank into the manure after only 3 months. Other natural permeable covers such as chopped corn stalks, saw dust, rice hulls, ground corn-cobs, and grass clippings also provide a reduction in

NH_3 emissions from manure storages (VanderZaag et al. 2008). Anew, these covers are limited by their chemical and biological degradation potential and their ability to float and maintain effective manure storage coverage. Successful natural permeable covers require durability over multiple months and resilient to biological degradation resulting in additional greenhouse gas emissions.

Biochar, produced by the pyrolysis of biomass, is composed of relatively stable carbon and has hydrophobic sites (Crombie et al. 2013; Mohan et al. 2014), both of which may increase durability and life span as a manure storage cover. Pyrolysis of biomass releases volatile matter that can be captured and used as an energy source, resulting in a high fraction of stable C (Crombie et al. 2013). The reduced amount of volatile matter may prevent additional emissions of CH_4 when using this material as a manure storage cover. An additional benefit of biochar as a manure storage cover is its ability to sequester nitrogen compounds of NH_3 and ammonium (NH_4) (Ding et al. 2010; Nelissen et al. 2012; Taghizadeh-Toosi et al. 2012a) and TAN precursors such urea and uric acid (Malińska et al. 2014). The absorbed NH_4 on biochar is generally stable, as when exposed to air for 12 days, the NH_4 was not hydrolyzed and volatilized as NH_3 (Spokas et al. 2012b). Nitrogen adsorbed to biochar is also bioavailable (Taghizadeh-Toosi et al. 2012b), making it a valuable fertilizer that can be applied to the field.

Nelissen et al. (2012) suggest that NH_4 absorption onto biochar is due to an elevated cation-exchange capacity (CEC). Feedstock and pyrolysis temperature are the driving forces in determining biochar CEC, and therefore adsorption of NH_4 (Gai et al. 2014). Increasing pyrolysis temperature tends to decrease CEC due to the removal of volatile matter at higher temperatures (Ippolito et al. 2015; Lin et al. 2012; Rajkovich et al. 2012). Biochar produced from corn has the highest CEC of previously measured feedstocks (Ippolito et al. 2015). However, the data used to develop feedstock influence on CEC was obtained from research conducted with varying production temperatures, so should be used cautiously. Borchard et al. (2012) suggest that the oxygen-containing functional groups present in biochar are responsible for overall sorption of NH_3 and NH_4 . These oxygen functional groups have a negative charge and therefore are directly correlated to the biochar CEC.

Steam treatment increases the hydrophobicity of wood and NH_3 sorption potential (Adjei 2007; Lam et al. 2011) and could also be a suitable manure storage

cover material. Steam explosion is a biomass pretreatment which uses pressure and steam and turns biomass into a pulp upon sudden release of the pressure and steam. Steam explosion enhances the microstructure and acidic properties of a biomass, giving it the potential to capture NH_3/NH_4 . Adeji (2007) found that biomass produced at a higher temperature and severity of explosion had a higher adsorption capacity and a lower pH. Packed column studies reported maximum adsorption capacities of 10.45 mg NH_3/g raw corncob and 59.8 mg NH_3/g steam-exploded cob resulting from physisorption and chemisorption (Adjei 2007). A study by Theuretzbacher et al. (2015) found that the biological methane potential of wheat straw used as a manure storage cover was not increased through steam explosion and therefore, additions of this material to manure storages will not result in an increase in CH_4 emission.

Currently, covering large manure storages (> 1 ha) with permeable covers is difficult (Nicolai et al. 2004). Applying covers by incorporating material during manure agitation, the recommended mixing of manure before pumping and application, could be an easy potential solution. However, this strategy requires that materials are durable and contact with manure would not accelerate degradation. Biochar and steamed natural materials are candidates for this installment technique as they are hydrophobic, durable, and could float to the surface after mixing to provide resistance to gaseous transfer from storage surface to air. Incorporating these materials could increase contact with TAN, urea, and uric acid further reducing NH_3 emissions and stabilizing these valuable sources of N fertilizer for crop use. Additionally, biochar could reduce the pH of manure shifting the NH_3/NH_4 equilibrium to NH_4 . These materials could also serve as a physical barrier, and if that is the primary mechanism should therefore be applied as a cover. This study investigates the effects of biomass covers processed by pyrolysis and steam treatment on NH_3 volatilization from manure storages, two different application strategies, and mechanisms for NH_3 reduction.

2 Methods and Materials

2.1 Experimental Design

The NH_3 emissions from four biomasses, (1) white birch (raw wood), (2) steam-treated white birch (steamed wood), (3) white birch biochar (wood biochar), and (4) corncob biochar (cob biochar) applied to digested dairy

manure were measured over 7 weeks. Laboratory studies on manure storage covers measuring the effects on gases abundant in the manure, such as NH_3 , are suitable for shorter-term studies as these gases are not largely produced by microbes (unlike CO_2 , CH_4 , and N_2O) (VanderZaag et al. 2008). Additionally, an experiment of 7 weeks would provide insight into the durability of covers. A field scale storage study of 30 days by Guarino et al. (2006) was used to determine biological degradation of biomass covers and was sufficient to examine the chemical and physical changes. The laboratory scale of manure storages (16 L of manure) enabled replication and the assessment of relative effects of biomass feedstock and application strategy on NH_3 emissions from manure storages. Each biomass treatment was applied to a manure by mixing directly into the manure (incorporated) or distributed evenly across the manure surface (unincorporated). The experiment was conducted as a complete factorial design with two factors: the four processed biomass materials and two manure storage application methods. The eight treatment combinations and a manure control with no added biomass were completed in triplicate for a total of 27 experimental units.

