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Ammonia volatilization from composting with oxidized biochar

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Abstract

Animal manure, agricultural residues, and other sources of biomass can be diverted from the waste stream and composted into valuable fertilizer. However, composting often results in substantial N loss through NH₃ gas volatilization. We investigated biochar's capacity to improve NH₃-N retention during composting of poultry manure and straw. After 7 wk, total N loss from composting with unoxidized biochar was twofold and sixfold higher than N loss from composting with oxidized biochar and without biochar (307, 142, and 51 mg N g⁻¹ N in the initial compost feedstocks, respectively). When cumulative NH₃-N loss was calculated relative to CO₂-C loss to account for differences in microbial activity, NH₃-N/CO₂-C loss from compost with oxidized biochar was 55% lower than from compost with unoxidized biochar (82% lower based on mass balance). Oxidized biochar particles removed from compost after 7 wk retained 16.0 mg N g⁻¹ biochar, compared with only 6.1 mg N g⁻¹ retained by unoxidized biochar, suggesting that N retention by biochar particles provides a mechanism for reduced NH₃-N loss. These data show that oxidized biochar enhanced microbial activity, doubled composting rate, and reduced NH₃-N loss compared with unoxidized biochar and that biochar's physiochemical characteristics modulate its performance in compost. In particular, the presence of oxidized surface functional groups, which can be increased artificially or through environmental weathering, appear to play an important role in key compost processes. This has implications for other natural and managed systems where pyrogenic organic matter may mediate biological activity and nutrient cycles.

1 | INTRODUCTION

Composting is a method used to convert animal manure, agricultural residues, sewage sludge, and other organic materials into a valuable soil amendment. Compost application can benefit agricultural production through its effect on edaphic conditions that favor plant growth and resilience, such as increased organic matter content, nutrient content and retention capacity, aeration, water infiltration and retention, and biotic diversity. Additionally, compost production is an

effective resource management strategy that transforms waste products into fertilizer while simultaneously reducing weed seed viability, pathogen populations that inhabit compost feedstocks, and the volume of organic materials that must be stored, applied, or transported. Livestock manure is a common compost feedstock with great agronomic potential due to its high nutrient content. Global livestock manure production exceeds 130 Tg N yr⁻¹ (Zhang et al., 2017). This is comparable to the quantity of fertilizer-N that is annually applied to agricultural soils and could provide a viable

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supplement or alternative to synthetic N fertilizers (Galloway et al., 2004). However, more than half of the original N contained in N-rich compost feedstocks can be lost as NH_3 gas during the composting process, thereby greatly reducing the compost's agronomic value and releasing reactive N into the environment (Eghball, Power, Gilley, & Doran, 1997; Tiquia, Richard, & Honeyman, 2002). Strategies to reduce NH_3 loss from compost include optimization of compost aeration, pH, temperature, and C/N ratio, inoculation with microorganisms, and incorporation of adsorbents, clay, minerals, and other materials (Bernal, Lopez-Real, & Scott, 1993; Chowdhury, de Neergaard, & Jensen, 2014; Eiland, Klamer, Lind, Leth, & Baath, 2001; Jeong & Kim, 2001; Kithome, Paul, & Bomke, 1999; Zhang et al., 2016).

Recently, biochar—the product that remains when biomass is heated under low-oxygen conditions—has also been investigated for its potential to reduce NH_3 loss and provide other benefits during composting. There is evidence that incorporation of biochar into compost can enhance microbial activity, speed compost maturation, improve nutrient retention and other agronomic properties of compost, and reduce emissions of greenhouse gases and NH_3 (Agyarko-Mintah et al., 2017; Awasthi et al., 2017; Chen et al., 2010; Chowdhury et al., 2014; Malinska, Zabochnicka-Swiatek, & Dach, 2014; Steiner, Das, Melear, & Lakly, 2010; Xiao et al., 2017). Despite its promise as a beneficial compost feedstock, biochar has been associated with both increased and decreased NH_3 emissions from compost and soil (Agyarko-Mintah et al., 2017; Awasthi et al., 2017; Chen et al., 2013; Fungo et al., 2019; Malinska et al., 2014; Mandal et al., 2016; Sha, Li, Lv, Misselbrook, & Liu, 2019; Spokas, Novak, & Venterea, 2012; Steiner et al., 2010; Sun, Li, Chen, Wang, & Xiong, 2014; Taghizadeh-Toosi, Clough, Sherlock, & Condrón, 2012a). Biochar's physical and chemical characteristics vary widely depending on the feedstock from which the biochar was made, pyrolysis conditions (e.g., temperature and atmospheric composition during pyrolysis), and post-pyrolysis processing (Enders, Hanley, Whitman, Joseph, & Lehmann, 2012; Zimmerman, 2010). The resulting variation in biochar's elemental composition, pH, porosity, surface chemistry, and other properties influence both its biotic and abiotic interactions in the environment (Clough, Condrón, Kammann, & Mueller, 2013; Enders et al., 2012; Wollet & Whitman, 2019). This variation may be partially responsible for the range of NH_3 emissions measured following biochar applications to soil and compost.

To assess biochar's potential to reduce NH_3 loss from compost, it is necessary to understand the mechanisms through which biochar can retain NH_3 -N and the physiochemical characteristics that enhance this retention capacity. This knowledge would aid in the development of “designer” biochars, which are produced to address specific agronomic or environmental constraints (Novak, Cantrell, Watts, Busscher, & Johnson, 2014). It would also help predict how different

Core Ideas

- Oxidized biochar doubled microbial decomposition in co-composted mixtures.
- NH_3 -N/ CO_2 -C loss was halved in co-composted mixtures containing oxidized biochar.
- Unoxidized biochar increased N losses sixfold during a 7-wk composting period.
- Oxidized biochar retained two- to threefold more compost N than unoxidized biochar.

types of biochar will behave across a broader range of applications and environmental conditions. There is evidence that oxidation greatly enhances biochar's NH_3 and NH_4^+ retention capacity (Hestrin et al., 2019; Wang, Lehmann, Hanley, Hestrin, & Enders, 2015, 2016). However, previous research has not explicitly investigated how oxidation influences biochar's behavior in compost. The objective of this study was to investigate whether oxidation enhances NH_3 -N retention during composting in compost-biochar mixtures and identify the mechanisms through which biochar reduces NH_3 emissions. We hypothesized that composting N-rich manure with oxidized biochar would result in higher NH_3 -N retention than composting with unoxidized biochar.

