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# Effects of Char on Nitrogen Management in Agricultural Soils of Semi-arid Western Nebraska

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# EFFECTS OF CHAR ON NITROGEN MANAGEMENT IN AGRICULTURAL SOILS OF SEMI-ARID WESTERN NEBRASKA

by

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A DISSERTATION

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# EFFECTS OF CHAR ON NITROGEN MANAGEMENT IN AGRICULTURAL SOILS OF SEMI-ARID WESTERN NEBRASKA

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Soils in western Nebraska are characterized by low soil organic C due to semi-arid environment in the region and further aggravated by disruption of soil aggregates and rapid C decomposition from intensive tillage, erosion, and frequent droughts. Proper management of soil C may improve soil properties, reduce N losses, and subsequently improve crop yields in this low C soil and low moisture condition. This dissertation focuses on C-rich coal char (henceforth “char”) as a potential strategy to overcome the existing problem of low C in semi-arid region. Char is an industrial by-product, resulting from inefficient coal burning during sugar beet processing in western Nebraska. It contains around 30 g $kg^{-1}$ total C by dry weight as well as other essential plant mineral nutrients. Laboratory results showed that addition of char reduced ammonia ($NH_3$) volatilization likely from increased ammonium ($NH_4$-N) sorption and retention due to its high surface area (82.1 $m^2$ $g^{-1}$) and high cation exchange capacity (CEC, 46.9 cmol $kg^{-1}$). Char also reduced soil pH in fertilized soil, thereby, contributing towards reduction of $NH_3$ loss. In field experiment, maize yield increased following char application which can be potentially due to increased micronutrient uptake and increased soil organic C. In field and lab experiments, char had a minimal positive effect on soil chemical

properties. Char is a promising soil amendment particularly in high pH and low C soil. However, it might take longer before measurable enhancement on soil properties can be observed following char application. There were no adverse effects of adding char, alone or in combination with other amendments, on crop yields. However, possible adverse effects of pesticide sorption and potential trace metal accumulation in soil, crop tissue, or grains on char addition need to be considered before using char on agricultural lands.

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## INTRODUCTION

Soil organic carbon (C) is the primary element in soil organic matter (SOM) and is used as a measurable basis for SOM estimation (Rossell et al., 2001). Among three forms of soil organic C pool; labile, intermediate, and passive, labile C is vital to soil organic C dynamics, nutrient cycling, and maintenance of soil environmental quality (D'andrea et al., 2002). Soil organic C is important since it sustains soil fertility, increases soil moisture storage, and mitigates droughts (Tiessen et al., 1994). The threshold level of soil organic C concentration in the semi-arid agricultural soils is around 9 g C $kg^{-1}$ (Hou et al., 2019). It would be challenging to attain the maximum agricultural production potential if soil organic C concentration is below the threshold level, regardless of soil types (Kay and Angers, 1999). Therefore, the maintenance of site-specific soil organic C concentration above the threshold level is a prerequisite to preserving soil functions.

Western Nebraska in semi-arid U.S. Great Plains occupies a unique geographic position in terms of soil, climate, hydrology, topography, vegetation, and land use cover compared to the rest of Nebraska. For instance, it receives annual precipitation of 385.6 mm as compared to the eastern NE of 736.6 mm (HPRCC, 2019). Tripp soils are the most extensive soils in agricultural landscapes of western NE, which have a thick, dark, non-limy surface and $CaCO_3$ rich sub-surface layers (Yost, 1968). Besides inherently low soil fertility, these soils are characterized by low soil organic C due to disruption of soil aggregates and rapid C decomposition from intensive tillage, erosion, high pH and frequent droughts

(Nielsen and Calderon, 2011; Mikha et al., 2013; He et al., 2017). Soils in this region have lost about 30-50% of the original C level since cultivation began. The average soil C level is around 10 g C kg$^{-1}$ compared to 15-20 g C kg$^{-1}$ in the eastern NE (Varvel and Wilhelm, 2010).

Intensive cropping systems, as well as cultivation of soil by plowing and other tillage methods, favor aeration and higher soil temperatures (Baker et al., 2007). These practices expose physically protected organic material to microbial breakdown and accelerate the rate of soil organic C mineralization (Reicosky et al., 1999; Zibilske et al., 2002). Strong winds could modify the texture of topsoil by removing fine particles that contain the most labile soil organic C fraction and soil nutrients (Ekhtesasi and Sepehr, 2009). Similarly, recurring drought and lower organic ion activity in semi-arid region further increased the process of calcium precipitation (Singh et al., 2007). The concentration of soluble salts in soil solution is increased as water is removed from the soil by evaporation and transpiration and soil pH reaches greater than 7 (Richards, 2012). Iron chlorosis could be a problem in the early growing season of crop due to high bicarbonate content in such calcareous soils (Lindsay, 1995; Lucena et al., 2018). Low soil productivity in semi-arid region is further aggravated by soil degradation (Gelaw et al., 2015). Hence, it is important to improve soil properties in this low C soil to enhance benefits of fertilizer inputs and increase crop yields.

Among inputs, nitrogen (N) fertilizer is the major input that contributes to soil fertility and crop production, including its impact on soil C dynamics (Wanniarachchi et al., 1999). Within just hours to days of being introduced to soil in reactive mineral forms, N undergoes a series of transformations where soils with the greatest C and clay content may have the greatest potential to retain added N (Zoggs et al., 2000; Barrett and Burke, 2002). Mineral N is stabilized in soil through a variety of mechanisms, including microbial immobilization of N and chemical reactions mediated by clay minerals (Holmes and Zak, 1999; Corre et al., 2007). Soil pH and temperature play a critical role in regulating soil $NH_4$-N retention. Numerous studies have reported that low soil temperature and pH could inhibit the $NH_4$ oxidation rate and suppress ammonia ($NH_3$) volatilization (Zhang et al., 2013; Delgado-Baquerizo et al., 2013; Jin et al., 2015), which are both beneficial to the soil $NH_4$-N retention. In general, $NH_4$-N retention efficiency is low as $NH_4$-N is sensitive to slight changes in soil local conditions (physical, chemical, and biological variables) that affect its concentration in soil (Gücker and Boëchat, 2004).

Crop production depends on sustained supply of mineral N which includes $NH_4$-N and its oxidation product, $NO_3$-N. Fertilization, as the main practice of crop management, has been found to be the major sources of N potentially available to crops (Sekhon et al. 2011). However, many findings report that crop N uptake efficiency is generally less than 50% of applied N (Dobermann et al., 2003; Meisinger et al., 2008). That leaves a significant amount of N in soil and may be lost to the environment as $NO_3$-N, $NH_3$, or nitrous oxide ($N_2O$) (Fageria and Baligar, 2005; Robertson et al., 2013; Maharjan et al., 2014). A decrease in N retention, N uptake, or N utilization may correlate with the reduction in N use efficiency (Dawson et al., 2008). Nitrate is the major form of N available to plants, but it is also highly mobile and susceptible to losses compared to $NH_4^+$ form (Crawford and Glass, 1998; Glass et al., 2002). An upward movement of water facilitates transfer of $NO_3^-$ from lower to upper zone whereas downward movement of water facilitates leaching of $NO_3$ up to a depth greater than 2 m (Di and Cameron, 2002; Qi-xiao, 2012) and may pollute aquatic ecosystem downstream (Kramer et al., 2006). Leached $NO_3$ may also continue to undergo recycling in soil-water-air system and convert to $N_2O$ and $N_2$ through denitrification process and released back to the atmosphere (Mosier et al., 1998).

Nitrous oxide is a major greenhouse gas (GHG) and the single most important ozone-depleting substance (Ravishankara et al., 2009). Microbial nitrification and denitrification, along with some abiotic processes contribute as a source of $N_2O$ production in soil (Bremner, 1997). Ammonium form of N can be lost to the atmosphere as $NH_3$ volatilization (Pacholski et al., 2008). It is widely reported that N fertilizer is the primary source for $NH_3$ volatilization and can increase with increasing application rate (Cai et al., 2002; Jantalia et al., 2012). Ammonia volatilization is also affected by management practices, weather conditions and soil attributed factors such as pH, organic matter, clay content, and water holding capacity (Kissel et al., 2008; Rochette et al., 2009; Cameron et al., 2013). Ammonia deposition from the atmosphere to land can cause soil acidification (Soares et al., 2012; Goulding, 2016) and promote eutrophication of surface water bodies (Sutton et al., 2008). Hence, N losses in any form from agricultural systems can be major limitations for crop production, soil sustainability, and environmental safeguard.

Numerous management technologies such as enhanced efficiency N fertilizers (controlled-release fertilizer, nitrification inhibitors, urease inhibitors) (Di and Cameron, 2002; Ni et al., 2011; Peng et al., 2015) have been proposed to mitigate N losses from agricultural systems. However, the challenges lie in selection of appropriate management tools that may vary from field to field, by soil type, local climate, other management practices and in cost associated compared to conventional management (Decock, 2014). In addition, extensive use of inorganic fertilizers in semi-arid regions is not favored due to soil with low crop yield potential and subsequent reduced return on input cost (Wang et al., 2016).

