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ORIGINAL RESEARCH ARTICLE

Agrosystems

Coal char affects soil pH to reduce ammonia volatilization from sandy loam soil

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Abstract

Ammonia (NH₃) volatilization loss adversely affects N availability in soil-plant systems, reduces crop yield, and negatively impacts environment. Char (coal combustion residue), which contains up to 293 g kg⁻¹ total C by weight, has been shown to reduce NH₃ volatilization due to its considerably high surface area and cation exchange capacity. The NH₃ loss can be greatly affected by a shift in soil pH or urea hydrolysis. A 21-d laboratory study was conducted to evaluate the effects of char on soil pH, N transformations, and subsequent NH₃ volatilization in sandy loam soil. Two char rates (0 and 13.4 Mg C ha⁻¹) and two urea rates (0 and 200 kg N ha⁻¹) were mixed in soil in four 2-way combinations with four replications of each. There were 11 sets of all treatment combinations and each set was analyzed for soil moisture, pH, NH₃ volatilization, and residual N (urea, NH₄, and NO₃) every other day for 3 wk. Char application reduced cumulative NH₃ loss in the fertilized treatment. Reduction in NH₃ loss due to char addition was evidenced by greater residual NH₄-N on certain days in treatments with char compared to treatments without char. Char did not affect urea hydrolysis process but it lowered soil pH in the fertilized treatments in the first week. This study supported our hypothesis that char altered soil pH and thereby reduced NH₃ volatilization loss from the fertilized soil.

1 | INTRODUCTION

A global meta-analysis of 824 observations revealed that up to 64% of surface-applied N fertilizer could volatilize as ammonia (NH₃) and be lost from the soils to the atmosphere (Pan, Lam, Mosier, Luo, & Chen, 2016). The volatilized NH₃ from fertilized agricultural land has adverse ecological impacts on environmental quality. In addition, NH₃ loss reduces N available for crop production (Shang et al., 2014; Zaman, Sagar, Blennerhassett, & Singh, 2009) and negatively influences crop N use efficiency. Upon depositing to ground, NH₃

can cause soil acidification, can be a secondary source of N₂O emissions, and promote eutrophication of surface water bodies (Sutton, Erismann, Dentener, & Möller, 2008).

Among all N fertilization type, urea accounted for nearly 56% of global fertilizer N consumption, as it contains comparatively high N content, safe to handle, and readily available in granular or liquid form (IFA, 2017). Ammonia volatilization accrues as the urea is applied to the soil surface through urea hydrolysis under favorable conditions (high soil pH and adequate moisture) and this process may continue up to 2 wk (Sommer, Schjoerring, & Denmead, 2004). Several modifications are applied to urea fertilizers such as adding urease inhibitor [e.g., N-(n-butyl) thiophosphoric triamide (NBPT)]

Abbreviations: CEC, cation exchange capacity.

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to slow the urea hydrolysis (Nascimento, Vitti, Faria, Luz, & Mendes, 2013; Silva, Sequeira, Sermarini, & Otto, 2017; Trenkel, 2010). High cation exchange capacity (CEC) of zeolite (aluminosilicate mineral) when mixed with urea is also reported to reduce NH_3 loss through volatilization (Palanivell, Ahmed, Susilawati, & Ab Majid, 2015). Biochar can retain NH_4 during soil N transformation and possibly reduce NH_3 emissions due to biochar high surface area (DeLuca, Gundale, MacKenzie, & Jones, 2015; Steiner, Das, Melear, & Lakly, 2010). Panday et al. (2020) reported that the addition of coal char up to $13.4 \text{ Mg C ha}^{-1}$ in a loam soil and $10.1 \text{ Mg C ha}^{-1}$ in a sandy loam soils decreased NH_3 volatilization loss by 24 and 26–37%, respectively. They also reported that the reduction in NH_3 volatilization was related to increased ammonium ($\text{NH}_4\text{-N}$) sorption and retention during soil N transformation due to char high surface area ($0.08 \text{ m}^2 \text{ kg}^{-1}$) and high CEC ($46.9 \text{ cmol}_c \text{ kg}^{-1}$). Previous research documented that the soil with low H^+ buffering capacities has a potential for NH_3 volatilization as the soil pH increases when added dry urea dissolves and hydrolyzes (Ferguson, Kissel, Koelliker, & Basel, 1984). In addition, NH_3 volatilization is enhanced in soil with pH above 7.5 (Fan & Machenzie, 1993; Kissel, Cabrera, & Paramasivam, 2008). The addition of coal char that has pH lower than a calcareous soil could potentially reduce soil pH and NH_3 volatilization during urea hydrolysis.

