Canadian Journal of Soil Science

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Journal:	<i>Canadian Journal of Soil Science</i>
Manuscript ID	CJSS-2021-0029.R3
Manuscript Type:	Article
Date Submitted by the Author:	07-Nov-2021
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Is the invited manuscript for consideration in a Special Issue?_:	Biochar Amendments for Sustainable Soil Management Special Issue
Keywords:	liquid manure, partially-decomposed solid manure, poultry, dairy cattle, Swine

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Ammonia volatilization from manure mixed with biochar

Short title: Nitrogen dynamics in biochar-manure mixtures

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ABSTRACT

Ammonia (NH_3) volatilization from ammonia-based fertilizer and animal manure reduces their nitrogen fertilizer value and is a source of environmental pollution. Mixing manure with biochar may lower NH_3 volatilization from manure by adding H^+ , adsorbing mineral nitrogen (N), or increasing N immobilization in microbial biomass. The objective of this study was to determine whether wood-based biochar could lower NH_3 volatilization from vented pails containing manure (liquid swine, dairy slurry, and solid poultry manure) or a urea ammonium nitrate solution (UAN). Two types of wood-based biochar (BlueLeaf and Dynamotive) were mixed with three types of manure and UAN fertilizer solution at 0, 2.5, 5, 10, and 25 % biochar by volume in vented pails. After 21 d storage in an outdoor shaded area, the greatest NH_3 volatilization was from poultry manure, which had pH 9.4 on average and low water content regardless of the biochar source and application rate. There was less NH_3 volatilization from UAN fertilizer solution when mixed with 25% (v/v) of Dynamotive biochar compared to NH_3 volatilization from UAN fertilizer solution mixed with 0–10% (%) of Dynamotive biochar, probably because pH decreased from 7.0 to 6.4 after 21 d contact. Mixing wood-based biochar with manure had no impact on NH_3 volatilization, suggesting that these biochar sources did not appreciably change the pH and N dynamics in stored manure after 21 d.

Keywords: liquid manure, slurry manure, partially-decomposed solid manure, poultry, swine, dairy cattle

INTRODUCTION

Ammonia (NH_3) volatilization lowers the value of nitrogen (N) fertilizer because the $\text{NH}_{3(g)}$ lost from fertilizer or fertilized soils is transferred into the atmosphere and eventually deposited. Atmospheric wet and dry N deposition across the landscape alters the biogeochemical cycling and associated processes in natural ecosystems (Aber et al., 2003) and affects human health (Domingo et al., 2021). Excessive N deposition lower plant species richness, e.g., in grasslands in the United Kingdom (Stevens et al., 2004), and an altered N:P (phosphorus) ratio in the lakes in North America and Northern Europe (Elser et al., 2009). Ammonia-based fertilizers and animal manure are most susceptible to NH_3 volatilization, and contribute to atmospheric N deposition of about $1\text{--}4 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in North America, and up to $30 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in East Asia (Dentener et al., 2006). The 4-R nutrient management strategies recommend incorporating N fertilizer in soils during the growing season, which should be effective at reducing NH_3 volatilization from fertilized soils (Pan et al., 2016). However, 4-R nutrient management strategies do not address the larger problem of global NH_3 volatilization from livestock facilities and manure storages, which release $272\text{--}9177 \text{ Gg NH}_3\text{-N y}^{-1}$ globally (Beusen et al., 2008). The NH_3 volatilization in animal manure occurs when fecal bacteria produce urease to hydrolyze urea contained in urine, a naturally occurring process in barns and manure piles (Whalen et al., 2019). Therefore, creative solutions are needed to control NH_3 volatilization from manure.