2 | MATERIALS AND METHODS

2.1 | Biochar preparation

Maple wood chips (*Acer rubrum*) were sieved to 2–16 mm and pyrolyzed at 500 °C under argon gas for 30 min in a modified muffle furnace. A subsample was incubated with 30% H_2O_2 at 25 °C for 3 mo (biochar/ H_2O_2 ratio, 1:10 g ml^{-1}). After oxidation, biochar was rinsed thoroughly with DI H_2O and dried at 25 °C. Oxidation altered many of biochar's physical and chemical characteristics (Table 1). Changes that were expected to be associated with reduced NH_3 emissions from compost include lower pH, higher cation exchange capacity, and higher NH_3 adsorption capacity. Because it is indicative of surface functional groups that might be involved in NH_3 -N retention, higher O content of oxidized biochar was also expected to be associated with lower NH_3 loss from compost.

2.2 | Compost production

Poultry manure and straw were adjusted to 50% water content by mass, mixed together, and subsampled for each treatment. For the control treatment, 500 g of the compost mixture was added to a 2-L glass jar. For treatments containing unoxidized

TABLE 1 Biochar and compost feedstock physical and chemical characteristics prior to composting

	pH (H ₂ O)	SSA ^a m ² g ⁻¹	CEC ^b mmolc kg ⁻¹	C	N	H	O	C/N	H/C	O/C	Ash	Volatile matter %	NH ₃ chemisorption capacity μmol g ⁻¹	NH ₃ physisorption capacity μmol g ⁻¹
Biochar	9.2	249.2	306.1	89.7	0.24	2.78	9.82	374	0.37	0.08	1.78	22.3	379.6	1,639.2
Oxidized biochar	3.6	216.3	1,331.6	69.7	0.21	2.49	21.21	331	0.43	0.23	1.30	36.1	1,599.1	3,716.1
Manure and straw	6.9	n.d. ^c	n.d.	35.5	4.56	n.d.	n.d.	7.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Manure, straw and biochar	6.9	n.d.	n.d.	49.1	4.17	n.d.	n.d.	11.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Manure, straw and oxidized biochar	6.3	n.d.	n.d.	44.7	3.96	n.d.	n.d.	11.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

^aSpecific surface area measured with CO₂. ^bCation exchange capacity. ^cNo data.

or oxidized biochar, 500 g of the compost mixture was mixed with 125 g of biochar (also pre-adjusted to 50% water content by mass) and added to jars. The ratio of biochar to compost was chosen based on observations by Steiner et al. (2010), who found that incorporation of biochar into poultry litter compost at a rate of 20% by dry weight resulted in substantial reductions in the concentration of compost NH₃ emissions and total compost N loss (up to 64 and 52%, respectively). Significant reductions in compost NH₃ emissions have also been observed with lower biochar incorporation rates; optimal dose rates appear to be context dependent and may need to be assessed separately for different types of biochar, compost systems, and intended outcomes (Awasthi et al., 2017; Chen et al., 2010; Liu et al., 2017; Malinska et al., 2014). All jars were sealed with tight-fitting lids that contained two ports: one for gas inflow and one for outflow (Supplemental Figure S1). A multichannel peristaltic pump set to 1.0095 ml min⁻¹ was used to control air flow in and out of the jars (IPC-N Low-Speed Digital Peristaltic Pump, Ismatec). Stainless steel tubing conducted inflow air to the bottom of each jar and maintained compost aeration. All jars were placed in an oven to standardize compost temperature and to simulate the interior of a compost pile (see Supplemental Figure S2 for temperature regime). The experiment was conducted twice, with two replicates of each treatment per experimental run, for a total of four replicates per treatment. The replicate jars were spatially distributed using a randomized complete block design. Each experimental run lasted 7 wk.

2.3 | Physical and chemical analyses

Biochar specific surface area was quantified using the Brunauer–Emmett–Teller method with CO₂ at 273.15 K (ASAP 2020, Micromeritics). Biochar ash and volatile content were measured according to the modified proximate analysis method described by Enders et al. (2012). Biochar NH₃ adsorption capacity was measured with an Autosorb iQ gas sorption analyzer (Quantachrome Instruments) (Hestrin et al., 2019). Briefly, samples were degassed at 300 °C for 3 h prior to NH₃ exposure, which was conducted from 80 to 800 mm Hg at 35 °C. Chemisorption capacity values indicate the quantity of NH₃ that was retained by biochar under vacuum, suggesting strong retention mechanisms, including covalent bonds (Hestrin et al., 2019). Physisorption capacity values indicate the quantity of NH₃ that was retained by biochar upon initial exposure but was removed under vacuum, suggesting a weak and easily reversible adsorption. See Table 1 for biochar physical and chemical characteristics.

At the beginning and end of each compost experiment, representative samples of compost and biochar were collected to measure moisture, pH, KCl-extractable N, and elemental content, as described below. Biochar and compost pH were

measured in DI H₂O at a ratio of 1:20 g ml⁻¹ following shaking for 1 h. Total C, N, H, and O were measured by combustion of powdered samples using automated Dumas combustion analysis (NC2500 Elemental Analyzer, Carlo Erba). At the beginning and end of each compost experiment, KCl-extractable NO₃⁻ and NH₄⁺ were measured from 8-g subsamples. The compost subsamples were mixed with 40 ml 2 N KCl, shaken for 1 h, and filtered through a qualitative filter (Whatman Grade 2V, GE Healthcare) prior to analysis with an autoflow analyzer using colorimetry (AA3 HR AutoAnalyzer, Seal Analytical). Net N mineralization was estimated by subtracting the quantity of KCl-extractable NO₃⁻ and NH₄⁺ measured in compost mixtures at the beginning of the experiment from the quantity measured after 7 wk of composting. At the beginning and end of the experiment, gravimetric moisture content of each compost mixture was calculated using the mass of subsamples weighed before and after drying at 105 °C for 48 h. Mass loss of compost was calculated by subtracting the dry mass of compost feedstocks after 7 wk of composting from the dry mass measured at the beginning of each experimental run. Total C and N content of each compost mixture were calculated by multiplying the total dry mass of each mixture by the percent C or N measured through combustion of powdered subsamples (NC2500 Elemental Analyzer, Carlo Erba). Total C and N mass loss were calculated by subtracting the C or N content of each compost mixture at the beginning of each experimental run from the C or N content measured after 7 wk of composting.

2.4 | NH₃ and CO₂ sampling

Concentrations of NH₃ and CO₂ in the headspace of each compost jar were measured once per minute for 25-to-30-min periods, repeated in 8-h cycles. Ammonia was measured with an infrared sensor (Manning AirScan IR-F9, Honeywell) connected to a microcontroller (Arduino Uno R3 Atmega328, Arduino), which performed a baseline and full-scale calibration once every 8-h cycle with N₂ and a premixed NH₃ gas standard (Cal Gas Direct Incorporated). Carbon dioxide was measured with an infrared sensor (COZIR WR 100% CO₂ Sensor GC-0016, CO2Meter.com). Sensors were flushed with N₂ gas for 30 min between measurements from each compost jar. Concentrations of NH₃ and CO₂ in ambient air were measured once during each 8-h cycle and subtracted from compost headspace measurements to calculate emissions from compost.