Proper management of soil C may improve soil properties, reduce N losses and subsequently improved crop N use since soil C affects soil properties and N cycling (Ding et al., 2010; Snapp et al., 2010; Dil et al., 2014). Understanding of soil organic C dynamics can contribute to N management (Wang et al., 2009). A wide range of management options are available to simultaneously restore/enhance soil C and improve soil productivity and some of such options are residue management, mulch farming, reduced or no tillage, diverse crop rotations and cropping/farming systems with avoidance of bare fallow (López-Fando and Pardo, 2011). Still, enrichment in soil organic C as influenced by those management practices are expected to be measurable under long-term rather than short term periods (Paustian et al., 1997; Hati et al., 2007).

Organic amendments can be a sustainable practice to increase soil C and subsequently, to enhance soil productivity (Uzoma et al., 2011). Organic amendments could supply essential plant nutrients as well as C to improve soil properties and productivity (Sanderman et al., 2009). The use of organic manures and compost enhances soil C in addition to supplying nutrients while that is not the case with inorganic fertilizers (Gregorich et al., 2001). Long-term manure applications increase the soil organic C pool and may improve aggregation (Gilley and Risse, 2000), and the effects may persist for a century or longer (Compton and Boone, 2000). However, in some cases, its benefits can be minimal (Lentz et al., 2014; Schulz et al., 2014).

Adding C rich materials can hasten the process in increasing soil organic C and improving soil properties and crop yields in semi-arid regions such as in agricultural landscapes of western Nebraska (Blanco-Canqui et al., 2020). High C products such as biochar can boost soil organic C, improve nutrient retention, reduce greenhouse gas emissions, increase crop yields (Filiberto and Gaunt, 2013; Singh et al., 2014). However, most of the reported benefits of biochar are in acidic soil, and that could be derived from the liming effect (Liu et al., 2012; Burell et al., 2016) and the use of biochar at large scale can be cost-prohibitive in agriculture.

This dissertation focuses on C-rich coal char (henceforth “char”), which is currently available in a considerable quantity and at low cost in western NE, as a potential strategy to overcome the existing problem of low C in semi-arid region. Char contains up to 30 g $kg^{-1}$ total C by dry weight and some plant essential nutrients. In addition, char has considerably higher CEC and surface area than biochar. Because of its agronomically beneficial properties and low cost, char is a low-cost potential soil amendment for low C soils in semi-arid western NE yet to be explored. It is an industrial by-product, resulting from inefficient coal burning during sugar beet processing in western NE.

## Production Process and Properties of Char

### a) Production of Char

Western Sugar Cooperative (WSC) is made up of over 850 growers and stakeholders who are engaged in beet sugar production. They have in total five manufacturing facilities in Nebraska, Colorado, Montana, and Wyoming. The NE facility is in Scottsbluff, Scotts bluff county. More than 31,820 Mg of char per year is produced in Scottsbluff, NE alone.

The WSC manufacturing facility in Scottsbluff, NE uses pulverized coal-fired furnace as an energy source at various stages of sugar extraction process. The coal source is sub-bituminous coal (moisture; 10-45%, fixed C; 35-45%, and ash; <10%) and mined in the Powder River Basin of Wyoming by Cloud Peak Energy Inc. Coal is first brought to the factory by rail car. The coal is then transferred from the coal rail cars through various conveyors to a pulverizing station and from there to a boiler house. The pulverized coal is then fed from above into the furnaces where blowers blow the pulverized coal into the combustion chambers of traveling grate type furnaces. The temperature in the furnace varies from 650 to 980 $^{o}$C.

Any coal that is not combusted in the hottest part of the chamber then falls into the moving grate. The moving grate temperature is considerably lower (around 165 $^{o}$C) than the hottest part of the combustion chamber. Residue on the moving grate is continuously moved forward and then dumped off the end into a water trough, which cools it and creates a slurry. This slurry contains bottom ash (mainly) and fly ash. Then all the slurry is pumped to holding ponds to settle out. Those holding ponds are periodically cleaned and the settled out char is moved to a holding pile (Appendix 1- 1).

As stated above, any unburned coal that falls to the grate has a chance of escaping the burning process. However, coal will have spent some cooking time in a high-temperature environment similar to biochar production, possibly giving it similar properties as those of biochar. Other elements will have also spent less cooking time or avoided the high-temperature, and thus, will have reduced chance to form oxides and therefore, remain in more plant available forms.

### b) Properties of Char

The physical, chemical, and mineralogical properties of char are heavily dependent on nature of parent coal, conditions of combustion, type of emission control devices and the storage and handling methods. The physical, chemical and mineralogical properties of char discussed here is the one produced at WSC in Scottsbluff, NE (Appendix 1- 2).

The physical dimension of char ranges from fine ash particles to medium to large fractions. Most particles are hollow spheres (cenospheres) filled with smaller particles of irregular shapes that contain unburnt C, anhydrate, calcite, and crystals. The bulk density and surface area of char is 750 kg $m^{-3}$ and 82 $m^2$ $g^{-1}$, respectively. Char has an amorphous and sandy clay loam structure with low fractions of silt and clay. These characteristics may be of use in water movement in soil; a similar product i.e., fly ash has shown a great water permeability and a small number of colloidal particles (Haynes, 2009).

Char has a slightly alkaline pH of 7.6 and high values of electrical conductivity as 6.6 $dSm^{-1}$, indicating that char contained a considerable amount of soluble salts (Ca, Mg and B). Carbon content in char is relatively higher, i.e., 293 g $kg^{-1}$ total C by weight compared to the other coal combustion residues (CCR) as a result of the incomplete combustion of the coal. It also contains some other essential plant mineral nutrients (N, P, K, Ca, Mg, S, Zn, Fe, Mn, Cu, B, Cl, and Mo). Due to the high surface area, these mineral nutrients have a higher ability to become bioavailable (Nyambura et al., 2011). Char also contains heavy metals (As, Cd, Cr, Pb, Hg, and Se). Their concentrations are below the US EPA's ceiling limits for heavy metal soil contamination or phytotoxicity in soil (Cameron, 1992).

The cation exchange capacity (CEC) of char is 46.9 cmol $kg^{-1}$. Glaser et al. (2003) suggested that improvement in CEC is related to the oxidation of the aromatic C and formation of carboxyl groups or other functional groups with a net negative charge. Higher CEC of char means it has a greater ability to adsorb cations per unit C. This feature is attributed to char's higher surface area, more negative surface charge, and greater charge density. Mineralogical analysis of char using X-ray powder diffraction shows the presence of $SiO_2$, $CaCO_3$, $CaSO_4.H_2O$ and C.

According to the International Energy Agency, the 2017 global coal consumption for energy production was 7,585 million megagram (Mg) (IEA, 2018) and generated 25.2 million Mg of total CCR (ECOBA, 2006). The utilization of coal residues reaches almost 100% in some developed countries. In many developing countries, the CCR utilization is low or nonexistent and is discarded in landfills as a “waste” product (EEA, 2006). Coal combustion residues such as fly ash, bottom ash, and flue gas desulfurization gypsum have been used as soil amendments to improve soil health and crop performance (Basu et al., 2009; Shaheen et al., 2014; Panday et al., 2018). In contrast to regular CCRs from coal-fired power plants, char resulting from inefficient coal burning contains a considerable amount of C as well as other essential plant mineral nutrients.

When char is added to fertilized soil, it might retain soil N, thereby minimizing environmental N loss from the soil system. The possible mechanisms that char might be useful to reduce N loss from fertilized soil may be due to (i) improved retention of applied N by electrostatic adsorption to exchange sites provided by char and/ or (ii) immobilization of N by microbial process due to high C:N ratio of char (Steiner et al., 2008).

If CCRs containing a high C content can be shown to be a beneficial soil amendment, additional value may be obtained from inefficient coal boiler systems. The safe use of char in cropland may also be mutually beneficial to the crop producers and regional industries. In addition, it can develop a partnership among generators of char, local landowners, extension scientists and regulators to expand char as agricultural soil amendment. Such information on agricultural reuse of C by product may be transferable to other regions/countries where there may be locally available similar high C by-product with potential reuse in farmland.

While evaluating potential use of char in agricultural soils in semi-arid western NE, the use of crop canopy sensor technology to determine in-season crop

N status could be an additional effective strategy to optimize N management and improve crop yields. In many recent studies, sensor-based in-season N application has been promoted to improve N use efficiency (NUE) in cropping systems (Solari et al., 2008; Krienke et al., 2015; Montealegre et al., 2019). These sensing tools provide information on crop N status based on leaf chlorophyll concentration or leaf greenness (Tremblay et al., 2011). There are limited studies of crop canopy sensor technology in semi-arid region (Shaver et al., 2011; Ballester et al., 2017; Pinar and Erpul, 2019).

In this dissertation, effectiveness of char in reducing environmental N losses and improving soil and crop yields in semi-arid western NE was evaluated. It was hypothesized that the C-enriched material i.e., char may reduce N losses from fertilized soils, improve soil C and properties, and crop yields since char has lower pH compared to calcareous soils of semi-arid region and has high surface area and high CEC. Results from laboratory experiments to determine the effect of char on soil properties and processes that affect N loss are also presented. In addition to char, soil amendments such as biochar, compost manure, and municipal compost were also evaluated in the field trials. There are four chapters in this dissertation which includes two laboratory and two field studies and char used in all these studies are the same.