Char is one of the C-rich organic amendments that make it a suitable material to enhance or recover soil C and it contains nutrients that are essential for plant growth. Adding organic C-rich materials can have a positive effect on increasing soil organic C, improving soil properties, and enhancing crop yields (Blanco-Canqui et al., 2020). Previous research documented a reduction in NH_3 volatilization due to the sorption properties of char (Panday et al., 2020). The effect of char on urea hydrolysis and soil pH would provide an understanding on how char is affecting soil processes that lead to reduced NH_3 volatilization. Hence, the objective of this study was to determine the effects of char addition on soil pH, urea-N transformation, and NH_3 emissions over a 21-d laboratory incubation under adequate environmental conditions. It is hypothesized that char would affect soil pH and processes that control urea hydrolysis and NH_3 volatilization and conserve soil N from loss to the atmosphere.

2 | MATERIALS AND METHODS

A 21-d laboratory study was conducted on the soil that was collected from 0-to-20-m depth from a farm field at the Panhandle Research and Extension Center, Scottsbluff, NE, at the University of Nebraska-Lincoln. The soil was Tripp fine sandy loam soil (coarse-silty, mixed, superactive, mesic Aridic Haplustolls) and had a 7.9 pH, 19 g kg^{-1} organic matter, 15.0 mg kg^{-1} initial extractable inorganic N ($\text{NH}_4\text{-N}$ and

Core Ideas

- Coal char application did not affect urea hydrolysis.
- Coal char application reduced soil pH in fertilized treatments in the first week.
- Coal char is a potential soil amendment particularly in high pH and low C soil.

$\text{NO}_3\text{-N}$) and $12.8 \text{ cmol}_c \text{ kg}^{-1}$ CEC. Soil was air-dried for a week and sieved through a 2-mm mesh size before the initiation of study.

A 10 g air-dried soil was added into multiple 250-ml glass beakers and was brought to 12% gravimetric water content (GWC) by adding deionized water and mixing thoroughly. The amount of water sprayed corresponded to 35% water-filled pore space for this soil. Char was mixed properly with soil, then urea-N was applied to the soil surface and left there in each beaker. Urea granules were ground to match the targeted N rate for each beaker content. Char properties used in this study was previously reported in Panday et al. (2020).

The study was arranged in a randomized complete block design with four replications (replication was considered as a block factor). The char was added at two rates that corresponded to 0 and $13.4 \text{ Mg C ha}^{-1}$ (equivalent to 0 and $44.6 \text{ Mg C ha}^{-1}$). The urea was also added at two rates that corresponded to 0 and 200 kg N ha^{-1} . The actual amounts of char and urea added were 0.2 g and 2.0 mg, respectively. The two rates each of char and urea generated four treatment combinations as follows: control with no char or urea (CON0), urea fertilizer at 200 kg N ha^{-1} with no char (CON1), char at $13.4 \text{ Mg C ha}^{-1}$ with no fertilizer (C1N0) and char at $13.4 \text{ Mg C ha}^{-1}$ with urea at 200 kg N ha^{-1} (C1N1).