2.5 | NH₃-N and CO₂-C loss calculations

Loss of NH₃-N was calculated as a portion of N present in the initial poultry manure and straw mixture, excluding the

quantity of N introduced through biochar additions. Because the quantity of both unoxidized and oxidized biochar added to the compost contained less than 2% of the N present in the poultry manure and straw and because typical mineralization rates of N in woody biochar are very low due to its persistent nature (Torres-Rojas et al., 2020), biochar-N was excluded from the denominator in calculations of NH₃-N loss per unit of initial compost N. If biochar-N did contribute to NH₃-N loss, then calculated losses of compost feedstock N presented in this manuscript could be up to 2% lower than the values reported per unit of initial compost N. Loss of CO₂-C was also calculated as a proportion of C present in the poultry manure and straw, excluding the quantity of C introduced through biochar additions. Similar to biochar-N, it is likely that a relatively low proportion of biochar-C was mineralized during composting, and the same error estimate applies.

2.6 | Data analysis

All statistical analyses were performed using the lsmeans package in the statistical computing language and environment R (R Development Core Team, 2011). First, a linear model was created including a fixed effect for treatment, a block effect to account for the spatially distributed randomized block design, and a run effect to account for the two separate experimental runs. Q-Q plots and plots of the residual versus fitted values were used to determine whether data met the assumptions of normality. Means comparisons were conducted using a Tukey's HSD test, which compared the means for all treatments while averaging for the effects of blocking and experimental run.

3 | RESULTS AND DISCUSSION

3.1 | Biochar pH effect

Because the pK_a of NH₃ is 9.2, the presence of NH₃ relative to NH₄⁺ is favored under alkaline conditions. If biochar additions to compost decrease the bulk compost pH, this could reduce NH₃ production and loss. Biochar's capacity to reduce NH₃ emissions has been associated with its acidity (Sha et al., 2019; Taghizadeh-Toosi, Clough, Sherlock, & Condon, 2012b), suggesting that biochar may either reduce NH₃-N loss from compost by lowering ambient pH (thereby favoring the protonation of NH₃ to NH₄⁺) or through retention mechanisms that are favored by acidic functional groups (Wang et al., 2015). Although the pH of the unoxidized biochar used in our study was 9.2, its addition to the other compost feedstocks (poultry manure and straw) did not alter bulk compost pH at the beginning of the experiment, which remained at 6.9 for both the compost without biochar and