Since NH_3 volatilization generally occurs in alkaline solutions ($\text{pH} > 7.3$), a common strategy to prevent $\text{NH}_{3(g)}$ loss is to add an acidic solution that protonates NH_3 to produce ammonium (NH_4^+), which will remain in the liquid fraction or bind to solid particles in manure (Sigudarson et al., 2018). For instance, adding alum ($[\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}]$) to solid poultry manure at the rate of $4 \text{ g alum } 100 \text{ g}^{-1} \text{ manure}$ decreased pH from 8.6 to 7.7 and reduced NH_3

volatilization from 31 g $\text{NH}_3\text{-N kg}^{-1}$ manure to 7 g $\text{NH}_3\text{-N kg}^{-1}$ manure (Choi and Moore Jr., 2008). Another option is to mix the urea-based fertilizer with an absorptive material like zeolites, which chemically adsorb 0.6–2.4 mg $\text{NH}_3\text{-N g}^{-1}$ zeolite from liquid swine slurry (Bernal et al., 1993). Similarly, adding C-rich residue like woodchip and straw bedding will increase the C:N ratio of manure, which induces N immobilization by microbial biomass. Straw addition to solid poultry manure reduced NH_3 volatilization from 44% to 9% of manure N, by increasing the C:N ratio from 18 to 36 (Kirchmann and Witter, 1989).

Wood-based biochar, i.e., pyrolyzed hardwoods, softwoods, and mixed woody by-products, may have the potential to lower NH_3 volatilization from manure by adding H^+ , adsorbing NH_4^+ and NO_3^- onto exchangeable surfaces, and supporting microbial biomass with greater N immobilization capacity (Fig. 1). It is possible to produce acidic biochar. Ippolito et al. (2016) reported that soil pH decreased from 7.6 to 7.2 within one month after 10% acidic wood-based biochar (pH 5.8) by weight was mixed with calcareous soil. However, adding neutral to alkaline biochar to soil stimulates microbial growth (i.e., by supplying substrates or physical space for microbial communities within its microporous structure; Gul et al., 2015) and could indirectly generate H^+ from proton pumps ($\text{H}^+\text{-ATPase}$) and nutrient transporters (H^+ /sugars and H^+/NO_3^- cotransporters; electrogenic NH_4^+ transporters) that operate during biological processes such as N immobilization (Jacoby et al., 2017; Wacker et al., 2014). Furthermore, wood-based biochar may be an effective sorbent since it can retain up to 0.8 mg $\text{NH}_4^+\text{-N g}^{-1}$ biochar and as much as 1.5 mg $\text{NO}_3^-\text{-N g}^{-1}$ biochar from water-based solutions containing 20 mg $\text{NH}_4^+ + \text{NO}_3^-\text{-N L}^{-1}$ (Fidel et al., 2018). Still, it is unclear whether biochar can effectively sorb NH_4^+ and NO_3^- from manure, which contains water with variable ionic strength, plus dissolved particulate material that could bind to sorptive surfaces. Biochar application on the surface of liquid swine

manure can create a thin layer of adsorbent (0.64 cm) to mitigate 40% NH_3 loss, and other odorous gas emissions, e.g., 20% H_2S , 90% p-cresol, and 70% skatole in a 30 d trial (Meiirkhanuly et al., 2020a; 2020b). Yet, biochar application to the surface of dairy slurry did not reduce NH_3 emissions from the control, which had a naturally-formed 10-cm thick crust (Holly and Larson, 2017). Finally, adding biochar to manure-amended soil often increases the microbial biomass, which is expected to immobilize NH_4^+ and NO_3^- from solutions (Gul et al., 2015), but it is not known whether N immobilization would lower the NH_3 volatilization from biochar-manure mixtures. Therefore, we wondered if these outcomes could be detected within a few weeks of adding biochar to a manure storage facility.

The objective of this study was to determine whether adding wood-based biochar reduces NH_3 volatilization and changes mineral N concentration (NH_4^+ and NO_3^-) in manure (liquid swine, dairy slurry, and solid poultry manure) compared to a urea-based fertilizer (urea ammonium nitrate, UAN). This experiment was designed to simulate a roofed (covered) manure storage where biochar was added and then left undisturbed for 21 d. We expect rapid fluctuations in N dynamics when manure is agitated and microbial communities are first exposed to biochar because NH_3 flux peaks in the first 7–14 d after manure is added or agitated in a manure storage facility, due to the microbial degradation of urea and its precursors (e.g. uric acid and allantoin; Al-Kanani et al., 1992; VanderZaag et al., 2010). Since the goal of this work was to examine whether biochar would affect the NH_3 volatilization after the system re-equilibrated from the initial disturbance, we took measurements after 21 d of contact between the manure and biochar.