Chapter 1. Optimum rate of surface applied coal char decreased soil ammonia volatilization loss (Journal of Environmental Quality, 2020)

The objective of this study was to evaluate effects of char on soil N losses via $NH_3$ volatilization, $N_2O$ emissions, and $NO_3$–N leaching from fertilized loam and sandy loam soils. Char was applied at five different rates (0, 6.7, 10.1, 13.4, and 26.8 Mg C ha$^{-1}$; char measured in C equivalent) to soils fertilized with urea ammonium nitrate (UAN) at 200 kg N ha$^{-1}$. In addition, there were two negative-UAN control treatments: no char (no UAN) and char at 26.8 Mg C ha$^{-1}$ (no UAN).

Chapter 2. Effects of char on ammonia volatilization from fertilized sandy loam soil

The objective of this study was to determine effects of char on soil pH, N transformations, and subsequent $NH_3$ 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 used and each treatment was analyzed for soil pH, $NH_3$ volatilization, and residual N (urea, $NH_4$ and $NO_3$) on every other day for 21 days.

Chapter 3. Potential amendments for improving productivity of a low carbon semi-arid soil

The objective of this study was to evaluate the effects of char, biochar, composted manure, and municipal compost on soil C, soil fertility properties, crop nutrient uptake, and crop yields in a low C sandy loam soil with limited productivity.

Chapter 4. Does application of coal char with urea or composted manure improve soil and crop yields in semi-arid region?

The objective of this study was to evaluate the effects of char applied together with urea or composted manure on soil properties and crop yields in sandy loam soil. Furthermore, this study evaluates the performance of active crop sensor in determining in-season N status in maize under furrow irrigation in fertilized sandy loam soil in western NE following char application.

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# CHAPTER 1 - OPTIMUM RATE OF SURFACE-APPLIED COAL CHAR DECREASED SOIL AMMONIA VOLATILIZATION LOSS

## Abstract

Fertilizer N losses from agricultural systems have economic and environmental implications. Soil amendment with high C materials, such as coal char, may mitigate N losses. Char, a coal combustion residue obtained from a sugar factory in Scottsbluff, NE, contained up to 293 g kg$^{-1}$ C by weight. A 30-d laboratory study was conducted to evaluate the effects of char addition on N losses via nitrous oxide ($N_2O$) emissions, ammonia ($NH_3$) volatilization, and nitrate ($NO_3$–N) leaching from fertilized loam and sandy loam soils. Char was applied at five different rates (0, 6.7, 10.1, 13.4, and 26.8 Mg C ha$^{–1}$; char measured in C equivalent) to soils fertilized with urea ammonium nitrate (UAN) at 200 kg N ha$^{–1}$. In addition, there were two negative-UAN control treatments: no char (no UAN) and char at 26.8 Mg C ha$^{–1}$ (no UAN). Treatment applied at 6.7 and 10.1 Mg C ha$^{–1}$ in fertilized sandy loam reduced $NH_3$ volatilization by 26–37% and at 6.7, 10.1, and 13.4 Mg C ha$^{–1}$ in fertilized loam soils by 24% compared with no char application. Nitrous oxide emissions and $NO_3$–N leaching losses were greater in fertilized compared with unfertilized soil, but there was no effect of char amendment on these losses. Because $NO_3$–N leaching loss was greater in sandy loam than in loam, soil residual N was twofold higher in loam than in sandy loam. This study suggests that adding coal char at optimal rates (up to 13.4 Mg C ha$^{–1}$ in fertilized loam and 10.1 Mg C ha$^{–1}$ in fertilized sandy loam soils) may reduce

agricultural reactive N to the atmosphere by decreasing $NH_3$ volatilization from fertilized soils.

## Introduction

Fertilizer N use increased globally at an annual rate of 1.4% from 2014 to 2018 (IFASTAT, 2019). Generally, crop N uptake efficiency is <50% of applied N, which leaves a significant amount of N in soil prone to loss via $NH_3$ volatilization, $NO_3$–N leaching, and/or denitrification as $N_2O$ emissions (Fageria and Baligar, 2005; Robertson et al., 2013). Nitrogen losses from agricultural systems can be a major limitation for crop production and environmental sustainability.

Numerous management technologies have been proposed to mitigate N losses from agricultural systems, including the proper management of soil C because of its effects on soil properties and processes, including N cycling (Ding et al., 2010; Dil et al., 2014). Carbon management practices that include amendments with high C content, such as biochar, can boost soil fertility and quality by improving water holding capacity, cation exchange capacity (CEC), and nutrient retention (Bridgwater, 2003; Filiberto and Gaunt, 2013; Singh et al., 2014).

Coal combustion residues (CCRs), such as fly ash, bottom ash, and flue gas desulfurization gypsum, have been used as soil amendments to improve soil health and crop performance (Basu et al., 2009; Shaheen et al., 2014; Panday et al., 2018). However, depending on the composition and nature of CCR, they can enhance mineralization of organic soil N and N losses (Siddaramappa et al., 1994). The CCRs in electric power generating stations obtained from the near-complete combustion of coal during energy production contain very little C. In contrast, coal char (henceforth “char”) resulting from inefficient coal burning contains up to 293 g $kg^{-1}$ C by dry weight as well as other essential plant mineral nutrients. This study includes char produced at Western Sugar Cooperative in Scottsbluff, NE. The physical, chemical, and mineralogical properties of char can be heavily dependent on nature of parent coal, conditions of combustion, type of emission control devices and the storage and handling methods.

Char stands midway between coal ash and biochar with respect to C content. Biochar and other hydrocarbons are typically produced from pyrolysis of biomass in the presence of little or no oxygen at a range of temperatures and can contain up to 70% of initial biomass C (Lehmann et al., 2006; Atkinson et al., 2010). Biochar can reduce $NH_3$ volatilization loss (Steiner et al., 2010) and $NO_3$–N leaching loss (Hagemann et al., 2017). However, the beneficial effect of biochar in reducing environmental N losses from fertilized soil is not consistent and depends on sources and production conditions (Ding et al., 2016). Char, which is different from regular CCRs and biochar but has a considerable amount of C, warrants exploration for its potential use in agricultural soil.

The objectives of this study were to evaluate the effects of char on soil N losses in the form of $NH_3$ volatilization, $N_2O$ emissions, and $NO_3$–N leaching from fertilized loam and sandy loam soils. We hypothesized (i) that adding char would reduce N losses from fertilized soil by improving the retention of applied N and (ii) that char effectiveness on retaining N would differ by soil type.

## Materials and methods

The char used in this study was a CCR from a sugar factory in Scottsbluff, NE, and contained up to 293 g $kg^{-1}$ C and some nutrients (Appendix 1- 1 and Appendix 1- 2). It also contained heavy metals (As, Cd, Cr, Pb, Hg, and Se), but their concentrations were below the USEPA's ceiling limits for heavy metal soil contamination or phytotoxicity in soil (Cameron, 1992). Char was sieved through a 2-mm sieve. The physical characteristics of char were determined by X-ray diffraction using a PANalytical Empyrean Diffractometer (Malvern Panalytical Ltd.) at the Nebraska Center for Materials and Nanoscience (Appendix 1- 3). Brunauer-Emmett-Teller surface area of char was analyzed with an ASAP 2460 Surface Area and Porosity Analyzer (Micromeritics Instrument Corporation) at the Nebraska Center for Materials and Nanoscience (Appendix 1- 4).

Two soils were used to evaluate the effects of char on N losses from fertilized soil at the Panhandle Research and Extension Center, University of Nebraska-Lincoln in Scottsbluff, NE. One soil was a Tripp fine sandy loam (coarse-silty, mixed, superactive, mesic Aridic Haplustolls, 0–3% slope) with pH 7.7; 13 g $kg^{–1}$ organic matter (OM); and 60, 28, and 12% of sand, silt, and clay contents, respectively. This soil was collected from the Panhandle Research and Extension Center. The other soil was a Duroc loam (fine-silty, mixed, mesic Pachic Haplustolls, 0–1% slope) with pH 7.2; 18 g $kg^{–1}$ OM; and 40, 33, and 27% of sand, silt, and clay, respectively. This soil was collected from farmland near the University of Nebraska-Lincoln High Plains Agricultural Laboratory in Sidney, NE. Both soils were collected at depths of 0–20 cm in the spring of 2018. Residual inorganic N ($NH_4$–N and $NO_3$–N) rates, extracted with 2 M KCl, in loam and sandy loam soils were 5.2 and 3.7 mg $kg^{-1}$, respectively.

Collected soils were air-dried and sieved through a 2-mm mesh. Soils were brought to 10% gravimetric water content (GWC) by applying water and mixing thoroughly, which corresponded to 70 and 50% of field capacity of sandy loam and loam, respectively. Soils were packed in 5-cm-diameter clear acrylic columns (Appendix 1- 5) to a height of 24 cm with a targeted bulk density of 1400 kg $m^{-3}$ (Peng et al., 2015). It is worth noting that although soil samples were collected from 0-20 cm depth from field, extended up to 24 cm in soil column.