2.2 Manure Characteristics

Digested dairy manure has greater NH_3 emissions than unprocessed dairy manure (Amon et al. 2006) and was therefore selected as the manure storage media to increase the likelihood of treatment differences. Digested manure was collected from a dairy farm with a mixed plug flow digester with an average retention time of 40 days, fed manure and milk house wastewater, and operated at mesophilic temperatures. This facility uses digested separated solids for bedding, and manure is collected with a skid steer three times per day. Manure was collected in four 208 L barrels and transported to the livestock laboratory at the University of Wisconsin – Madison. Manure was then added to 31 individual 20 L buckets and stored in a temperature controlled laboratory at 20–21 °C. To ensure uniform manure characteristics between buckets, manure in the four barrels was stirred for 1 min with a power drill connected to a 0.85-m long mixer with three blades (6 cm × 1.5 cm). Four liters were then added from each of the four barrels to buckets at random with mixing between each bucket distributed. In total, 16 L of manure were added to each bucket, leaving sufficient headspace for biomass additions. The mass of manure for each treatment was

recorded at the beginning and end of the experiment (Table 1). Upon completion of manure distribution, each bucket mixed with a 5-gal paint stirrer attached to a power drill for 15 s and a 100-mL sample was taken before addition of biomass. Initial manure samples were analyzed, as recommended by Peters et al. (2003), for pH using a glass electrode for potentiometric analysis, total solids by drying (approximately 5 g) at 105 °C, volatile solids by loss-on-ignition at 550 °C, total Kjeldahl nitrogen by acid digestion (TKN), and TAN by phenol-hypochlorite reaction. Samples were refrigerated to 4 °C before analyzing for pH, total solids, and volatile solids, which was completed within 1 week of sampling. An IntelliCAL™ PH191 gel-filled electrode was used for pH measurements (Hach Company, Loveland, CO, USA). A diluted portion of the subsample (50 ml) was preserved with sulfuric acid pH < 2 and refrigerated to 4 °C until analyzed for TKN. Colorimetric analysis was completed using a Seal AQ2 discrete analyzer (Seal Analytical Inc., Menquon, WI, USA).

2.3 Biomass Covers

The wood used in this study was a *Betula papyrifera* (white birch) variety grown in northern Wisconsin. Corncoobs were obtained from a field growing hybrid dent corn, *Zea mays var. indentata*, in South Central Wisconsin after grain separation during fall harvest. Prior to processing, the biomasses were air dried using

fans for 4 days. Biochar was produced in 5 L reactor by Biochar Options, LLC. Kiln temperature was raised to 400 °C and held for 1 h. This temperature was selected in an attempt to maximize the CEC in order to increase adsorption of NH₄ (Ippolito et al. 2015). Wood chips were steam treated at the USDA Forest Products Laboratory in Madison, WI, where a reactor was held for 120 min at a temperature of 190 °C and a pressure of 1207 kPa. Biomass was analyzed for pH, Brunauer-Emmett-Teller (BET) surface area, elemental composition (C, H, N, and O), functional groups, and TAN, and the initial physiochemical properties are provided in (Table 2). The pH was measured using a HACH HQ440b benchtop multimeter pH probe in a 1:20 mass ratio of biochar to deionized water. A Quantachrome Nova 4200e (Quantachrome Instruments) was used to determine surface area using the multipoint BET ASTM method D3663-03 (ASTM International 2015). Elemental composition was determined using ultimate analysis following the recommendations of ASTM D5373 using a PerkinElmer elemental analyzer (ASTM International 2016). Oxygen content was determined as the remaining mass after subtracting C, H, N, ash, and moisture using the ASTM method E871 (ASTM International 2013).

Initial sorption of NH₄ was determined by extraction differences before and upon completion of the study. KCL extractions for NH₄ are common for soils and biochar; however, recent literature suggests this method is capable of only partial recovery due to strong bonds between NH₄

Table 1 Initial and final mass of manure and mass of biomass added by treatment

	Initial manure mass (kg)	Final manure mass (kg)	Change in mass (kg)	Mass of biomass cover (kg)
Control	16.8	12.4	4.4	
Raw wood				
Incorporated	16.6	12.9	3.7	1.2
Cover	16.9	13.8	3.1	1.3
Steamed wood				
Incorporated	16.5	12.3	4.2	1.2
Cover	16.7	13.3	3.4	1.2
Wood biochar				
Incorporated	16.7	14.8	1.9	0.6
Cover	16.7	16.0	0.7	0.6
Cob biochar				
Incorporated	16.5	13.5	3	0.4
Cover	17.0	15.7	1.3	0.4

Table 2 Biomass physical and chemical composition. Values expressed as mean and standard deviation (in parentheses)

	Raw wood	Steam-treated wood	Wood biochar	Cob biochar
Carbon (%)	44 (0.57)	46 (5.7)	74 (2.5)	70.5 (8.5)
Hydrogen (%)	4.1 (0.06)	4.3 (0.55)	7.0 (0.27)	6.8 (0.92)
Nitrogen (%)	0.09 (0.01)	0.08 (0.01)	0.17 (0.01)	0.67 (0.11)
Oxygen (%)	52	50	19	22
O:C ratio	1.2	1.09	0.26	0.31
pH	5.53 (0.06)	4.22 (0.04)	7.7 (0.03)	9.88 (0.10)
Total solids (%)	95 (0.05)	95 (0.14)	99 (0.25)	97 (0.44)
Volatile solids (as a % of total solids)	99.5 (0.001)	99.7 (0.001)	98.8 (0.003)	94.5 (0.01)
Pore diameter (Å or 10^{-10} m)	51.2 (23.4)	46 (7.5)	87	48
Surface area (m^2 per g)	28.9 (16.2)	17.8 (18.8)	< 5	27.2
Pore volume (cc per g)	0.04 (0.04)	0.02 (0.02)	0.003	0.03

and biochar (Sika and Hardie 2014; Taghizadeh-Toosi et al. 2012b; Zhao et al. 2014). Extractions on the biomass treatments were accomplished using a method by Wang et al. (2015) who found that additional water extractions followed by an additional KCL extraction over 24 h increased recovery of NH_4 from biochar to 99%. The supernatant was filtered (8 to 10 μm) and preserved at a rate of 2 ml H_2SO_4 and TAN was analyzed using a Seal Analytical AQ2 discrete analyzer within 1 week (Supplemental Table S4). At the completion of the study, a portion of the manure covers was sampled, rinsed with DI to remove physically bound manure biomass and filtered (8 to 10- μm pore size), and TAN was extracted using the method by Wang et al. (2015).