MATERIAL AND METHODS

Biochar and manure

We used two types of wood-based biochar, BlueLeaf (softwood, pyrolysis at 450 °C; BlueLeaf Inc., Drummondville, Quebec, Canada) and Dynamotive (hardwood, pyrolysis at 750 °C; Dynamotive Energy Systems Corporation, West Lorne, Ontario, Canada), both described by Glodowska et al. (2016). Briefly, BlueLeaf biochar has higher pH (8.6), lower total pore space ($2.5 \text{ m}^2 \text{ g}^{-1}$), and lower mineral N concentration ($18 \text{ mg NH}_4\text{-N} + \text{NO}_3\text{-N kg}^{-1}$) compared with Dynamotive biochar that has pH 7.4, total pore space of $13.4 \text{ m}^2 \text{ g}^{-1}$, and higher mineral N ($42 \text{ mg NH}_4\text{-N} + \text{NO}_3\text{-N kg}^{-1}$). The particle size of the wood-based biochars was $< 2 \text{ mm}$. The manure sources were liquid swine, dairy slurry, and solid poultry manure, which were obtained from the Macdonald Campus Farm of McGill University, Sainte-Anne-de-Bellevue, Quebec, Canada. We applied UAN fertilizer solution, a common N fertilizer for field crops in Quebec with a guaranteed analysis of 32-0-0 as a control to assess how biochar sorption of soluble NH_4^+ and NO_3^- occurred in a solution with high ionic strength. The basic physicochemical properties of the fertilizers are summarized in Table 1.

Experimental design

The experiment was a completely randomized factorial design, with two biochar sources (BlueLeaf, Dynamotive) combined with the four nutrient sources (liquid swine, dairy slurry, solid poultry manure and UAN) at 0, 2.5, 5, 10, and 25 % biochar by volume, i.e., 0, 0.125, 0.25, 0.50, and 1.25 L biochar. The experimental unit was a 20 L plastic pail (12.9 cm dia., 38.1 cm height), which contained 5 L manure or UAN fertilizer solution and was stored in an outdoor shaded area for a week before biochar application (mean air temperature 21°C). Each treatment had three

replicates for a total of 120 plastic pails in the study. After adding biochar to the nutrient sources, we sealed the pails with leak-tight lids and mixed them thoroughly using a mechanical shaker for 1 h. To ensure even distribution of biochar in the UAN fertilizer solution, the biochar was pre-soaked for 12 h in the surfactant Agral 90 (90% nonylphenoxy polyethoxy ethanol, Syngenta Crop Protection Canada, Guelph, ON). After shaking, the lid was removed and a 400 mL subsample of the biochar-fertilizer mixture (i.e., biochar mixed with manure; biochar mixed with UAN fertilizer solution) was collected for analysis. Visual observation indicated that most of the biochar settled to the bottom after a day in the pails. Each pail was fitted with a two-way vented lid to avoid a buildup of noxious gases and placed in an outdoor shaded area for three weeks (Fig. 2, mean air temperature 21 °C). A 100 g subsample of the biochar-fertilizer mixture was collected from the pail each week and stored at -20 °C until analysis.

The vented pail is a small-scale representation of a manure storage facility. It was considered analogous to an above-ground concrete tank filled with liquid manure or an above-ground concrete bunker containing solid manure. Covering the pail with a two-way vented lid, which allows for air exchange, resembles a liquid manure tank with a semi-permeable cover such as a floating geotextile membrane or a solid manure pile covered with a permeable plastic tarp.

NH₃ gas analysis

The NH₃ gas concentration was measured in the pail headspace, 21 d after the biochar-fertilizer mixtures were prepared. The NH₃ amount in the headspace after 21 d was considered an indicator of the NH₃ volatilization from a simulated manure storage facility after the microbial community re-equilibrated from the disturbance associated with transferring manure into the pails, adding biochar, and agitating the manure-biochar mixture. The partial NH₃ accumulation in the