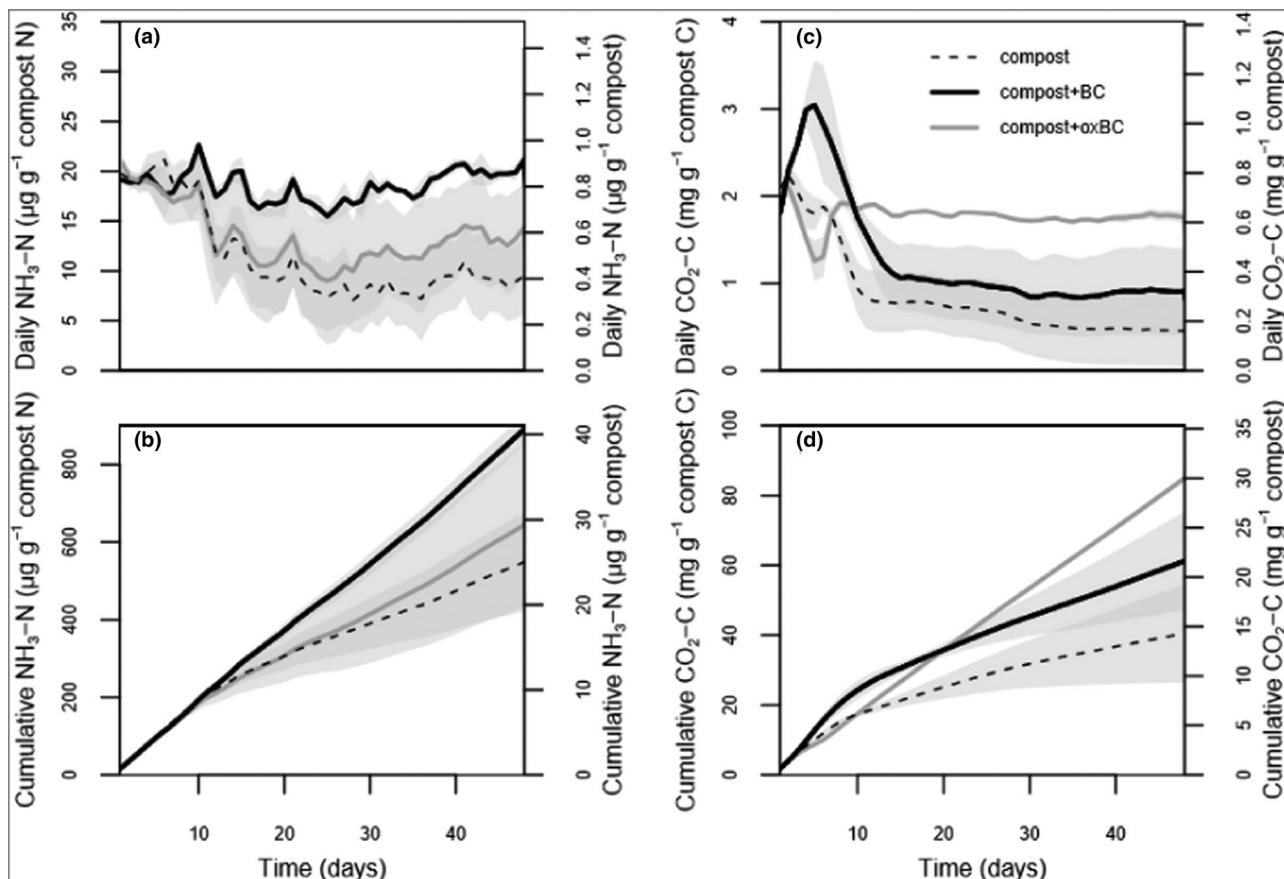


FIGURE 1 Daily and cumulative $\text{NH}_3\text{-N}$ and $\text{CO}_2\text{-C}$ emissions from compost over 7 wk. Emissions from the compost without biochar (compost), compost with unoxidized biochar (compost+BC), and compost with oxidized biochar (compost+oxBC) are represented with a dashed line, solid black line, and solid grey line, respectively. (a) Daily $\text{NH}_3\text{-N}$ emissions are shown in $\mu\text{g NH}_3\text{-N g}^{-1}\text{ N}$ in the initial manure and straw mixture (excluding biochar) on the left axis and $\mu\text{g NH}_3\text{-N g}^{-1}$ initial dry mass on the right. (b) Cumulative $\text{NH}_3\text{-N}$ emissions are shown in total $\mu\text{g NH}_3\text{-N g}^{-1}\text{ N}$ in the initial manure and straw mixture (excluding biochar) on the left axis and total $\mu\text{g NH}_3\text{-N g}^{-1}$ initial dry mass on the right. (c) Daily $\text{CO}_2\text{-C}$ emissions are shown in $\text{mg CO}_2\text{-C g}^{-1}\text{ C}$ in the initial manure and straw mixture (excluding biochar) on the left axis and $\text{mg CO}_2\text{-C g}^{-1}$ initial dry mass on the right. (d) Cumulative $\text{CO}_2\text{-C}$ emissions are shown in total $\text{mg CO}_2\text{-C g}^{-1}\text{ C}$ in the initial manure and straw mixture (excluding biochar) on the left axis and total $\text{mg CO}_2\text{-C g}^{-1}$ initial dry mass on the right. The shaded bands represent the SE for each day ($n = 4$). Standard errors were calculated by dividing the SD of daily measurements taken from each compost treatment by the square root of the sample size. The SEs associated with some treatments are too small to see in this figure (e.g., daily and cumulative $\text{CO}_2\text{-C}$ emissions from compost+oxBC)

the compost with unoxidized biochar (Table 1; Supplemental Figure S3). The addition of oxidized biochar, whose pH was 3.6 (Table 1), significantly decreased the pH of the bulk compost to 6.3 at the beginning of the experiment, but the effect was temporary ($p < .05$; Supplemental Figure S3). By the end of the 7-wk experiment, compost pH was not significantly different with or without either unoxidized or oxidized biochar (Supplemental Figure S3). It is possible that the higher starting pH of the compost without biochar and compost with unoxidized biochar promoted greater NH_3 emissions from these mixtures at the beginning of the experiment, especially in microsites directly surrounding the biochar particles, which may have a different pH than the bulk compost and biochar mixture, as has been observed in soil–biochar mixtures (Lehmann, Kuzyakov, Pan, & Ok, 2015). However, because compost pH was dynamic and pH differences were

not significant by the end of the experiment, it is unlikely that biochar's effect on bulk compost pH was solely responsible for differences in N cycling. Other authors have also concluded that biochar's effect on compost pH was not a likely driver of reduced NH_3 losses (Agyarko-Mintah et al., 2017; Steiner et al., 2010).

3.2 | NH_3 and CO_2 emissions

Mean daily NH_3 emission rates were highest within the first week, averaging $16.9\text{--}21.2 \mu\text{g NH}_3\text{-N g}^{-1}\text{ N d}^{-1}$ in initial compost feedstocks during that time, irrespective of biochar additions (Figure 1a).

Daily NH_3 emission rates from compost with unoxidized biochar remained relatively stable throughout the 7 wk of

composting, ending at $21.2 \mu\text{g NH}_3\text{-N g}^{-1} \text{N d}^{-1}$ in initial manure and straw mixture. Within 2 wk, daily NH_3 emission rates from the compost without biochar and compost with oxidized biochar had decreased substantially compared with emission rates from compost with unoxidized biochar, reaching 9.5 and $14.4 \mu\text{g NH}_3\text{-N g}^{-1} \text{N d}^{-1}$ in the initial manure and straw mixture, respectively, by the end of the 7-wk composting period. Although a general trend in emission rates was noticeable within 2 wk, statistically significant differences did not emerge until 4 wk, at which point daily NH_3 emission rates from the compost with unoxidized biochar were significantly higher than NH_3 emission rates from compost without biochar ($p = .075$ and $p = .038$ at Days 30 and 48, respectively; Figure 1a). Although the addition of either unoxidized or oxidized biochar resulted in higher daily NH_3 emissions from co-composted mixtures than from compost without biochar, only the emissions from compost with unoxidized biochar were significantly higher, exceeding a twofold difference in daily NH_3 emissions by the end of the 7-wk composting period. This suggests that variation in biochar's physiochemical properties influences how it performs in compost and mediates NH_3 emissions. Future research investigating co-composted mixtures should consider how biochar's physiochemical properties affect processes of interest and whether these properties can be optimized for the intended application.

Cumulative $\text{NH}_3\text{-N}$ loss followed a similar pattern to that of daily NH_3 emission rates (Figure 1b). After 7 wk of composting, cumulative $\text{NH}_3\text{-N}$ loss reached 549.4, 891.3, and $645.5 \mu\text{g NH}_3\text{-N g}^{-1} \text{N}$ of the initial manure and straw mixture and 25.1, 40.7, and $29.5 \mu\text{g NH}_3\text{-N g}^{-1}$ of initial dry mass for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively. The observed $\text{NH}_3\text{-N}$ losses were low compared with other reported N losses from compost, which often exceed $400 \text{ mg N g}^{-1} \text{N}$ in initial compost feedstocks (Ogunwande, Osunade, Adekalu, & Ogunjimi, 2008; Raviv, Medina, Krasnovsky, & Ziadna, 2002; Steiner et al., 2010). The lower $\text{NH}_3\text{-N}$ losses observed in this study may be due to the small size of the compost incubators, the short duration of the compost experiment, or other variations in composting conditions that influence NH_3 emissions. Because the C/N ratio of the initial poultry manure and straw mixture was relatively low (8:1), it is unlikely that N limitation inhibited NH_3 emissions compared with other studies.

Mean daily CO_2 emission rates peaked during the first week of composting, reaching 2.24, 3.04, and $2.09 \text{ mg CO}_2\text{-C g}^{-1} \text{C}$ of the initial manure and straw mixture from the compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively (Figure 1c), which is within the same range reported elsewhere (Changa, Wang, Watson, Hoitink, & Michel, 2003; Nada, 2015). Within the first 3 d, the daily CO_2 emission rate from compost with unoxidized biochar increased significantly compared with the

CO_2 emission rates from both the compost without biochar and compost with oxidized biochar ($p < .05$; Figure 1c). During the rest of the first week, the daily CO_2 emission rates from both the compost without biochar and the compost with unoxidized biochar began decreasing rapidly, reaching a slower rate of decline within 2 wk. Conversely, the daily CO_2 emission rate from compost with oxidized biochar fluctuated within the first week but soon plateaued at a rate only slightly lower than that of the initial daily CO_2 emission rate. In less than 2 wk, the daily CO_2 emission rate from compost with oxidized biochar was significantly greater than the daily CO_2 emission rate from the compost without biochar but was not different from the compost with unoxidized biochar ($p < .05$; Figure 1c). After 7 wk of composting, daily CO_2 emission rates had decreased to 0.46, 0.91, and $1.75 \text{ mg CO}_2\text{-C g}^{-1} \text{C}$ of the initial manure and straw mixture for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively. The high sustained rate of daily CO_2 emissions from compost with oxidized biochar throughout the 7 wk of composting is remarkable because CO_2 emissions from experimentally produced compost usually begin decreasing within this time (Changa et al., 2003; Nada, 2015; Steiner et al., 2010). Because CO_2 emissions are often used as a proxy for microbial activity, this suggests that the addition of oxidized biochar to compost enhanced microbial activity.