Previous studies on natural permeable covers were installed on manure storages at depths of 5 to 15 cm (VanderZaag et al. 2008). The manure cover treatments without incorporation were applied to the surface of the laboratory scale storages of manure at a thickness of 5 cm to determine potential treatment effects. For these treatments, the biomass was undisturbed for the duration of the storage study. Manure covers applied through incorporation were applied at the identical mass applied to the unincorporated covers (Table 1).

2.4 Gas Emission Measurements

The study took place in ventilated room and the buckets were arranged in a random block design to determine variability from inconsistent exposure to air turbulence from spatial distribution. Each bucket was left uncovered outside of gas measurement

periods; to measure weekly manure NH_3 emissions buckets were left in situ and measured by block sequentially. A steady-state chamber was used for measurement and connected to a Fourier transform infrared spectroscopy (FTIR) gas analyzer was used for NH_3 concentration measurement (Altair© 5X Gas Detector, MSA, Houston, TX, USA). The gas analyzer had a detection limit of 0 to 100 ppm NH_3 and a resolution of 1 ppm NH_3 . The MSA Altair® 5X multigas analyzer measured chamber outlet concentrations at 20 s increments and pumped gas through from the chamber at rate of 250 mL per minute. Chamber gas pumped out of the headspace for measurement was replaced by ambient laboratory air through an 18-mm vent. The temperature, pressure, and NH_3 concentration of the ambient air was measured seconds before measurement. Polytetrafluoroethylene tubing (1 m in length) used to connect the lid to the chamber lid to the gas analyzer. Upon completion of 5 min of sampling, measurements were terminated and subsequent emissions did not continue until sample lines were cleared with ambient air and a zero NH_3 was measurement was obtained. the enclosed area between manure surface and chamber lid (bucket headspace was measured just before sampling), molar mass of air, and change of concentration over time (Formulas 1, 2, and 3) where F = flux rate ($mg s^{-1}$) (Formula 1), S = to slope of the change in concentration over time ($mg s^{-1} L^{-1}$) (Formula 2), V_C = enclosed gas area (L), C_f = final gas concentration ($mg L^{-1}$) (Formula 3), C_i = initial gas concentration ($mg L^{-1}$), T = measurement time (s), c = final

gas concentration (ppm), MW = molecular weight of NH_3 (17.03 mg L^{-1}), R = gas constant ($0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$), T = temperature of headspace at time of measurement (K), and P = ambient pressure (atm).

$$F = S \times V_c \quad (1)$$

$$S = \frac{C_f - C_i}{T} \quad (2)$$

$$C_f = \frac{c}{10^6} \times \text{MW} \times \frac{1 \times R \times T}{P} \quad (3)$$

Cumulative emissions for each experimental unit were calculated using piecewise interpolation between sampling points for each date of data collection. To account for variability in bucket manure mass, each measurement was adjusted to report NH_3 emissions per kilogram of manure. A one-way ANOVA (Proc ANOVA) was conducted to compare the effect of treatment on cumulative gas emissions of NH_3 by the different biomasses using SAS software version 9.4 (SAS Institute Inc., Cary, NC). A Tukey's studentized range test (HSD) was conducted to compare differences between all treatments ($\alpha = 0.05$). A factorial ANOVA (Proc GLM) was conducted to compare the main effects of biomass, application method, and the interaction effect of biomass and application method on the amount of NH_4 adsorbed by biomass and the cumulative emission of NH_3 . Comparisons were made using least square means on the averages for all treatments of biomass type and application method. A Tukey's adjustment was used for multiple comparisons. A paired t test was conducted to compare the effect of treatment on manure characteristics at the beginning and the end of the study.

3 Results

All treatments regardless of their application method significantly reduced emissions of NH_3 from the control (Fig. 1). Wood biochar cover (unincorporated) had the greatest reduction in NH_3 emissions, 96%, when compared to the control digested manure storage (Fig. 1). The incorporated raw wood cover was the least effective at reducing NH_3 emissions with a reduction of 40% (Fig. 1). The main effect of biomass was statistically

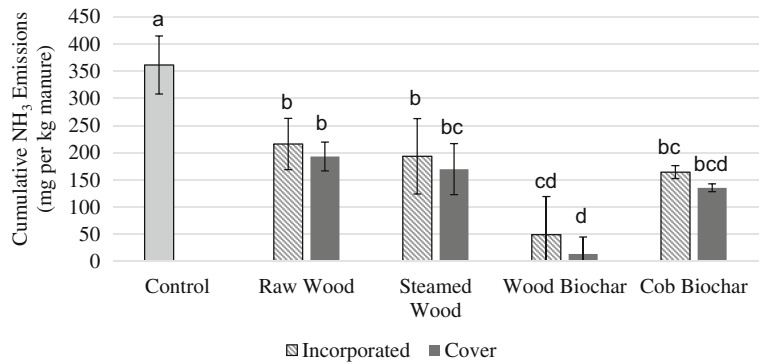
significant ($p < 0.001$); the average of the two applications of wood biochar treatments had significantly less NH_3 gaseous losses when compared to the other treatments ($p < 0.0016$). Statistical analysis for effects of biomass and application effects on NH_3 emissions and extracted ammoniacal N is reported in (Tables S1, S2, S3, and S4) (Online resource 1).