headspace after 21 d was measured with a Dräger X-am[®] 5000 gas detector equipped with Catalytic Ex sensors 125PR (Dräger AG & Co., Lübeck, Germany). The detector was connected to Dräger X-am[®] 125 pump (flow rate: 0.4 L min⁻¹, with a 0.1 µm PTFE filter) and a hose that was inserted into the plastic pail through a hole in the lid. The NH₃ concentration was recorded after the hose was inserted into the pail (> 10 s) or the highest value when an A2 alarm (i.e., NH₃ > 50 ppm) was triggered. Dilution of the headspace NH₃ concentration caused by about 0.07 L ambient air entering due to pressure compensation was assumed to be negligible. The detector pumped fresh air (50 m away from the pails) into the sensor to eliminate possible gas saturation of electrodes after every five measurements. The amount of NH₃-N (µg N) in the headspace was calculated by ideal gas law based on the NH₃ concentration (ppm), air temperature (21°C), the molecular weight of N and NH₃, and the headspace volume of the pail (assumed to be 15 L with 0% biochar by volume, and declining to 13.75 L in pails receiving 25% biochar by volume).

Analytical methods

Every subsample of the biochar-fertilizer mixture was analyzed for pH, dissolved organic carbon, and mineral N (NH₄⁺-N and NO₃⁻-N). The pH of the samples was determined in a 1:5 mixture: deionized water suspension. Mixtures containing appreciable liquid (liquid swine, dairy slurry, and UAN fertilizer solution) with biochar were filtered through Q5 filter paper (Thermo Fisher Scientific Inc., Waltham, MA, US), while the biochar-solid poultry manure mixture was extracted (1:20, w/v with deionized water) after 30 min shaking and filtered through Q5 filter paper before the filtrate was analyzed for dissolved organic carbon on a Sievers Innovox TOC analyzer (GE Analytical Instrument, Boulder, CO, USA). The NH₄⁺-N and NO₃⁻-N extracted with 2M KCl

(1:10, w/v) during 1 h shaking was quantified by the modified indophenol blue method (Sims et al., 1995).

Statistical Analysis

The responses of different manure types, biochar types, and biochar rates on NH_3 amount in the headspace were analyzed by three-way ANOVA. We used linear or exponential regression to show the correlations between biochar rate and the amount of NH_3 in the headspace, the pH, and the NH_4^+ , and mineral N concentrations in biochar-manure mixtures. Data presented in the text are the mean $\pm$ standard error, and statistical analysis was done with R v. 3.6.1 (R Core Team, 2017).

RESULTS AND DISCUSSION

As expected, the NH_3 volatilization differed among animal manures (data not shown, $P < 0.001$), regardless of the biochar source and application rate. There was more NH_3 in the headspace of pails with solid poultry manure ($1555 \pm 155 \mu\text{g N}$) than other manure types or the UAN fertilizer solution ($504 \pm 18 \mu\text{g N}$ for liquid swine, $777 \pm 46 \mu\text{g N}$ for dairy slurry, and $450 \pm 39 \mu\text{g N}$ for UAN; Fig. 3). Greater NH_3 volatilization from solid poultry manure is expected due to its high initial pH (9.4) and low water content (31%), which means that $\text{NH}_{3(\text{g})}$ is more likely to diffuse from the solid poultry manure than remain dissolved in water as $\text{NH}_{3(\text{aq})}$, which can be protonated to $\text{NH}_4^+(\text{aq})$. Consequently, livestock operators should cover piles of solid poultry manure to prevent NH_3 volatilization during storage (Whalen et al., 2019).

Adding biochar into manure or UAN fertilizer solution did not decrease NH_3 volatilization after 21 d storage for any treatments, except that there was less NH_3 volatilization from UAN