A porous ceramic plate (0.1 MPa strength) was inserted in the bottom of the column and topped with Whatman no. 42 filter paper to prevent soil from clogging the ceramic plate. Soil columns had lid systems at either end. A vacuum port located on the bottom lid allowed suction to be applied during the collection of leachate. The top lid had two parts (lower and upper). The lower lid part is an elongated connector (height, 5 cm) threaded onto the main column and the upper lid, which was used to install the $NH_3$ acid trap. The upper lid part (height, 5 cm) terminates the column with a closed end fitted with a septum port for $N_2O$ sampling from the headspace above the soil.

Char (measured in C equivalent) and UAN were applied to each soil column and mixed in the top 6-cm soil layer. There were seven treatments, each with four replications: (i) C0N0, no char or UAN; (ii) C0N1, no char and UAN; (iii) C1N1, char rate at 6.7 Mg C $ha^{-1}$ and UAN; (iv) C2N1, char rate at 10.1 Mg C $ha^{-1}$ and UAN; (v) C3N1, char rate at 13.4 Mg C $ha^{-1}$ and UAN; (vi) C4N1, char rate at 26.8 Mg C $ha^{-1}$ and UAN; and (vii) C4N0, char rate at 26.8 Mg C $ha^{-1}$ and no UAN. Char rates 0, 6.7, 10.1, 13.4 and 26.8 Mg C $ha^{-1}$ corresponds to 0, 22.3, 33.6, 44.6 and 89.2 Mg char $ha^{-1}$. All treatments that were fertilized (CxN1) received $39.5 \times 10^{-3}$ g UAN-N that was equivalent to 200 kg N $ha^{-1}$. Char rates were chosen to generate a measurable crop yield response around application rate of 13.4 Mg C $ha^{-1}$ recommended by Western Sugar Cooperatives, Scottsbluff, NE to their cooperative growers.

After soil columns were prepared, water was periodically added to simulate rainfall (100.8 mm in total) in May 2017 in Scottsbluff, NE (Appendix 1- 6 and Appendix 1- 7). Water was added slowly on the surface of soil using a syringe to prevent ponding on the surface. Columns were kept on the laboratory benchtop at constant room temperature (25°C) throughout the 30-d experimental period.

**Sample collection**

Ammonia volatilization was measured using an acid trap method (McGinn and Janzen, 1998). The acid trap was made up of a sponge (diameter, 5 cm; thickness, 1.3 cm) with 5 ml of $H_3PO_4$–glycerol solution (40 ml glycerol, 50 ml $H_3PO_4$ acid, and 910 ml deionized water) placed inside the lower part of the column top lid. The acid traps were installed on Day 0 after all treatments were applied to soil. All $NH_3$ traps were exchanged with fresh ones on Days 1, 2, 3, 5, 7, 9, 11, 13, 17, 21, and 25 (Appendix 1- 7). Each used trap was thoroughly rinsed in 2 M KCl solution and squeezed several times to extract the solution. The collected extracts were analyzed for $NH_4$–N using a flow injection method (Ahmed et al., 1997). Cumulative $NH_3$ loss was calculated by summing $NH_4$–N across all collection dates. Cumulative $NH_3$ loss was converted to kg N ha$^{-1}$ by multiplying the total volatilization loss and the given soil surface area.

Nitrous oxide emissions were measured by collecting gas samples through the septum port on the upper terminal lid. Gas samples were collected on alternate days (Days 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, and 29) (Appendix 1- 7). During the $N_2O$ sampling period, the $NH_3$ trap was removed from the column, which gave a headspace of 315 cm$^3$. Gas samples were collected at 0, 10, and 20 min using a 12-ml syringe. The 0-min samples were collected before closing the lid. At each sampling, gas was transferred to a 10-ml glass sample vial (Wheaton). Samples were analyzed for $N_2O$ concentrations with a gas chromatograph (450-GC, Varian) using an electron capture detector. The $N_2O$ concentration values were converted to mass per volume using the universal gas law equation. Daily gas flux rates (mg m$^{-2}$ min$^{-1}$) were calculated as the linear or quadratic change in headspace $N_2O$ concentration over time (Wagner et al., 1997) based on regression analysis with the highest $r^2$ value. Cumulative $N_2O$ emissions (kg N ha$^{-1}$) were determined by integrating daily $N_2O$ fluxes using the trapezoidal integration method (Dunmola et al., 2010).

An attempt was made to collect column leachate on each day after water addition (Appendix 1- 7). On each collection date, suction with a 0.25-horsepower air motor (Model 1603007402, Bluffton Motor Works) was applied to the bottom lid of the column to facilitate drainage of water through a porous ceramic plate (Peng et al., 2015). Leachate samples were frozen until analysis for $NO_3$–N using a flow injection method (Ahmed et al., 1997). The total amount of $NO_3$–N leached in each treatment was calculated by multiplying $NO_3$–N concentration with leachate volume and summing over collection dates.

All samplings were done in the morning (8:00 AM–12:00 PM). At the end of the experiment, the porous ceramic plate was removed from the bottom of the soil column, and soil was divided into 6-cm increments. For each increment, 10 g of soil was collected for determination of GWC, and the remaining soil was analyzed for $NH_4$–N and $NO_3$–N concentrations. Soil residual inorganic N was calculated as the sum of $NH_4$–N and $NO_3$–N concentrations across all soil increments for each column.

### Data analysis

The N losses via $NH_3$ volatilization, $NO_3$–N leaching, and $N_2O$ emissions and soil residual N in unfertilized treatment (C0N0) were subtracted from those in fertilized treatments and divided by the amount of UAN-N applied (i.e., 39.5 mg N) to estimate those losses per applied UAN-N. Fertilizer N recovery (FNR) was estimated by two methods. Equation (1) represents the "N difference" method, where N losses and residual N at the end of the experiment in control treatment (C0N0) were subtracted from those in fertilized treatment to estimate FNR based on "N difference" method ($FNR_{CTRL}$) (adapted from Mahal et al. [2019]). Equation (2) estimated FNR based on the initial extractable N ($FNR_{ResN}$), which accounted for initial extractable N at the beginning of the experiment (adapted from Li et al., 2007).

$$\mathrm{FNR_{CTRL}} = \frac{(\mathrm{N\,loss_{Treatment}} - \mathrm{N\,loss_{C0N0}}) + (\mathrm{Soil\ residual\ N_{Treatment}} - \mathrm{Soil\ residual\ N_{C0N0}})}{\mathrm{Applied\,N}} \times 100$$

(1)

$$\mathrm{FNR_{ResN}} = \frac{\mathrm{N\,loss_{Treatment}} + \mathrm{Soil\,residual\,N_{Treatment}}}{(\mathrm{Applied\,N} + \mathrm{Initial\ extractable\ N})} \times 100 \quad (2)$$

The effects of treatment and soil on dependent variables' cumulative values were tested using the PROC MIXED procedure in SAS, with treatment, soil, and their interaction as the fixed effects and rep as random effect (Littell et al., 2006; SAS, 2015). When main or interaction effects were significant, means were separated by the LSD test (Littell et al., 2006). Ammonia volatilization and $N_2O$ emissions data were analyzed using repeated measures in ANOVA to determine the differences among treatments by sampling dates. Statistical significance was evaluated at $P < .05$ unless otherwise stated.

## Results

### Ammonia volatilization

Daily $NH_3$ volatilization loss with the C4N1 treatment was higher than with other treatments in the first 10 acid trap sample collection dates ($n = 12$) in loamy soil (Figure 1-1a). The same was true for sandy loam on five different sampling dates (Figure 1-2b). After Day 17, all treatments showed no or minimal volatilization loss in both soil types. In fertilized treatments, all daily $NH_3$ losses were >2% of applied N and occurred within the first 2 wk of the experiment, and losses were >1% by the third week in both soil types.

Cumulative $NH_3$ loss across treatments ranged from 0.2 to 9.1 mg (equivalent to 1.0–46.4 kg N $ha^{-1}$) in loam and from 0.2 to 6.9 mg (equivalent to 1.0–35.2 kg N $ha^{-1}$) in sandy loam soils. There was a significant treatment × soil interaction effect on cumulative $NH_3$ loss and cumulative $NH_3$ loss per applied N (Table 1-1 and Table 1-2). Compared with C0N1, cumulative $NH_3$ loss (per applied N) was significantly lower for C1N1, C2N1, and C3N1 in loam soil and for C1N1 and C2N1 in sandy loam soil (Table 1-2). The C3N1 and C4N1 in sandy loam and C4N1 in loam increased $NH_3$ loss (per applied N) compared with C0N1. The C0N0 and C4N1 had minimal $NH_3$ losses in both soil types (Figure 1-1). Among fertilized treatments (C0N1, C1N1, C2N1, C3N1, and C4N1), cumulative $NH_3$ loss per applied N ranged from 3.2 to 22.3% in loam and from 6.6 to 16.8% in sandy loam soils.

**Nitrous oxide emissions**

Daily $N_2O$ fluxes varied from 0 to 0.4 mg $m^{-2}$ $h^{-1}$ in loam and were 0.3 mg $m^{-2}$ $h^{-1}$ in the sandy loam soil across treatments throughout the experiment (Figure 1-2). Variability in daily $N_2O$ fluxes was high among replications in both loam (coefficient of variance [CV], 32.1–166.1%) and sandy loam (CV, 12.1–176.2%). Of the 15 sampling dates, C0N1 had the highest daily $N_2O$ flux on the final sampling date in loam and on Days 7 and 9 in sandy loam. Control treatments always had minimal $N_2O$ fluxes in both soil types.