Application strategy (incorporation vs. unincorporation) did not affect cumulative emissions as the main effect of application method was not statistically significant (p value = 0.15) although individual sample points were statistically different between the two cover application strategies within the first week to month of the study. In general, unincorporated cover applications for all biomasses had a stronger mitigation potential initially but treatment differences between application strategy were reduced at the end of the study (no statistical difference between application methods) (Fig. 2). Effectiveness of the unincorporated cover over the incorporated cover with time was dependent on the biomass. Raw wood, steam-treated wood, and the cob biochar cover had significantly less NH_3 emitted on some days within the first 4 days of the study, after which NH_3 flux measurements between the application methods were statistically similar (Fig. 2a, b, and c). Unincorporated wood biochar covers maintained a statistical difference from the incorporated biochar covers manure through day 13 (Fig. 2d).

The main effects of application method and biomass type had a significant effect on the sorption of TAN (p value < 0.001). Sorption of TAN by the unincorporated biomass covers was statistically greater than those which were incorporated, with nearly twice as much TAN extracted for all treatments (Table 3). Wood and cob biochar had 4.4 and 1.12 times greater the amount of NH_3 extracted than the raw wood, respectively (Table 3). TAN extracted from wood biochar was significantly greater (p value < 0.0001) than the other biomasses. The sorption of TAN by each biomass was less than the total measured reductions in NH_3 emissions (Table 3) indicating sorption is not the main mechanism for mitigation. For example, sorption of TAN by the unincorporated wood biochar cover was only 1% of the total NH_3 retained in the bucket when compared to the control.

Manure TKN significantly decreased from the beginning to the end of the study in all treatments except the raw wood cover, incorporated wood biochar, and wood biochar cover ($p < 0.15$) (Table 4). Initial and final manure TKN concentrations for these treatments were statistically

Fig. 1 Cumulative NH₃ emissions per initial manure mass. Treatments with similar letters are not statistically significantly difference at $\alpha = 0.05$. Vertical bars represent the standard error of the mean ($N = 3$)



similar. NH₃ emissions from the wood biochar were lower than all other treatments supporting the retention of TKN within the manure. However, the raw wood cover had substantial emissions of NH₃ but actually had an increase in TKN. The raw wood cover may have been partially degraded in the manure, adding additional N, but if this was the case, degradation would have likely occurred in the incorporated raw wood as well. Conversely, in the incorporated raw wood, there was not a representative increase in TKN nor were the emissions significantly different from the raw wood cover. White mold was observed on the raw wood cover treatments only indicating some biological transformation for this treatment.

Initial manure TAN concentrations significantly decreased in the control, incorporated raw wood, incorporated steam wood, and cob biochar. In these treatments, the reduction was caused by the loss of NH₃ through volatilization, supported by the measured ammonia emissions. TAN concentrations were statistically similar at the beginning and end of the experiments for the treatments of raw wood cover and both wood biochars. Both wood biochars had minimal losses of NH₃, supporting the minimal losses of NH₃ seen in emissions.

Total solids significantly increased for all treatments except the raw wood cover, the incorporated wood biochar, wood biochar cover, and the cob biochar cover

Fig. 2 NH₃ fluxes from (a) control and raw wood, (b) steam-treated wood, (c) cob biochar, and (d) wood biochar. Raw I, incorporated raw wood; Raw C, raw wood cover; Steamed I, incorporated steamed wood; Steamed Wood C, steamed wood cover; Cob BC I, incorporated cob biochar; Cob BC C, cob biochar cover; Wood BC I, incorporated wood biochar; and Wood BC C, wood biochar cover. Vertical bars represent the standard error of the mean ($N = 3$)

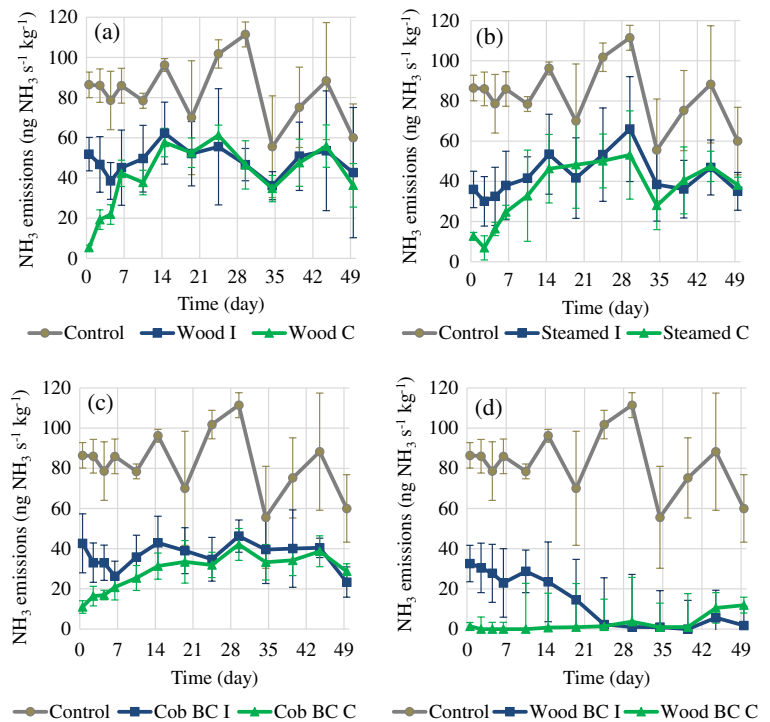


Table 3 NH₃ lost and sorption of TAN by treatments per initial manure mass. Values expressed as mean and standard deviation (in parentheses)