fertilizer solution mixed with a 25% Dynamotive biochar, by volume (Fig. 3). Greater NH_3 volatilization is associated with higher NH_4^+ concentration and elevated pH because the NH_3 produced from urea hydrolysis is likely to be protonated to NH_4^+ in acidic solutions (Fig. 4). As there was abundant NH_4^+ in all biochar-fertilizer mixtures, the greater NH_3 volatilization therefore might be related to the solution pH. In all biochar-manure mixtures, the pH was stable (on average, 7.3 ± 0.0 in mixtures with dairy slurry; 9.0 ± 0.1 in mixtures with solid poultry manure) or the pH increased during the 21-d storage period (from 7.3 ± 0.0 on day 0 to 7.6 ± 0.0 on day 21 in the biochar-liquid swine mixtures; $P < 0.05$, data not shown). However, pH in biochar-UAN mixtures declined from 7.0 ± 0.0 on day 0 to 6.4 ± 0.0 on day 21 ($P < 0.01$, data not shown), and pH dropped from 6.4 to 6.1 when UAN fertilizer solution was mixed with the highest rate of Dynamotive biochar (Fig. 5). The decline of pH in the biochar-UAN mixture might be related to NH_4^+ oxidation through biological N immobilization, which increases the H^+ concentration in solution (Havlin et al., 2005). Thus, the biochar-fertilizer mixtures with the lowest pH values had less NH_3 volatilization. This finding is consistent with other reports of greater NH_3 volatilization with an increase in soil pH and solution pH (Ernest and Massey, 1960; Havlin et al., 2005).

We did not find lower NH_3 volatilization from simulated manure storage after adding wood-based biochar, but there might be other ways to integrate biochar into livestock systems to achieve this goal. Some authors have proposed adding biochar to animal diets, based on the assumption that urea and amino acids from degradable proteins in animal digestive systems may be sorbed to biochar (Hagemann et al., 2017, Kasozi et al., 2010, Zimmerman et al., 2004), which would prevent urea hydrolysis during manure storage. Although urea enters the gastrointestinal system of ruminants and monogastric animals like dairy and swine, it is a relatively minor amount because most urea is excreted through the renal system of these animals, and this may account for

the negligible fraction of the total urea produced in these ruminants and monogastric animals (Getahun, et al., 2019; Krone et al., 2019). Poultry that ingest biochar might have lower NH_3 volatilization from their manure, based on the fact that urine and feces are combined in the digestive tract before they are excreted together through the cloaca, but inconsistent results were reported after feeding biochar to broilers and laying hens (Kalus et al., 2020; Parasai et al., 2018). Covering the manure with a layer of biochar is another way we might reduce NH_3 volatilization from manure. Dougherty et al. (2017) showed wood-based biochar made from a mixture of Douglas fir bark and center wood pyrolyzed at 600 °C reduced NH_3 concentration by 72 to 80%. A thin layer (6.4 mm) of biochar made from red oak on the surface of a swine manure storage reduced NH_3 volatilization by 19–39% in a 30-d trial (Meiirkhanuly et al., 2020a). However, wood-based biochar made from Douglas fir chips pyrolyzed at 650 °C did not reduce NH_3 volatilization (Dougherty et al. 2017). It remains to be determined whether biochar acted as a physical barrier or changed the chemistry and biological activity at the manure-atmosphere interface in a way that altered NH_3 volatilization. Although covering manure with biochar is simpler and requires less energy than agitating the storage to create a biochar-manure mixture, we acknowledge that floating biochar has a low density and can be displaced by strong winds, which can create a dust problem and may not prevent NH_3 loss. Further study is needed to determine the best way to integrate biochar into livestock systems for control of NH_3 volatilization, considering that biochars may be more or less suitable for this purpose depending on their origin (e.g., feedstock and pyrolysis temperature), particle size, and chemical properties. Finally, we have to consider the economics of biochar application in manure storages, since biochar may sell for CAD \$350 and CAD \$500 per metric tonne, dry weight (B. Husk, personal communication). If a farm was using a commercial, aboveground tank with a capacity of 2528 m³ (e.g., Boerger, 2021) that contained 2000 m³ of solid

poultry manure, and they added 5% wood-based biochar by volume with a density of 342 kg m^{-3} (density of Dynamotive biochar, Glodowska et al., 2016), the cost would be CAD \$11,970 to CAD \$17,100 for the biochar-manure mixture per tank. The economic and environmental costs and benefits of biochar application requires further study, considering the product life cycle of biochar and manure, to justify this practice.