The beakers containing soil and different treatments were closed with lids and the 1st day of the experiment was considered as Day 0. The beakers were placed in a constant room temperature (25°C) which was maintained during the entire 21-d experiment. Every other day, beakers lids were opened for 15 min for air circulation and to avoid CO_2 gas accumulation inside the beakers. There were 11 sets of all treatment combinations and one set each was analyzed for moisture content, pH, NH_3 volatilization, and residual mineral N (urea, NH_4 , and NO_3) at each sampling event which was on every other day (Day 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20).

Ammonia volatilization loss was measured using the acid trap method. A sponge of 2 cm diam. and 1.3 cm thickness was used as an acid trap with 2 ml of H_3PO_4 -glycerol solution (40 ml glycerol, 50 ml H_3PO_4 acid, and 910 ml deionized water) and placed inside the mouth of beaker. The first set of acid traps was installed on Day 0 and removed from beakers on Day 2. Such collected traps were rinsed with a 2 M KCl

solution and squeezed multiple times to extract the solution which was frozen until analyzed for NH_4 .

After removing the acid traps, deionized water was added to soil in beakers to adjust for any water losses and maintain the 12% gravimetric water content (GWC) during the experiment. At each sampling date, soil pH was determined by a glass electrode (soil/water ratio, 1:1). The urea-N, NH_4 -N, and NO_3 -N were evaluated by extraction using 2 M KCl-potassium chloride-phenyl mercuric acetate (PMA) solution prepared by mixing 149.1 g KCl in 900 ml deionized water and 5 mg PMA in 100 ml deionized water. The addition of PMA was to inhibit urease activity during extraction of soil with 2 M KCl (Douglas & Bremner, 1970). Each beaker containing soil suspension (10 g soil) was placed in a shaker for 15 min at a speed of 250 rpm. The resulting suspension was filtered through Whatman no. 42 filter paper and analyzed for urea-N, NH_4 -N, and NO_3 -N. The urea-N was determined by using a colorimetric diacetyl monoxime method (Chen, Ma, Huang, Dai, & Li, 2015). Ammonia (NH_3) trapped in acid trap solution, and NH_4 -N and NO_3 -N present in soil solutions were determined by using a flow analyzer (SEAL Analytical).

Cumulative NH_3 loss for each treatment was calculated by adding up NH_3 loss across all sampling dates. To estimate the cumulative NH_3 volatilization loss per applied N for each treatment, cumulative NH_3 volatilization loss in fertilized soil with char or no char was subtracted from control treatment (C0N0) and divided by the amount of urea-N applied. Total inorganic N was estimated by summing NH_3 loss, residual urea-N, residual NO_3 -N, and residual NH_4 -N on each sampling date.

The effect of treatments on cumulative NH_3 loss was tested using the PROC MIXED procedure in SAS software v. 9.4 (SAS Institute, 2003) with treatment as fixed effect and replication as random effect. The ANOVA was used to evaluate the influence of the sampling dates on the measured parameters (pH, NH_3 volatilization, residual N [urea, NH_4 and NO_3] and total N). Statistical difference of $P < .05$ was considered significant unless otherwise indicated.

3 | RESULTS

3.1 | Ammonia volatilization

About 70% of total NH_3 volatilization in the fertilized treatment that received 200 kg N ha^{-1} occurred within the 1st week of the experiment (Figure 1). The highest peak of daily NH_3 volatilization loss was observed on Day 4 for the fertilized treatments following treatment application. There was a significant effect of treatment on NH_3 volatilization loss up to Day 8 (Figure 1). The daily NH_3 volatilization loss in the treatment C0N1 was greater than C1N1 on Day 6. Both fertilized treatments (with and without char) had greater daily NH_3 loss