	NH ₃ lost (mg per kg manure)	Difference in NH ₃ emission (mg per kg manure)	Sorption of NH ₃ by biomass (mg per kg manure)
Control	325 (41)		
Raw wood			
Amended	199 (70)	126	0.7 (0.1)
Cover	180 (32)	145	0.9 (0.5)
Steam-exploded wood			
Amended	174 (66)	151	0.8 (0.1)
Cover	153 (43)	172	1.1 (0.5)
Wood biochar			
Amended	52 (12)	273	1.6 (1.3)
Cover	13 (7)	312	4.3 (0.4)
Cob biochar			
Amended	153 (48)	172	0.6 (1)
Cover	133 (27)	192	1.0 (1.3)

(Table 4). These treatments were more efficient at preventing evaporation and therefore inhibited an increase in total solids concentration. Additionally, the mass of these manures was higher at the end of the experiment than the other manure storage treatments, confirming conservation of moisture. Preventing evaporation may correspond to these treatments ability to act as a physical barrier and prevent emissions of NH₃. The pH of the control significantly increased while the other treatments significantly decreased or stayed the same. The increase in pH in the control is likely a result of ammonia loss and or the increased buffering capacity of the covers from the addition of carbon. Increasing the pH of manure will increase emissions of NH₃ as the NH₄/NH₃ shifts from NH₄ to NH₃.

4 Discussion

The raw wood had the highest amount of NH₃ emitted compared to any other treatment but still resulted in a 40% decrease from the control. A similar study by Guarino et al. (2006) measured a 17% reduction in NH₃ lost during a 1-week study with a raw wood cover depth of 7 cm. Guarino et al. (2006) immersed dried raw wood chips measuring 20 to 30 mm long in dairy slurry for 30 days prior to measuring the emission to achieve some

biological degradation. In this study, the wood was dried which would create more buoyancy increasing the performance as a physical barrier to NH₃ emissions.

The physical and chemical compositions of the raw and steamed wood were similar, which may explain the similar emissions of NH₃ (Table 2). Steam-treated wood was more acidic than raw wood, but once introduced to the manure, it did not impact the pH of the manure mixture significantly (Table 4). As expected, the raw wood had the lowest TAN extracted from its biomass at the end of the study. Contrary to expectations, the steam-treated wood did not increase the TAN sorption potential of white birch. This opposes laboratory results by Adjei (2007) where steam explosion of corncobs increased the NH₃ sorption potential from 10 mg NH₃ per gram raw corncob to 60 mg NH₃ per gram steam-exploded corncob. Adjei (2007) also measured the adsorption capacity of NH₄ of steam-exploded material and found only a slight increase in sorption through steam explosion, 0.0328 mg NH₄OH per gram raw biomass and 0.4725 mg NH₄OH per gram steam-exploded biomass. Therefore, steam-exploded or -treated material may have preference for sorption of NH₃ gas, and this cover may have to be completely suspended above a manure storage for sorption of TAN. Steam explosion and steam treatment had the same impact on the physical properties of biomasses

Table 4 Initial and final manure characteristics by treatment. Values expressed as mean and standard deviation (in parentheses) including the *p* value from *t* tests

		pH	TS (g per kg manure)	VS (g per kg manure)	TAN (g per kg manure, dry basis)	TKN (g per kg manure, dry basis)
Control	Initial	7.6 (0.06)	42 (1)	33 (1)	30 (3)	58 (8)
	Final	7.8 (0.03)	54 (2)	43 (1)	18 (2)	37 (2)
	<i>p</i> value	0.017	0.009	0.003	0.001	0.03
Raw wood incorporated	Initial	7.7 (0.01)	42 (1)	33 (1)	29 (5)	50 (8)
	Final	7.6 (0.07)	55 (4)	44 (3)	20 (2)	40 (1)
	<i>p</i> value	0.070	0.038	0.043	0.07	0.13
Raw wood cover	Initial	7.7 (0.08)	40 (1)	32 (1)	32 (2)	54 (4)
	Final	7.5 (0.01)	42 (8)	44 (7)	32 (7)	59 (12)
	<i>p</i> value	0.060	0.674	0.203	0.98	0.63
Steamed wood incorporated	Initial	7.7 (0.03)	37 (8)	35 (3)	35 (6)	60 (9)
	Final	7.6 (0.03)	59 (6)	48 (4)	18 (1)	39 (2)
	<i>p</i> value	0.017	0.051	0.065	0.04	0.06
Steamed wood cover	Initial	7.7 (0.04)	41 (1)	33 (1)	28 (4)	48 (7)
	Final	7.5 (0.03)	58 (4)	48 (4)	21 (1)	37 (3)
	<i>p</i> value	0.033	0.014	0.016	0.14	0.04
Wood biochar incorporated	Initial	7.7 (0.08)	28 (14)	35 (1)	50 (26)	88 (38)
	Final	7.6 (0.03)	47 (3)	37 (3)	27 (3)	44 (2)
	<i>p</i> value	0.460	0.154	0.332	0.25	0.18
Wood biochar cover	Initial	7.7 (0.08)	41 (1)	33 (1)	28 (5)	46 (10)
	Final	7.6 (0.04)	41 (9)	36 (1)	32 (9)	53 (10)
	<i>p</i> value	0.273	0.840	0.075	0.65	0.51
Cob biochar Incorporated	Initial	7.7 (0.04)	42 (2)	36 (2)	28 (2)	50 (5)
	Final	7.7 (0.04)	55 (2)	43 (2)	22 (2)	41 (2)
	<i>p</i> value	0.438	0.012	0.034	0.24	0.08
Cob biochar cover	Initial	7.7 (0.06)	27 (20)	34 (2)	29 (0.1)	54 (1)
	Final	7.7 (0.05)	47 (1)	38 (1)	25 (1)	44 (1)
	<i>p</i> value	0.038	0.239	0.062	0.01	0.01

used in each study, the surface area and pore volume of the biomasses was decreased; therefore, not likely to be the cause of the difference in NH_3 emissions. Differences in results were most likely caused by experimental design as Adjei (2007) passed volumes of NH_3 gas through steam-exploded biomass to determine NH_3 adsorption. Since both applications of steam-treated material were submerged after application, there may not have been much contact between the volatilized NH_3 gas and the biomass.