Cumulative $N_2O$ emissions differed by treatment but did not differ by soil type or their interaction (Table 1-1). Emissions were greater in fertilized treatments compared with unfertilized treatments at $P < .001$. Cumulative $N_2O$ emissions among fertilized treatments were not different. Averaged cumulative $N_2O$ emissions in fertilized treatments were 0.7 kg N $ha^{-1}$ in both soil types and 0.03 and 0.05 kg N $ha^{-1}$ in unfertilized loam and sandy loam, respectively (Appendix 1-8). Among fertilized treatments (C0N1, C1N1, C2N1, C3N1, and C4N1), cumulative $N_2O$ emissions per applied N ranged from 0.1 to 0.5% in loam and from 0.1 to 0.4% in sandy loam soils.

### Nitrate leaching

In loam, one leaching event occurred on Day 29 after N fertilization across all treatments. In contrast, three leaching events occurred in sandy loam (Days 20, 21, and 29), with 44.3% of the total $NO_3$–N leaching observed on Day 29 (Figure 1-3). There was a significant treatment × soil interaction effect on cumulative $NO_3$–N leaching (Table 1-1 and Table 1-2). Cumulative $NO_3$–N leaching was consistently greater for all fertilized treatments in sandy loam than in loam (Table 1-2). Averaged across all treatments, cumulative $NO_3$–N leaching was almost fourfold greater for sandy loam ($17.6 \times 10^{-3}$ g) than for loam ($4.3 \times 10^{-3}$ g) (Table 1-1).

Among fertilized treatments, cumulative $NO_3$–N leaching per applied N was higher in sandy loam (32.4%) than in loam (2.6%) (Table 1-1). In sandy loam, C3N1 had lower $NO_3$–N leaching ($16.9 \times 10^{-3}$ g or 21.1% of applied N) than C0N1 ($24.3 \times 10^{-3}$ g or 39.9% of applied N) (Table 1-2).

### Soil residual mineral nitrogen and fertilizer nitrogen recovery

There was a significant treatment × soil interaction effect on soil residual mineral N throughout the column (Table 1-1). Control treatments (C0N0 and

C4N0) had lower soil residual mineral N than fertilized treatments in both soil types (Table 1-2). Among fertilized treatments, soil residual mineral N was similar in sandy loam but was significantly lower in C4N1 ($26.4 \times 10^{-3}$ g or 49.8% of applied N) than in the other treatments in loam (Table 1-2).

When separated by depth, soil residual N was greater in fertilized treatments than in the control treatments at 18–24 cm in both soil types. Fertilized treatments (C0N1, C1N1, C2N1, C3N1, and C4N1) in loam had greater residual N than the control treatments (C0N0 and C4N0) at other depths as well. Soil residual mineral N at 18–24 cm was higher with C1N1 and C3N1 in loam soil than other treatments in both soil types (Figure 1-4). In loam, C4N1 had lower soil residual N at 18–24 cm than other fertilized treatments. In sandy loam, soil residual N were greater with C3N1 than other treatments except C1N1. Among fertilized treatments in sandy loam, C4N1 and C0N1 had lower soil residual N than others.

There were no significant differences by treatment or soil in fertilizer N recovery (Table 1-1). The $\mathrm{FNR}_{\mathrm{CTRL}}$ ranged from 67.6 to 77.3% by soil type and from 69.0 to 74.2% by treatment. The UAN-N applied among fertilized treatments (C0N1, C1N1, C2N1, C3N1, and C4N1) that remained unaccounted ranged from 26.3 to 34.4%. However, $\mathrm{FNR}_{\mathrm{ResN}}$ ranged from 94.0 to 98.3% in treatments and from 96.2 to 96.7% by soil type (Table 1-1).

## Discussion

### Ammonia volatilization

Ammonia volatilization loss observed in this study aligned with other studies that reported $NH_3$ losses from 8 to 13% (Ma et al., 2010a; Peng et al., 2015;

Vaio et al., 2008). Char addition had no effect on $NH_3$ volatilization in unfertilized treatments. Fertilization is the major source for $NH_3$ volatilization loss, as evidenced by a positive correlation between $NH_3$ volatilization and N fertilization reported in Jantalia et al. (2012) and Jones et al. (2013).

The higher clay content and CEC in loam than in sandy loam promoted better retention of $NH_4$ and subsequently reduced $NH_3$ loss in loam compared with sandy loam in this study. In addition, a higher sand content would enhance the loss of $NH_3$ in sandy loam (McDowell et al., 1958). As the particle sizes increased (higher hydraulic conductivity) and the clay content and organic matter content decreased, $NH_3$ volatilization rate increased (Watson, 1994).

Reduction in $NH_3$ volatilization observed at lower char rates in both soil types was likely from increased sorption due to the high surface area (82.1 $m^2\ g^{-1}$) and the high CEC (46.9 cmol $kg^{-1}$) of char. The surface area of char exceeds that of clay-sized particles (Qi and Zhang, 2015) by one or two orders of magnitude and exceeds that of sand particles by three or four orders of magnitude. The increased in surface area is due to greater degree of microporosity, derived from thermal or chemical activation that are available for sorption or chemical reactions. Similarly, the improvement in CEC of char is thought to take place through two mechanism: surface oxidation of black C particles and sorption of highly oxidized organic matter onto C surfaces (Glaser et al., 2003; Nanda et al., 2016). These results suggest that char functions more like biochar from various sources that have been reported to capture $NH_3$ and reduce $NH_3$ volatilization loss (Steiner et al., 2010; Taghizadeh-Toosi et al., 2012). However, the beneficial effect of high-C products, such as char and biochar, in reducing $NH_3$ loss depends on their sources, production conditions, containments and quality, and application rates (Ding et al., 2016; Steiner et al., 2008).

Soil pH is another important factor for retention or release of $NH_4$/$NH_3$ in the soil. At pH below 7.5, $NH_4$ is the predominant form, rather than volatile $NH_3$ (Fan et al., 1993). As pH increases above 7.5, the $NH_3$ form quickly becomes dominant and is susceptible to loss via volatilization (Behera et al., 2013). The initial pH of sandy loam in this study was 7.7, which is above the 7.5 pH threshold for $NH_3$ volatilization, whereas the loam soil had a pH of 7.2, which is slightly below this threshold. The pH of the char was 7.6, and char contained 19% calcium carbonate. Calcium carbonate aids in increasing soil alkalinity, and hydrolysis of urea to form $NH_4$ also raises the pH (Jones et al., 2013). Depending on the nature and composition of CCRs, they could be useful to increase or buffer soil pH (Elseewi et al., 1978a; Elseewi et al., 1978b; Phung et al., 1978). There could have been a considerable soil alkalization effect with higher char rates that counteracted and exceeded sorption benefits of char.

### Nitrous oxide emissions

The average $N_2O$ emission rate of 0.7 kg N $ha^{-1}$ from fertilized treatments in this study is comparable to the 0.6 kg N $ha^{-1}$ emission rate from UAN at 150 kg N $ha^{-1}$ in a 28-d field study in eastern Canada (Ma et al., 2010b). In this study, a considerable amount of N moved down the soil profile and/or leached, and char addition would have only facilitated that downward N movement due to presence of micropores in char that allow the penetration of air and water (Basu et al., 2009).

A slight increase in $N_2O$ emissions in loam soil compared with sandy loam (Table 1-1) could be related to anaerobic conditions at some pockets in loam soil, which promotes denitrification (Weier et al., 1993).

A previous laboratory incubation study documented that $N_2O$ emissions may vary by soil texture (Harrison-Kirk et al., 2013), but no significant differences in $N_2O$ emissions by soil types were found in our study. Nitrous oxide emissions are primarily driven by N fertilization (Maharjan et al., 2014; Shcherbak et al., 2014), as evidenced by greater emissions in fertilized than unfertilized treatments in this study. The high variability in daily $N_2O$ fluxes among laboratory replicates, which is likely be larger under field conditions, was one reason for the non-significant differences and should be kept in mind for evaluation of N losses from agricultural systems because it points toward a highly dynamic pathway. Johnson and Welch (1939) suggested 33% as permissible upper fiducial limit of CV. Although the acceptable range of CV may vary among experiments, the high CV observed in daily fluxes in this study failed to detect differences in treatment means (Patel et al., 2001). Another potential pitfall in this study could be the small headspace used for gas sampling, which reduces minimum detectable flux (De Klein and Harvey, 2012).

### Nitrate leaching

The contrasting effect of C3N1 and C0N1 in sandy loam with respect to $NH_3$ loss and $NO_3$–N leaching underscores the need to account for all possible pathways of N losses i.e., leaching, runoff, and denitrification. The lower $NO_3$–N leaching loss in C3N1 than in C0N1 is due to greater soil mineral residual N at the lower bottom of the column (18–24 cm depth) and greater $NH_3$ loss in C3N1 than in C0N1. When there are multiple possible pathways for loss, as is the case with mineral N, an effort to reduce N loss via a particular pathway may be undermined or even outweighed by loss via other pathway(s) (Lam et al., 2016).