Cumulative $\text{CO}_2\text{-C}$ loss was similar for all treatments during the first 3.5 wk (Figure 1d). After 4 wk, cumulative $\text{CO}_2\text{-C}$ loss from the compost with oxidized biochar was more than 50% greater than $\text{CO}_2\text{-C}$ loss from the compost without biochar ($p < .05$; Figure 1d) but was not significantly greater than $\text{CO}_2\text{-C}$ loss from the compost with unoxidized biochar. After 7 wk of composting, cumulative $\text{CO}_2\text{-C}$ loss reached 40.5, 61.3, and $85.0 \text{ mg CO}_2\text{-C g}^{-1} \text{C}$ of the initial manure and straw mixture and 14.3, 21.6, and $30.0 \text{ mg CO}_2\text{-C g}^{-1}$ of initial dry mass from compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively. Although biochar additions to compost resulted in greater total C contents in the biochar-compost mixtures, other authors have found that mineralization of biochar-C did not contribute to greater CO_2 loss from compost (Steiner et al., 2010). In the work presented here, CO_2 loss from compost with unoxidized biochar was similar to CO_2 loss from compost without biochar, suggesting that unoxidized biochar-C was not mineralized in substantial quantities and did not influence microbial respiration through other means, including priming (DeCiucies, Whitman, Woolf, Enders, & Lehmann, 2018), to an extent that would alter the conclusions drawn here. In comparison, CO_2 loss from compost with oxidized biochar was significantly higher than with unoxidized biochar. This could be due to microbial mineralization of C in oxidized biochar or other effects of biochar on the compost environment that facilitate microbial activity, including enhanced

extracellular electron transfer rates or interference with microbial quorum sensing (Masiello et al., 2013; Sun et al., 2016; Wang, Lehmann, Hanley, Hestrin, & Enders, 2016). Further research is necessary to determine how biochar oxidation influences interactions between biochar and microorganisms in co-composted mixtures.

3.3 | Mechanisms responsible for variation in NH_3 emissions

Compost CO_2 emissions are correlated with microbial decomposition processes and can therefore be used as a proxy for microbial activity in compost (Benito, Masaguer, Moliner, Cogger, & Bary, 2005; Tiquia, 2005). Because the majority of compost N is present in organic form, it must be mineralized before it is susceptible to volatilization as NH_3 (Nahm, 2003). We expected that compost CO_2 emissions (a result of microbial activity and organic matter decomposition) would be associated with proportionally higher NH_3 emissions due to the link between microbially driven C and N mineralization. However, when differences in microbial activity were accounted for by calculating cumulative $\text{NH}_3\text{-N}$ loss from compost relative to cumulative $\text{CO}_2\text{-C}$ loss, relative N/C loss from compost with oxidized biochar after 7 wk ($0.00754 \text{ mg N mg}^{-1} \text{ C}$) was 55.3 and 49.1% lower than N/C loss from compost with unoxidized biochar ($0.01687 \text{ mg N mg}^{-1} \text{ C}$) and compost without biochar ($0.01482 \text{ mg N mg}^{-1} \text{ C}$), respectively (Figure 2b). Thus, in compost with oxidized biochar, NH_3 loss did not increase proportionally to an increase in microbial activity. The lack of correlation between daily NH_3 and CO_2 emissions from compost with oxidized biochar further suggests that the processes leading to the emission of these gases were decoupled (adjusted $R^2 = .029$; $p < .01$; $F_{1,194} = 6.84$; $\text{RSE}_{194} = 0.0000087$; $n = 196$) (Supplemental Figure S4). Even if organic C and N mineralization remained coupled, enhanced microbial activity might be accompanied by greater NH_3 oxidation into nitrate or N immobilization into microbial biomass, both of which could account for lower NH_3 emissions despite high CO_2 loss from compost with oxidized biochar. We did not measure microbial biomass or community composition in our compost mixtures. However, previous work shows that biochar additions to compost influence microbial community composition and enzymatic activity, with implications for decomposition processes and N emissions (Agyarko-Mintah et al., 2017; Awasthi et al., 2017; Jindo et al., 2012; Wang, Xiong, & Kuzyakov, 2016; Wei, Shutao, Jin, & Tong, 2014; Zhang, Marchant-Forde, Zhang, & Wang, 2020). It is also possible that oxidized biochar inhibited emission of mineralized N through abiotic N retention. Although oxidation can enhance biochar's NH_3 and NH_4^+ retention capacity in simplified experimental systems (Hestrin et al., 2019; Wang et al., 2015, 2016), the