The NH_4^+ and mineral N concentration in the nutrient sources are important indicators of its agronomic value. In biochar-manure mixtures, there was $3.4 \pm 0.2 \text{ g NH}_4^+\text{-N kg}^{-1}$ (wet weight) and this was generally not affected by adding biochar. However, NH_4^+ and mineral N concentration in the biochar-UAN fertilizer solution showed an exponential decline with increasing rates of both biochar types (Fig. 4 and Fig. 6). The NH_4^+ concentrations of biochar-UAN mixtures after 21 d were in the same order of magnitude, but declined from $5.1 \pm 0.1 \text{ g NH}_4^+\text{-N kg}^{-1}$ (wet weight) when no biochar was incorporated to $0.6 \pm 0.4 \text{ g NH}_4^+\text{-N kg}^{-1}$ with the 25% Dynamotive biochar treatment (Fig. 4). The lower NH_4^+ concentration in biochar-UAN mixtures could be the result of microbial immobilization and sorption to biochar, instead of net nitrification in the UAN fertilizer solution because of anaerobic conditions in the solution and stable NO_3^- concentration. Likewise, the exponential decline of the mineral N concentration with biochar rate is related to the NH_4^+ dynamics because of stable NO_3^- concentration. A possible reason to explain why NH_4^+ concentration decreased more in Dynamotive biochar is due to the higher pore space in Dynamotive biochar (13.4 vs. $2.5 \text{ m}^2 \text{ g}^{-1}$), but we cannot rule out the possibility of greater N immobilization with the BlueLeaf biochar, which was pyrolyzed at a lower temperature and may contain more labile organic C that might be a substrate for microbial growth (Weber and Quicker, 2018). In the future, we need to estimate the C availability to microorganisms and N immobilization rates of these biochar sources.

The mineral N concentration in the biochar-manure mixtures was not influenced by the biochar type or application rate (Fig. 6). This is possibly due to interactions between urea hydrolysis, mineralization, and immobilization that produce highly variable mineral N concentrations in the mixtures. Manure contained sufficient dissolved organic C (data not shown, 132–206 mg C kg regardless of the manure type) for microbial metabolic processes, even before biochar was added. We did not account for gaseous N loss resulting from nitrification and denitrification, i.e., nitrogen gas (N_2) and nitrous oxide (N_2O) emission, in the manure-biochar mixtures. Manure storages typically emit N_2 and N_2O from denitrification, due to the presence of many anaerobic microsites, while nitrification at the manure surface contributes to N_2O emission (Maeda et al., 2010). Admittedly, the expected proportion of the N losses may be as low as 0.0006–0.01 kg N_2O kg⁻¹ N in manure (Gavrilova et al., 2019). We need to measure N dynamics following biochar application to manure storage, including N_2 and N_2O losses and microbial N immobilization, based on net changes in pools or using isotopic tracers to track specific N transformation after mixing biochar with manure.

CONCLUSION

Stored manure is susceptible to NH_3 volatilization, which reduces its value as an N fertilizer and adds to the atmospheric N load, which is generally deposited in non-agricultural ecosystems. Wood-based biochar had no impact on NH_3 volatilization after 21-day storage, probably due to internal regulation of microbial processes in the manure, which were not affected by biochar. When mixed with UAN fertilizer solution, wood-based biochar tended to reduce the pH, leading to greater NH_4^+ sorption or immobilization. Biochar-induced changes in N dynamics of UAN fertilizer solution will require further study. Mixing biochar with manure during storage is unlikely

to be an effective measure at conserving the N fertilizer value of manure, and the extra cost associated with adding biochar to manure storage is not justified in this study. We suggest alternative methods of integrating biochar into livestock systems to reduce NH_3 volatilization, and these could be examined in the future.

ACKNOWLEDGEMENTS

This research was supported in part by funding from the Discovery program (grant #238323-2010) of the Natural Sciences and Engineering Research Council of Canada. We greatly appreciate the fieldwork and lab work supported by Hicham Benslim, Blake Bissonnette, Dr. Grant Clark, Andrea Ellison Aidan Prado, Dr. Yung-Chien Sun, and Aissa Zaouia. We also thank Dr. Noura Ziadi and three anonymous reviewers for their helpful comments and suggestions to improve an earlier version of this manuscript.