The effect of high-C-content amendments on $NO_3$–N leaching depends on complex physical, chemical, and biological processes. It has been suggested that leaching of soil $NO_3$–N depends on the ability of biochar to retain $NO_3$–N and $NH_4$–N or on the inhibition of nitrification by clay particles (Clough et al., 2013; Liu et al., 2017). Some biochar studies have found decreased $NO_3$–N leaching depending on fertilizer type, soil type, and leaching conditions, but other studies showed inconsistent effects of biochar on leaching (Sika and Hardie, 2014; Haider et al., 2017; Fidel et al., 2018).

Ventura et al. (2013) observed a reduction in $NO_3$–N leaching only in the second year after biochar application, suggesting an increase in biochar sorption properties over time, possibly due to the oxidation and interaction of biochar and soil particles and an increase in the adsorbing surface due to particle fragmentation with aging (Singh et al., 2010; Hagemann et al., 2017). In contrast, Gronwald et al. (2015) observed that the sorption capacity of biochar decreased by 60–80% to less or observed no $NO_3$/$NH_4$–N sorption after 7 mo of aging in the field compared with the fresh hydrochar, obtained from hydrothermal carbonization process. A similar trend of decreasing sorption capacity with biochar from beetroot chips was reported from a laboratory study on loam soil (Bargmann et al., 2014). Possible reasons for decreased sorption capacity over time can be binding sites of biochar being blocked with organic matter or mineral particles and microbial degradation with subsequent possible changes in surface properties (Cheng et al., 2008). In this study, a leaching event was observed on Day 29 after fertilization in loamy soil. The later and lower $NO_3$–N leaching observed in fertilized loam than in sandy loam in this study may be due to a lower water infiltration rate and greater nutrient retention in loamy soil because of greater clay and OM content (Lehmann and Schroth, 2003). Long-term evaluation is required to understand how char properties might change and affect soil $NO_3$–N leaching over time.

### Soil residual mineral nitrogen and fertilizer nitrogen recovery

Lower soil residual mineral N at a depth of 18–24 cm and subsequently lower residual mineral N in the whole soil column with C4N1 compared with other fertilized treatments in loam soil are likely the result of higher $NH_3$ volatilization loss (cumulative loss of $7.6 \times 10^{-3}$ g N or 17.1% of applied N) (Figure 1-1) or a slightly higher $NO_3$–N leaching loss (Table 1-1).

In all fertilized treatments, most of N moved down the profile and accumulated at the lower soil layers of the columns 30 d after N addition. This suggests the movement of $NO_3$–N down the soil profile with water (Pierzynski et al., 2005; Bahmani et al., 2009). Previous research documented that 25.4 mm of irrigation or rainfall can transport soil $NO_3$–N to 150–200 mm in a loamy sand (Endelman et al., 1974). During the 30-d experiment, 100.8 mm of water was added. In the case of sandy loam soil, N moved down the profile and leached out of the column; therefore, residual mineral N was overall lower in sandy loam than in loam across fertilized treatments, including C4N1.

The $\mathrm{FNR}_{\mathrm{CTRL}}$ was much smaller than $\mathrm{FNR}_{\mathrm{ResN}}$ (Table 1-1). The $\mathrm{FNR}_{\mathrm{CTRL}}$ estimate assumes that fertilizer N enhances OM mineralization (Khan et al., 2007; Robertson et al., 2013). However, inorganic N inputs can also decrease OM mineralization by decreasing the decomposition of energy-poor OM substrates that are mineralized solely to access N-containing compounds (Moorhead and Sinsabaugh, 2006; Craine et al., 2007). Particularly, in the current study, no crops were grown, and therefore there was no OM to mineralize to make up for potential N deficiency. In a laboratory incubation study with no crops involved, Mahal et al. (2019) demonstrated that fertilizer N suppressed OM mineralization. In contrast, Kaleeem Abbasi et al. (2015) reported that control soil without amendment released a maximum of 30.9 mg N $\mathrm{kg}^{-1}$ soil on Day 28 compared with 13.7 mg $\mathrm{kg}^{-1}$ at Day 0 at 25°C and 58% water filled pore space under laboratory conditions, showing a substantial release of N into the mineral N pool. The wide variation reported in the N mineralization from soils with or without fertilizer N can be affected by applied N rate (Cahill et al., 2007), soil temperature and moisture (Deenik, 2006), and amount and type of clay in soil (Breland, 1994; Deenik, 2006). In the current study, mineralization under different treatments was not measured, and the long-term effect of char-C in soil N mineralization/immobilization is yet to be explored. Irrespective of the methods of estimating FNR, it did not vary by treatment or soil. However, the differences in $\mathrm{FNR}_{\mathrm{CTRL}}$ and $\mathrm{FNR}_{\mathrm{ResN}}$ observed in this study underscore the implications of different methods used in calculating fertilizer N recovery or use efficiency (Mahal et al., 2019) and a critical role that soil OM mineralization might play in soil N availability and N use efficiency.

## Conclusion

The benefits of decreasing $NH_3$ volatilization loss were observed with optimum rates of char addition in coarse (sandy loam) and fine-textured (loam) soils. Those char rates were up to 13.4 Mg C $ha^{-1}$ in fertilized loam and 10.1 Mg C $ha^{-1}$ in fertilized sandy loam soils. There were no adverse effects of adding char on leaching losses or $N_2O$ emissions. Field research is warranted to evaluate the potential use of char and other similar high-C-content by-products to improve N management. Further evaluation is warranted to investigate the possible adverse effects of pesticide/herbicide sorption and potential trace metal accumulation in soil, crop tissue, or grains before recommending char for agricultural use.

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**Table 1-1.** Analysis of variance results with means for different dependent variables as affected by char, soil, and their interaction.

| **Treatment** | **$NH_3$ volatilized** | | **$N_2O$ emissions** | | **$NO_3$-N leached** | | **Soil residual mineral N** | | **FNR$_{CTRL}$**[§] | **FNR$_{ResN}$**[¶] |
|---|---|---|---|---|---|---|---|---|---|---|
| **Char**[†] | g ($10^{-3}$) | % per applied N | g ($10^{-3}$) | % per applied N | g ($10^{-3}$) | % per applied N | g ($10^{-3}$) | % per applied N | % | |
| C0N0 | 0.4 | - | 0.01 b[‡] | - | 6.1 | - | 6.2 | - | - | - |
| C0N1 | 4.0 | 9.2 | 0.12 a | 0.28 | 14.3 | 20.9 | 22.8 | 42.1 | 72.5 | 97.3 |
| C1N1 | 2.8 | 6.2 | 0.11 a | 0.28 | 12.2 | 15.4 | 26.4 | 51.2 | 73.1 | 97.8 |
| C2N1 | 3.0 | 6.8 | 0.15 a | 0.34 | 14.1 | 20.4 | 24.6 | 46.7 | 74.2 | 95.0 |
| C3N1 | 3.9 | 8.9 | 0.10 a | 0.25 | 10.8 | 11.9 | 25.1 | 48.0 | 69.0 | 94.0 |
| C4N1 | 7.1 | 17.1 | 0.15 a | 0.36 | 13.6 | 19.1 | 20.9 | 37.1 | 73.7 | 98.3 |
| C4N0 | 0.3 | - | 0.01 b | - | 5.4 | - | 7.0 | - | - | - |
| *Significance* | *** | *** | *** | NS | *** | NS | *** | NS | NS | NS |
| **Soil** | | | | | | | | | | |
| Loam | 2.7 | 8.7 | 0.10 | 0.32 | 4.3 | 2.6 b | 25.4 | 66.1 a | 77.3 | 96.2 |
| Sandy Loam | 3.4 | 11.0 | 0.09 | 0.28 | 17.6 | 32.4 a | 12.5 | 23.9 b | 67.6 | 96.7 |
| *Significance* | *** | *** | NS | NS | *** | *** | *** | *** | NS | NS |
| Char X Soil | *** | *** | NS | NS | *** | NS | *** | NS | NS | NS |

[†]Char treatments were C0N0; no char and urea ammonium nitrate (UAN), C0N1; no char but UAN, C1N1; 6.7 Mg C ha$^{-1}$ and UAN, C2N1; 10.1 Mg C ha$^{-1}$ and UAN, C3N1; 13.4 Mg C ha$^{-1}$ and UAN, and C4N1; 26.8 Mg C ha$^{-1}$ and UAN, C4N0; 26.8 Mg C ha$^{-1}$ but no UAN, and UAN was applied at rate of 200 kg N ha$^{-1}$.

[‡]Means in a column followed by same lowercase letter are not significantly different. When interaction effect was significant, main effect was not reported. [§] Fertilizer N recovery based on "N difference" method. [¶] Fertilizer N recovery based on initial extractable N. ***$P < 0.001$, **$P < 0.01$, *$P < 0.05$, NS = not significant.