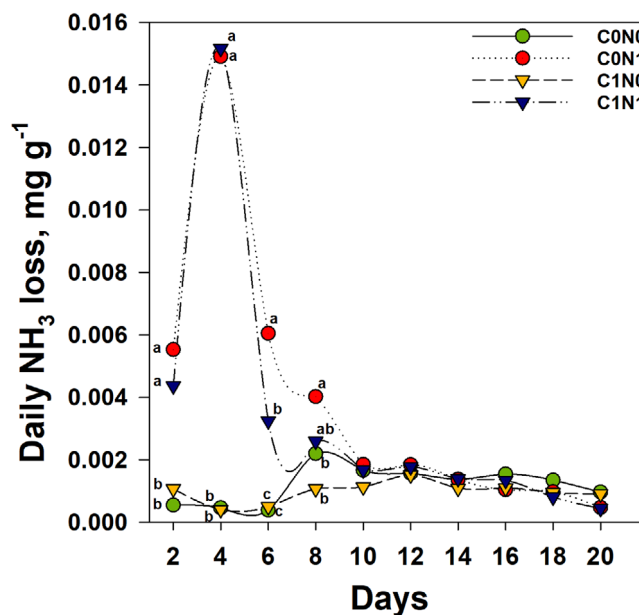


FIGURE 1 Daily NH_3 volatilization losses under different treatments. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha^{-1} with no char (C0N1), char at $13.4 \text{ Mg C ha}^{-1}$ with no fertilizer (C1N0) and char at $13.4 \text{ Mg C ha}^{-1}$ with urea at 200 kg N ha^{-1} (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

TABLE 1 Mean cumulative NH_3 volatilized as affected by treatment

Treatment ^a	Cumulative NH_3 volatilized g N kg^{-1}
C0N0	0.012 c ^b
C0N1	0.039 a
C1N0	0.010 c
C1N1	0.033 b

^aTreatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha^{-1} with no char (C0N1), char at $13.4 \text{ Mg C ha}^{-1}$ with no fertilizer (C1N0) and char at $13.4 \text{ Mg C ha}^{-1}$ with urea at 200 kg N ha^{-1} (C1N1).

^bMeans in a column followed by same lowercase letter are not significantly different.

than the unfertilized on Days 2, 4, and 6. The C0N1 treatment had the highest total NH_3 volatilization than any other treatment. Cumulative NH_3 volatilization loss across treatments ranged from 0.006 to $0.042 \text{ g kg}^{-1} \text{ N}$ in this 21-d laboratory study. There was a significant treatment effect on cumulative NH_3 volatilization loss (Table 1). Both fertilized treatments (C1N1 and C0N1) had a greater cumulative NH_3 loss than the unfertilized. Between the fertilized treatments, char application reduced cumulative NH_3 loss by 15.3% (C1N1 < C0N1). However, NH_3 volatilization did not differ by char addition in the unfertilized treatments (C0N0 = C1N0).

3.2 | Soil pH

There was a significant effect of treatment on soil pH throughout the study period (Figure 2). At the beginning of experiment, soil pH increased to around 8.0 in the treatment CON1 (Figure 2). The same treatment continued to have the highest soil pH among all treatments until Day 6 and then the pH dropped by 0.5 units. Soil pH was consistently lower in the treatment C1N1 than CON1 until Day 10, except on Day 8. During and after Day 10, soil pH with the CON1 was ≤ 7.1 and with the C1N1 was between 7.1 and 7.3. In the unfertilized treatments, soil pH was around 7.8 in the beginning of the study, but on Day 8 and forward, the pH dropped to 7.7 for CON0 and around 7.5 for the treatment C1N0.

3.3 | Soil residual nitrogen (urea, ammonium, and nitrate)

Soil residual urea-N was not influenced by char addition to the fertilized treatments (Figure 3). Soil residual $\text{NH}_4\text{-N}$ were greater with char added fertilized treatments than no char (C1N1 > C0N1) on Days 4 and 6 (Figure 4). Soil residual urea-N and $\text{NH}_4\text{-N}$ in the fertilized treatments were greater than in the unfertilized treatments up to Day 6 and Day 10, respectively. The addition of char did not influence soil residual urea-N or $\text{NH}_4\text{-N}$ in the unfertilized treatments. There was a significant treatment effect on soil residual $\text{NO}_3\text{-N}$ throughout the study period (Figure 5). Both fertilized treatments had higher soil residual $\text{NO}_3\text{-N}$ compared to the unfertilized treatments from Day 6 to the end of the study period. Soil residual $\text{NO}_3\text{-N}$ in the C1N1 was higher than C0N1 on Days 8, 10, 14, 16, and 18.