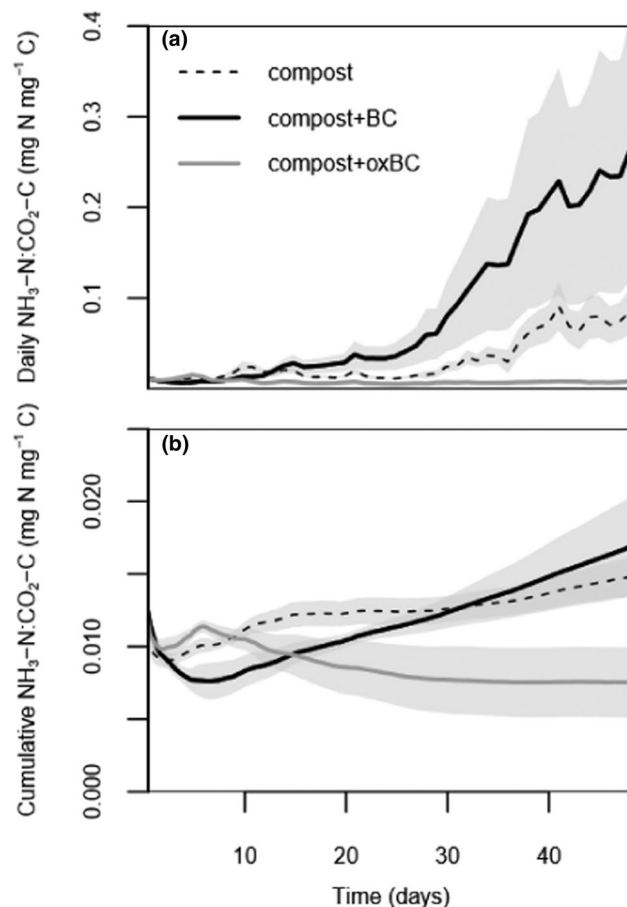


FIGURE 2 Daily and cumulative $\text{NH}_3\text{-N}/\text{CO}_2\text{-C}$ emissions from compost over 7 wk. Emissions of $\text{NH}_3\text{-N}/\text{CO}_2\text{-C}$ from the compost without biochar (compost), compost with unoxidized biochar (compost+BC), and compost with oxidized biochar (compost+oxBC) are represented with a dashed line, solid black line, and solid grey line, respectively. Daily (a) and cumulative (b) $\text{NH}_3\text{-N}/\text{CO}_2\text{-C}$ emissions were calculated from $\text{NH}_3\text{-N}$ and $\text{CO}_2\text{-C}$ emission values normalized by initial compost N and C contents (excluding biochar N and C content). Shaded bands represent the SE for each day ($n = 4$). Standard errors were calculated by dividing the SD of daily measurements taken from each compost treatment by the square root of the sample size. The SEs associated with daily $\text{NH}_3\text{-N}/\text{CO}_2\text{-C}$ emissions from compost+oxBC are too small to see in this figure

effect of oxidation on biochar's performance in compost has only been hypothesized (Agyarko-Mintah et al., 2017).

Taken together, these data show that biochar's performance in compost is mediated by its specific physiochemical characteristics. We found that unoxidized biochar increased both CO_2 and NH_3 emissions from co-composted mixtures, whereas oxidized biochar increased CO_2 emissions substantially but NH_3 emissions only marginally compared with emissions from compost without biochar. This illustrates that oxidation can improve biochar's capacity to reduce $\text{NH}_3\text{-N}$ loss from compost, even when microbial respiration and decomposition processes are sustained or increased. These

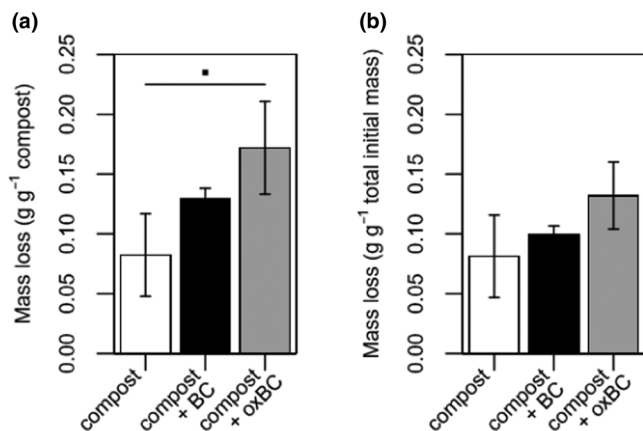


FIGURE 3 Mass loss from compost after 7 wk. Mass loss is represented as g g^{-1} dry mass of the initial poultry manure and straw mixture (a) and as g g^{-1} dry mass of the initial complete compost mixture including biochar (b) for compost without biochar (compost), compost with unoxidized biochar (compost+BC), and compost with oxidized biochar (compost+oxBC). Error bars represent the SE ($n = 4$). The dot denotes a significant difference between treatments based on a Tukey's HSD test ($p < .1$)

results also indicate that adding oxidized biochar to compost may accelerate the rate of composting. Previous investigation of co-composted mixtures has found that biochar can increase compost temperature, which is associated with microbial activity (Steiner et al., 2010). Because the compost temperature was controlled in this experiment, we could not use temperature as an indicator of microbial activity or composting rate. However, higher CO_2 emissions from compost with oxidized biochar suggest that the rate of composting was accelerated compared with that of the compost with unoxidized biochar or compost without biochar.

3.4 | Mass loss, C and N balance, and N mineralization

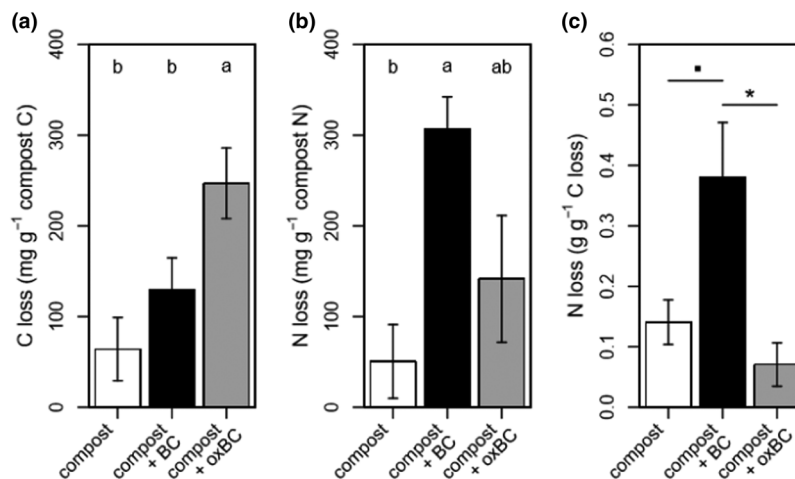
After 7 wk of composting, total mass loss reached 0.08, 0.13, and 0.17 g g^{-1} dry mass of the initial manure and straw mixture for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively (Figure 3a).

Mass loss from compost with oxidized biochar was significantly higher than mass loss from compost without biochar, which corresponds with trends in daily and cumulative NH_3 and CO_2 emissions ($p < .1$; Figure 3a). When mass loss was calculated as a portion of total initial dry mass including biochar in the biochar–compost mixtures, there were no significant differences in mass loss (Figure 3b). This suggests that the majority of mass loss from the compost–biochar mixtures was from the poultry manure and straw rather than from the unoxidized or oxidized biochar. Previous studies

have documented varying effects of biochar on compost mass loss, ranging from a decrease to an increase in mass loss compared with compost without biochar (Agyarko-Mintah et al., 2017; Dias, Silva, Higashikawa, Roig, & Sánchez-Monedero, 2010; Liu et al., 2017; Steiner et al., 2010). Biochar may facilitate decomposition by enhancing compost aeration, which provides an oxygenated environment necessary for aerobic microorganisms and enzymes that drive many key decomposition reactions. Agyarko-Mintah et al. (2017) found that β -glucosidase and leucine–aminopeptidase activity were higher in compost amended with greenwaste biochar than in compost without biochar. Similarly, Awasthi et al. (2017) found that dehydrogenase enzyme activity was higher in compost amended with wheat straw biochar and that biochar dose rates were generally positively associated with enzyme activity. Compost temperature is also used as a proxy for microbial activity and decomposition rate. Several studies have found that incorporation of biochar into compost is associated with higher maximum temperatures or faster temperature rise in co-composted mixtures (Chen et al., 2010, 2017; Steiner et al., 2010). Because many laboratory compost experiments are conducted on shorter timescales and in smaller batches than agricultural- or industrial-scale compost production, it is important to consider how outcomes might vary in more realistic field conditions.