The wood biochar treatments had the greatest reductions in NH_3 , followed by the cob biochar. Wood biochar's success was due to its effectiveness as a physical barrier. At the end of the experiment, the

average cover thickness above the manure surface was deeper for both biochars than the other biomass covers. Cover depths for wood biochar and cob biochar were 3.1 and 2.5 cm, respectively, while raw wood and steamed wood had cover depths of 0.7 cm. A greater cover depth could retain more gases at the liquid air interface by trapping or slowing the transfer of NH_3 emissions. Between the wood and cob biochar, the wood biochar was more effective in reducing emissions as it completely covered the manure storage surface. Wood biochar was able to layer and overlap, where the cob biochar has larger gaps between the biomass exposing some of the manure surface as seen in Fig. S1 (Online resource 2). Any

disturbance to a manure storage surface, resulting in shifting of material, could expose the manure surface and increase NH_3 emissions. Therefore, farm-scale NH_3 emission reductions from the use of a permeable manure storage covers would be affected by wind shear across the manure storage, rain, and installation method and implementation of covers requires innovation to reduce the impact of these concerns.

Even though sorption of TAN by biochars was not the main mechanism for NH_3 emission reduction, it is still important to the end use of these materials. Biomass treatments could be incorporated with manure and applied to the field and nitrogen retained by these materials is stable and is plant available (Spokas et al. 2012b), potentially reducing commercial N fertilizer requirements. Previous literature measurements of wood biochar CEC were lower (140 to 150 mmolc/kg) than cob biochar (610 mmolc/kg); the measured wood biochar's higher sorption potential over cob biochar of the current study was in contrary to literature supporting CEC and sorption of TAN (Gai et al. 2014). Biochar's ammonium retention with increased may be explained by electrostatic adsorption to negatively charge oxygen-containing functional groups (Cheng and Lehmann 2009; Hale et al. 2013), and or the functional groups of oxygen are acidic and can remove alkaline ammonia gas via acid-base reactions (Hale et al. 2013; Spokas et al. 2012a). In accordance, cob biochar had a slightly higher measured percentage of oxygen (Table 1) and may have had a higher amount of functional groups containing oxygen. Deviance from expectations could be due to differences in the physical structures of the two biochars. The wood biochar pieces were smaller and had significantly lower surface area and volume likely resulting and in more readily exposed functional groups. The porous structure of the cob may have reduced the diffusivity of NH_3 and NH_4 to sorption sites. Grinding would reduce the particle size of the cob biochar and could expose more functional groups and increase TAN sorption. The functional groups of biochar should be readily exposed to manure TAN for the greatest sorption of TAN.

Biomass application method had little impact on reducing NH_3 emissions, although the covers were more effective during the first week and up until the first month for the wood biochar. Based on visual observations, the incorporated material did not stay suspended in the liquid and within an hour of application, vertical distribution between covers and incorporated biomass

appeared to be similar. Biomass that migrated towards the surface of manure reduced NH_3 emissions as the main mechanism for gas reduction was a physical barrier. Application as a cover increased sorption of TAN compared to those that were incorporated; the sorption sites of the materials may have been blocked by manure particles after materials were submerged in the manure reducing the TAN sorption potential of the incorporated biomasses.

Emissions of NH_3 from dairy manure in the USA including emissions from housing, storage, and land application is estimated to be 370 Gg NH_3 per year from 2005 to 2008 (Paulot et al. 2014). Assuming uniform adoption of AD, manure is incorporated immediately after broadcasting, and all dairies in the USA are free-stall tie barns with manure storage. Digestion can increase emissions of NH_3 by 81% resulting in an increase of 143 Gg NH_3 per year in NH_3 emission (Holly et al. 2017). Using a wood biochar cover during storage in a similar scenario to this study would reduce emissions almost completely, eliminating the increase in NH_3 from incorporating AD into manure systems.

5 Conclusions

Floating covers and incorporation of raw wood, steamed wood, wood biochar, and cob biochar significantly reduce emissions of NH_3 from lab-scale digested manure storages. Biochars were the most successful in mitigating emissions, the success of which is related to its ability to serve as a physical barrier and effectively cover the surface of the manure storage. Sorption of NH_3 was greatest for wood biochar manure treatments; however, sorption of NH_3/NH_4 is not the main treatment mechanism as it only accounts for a small fraction of the NH_3 mitigated. Manure storage covers are only slightly more effective in reducing NH_3 emissions within the first month than biomass incorporation as many of the incorporated covers float to the manure surface resulting in no difference in cumulative emission. Sorption of biomass was greater for unincorporated manure storage covers as sorption sites after incorporation may have been blocked by manure. Wood biochar covers greatly reduced NH_3 emissions from lab-scale manure storages and further investigation including farm-scale testing, technologies for

installation, and cost benefit analysis would elucidate practicality (USEPA 1983).

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Compliance with ethical standards

Ethic Statement Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the U.S. Department of Agriculture.