3.4 | Soil total inorganic nitrogen

Soil used in the study had 0.015 g kg^{-1} residual inorganic N ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) and 0.1 g kg^{-1} urea-N was added to fertilized treatments. Total inorganic N ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) in glass beaker ranged from 0.013 to 0.022 g kg^{-1} N in the unfertilized treatments and 0.703 to 0.122 g kg^{-1} N in the fertilized treatments (Figure 6). Total inorganic N was always greater in the fertilized than in the unfertilized treatments (Figure 2–6). Both fertilized treatments had 0.075 g kg^{-1} N on Day 0 compared to other days which had a total N of $> 0.10 \text{ g kg}^{-1}$.

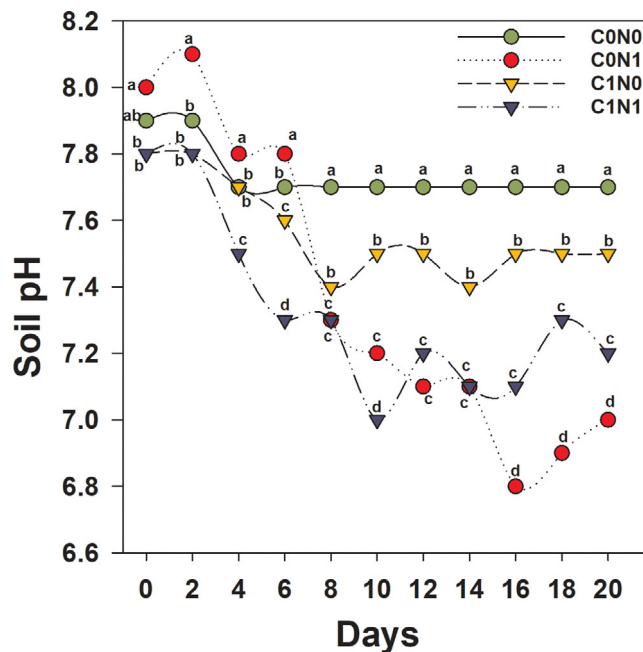


FIGURE 2 Daily soil pH under different treatments. Treatments included control with no char or urea (CON0), urea fertilizer at 200 kg N ha^{-1} with no char (CON1), char at $13.4 \text{ Mg C ha}^{-1}$ with no fertilizer (C1N0) and char at $13.4 \text{ Mg C ha}^{-1}$ with urea at 200 kg N ha^{-1} (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