**Table 1-2.** Interaction effect of char and soil on $NO_3$-N leached and soil residual N.

| **Treatment** | **$NH_3$ volatilized** | | **$NO_3$-N leached** | | **Soil residual N** | |
|---|---|---|---|---|---|---|
| **Char**[†] | Loam | Sandy loam | Loam | Sandy loam | Loam | Sandy loam |
| | mg N | | | | | |
| C0N0 | 0.4 g[‡] | 0.3 g | 3.6 cd | 8.5 c | 6.7 e | 5.6 e |
| C0N1 | 3.5 e | 4.5 d | 4.4 cd | 24.3 a | 33.3 a | 12.4 cd |
| C1N1 | 2.2 f | 3.4 e | 1.5 d | 22.9 ab | 36.6 a | 16.2 c |
| C2N1 | 2.6 f | 3.4 e | 5.8 cd | 22.5 ab | 35.1 a | 14.2 c |
| C3N1 | 2.3 f | 5.4 c | 4.6 cd | 16.9 b | 32.8 a | 17.5 c |
| C4N1 | 7.6 a | 6.6 b | 7.0 cd | 20.2 ab | 26.4 b | 15.2 c |
| C4N0 | 0.3 g | 0.3 g | 3.2 cd | 7.7 cd | 7.0 de | 6.4 e |

[†] Char treatments were C0N0; no char and urea ammonium nitrate (UAN), C0N1; no char but UAN, C1N1; 6.7 Mg C $ha^{-1}$ and UAN, C2N1; 10.1 Mg C $ha^{-1}$ and UAN, C3N1; 13.4 Mg C $ha^{-1}$ and UAN, and C4N1; 26.8 Mg C $ha^{-1}$ and UAN, C4N0; 26.8 Mg C $ha^{-1}$ but no UAN, and UAN was applied at rate of 200 kg N $ha^{-1}$.

[‡] Means for each variable followed by same lowercase letters are not significantly different.

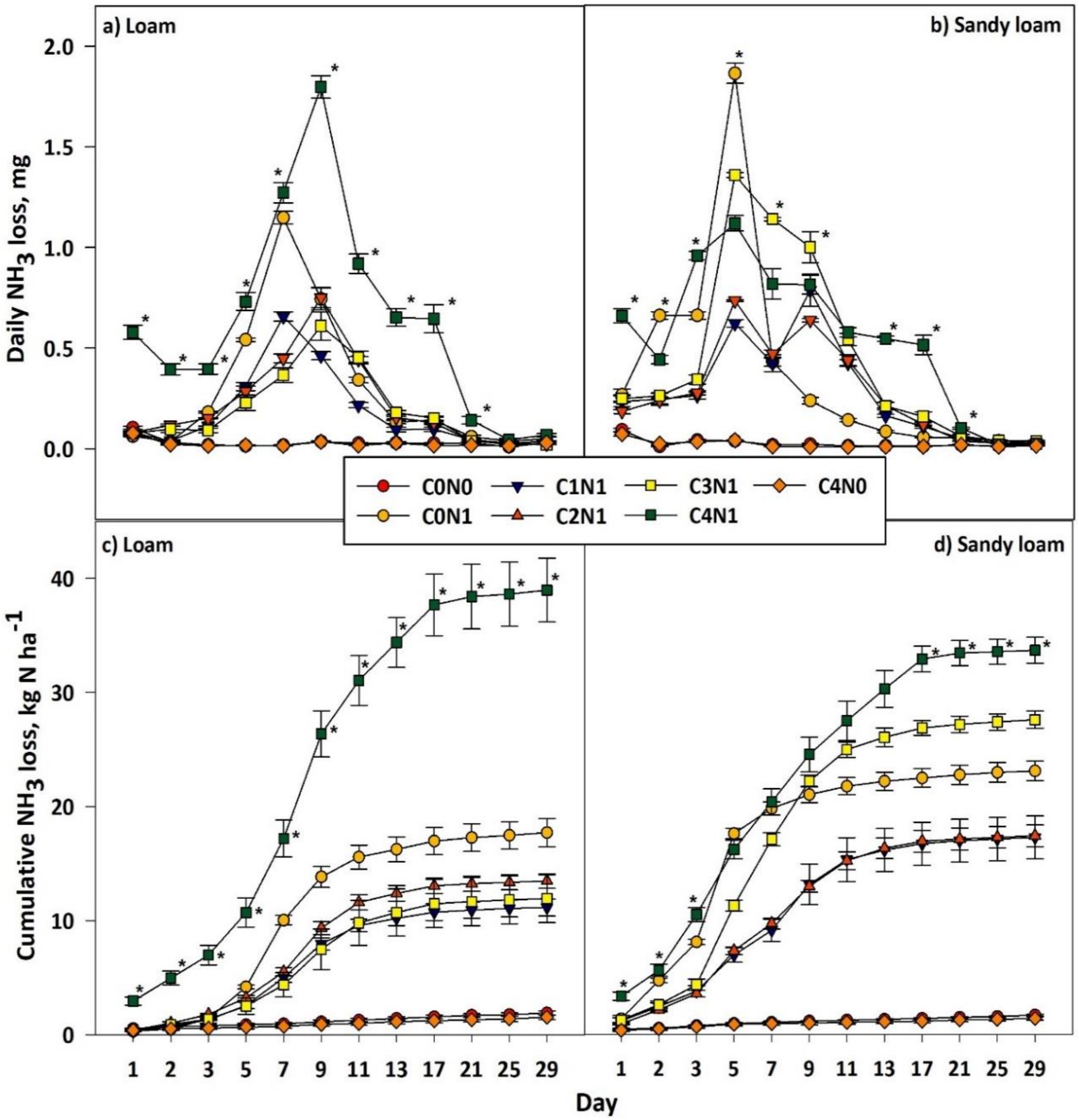

**Figure 1-1.** Daily and cumulative $NH_3$-N volatilization loss (mean ± SE; n=4) with different char treatments in a, c) loam and b, d) sandy loam soils. C0N0, no char and no urea ammonium nitrate (UAN); C0N1–C4N1, UAN at 200 kg N $ha^{-1}$ and char at 0, 6.7, 10.1, 13.4, and 26.8 Mg C $ha^{-1}$, respectively; C4N0, 26.8 Mg C $ha^{-1}$ and no UAN. *Treatment with significantly higher loss than all other treatments on a given sampling day.

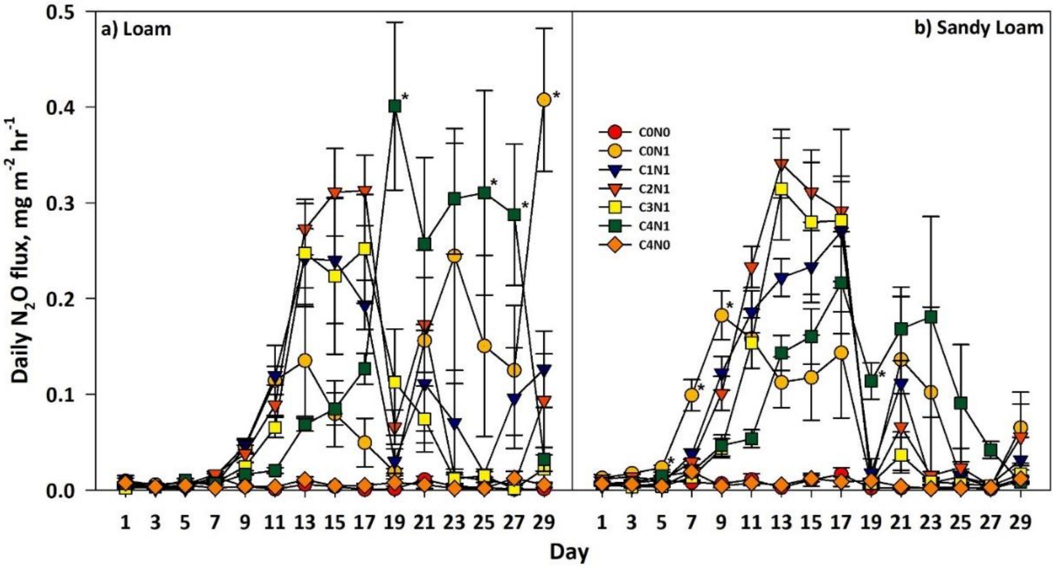

**Figure 1-2.** Daily $N_2O$ flux (mean ± SE; n=4) with different char treatments in a) loam and b) sandy loam soils. C0N0, no char and no urea ammonium nitrate (UAN); C0N1–C4N1, UAN at 200 kg N $ha^{-1}$ and char at 0, 6.7, 10.1, 13.4, and 26.8 Mg C $ha^{-1}$, respectively; C4N0, 26.8 Mg C $ha^{-1}$ and no UAN. *Treatment with significantly higher loss than all other treatments on a given sampling day.