Total C mass loss measured by dry combustion reached 64.2, 129.0, and 247.0 mg g^{-1} C of the initial compost feedstocks for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively, after 7 wk of composting (Figure 4a). Total C mass loss from compost with oxidized biochar was significantly greater than C mass loss from compost without biochar and compost with unoxidized biochar, also corresponding with trends measured by mass loss and CO_2 emissions ($p < .05$; Figures 1d, 3, and 4a). Total N mass loss measured by N stock differences before and after composting reached 50.5, 307.3, and $141.6 \text{ mg N g}^{-1}$ N of the initial compost feedstocks for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively (Figure 4b). Total N mass loss from compost with unoxidized biochar was significantly greater than N mass loss from compost without biochar but not from compost with oxidized biochar ($p < .05$; Figure 4b). When N mass loss was calculated as a proportion of C mass loss to account for differences in microbial activity, relative N/C mass loss from compost with oxidized biochar was 81.4% lower than N/C mass loss from compost with unoxidized biochar and comparable to N/C mass loss from the compost without biochar (Figure 4c). This corresponds with the trends observed in cumulative NH_3 –N loss normalized by cumulative CO_2 –C loss (Figure 2b), which also showed that relative N/C loss from compost with oxidized biochar was lower than relative N/C loss

FIGURE 4 Total C and N mass loss from compost feedstocks after 7 wk. After 7 wk of composting, compost C (a) and N (b) content were measured in compost without biochar (compost), compost with unoxidized biochar (compost+BC), and compost with oxidized biochar (compost+oxBC). (c) Total N mass loss from compost and compost–biochar mixtures represented as a proportion of C mass loss after 7 wk. Error bars represent the SE ($n = 4$). Letters in (a) and (b) denote the results of a Tukey's HSD test ($p < .05$). Statistically significant results of a Tukey's HSD test in (c) are indicated with the following symbols: ■ $p < .1$ and * $p < .05$



from compost without biochar and compost with unoxidized biochar.

Previous investigations of co-composted mixtures show that biochar can improve compost N retention through reduced NH_3 emissions and other effects on decomposition processes (Agyarko-Mintah et al., 2017; Awasthi et al., 2017; Chen et al., 2010, 2017; Malinska et al., 2014; Steiner et al., 2010). Because each study uses different biochar types, compost feedstocks, production conditions, and analysis methods, it is difficult to assess specific mechanisms driving changes in N cycling. Both Steiner et al. (2010) and Chen et al. (2010) found that higher biochar dose rates were associated with higher N retention. Agyarko-Mintah et al. (2017) found that incorporation of greenwaste biochar reduced total compost N loss by 51% compared with compost without biochar, whereas poultry litter biochar resulted in only a 33% decrease in total compost N loss. Similarly, Chen et al. (2017) found that biochar made from corn or woody biomass reduced NH_3 emissions more than biochar made from poultry litter, coir, or bamboo. Both groups of authors attributed this variation to differences in biochar physiochemical characteristics, such as surface area, pore volume, cation exchange capacity, acidic functional groups, and N adsorption capacity. However, because many of these characteristics vary simultaneously in biochar made from different feedstocks, it was not possible to evaluate which characteristic contributed most to biochar's effect on compost N cycling.

We found that unoxidized biochar made from woody biomass significantly increased N loss from compost, whereas oxidized biochar did not. Other authors have posited that variation in biochar N retention mechanisms could drive differences observed in N loss from co-composted mixtures (Agyarko-Mintah et al., 2017; Chen et al., 2017; Malinska et al., 2014). Our previous work shows that surface oxidation substantially increases biochar's N retention capacity, supporting the hypothesis that biochar may reduce compost N emissions by physiochemically immobilizing N and inhibit-

ing its volatilization as NH_3 gas (Hestrin et al., 2019; Wang et al., 2015, 2016). Net N mineralized after 7 wk of composting reached 3.58, 14.61, and 5.20 mg N g^{-1} compost for compost without biochar, compost with unoxidized biochar, and compost with oxidized biochar, respectively, and was significantly higher in compost with unoxidized biochar than in compost without biochar and compost with oxidized biochar ($p < .05$; Figure 5). Combined with our previous findings, greater mineral N availability in co-composted mixtures containing unoxidized biochar further supports the hypothesis that unoxidized biochar is less able to inhibit NH_3 emissions from compost due to its lower N retention capacity. It is also possible that greater microbial activity in compost with oxidized biochar resulted in greater N assimilation into microbial biomass, thereby reducing N susceptibility to volatilization. Future work should measure gross N mineralization and microbial biomass to further evaluate divergent mechanisms of N retention.

3.5 | N capture by biochar

To further evaluate whether patterns in N loss were driven specifically by biochar N retention, we measured the N content of biochar particles before and after co-composting. Unoxidized and oxidized biochar removed from the bulk compost at the end of the experiment contained 6.06 and 16.04 mg N g^{-1} biochar more than the original 2.44 and 2.09 mg N g^{-1} contained in the unoxidized and oxidized biochar, respectively (Figure 6).

Because this biochar was sampled from the bulk compost mixture, its increased N content could be due to retention of a combination of mineral N (e.g., NH_3 or NH_4^+), manure, microbial biomass, N-rich metabolites, and other compost residues adhered to biochar's surfaces. Nitrogen enrichment was significantly greater in oxidized biochar particles compared with unoxidized biochar particles, further supporting