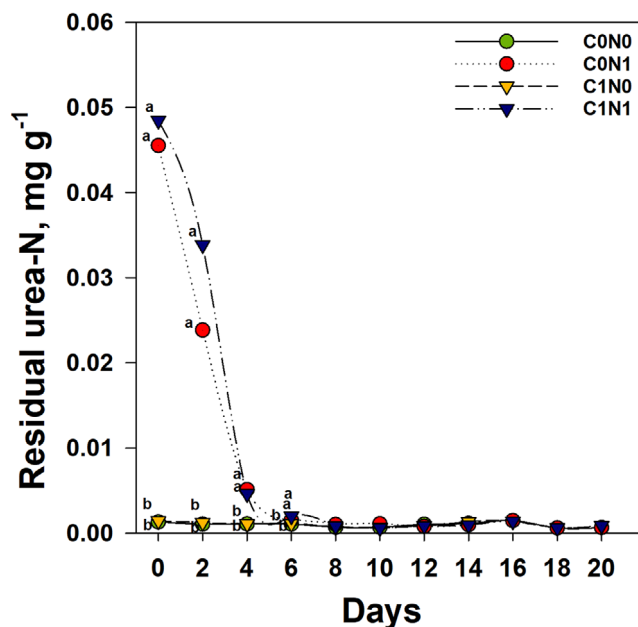


FIGURE 3 Daily soil residual urea-N under different treatment. Treatments included control with no char or urea (CON0), urea fertilizer at 200 kg N ha^{-1} with no char (CON1), char at $13.4 \text{ Mg C ha}^{-1}$ with no fertilizer (C1N0) and char at $13.4 \text{ Mg C ha}^{-1}$ with urea at 200 kg N ha^{-1} (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

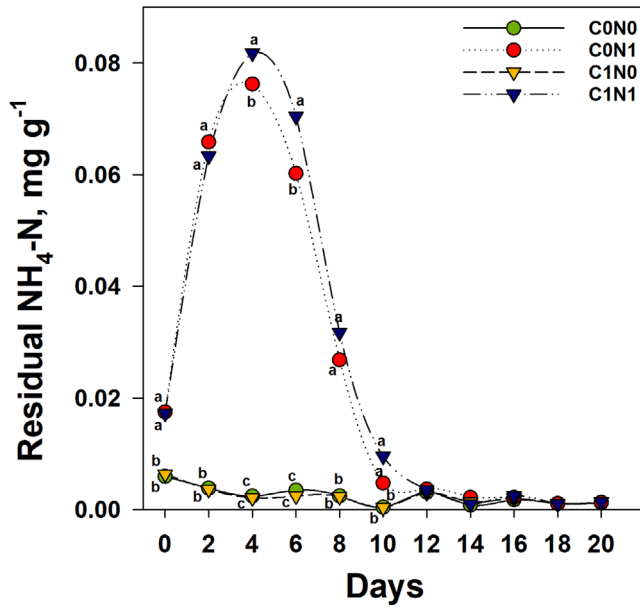


FIGURE 4 Daily soil residual NH₄-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha⁻¹ with no char (C0N1), char at 13.4 Mg C ha⁻¹ with no fertilizer (C1N0) and char at 13.4 Mg C ha⁻¹ with urea at 200 kg N ha⁻¹ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

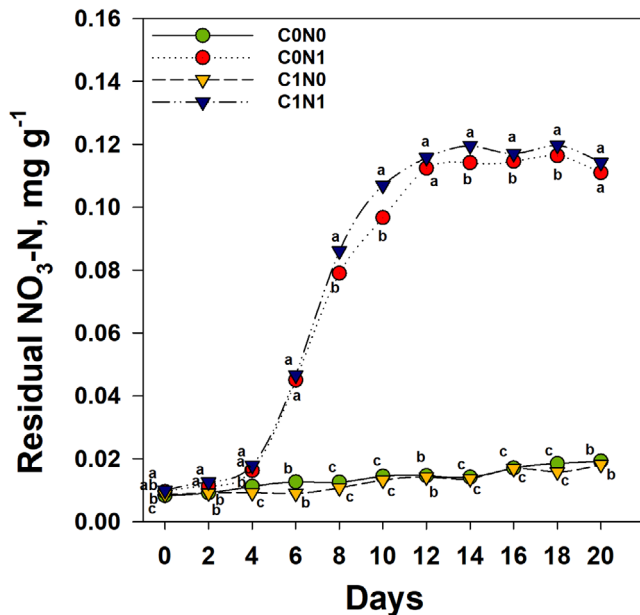


FIGURE 5 Daily soil residual NO₃-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha⁻¹ with no char (C0N1), char at 13.4 Mg C ha⁻¹ with no fertilizer (C1N0) and char at 13.4 Mg C ha⁻¹ with urea at 200 kg N ha⁻¹ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