Abbreviations AD, Anaerobic digestion; BET, Brunauer-Emmett-Teller method; CEC, Cation-exchange capacity; CH₄, Methane; CO₂, Carbon dioxide; Cob BC C, Cob biochar cover; Cob BC I, Incorporated cob biochar; N₂O, Nitrous oxide; NH₃, Ammonia; NH₄, Ammonium; Steamed C, Steamed wood cover; Steamed I, Incorporated-steamed wood; TAN, Total ammoniacal nitrogen; TKN, Total Kjeldahl nitrogen; Wood BC I, Incorporated wood biochar; Wood C, Wood cover; Wood I, Incorporated wood cover; Wood BC C, Wood biochar cover

References

- Adjei, T. (2007). Characterization of a novel biodegradable material to reduce emission of ammonia [Thesis]. Virginia Polytechnic Institute and State University. <http://hdl.handle.net/10919/30949>. Accessed 27 Oct 2017.
- Amon, B., Kryvoruchko, V., Amon, T., & Zechmeister-Boltenstern, S. (2006). Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agriculture, Ecosystems & Environment*, 112(2–3), 153–162. <https://doi.org/10.1016/j.agee.2005.08.030>.
- ASTM International. (2013). *ASTM E871-82 (2013), Standard test method for moisture analysis of particulate wood fuels*. PA, U.S.A: West Conshohocken www.astm.org.
- ASTM International. (2015). *ASTM D3663-03 (2015), Standard test method for surface area of catalysts and catalyst carriers*. PA, U.S.A: West Conshohocken www.astm.org.
- ASTM International. (2016). *ASTM D5373-16, Standard test methods for determination of carbon, hydrogen and nitrogen in analysis samples of coal and carbon in analysis samples of coal and coke*. PA, U.S.A: West Conshohocken www.astm.org.
- Berg, W., Brunsch, R., & Pasiczki, I. (2006). Greenhouse gas emissions from covered slurry compared with uncovered during storage. *Agriculture, Ecosystems and Environment*, 112(2–3), 129–134. <https://doi.org/10.1016/j.agee.2005.08.031>.
- Borchard, N., Prost, K., Kautz, T., Moeller, A., & Siemens, J. (2012). Sorption of copper (II) and sulphate to different biochars before and after composting with farmyard manure. *European Journal of Soil Science*, 63(3), 399–409. <https://doi.org/10.1111/j.1365-2389.2012.01446.x>.
- Cheng, C. H., & Lehmann, J. (2009). Ageing of black carbon along a temperature gradient. *Chemosphere*, 75(8), 1021–1027. <https://doi.org/10.1016/j.chemosphere.2009.01.045>.
- Christensen, M. L., Christensen, K. V., & Sommer, S. G. (2013). Solid-liquid separation of animal slurry. In S. G. Sommer, M. L. Christensen, T. Schmidt, & L. S. Jensen (Eds.), *Animal manure recycling: treatment and management* (First., pp. 105–130). Chichester: John Wiley & Sons, Ltd.
- Clemens, J., Trimborn, M., Weiland, P., & Amon, B. (2006). Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. *Agriculture, Ecosystems & Environment*, 112(2–3), 171–177. <https://doi.org/10.1016/j.agee.2005.08.016>.
- Crombie, K., Masek, O., Sohi, S. P., Brownsort, P., & Cross, A. (2013). The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy*, 5(2), 122–131. <https://doi.org/10.1111/gcbb.12030>.
- Ding, Y., Liu, Y.-X., Wu, W.-X., Shi, D.-Z., Yang, M., & Zhong, Z.-K. (2010). Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. *Water, Air, & Soil Pollution*, 213(1–4), 47–55. <https://doi.org/10.1007/s11270-010-0366-4>.
- Gai, X., Wang, H., Liu, J., Zhai, L., Liu, S., Ren, T., & Liu, H. (2014). Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. *PLoS One*, 9(12), e113888. <https://doi.org/10.1371/journal.pone.0113888>.
- Guarino, M., Fabbri, C., Brambilla, M., Valli, L., & Navarotto, P. (2006). Evaluation of simplified covering systems to reduce gaseous emissions from livestock manure storage. *Transactions of the ASABE*, 49(3), 737–748.
- Hale, S. E., Alling, V., Martinsen, V., Mulder, J., Breedveld, G. D., & Comelissen, G. (2013). The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. *Chemosphere*, 91(11), 1612–1619. <https://doi.org/10.1016/j.chemosphere.2012.12.057>.
- Holly, M. A., Larson, R. A., Powell, J. M., Ruark, M. D., & Aguirre-Villegas, H. (2017). Greenhouse gas and ammonia emissions from digested and separated dairy manure during storage and after land application. *Agriculture, Ecosystems and Environment*, 239, 410–419. <https://doi.org/10.1016/j.agee.2017.02.007>.
- Hou, Y., Velthof, G. L., & Oenema, O. (2015). Mitigation of ammonia, nitrous oxide and methane emissions from manure management chains: A meta-analysis and integrated assessment. *Global Change Biology*, 21(3), 1293–1312. <https://doi.org/10.1111/gcb.12767>.
- Ippolito, J. A., Spokas, K. A., Novak, J. M., Lentz, R. D., & Cantrell, K. B. (2015). *Biochar elemental composition and factors influencing nutrient retention*. In Biochar for environmental management: science, technology and implementation (pp. 139–165).
- Lam, P. S., Sokhansanj, S., Bi, X., Lim, C. J., & Melin, S. (2011). Energy input and quality of pellets made from steam-exploded douglas fir (*Pseudotsuga menziesii*). *Energy and Fuels*, 25(4), 1521–1528. <https://doi.org/10.1021/ef101683s>.
- Lin, Y., Munroe, P., Joseph, S., Henderson, R., & Ziolkowski, A. (2012). Water extractable organic carbon in untreated and chemical treated biochars. *Chemosphere*, 87(2), 151–157. <https://doi.org/10.1016/j.chemosphere.2011.12.007>.