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Table 1 Physiochemical characteristics of two biochars (BlueLeaf and Dynamotive) and four nutrient sources (liquid swine, dairy slurry, solid poultry manure and urea ammonium nitrate), on a fresh weight basis

Characteristics ^a	BlueLeaf (Softwood)		Dynamotive (Hardwood)	
pH	8.6		7.4	
NH ₄ ⁺ -N + NO ₃ ⁻ -N (mg N kg ⁻¹)	18		42	
Organic C (g kg ⁻¹)	680		440	
Water holding capacity (g 100g ⁻¹)	80.1		70.7	
Total pore area (m ² g ⁻¹)	2.5		13.4	
Median pore diameter: area (μm)	2.95		9.8 × 10 ⁻³	
Median pore diameter: volume (μm)	12.2		42.5	
Average pore diameter (4V/A, μm)	6.03		0.68	
	Liquid swine	Dairy slurry	Solid poultry	Urea ammonium nitrate
Phase	liquid	slurry	solid	liquid
pH	7.4	7.5	9.4	7.1
Dry matter content (g kg ⁻¹)	49	38	591	NA ^b
Total nitrogen ^c (mg N L ⁻¹)	11.1	20.4	44.5	2678
Dissolved organic carbon (mg C kg ⁻¹)	208	219	177	183
Total phosphorus ^c (mg P L ⁻¹)	2.4	3.8	18.8	0.4
Total potassium ^c (mg K L ⁻¹)	11.7	14.7	36.9	0

^a Characteristics of BlueLeaf and Dynamotive biochar were described by Glodowska et al. (2016).

^b NA = not available.

^c The total nitrogen, phosphorus, and potassium were measured by the acid digestion method with concentrated H₂SO₄ and 30% H₂O₂, and the digestate was analyzed with an inductively coupled plasma atomic emission spectrometry.

Figure captions

Fig. 1 Conceptual model illustrating the ways that biochar could reduce ammonia volatilization during manure storage. The NH_4^+ in manure, excreted by animals or produced by urea hydrolysis, may be sorbed to biochar surfaces, or immobilized by microbes living in the charosphere (niches on the surface and within the micropores of biochar). Biochar that releases H^+ into the fertilizer solution will protonate NH_3 to NH_4^+ , thereby reducing the $\text{NH}_3(\text{g})$ lost from the biochar-fertilizer mixture.

Fig. 2 Biochar-manure was stored in a 20 L pail with a vented lid that had 7–8 small holes in the lid and a big hole (covered with duct tape) for headspace gas measurement with a Dräger X-am® 5000 gas detector. The pails were randomly placed in an outdoor shaded area and rotated weekly.

Fig. 3 $\text{NH}_3\text{-N}$ in the headspace of vented pails containing manure or urea ammonium nitrate fertilizer solution mixed with two biochar types (BlueLeaf and Dynamotive), after 21 d storage. Pails were stored in a shaded area with an average temperature of 21°C . Data were from the replicated pails ($n=3$, except that $n=2$ in the biochar mixtures with poultry manure).

Fig. 4 $\text{NH}_4^+\text{-N}$ concentration of manure or urea ammonium nitrate solution mixed with biochar, after 21 d storage. Pails ($n=3$ for each biochar-fertilizer mixture) were stored in a shaded area with an average temperature of 21°C . Higher Dynamotive biochar rates reduced the $\text{NH}_4^+\text{-N}$ concentration in the liquid swine and the urea ammonium nitrate solution. Higher BlueLeaf biochar rates reduced the $\text{NH}_4^+\text{-N}$ concentration in the urea ammonium nitrate solution.

Fig. 5 pH values of manure or urea ammonium nitrate solution mixed with two biochar types (BlueLeaf and Dynamotive), after 21 d storage. Pails ($n=3$ for each biochar-fertilizer mixture) were stored in a shaded area with an average temperature of 21°C .

Fig. 6 Mineral N ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) concentration of manure or urea ammonium nitrate solution mixed with two biochar types (BlueLeaf and Dynamotive), after 21 d storage. Pails ($n=3$ for each biochar-fertilizer mixture) were stored in a shaded area with an average temperature of

21°C. There was less mineral N when higher rates of Dynamotive biochar and BlueLeaf were added to the urea ammonium nitrate solution.

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Fig. 2

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Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6