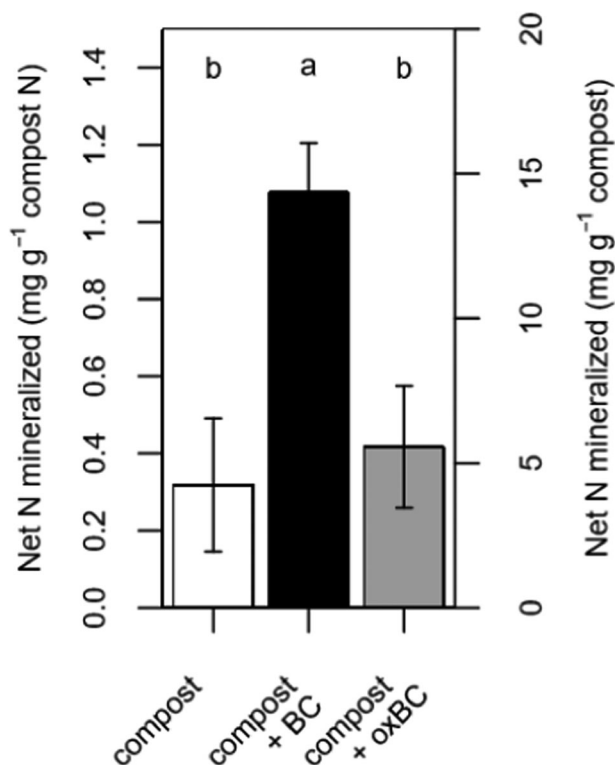


FIGURE 5 Net N mineralized during 7 wk. Net N mineralized after 7 wk of composting shown in mg g⁻¹ N in compost and compost–biochar mixtures on the left axis and mg g⁻¹ dry mass compost and biochar–compost mixtures on the right for compost without biochar (compost), compost with unoxidized biochar (compost+BC), and compost with oxidized biochar (compost+oxBC). Error bars represent the SE ($n = 4$). Letters denote the results of a Tukey's HSD test ($p < .01$)

the hypothesis that oxidized biochar is better able to retain N in compost ($p < .01$; Figure 6). Although the mechanisms responsible for N retention were not unequivocally identified using the analyses presented here, previous work suggests that NH₃ gas sorption, protonation into NH₄⁺ and subsequent electrostatic interactions with biochar's surface functional groups, and nucleophilic reactions forming new functional groups could play a role in biochar's N retention capacity in compost (Hestrin et al., 2019; Wang et al., 2015, 2016). Future work should explore a wider variety of N retention mechanisms in compost through sequential extractions and chemical characterization.

3.6 | Trade-off between C and N emission reductions

The trade-off between CO₂ and NH₃ emissions has implications for compost efficiency, nutritive value, and environmental impacts. The primary aim of this study was to explore the mechanisms through which biochar could reduce NH₃ loss and improve N retention. Agricultural N management has

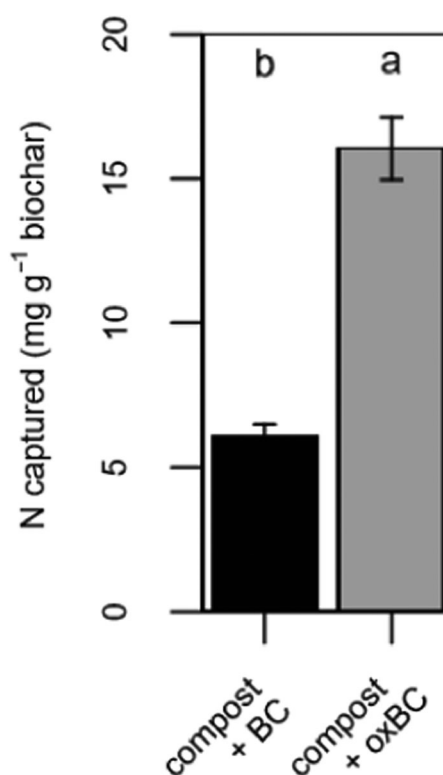


FIGURE 6 Compost N captured by bulk biochar after 7 wk. Biochar was removed from bulk compost mixtures containing compost feedstocks with unoxidized biochar (compost+BC) and compost feedstocks with oxidized biochar (compost+oxBC) following 7 wk of composting. The biochar particles may contain adsorbed gases, mineral N, manure, microbes, metabolites, and other compost residues adhered to the surface. Error bars represent the SE ($n = 4$). Letters denote the results of a Tukey's HSD test ($p < .01$)

been a persistent challenge: insufficient N limits crop productivity, and excessive N applications can result in eutrophication and greenhouse gas emissions (Galloway et al., 2004, 2008). Management of N-rich materials such as manure is also challenging due to the potential for substantial NH₃ emissions, which simultaneously represent lost nutritive potential and release of a noxious and corrosive gas (Beusen, Bouwman, Heuberger, Van Drecht, & Van Der Hoek, 2008). Although compost CO₂ emissions are often viewed favorably as a sign of microbial activity and progress toward compost maturity, they also contribute to atmospheric CO₂ concentrations. However, alternative fates of compost feedstocks, such as storage in a landfill, may favor higher emissions of CH₄, which is a greenhouse gas far more potent than CO₂ (Lashof & Ahuja, 1990; Luo & Nair, 2009). Additionally, there are many other aspects of compost production that must be evaluated to assess its ultimate environmental impact, such as competing uses of compost feedstocks, downstream applications, and potential agronomic benefits. We observed that, within a 7-wk composting period, oxidized biochar greatly stimulated

compost CO₂ emissions but had little effect on NH₃ emissions, whereas unoxidized biochar greatly stimulated NH₃ emissions and only temporarily stimulated CO₂ emissions (Figure 1). This suggests that there was a trade-off between emission of these two gases and that it may be possible to optimize biochar's physiochemical characteristics to favor one or the other. Whether the suppression of CO₂ or NH₃ emissions is preferable will depend on the agronomic constraints and purpose of a particular composting system.

4 | CONCLUSION

Incorporation of unoxidized biochar into compost resulted in significantly higher N loss compared with compost without biochar. Adding oxidized biochar to compost resulted in significantly greater respiration and C loss but did not significantly increase N loss compared with compost without biochar. When greater microbial activity in compost with oxidized biochar is accounted for, these results suggest that adding oxidized biochar to compost can simultaneously speed the rate of composting and improve N retention efficiency. Nitrogen retention by oxidized biochar particles was directly responsible for a portion of the reduced NH₃ emissions. Oxidized biochar may have also reduced compost N loss through indirect mechanisms, such as localized reduction in compost pH around biochar particles, which might reduce the relative proportion of N present as NH₃ versus NH₄⁺. These data show that biochar can improve compost N use efficiency but that each biochar's specific physiochemical characteristics can determine its performance during composting and the degree to which it may improve N management in crop residue and animal manure composting. Future research should explore the mechanisms responsible for biochar's N retention capacity and ability to enhance microbial activity in compost, including but not limited to effects on microbial community composition, electron shuttling, or microbial signaling. In addition, agronomic effects of oxidized biochar should be considered when co-composted mixtures are added to soil.

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DATA AVAILABILITY STATEMENT

Data that support the findings of this study are available in Cornell University's digital repository eCommons with the identifier <https://doi.org/10.7298/p9wj-nk83>

AUTHOR CONTRIBUTIONS

R.H. and J.L. conceived the experiments; A.E. and R.H. constructed the compost incubators and gas monitoring system; R.H. conducted the experiments and analyzed the data; R.H. wrote the paper; all authors contributed to the final manuscript.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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