- Malińska, K., Zabochnicka-Świątek, M., & Dach, J. (2014). Effects of biochar amendment on ammonia emission during composting of sewage sludge. *Ecological Engineering*, *71*, 474–478. <https://doi.org/10.1016/j.ecoleng.2014.07.012>.
- Mohan, D., Kumar, S., & Srivastava, A. (2014). Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars. *Ecological Engineering*, *73*, 798–808. <https://doi.org/10.1016/j.ecoleng.2014.08.017>.
- Nelissen, V., Rütting, T., Huygens, D., Staelens, J., Ruyschaert, G., & Boeckx, P. (2012). Maize biochars accelerate short-term soil nitrogen dynamics in a loamy sand soil. *Soil Biology and Biochemistry*, *55*, 20–27. <https://doi.org/10.1016/j.soilbio.2012.05.019>.
- Nicolai, R., Pohl, S., & Schmidt, D. (2004). Covers for manure storage units. *South Dakota Cooperative Extension Service Publication*. pubstorage.sdstate.edu/AgBio_Publications/articles/FS925-D.pdf. Accessed 27 Oct 2017.
- Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., & Henze, D. K. (2014). Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE-NH3). *Journal of Geophysical Research: Atmospheres*, *119*(7), 4343–4364. <https://doi.org/10.1002/2013JD021130>.
- Peters, J., Combs, S., Hoskins, B., Jarman, J., Kovar, J., Watson, M., et al. (2003). Recommended Methods of Manure Analysis (A3769). <http://learningstore.uwex.edu/assets/pdfs/A3769.pdf>. Accessed 27 Oct 2017.
- Rajkovich, S., Enders, A., Hanley, K., Hyland, C., & Zimmerman, A. R. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils*, *48*, 271–284. <https://doi.org/10.1007/s00374-011-0624-7>.
- Sika, M. P., & Hardie, A. G. (2014). Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil. *European Journal of Soil Science*, *65*(1), 113–119. <https://doi.org/10.1111/ejss.12082>.
- Smith, K., Cumby, T., Lapworth, J., Misselbrook, T., & Williams, A. (2007). Natural crusting of slurry storage as an abatement measure for ammonia emissions on dairy farms. *Biosystems Engineering*, *97*(4), 464–471. <https://doi.org/10.1016/j.biosystemseng.2007.03.037>.
- Sommer, S. G., Christensen, B. T., Nielsen, N. E., & Schjørring, J. K. (1993). Ammonia volatilization during storage of cattle and pig slurry: effect of surface cover. *The Journal of Agricultural Science*, *121*(1), 63. <https://doi.org/10.1017/S0021859600076802>.
- Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., et al. (2012a). Biochar: a synthesis of its agronomic impact beyond carbon sequestration. *Journal of Environment Quality*, *41*(4), 973. <https://doi.org/10.2134/jeq2011.0069>.
- Spokas, K. A., Novak, J. M., & Venterea, R. T. (2012b). Biochar's role as an alternative N-fertilizer: ammonia capture. *Plant and Soil*, *350*(1–2), 35–42. <https://doi.org/10.1007/s11104-011-0930-8>.
- Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., & Condon, L. M. (2012a). A wood based low-temperature biochar captures NH₃-N generated from ruminant urine-N, retaining its bioavailability. *Plant and Soil*, *353*(1–2), 73–84. <https://doi.org/10.1007/s11104-011-1010-9>.
- Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., & Condon, L. M. (2012b). Biochar adsorbed ammonia is bioavailable. *Plant and Soil*, *350*(1–2), 57–69. <https://doi.org/10.1007/s11104-011-0870-3>.
- Theuretzbacher, F., Lizasoain, J., Lefever, C., Saylor, M. K., Enguidanos, R., Weran, N., et al. (2015). Steam explosion pretreatment of wheat straw to improve methane yields: investigation of the degradation kinetics of structural compounds during anaerobic digestion. *Bioresource Technology*, *179*, 299–305. <https://doi.org/10.1016/j.biortech.2014.12.008>.
- Uludag-Demirel, S., Demirel, G. N., Frear, C., & Chen, S. (2008). Anaerobic digestion of dairy manure with enhanced ammonia removal. *Journal of Environmental Management*, *86*(1), 193–200. <https://doi.org/10.1016/j.jenvman.2006.12.002>.
- USEPA. (1983). *Methods of chemical analysis of water and waste*, Section 9.3. Cincinnati: EPA/600/4-79/020.
- VanderZaag, A. C., Gordon, R. J., Glass, V. M., & Jamieson, R. C. (2008). Floating covers to reduce gas emissions from liquid manure storages: a review. *American Society of Agricultural and Biological Engineers*, *24*(5), 657–672.
- VanderZaag, A. C., Gordon, R. J., Jamieson, R. C., Burton, D. L., & Stratton, G. W. (2009). Gas emissions from straw covered liquid dairy manure during summer storage and autumn agitation. *Transactions of the ASABE*, *52*(2), 599–608.
- Wang, B., Lehmann, J., Hanley, K., Hestrin, R., & Enders, A. (2015). Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. *Chemosphere*, *138*, 120–126. <https://doi.org/10.1016/j.chemosphere.2015.05.062>.
- Webb, J., Menzi, H., Pain, B. F., Misselbrook, T. H., Dammgen, U., Hendriks, H., & Dohler, H. (2005). Managing ammonia emissions from livestock production in Europe. *Environmental Pollution*, *135*(3 SPEC. ISS), 399–406. <https://doi.org/10.1016/j.envpol.2004.11.013>.
- WHO. (2005). *Ambient (outdoor) air quality and health*. Fact sheets. World Health Organization. <http://www.who.int/mediacentre/factsheets/fs313/en/>. Accessed 14 Aug 2016.
- Zhao, X., Wang, S., & Xing, G. (2014). Nitrification, acidification, and nitrogen leaching from subtropical cropland soils as affected by rice straw-based biochar: Laboratory incubation and column leaching studies. *Journal of Soils and Sediments*, *14*(3), 471–482. <https://doi.org/10.1007/s11368-013-0803-2>.