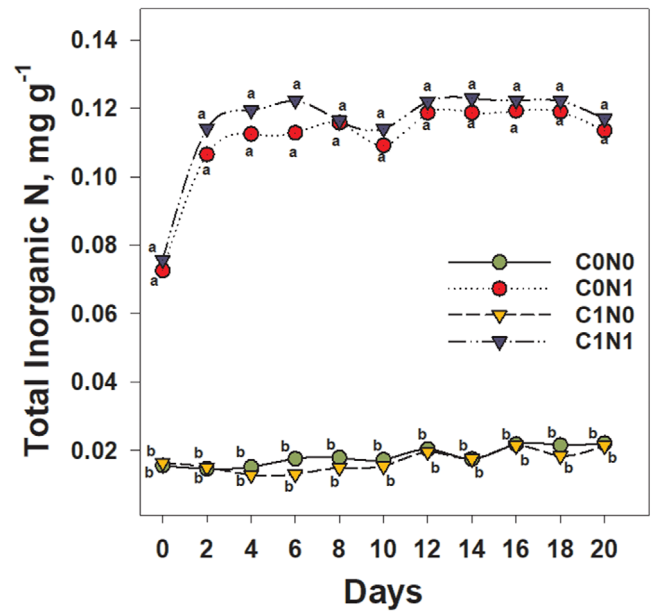


FIGURE 6 Daily soil total-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha⁻¹ with no char (C0N1), char at 13.4 Mg C ha⁻¹ with no fertilizer (C1N0) and char at 13.4 Mg C ha⁻¹ with urea at 200 kg N ha⁻¹ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < .05$

4 | DISCUSSION

Fertilizer is the primary source for NH₃ volatilization which can increase with increasing N application rate, especially with surface broadcast compared to subsurface banding or deep placement (Cai et al., 2002; Jantalia et al., 2012). Sommer et al. (2004) and Reichmann, Sala, and Peters (2013) demonstrated that NH₃ volatilization is dependent on urea hydrolysis as influenced by soil temperature and moisture which may raise NH₄/NO₃ ratio in the application area. Ammonia volatilization may reach up to 35% of applied N over a week at 20–25 °C (Franzen et al., 2011). Maintaining the incubation temperature (25 °C) and soil moisture content around 35% water-filled pore space throughout the experiment period allowed for considerable NH₃ volatilization loss (up to 38% of applied N). These losses aligned with other studies that reported NH₃ loss of 15 to 64% of applied N from a surface applied urea-N fertilizer (San Francisco, Urrutia, Martin, Peristeropoulos, & Garcia-Mina, 2011; Siddique et al., 2020; Vaio et al., 2008).

Cation exchange capacity and N₂ fixation capacity can affect soil NH₃ volatilization, likely because these soil properties control the amount of available total applied N near soil surface (Ferguson et al., 1984). Clay minerals can fix total applied N in soil, which can reduce the pool of available N for NH₃ volatilization (Pelster et al., 2018). The reduction in NH₃

volatilization in char added fertilized treatment by 15.3% compared to no char treatment was due to increased N sorption due to higher surface area and CEC associated with char compared to soil (Panday et al., 2020). This observation agreed with previous research that documented a reduction in NH_3 volatilization with char addition to the fertilized treatment (Wang & Alva, 2000).

Ammonium (NH_4) is the predominant form at pH below 7.5 (Fan et al., 1993; Sherlock, Freney, Bacon, & Van der Weerden, 1994). The NH_3 forms quickly and becomes dominant as soil pH increases above 7.5 and it becomes susceptible to loss via volatilization (Behera et al., 2013). The reduction in soil pH in fertilized soil is due to acidifying nature associated with NH_3 -based fertilizer transformation (Stewart, 2008). Further reduction in soil pH observed due to char can be attributed to dilution effect of adding char that has lower pH (7.6) than soil (7.9). Similarly, the dilution effect of soil pH associated with organic amendment, such as fly ash, has been reported previously by Lai, Ye, and Wong (1999).

Reduction in NH_3 loss in the char-added fertilized treatment coincided with greater residual $\text{NH}_4\text{-N}$ in that treatment than in no char treatment on Days 4 and 6. Prolonged and higher presence of $\text{NH}_4\text{-N}$ can eventually lead to a greater NH_3 emission (Peng et al., 2015; Zaman, Nguyen, & Blennerhassett, 2008). However, it is important to note that KCl-extractable $\text{NH}_4\text{-N}$ does not directly correlate with NH_3 emissions because it includes the proportion of free $\text{NH}_4\text{-N}$ in solution and bound $\text{NH}_4\text{-N}$ in CEC pools (Pelster et al., 2018). Those $\text{NH}_4\text{-N}$ bound to CEC pools are only moderately available and most of the NH_3 volatilization loss would derive from free $\text{NH}_4\text{-N}$ in soil solution (Pelster et al., 2018; Witter et al., 1989). Therefore, a greater $\text{NH}_4\text{-N}$ in char treatment in the current study suggests enhanced N retention in that treatment and subsequently, reduced NH_3 loss. Di and Cameron (2004) also observed a negligible NH_3 volatilization loss once the pH was reduced to below 7.5 after 2 wk of urea application despite the presence of KCl-extractable $\text{NH}_4\text{-N}$ in soil.

The residual $\text{NH}_4\text{-N}$ was higher in char-added fertilized treatment (C1N1) compared to no char treatment (C0N1) on Days 4 and 6. In addition to char properties of increasing N sorption, the addition of char with pH 7.6 reduced soil pH from 7.9 to 7.3 compared to no char-treated soil of pH = 7.8 on Day 6, thus reducing NH_3 volatilization with the char treatment. This explains why there was lower daily NH_3 volatilization in the treatment C1N1 compared to C0N1 only on Day 6. This observation is supported by previous research that demonstrates an importance of soil pH in retaining or releasing soil NH_4/NH_3 (Fan et al., 1993; Panday et al., 2020; Sherlock et al., 1994). When comparing between char and no char fertilized treatments, a reduction in NH_3 loss with char treatment also coincided with a trend for higher residual $\text{NH}_4\text{-N}$ with that treatment than no char from Day 4 to 8. From

Day 8 and onward, soil pH in both C0N1 and C1N1 treatments were similar and below 7.5 threshold and therefore no differences in NH_3 loss or residual $\text{NH}_4\text{-N}$ were observed in fertilized treatments with or without char.

Total inorganic N in the fertilized treatments on Day 0 was much lower than on other days. Any increase in total inorganic N during the experiment compared to that at the onset of the experiment could be related to N added and to soil N mineralization (Anderson, Hart, Christensen, Mellbye, & Flowers, 2010; Robertson & Groffman, 2007). Maximum N mineralization occurs when soil temperatures are between 25 and 35 °C (Stark & Firestone, 1996) and soil moisture is near field capacity (Cassman & Munns, 1980; Stanford & Epstein, 1974). After 28 d of laboratory study, Knoepp and Swank, (2002) observed a 3.5 mg N kg⁻¹ mineralization in sandy loam soil. Another study reported an approximately 310 mg N kg⁻¹ mineralization in a 312-d incubation experiment under Waimea sandy loam soil (medial, amorphous, isothermic Humic Haplustands) (Deenik, 2006).

5 | CONCLUSION

Char rate at 13.4 Mg C ha⁻¹ was effective in reducing NH_3 volatilization from soil by lowering soil pH. In addition to char properties of high surface area, CEC, and total C content, its effect on soil pH makes it a promising soil amendment particularly in high pH and low C soil. As it improves soil N retention, char may directly or indirectly affect soil N cycle processes as well. This study supported our hypothesis that char reduced soil pH and NH_3 volatilization loss from the soil. Further research is warranted to evaluate the potential use of char in farmland to reduce NH_3 losses and enhance N use efficiency for crop production.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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