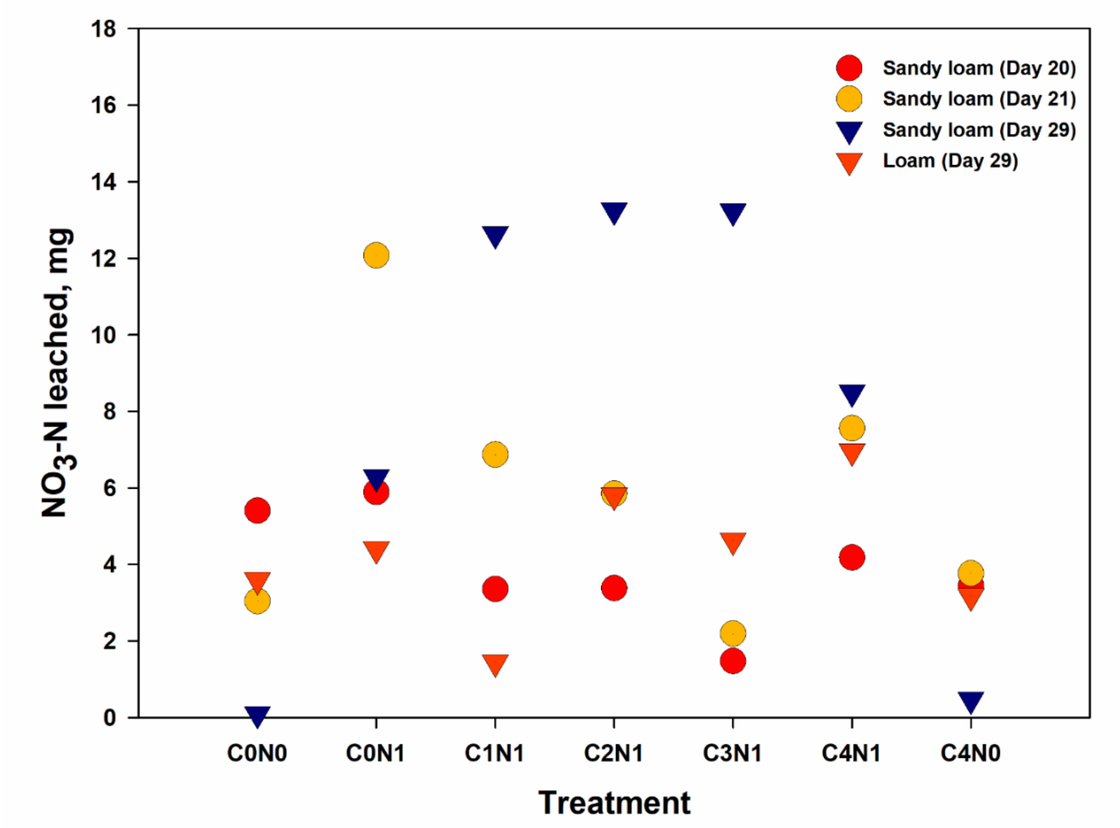

**Figure 1-3.** Amount of $NO_3$-N leached with different char treatments in loam and sandy loam soils at different leaching events. C0N0, no char and no urea ammonium nitrate (UAN); C0N1–C4N1, UAN at 200 kg N $ha^{-1}$ and char at 0, 6.7, 10.1, 13.4, and 26.8 Mg C $ha^{-1}$, respectively; C4N0, 26.8 Mg C $ha^{-1}$ and no UAN. *Treatment with significantly higher loss than all other treatments on a given sampling day.

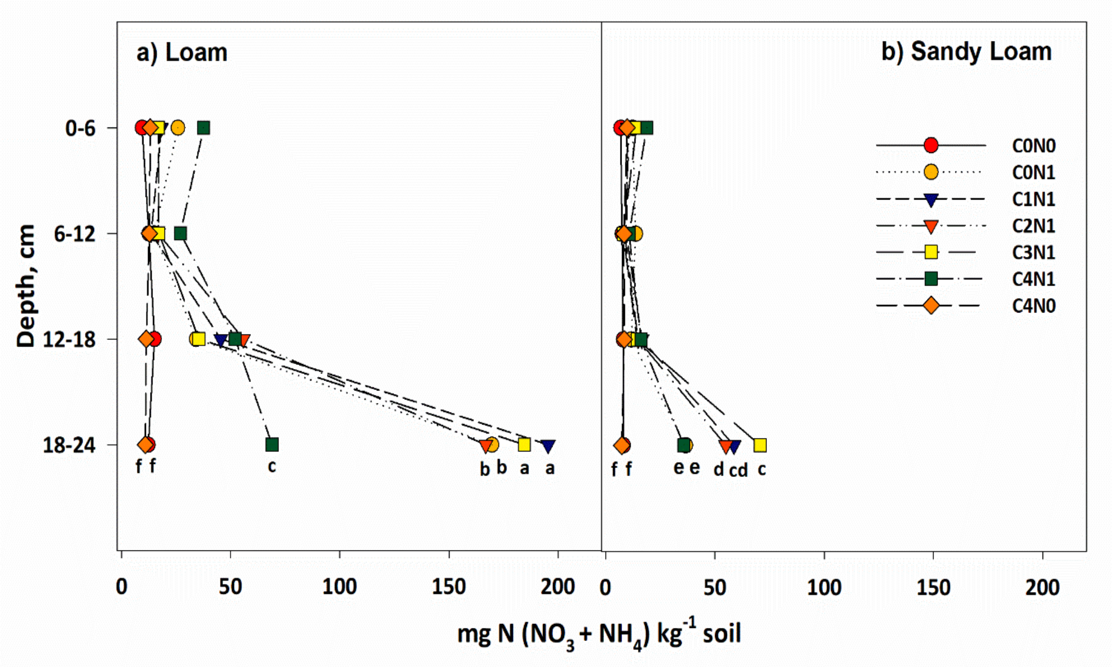

**Figure 1-4.** Soil residual N (mean; n=4) in soil profile at different char treatments in a) loam and b) sandy loam soils. C0N0, no char and no urea ammonium nitrate (UAN); C0N1–C4N1, UAN at 200 kg N $ha^{-1}$ and char at 0, 6.7, 10.1, 13.4, and 26.8 Mg C $ha^{-1}$, respectively; C4N0, 26.8 Mg C $ha^{-1}$ and no UAN. Means at 18-24 cm with different letters across both soil types are significantly different at $P < 0.05$.

# CHAPTER 2 - EFFECTS OF CHAR ON AMMONIA VOLATILIZATION FROM FERTILIZED SANDY LOAM SOIL

## Abstract

Ammonia ($NH_3$) volatilization loss adversely affects N availability in soil-plant systems and reduces crop yield as well as negatively impacts environment. Char, coal combustion residue, which contains up to 293 g $kg^{-1}$ total C by weight, has shown a reduction of $NH_3$ volatilization due to its considerably high surface area and cation exchange capacity. Besides chemical N sorption, $NH_3$ loss can be greatly affected by a shift in soil pH or urea hydrolysis due to additives. A 21-day laboratory study was conducted to determine the effects of char on soil pH, N transformations, and subsequent $NH_3$ 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 of treatment combinations were analyzed for soil pH, $NH_3$ volatilization, and residual N (urea, $NH_4$ and $NO_3$) every other day for three weeks. Daily $NH_3$ volatilization loss in fertilized treatment with char was lower than with no char on Day 6. Char application reduced cumulative $NH_3$ in fertilized treatment. Reduction in $NH_3$ loss due to char addition was evidenced by greater residual $NH_4$-N on certain days in fertilized treatment with char compared to without. Char lowered soil pH in fertilized treatments in the first week. Char did not affect urea hydrolysis process but altered soil pH and thereby reduced $NH_3$ volatilization loss in fertilized soil.

## Introduction

A global meta-analysis of 824 observations revealed that up to 64% (with an average of 18%) of applied fertilizer N at the soil surface could volatilize as ammonia ($NH_3$) and lost from the soils system (Pan et al., 2016). Besides reduction in crop N use efficiency, the volatilized $NH_3$ from fertilized agricultural land has adverse ecological impacts on environmental quality in addition to the reduction in N available for crop N production (Zaman et al., 2009; Shang et al., 2014). Ammonium ($NH_4$) based fertilizers and urea can cause soil acidification upon deposition to the ground through the process of nitrification (Van Der Eerden et al., 1998; Dong et al., 2012). Ammonia can also be a secondary source of $N_2O$ emissions and promote eutrophication of surface water bodies (Sutton et al., 2008). Among all N formulations associated with urea accounted for nearly 56% of global fertilizer N consumption, as it contains comparatively high N content, is safe to handle and readily available in granular or liquid form (Bouwman et al., 1997; IFA, 2017).

Ammonia volatilization accrues as the urea is applied to the soil surface through urea hydrolysis under favorable conditions and this process continue up to two weeks (Sommer et al., 2004). Several modifications were applied for urea fertilizers such as adding urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) to slow the urea hydrolysis (Trenkel, 2010; Nascimento et al., 2013; Silva et al., 2017). High cation exchange capacity (CEC) of zeolite (aluminosilicate mineral) when mixed with urea is also reported to reduce $NH_3$ loss (Bernardi et al., 2007; Palanivell et al., 2015). Biochars, due to presence of high surface area, can retain $NH_4$ during soil N transformation and possibly reduce $NH_3$ emissions (Steiner et al., 2010;

DeLuca et al., 2015).

In a recent publication, we reported that addition of coal char up to 13.4 Mg C $ha^{-1}$ in fertilized loam and 10.1 Mg C $ha^{-1}$ in fertilized sandy loam soils decreased $NH_3$ volatilization (Panday et al., 2020). The study documented that char reduced $NH_3$ volatilization loss from fertilized soils by 24% in loam and 26-37% in sandy loam likely from increased ammonium ($NH_4$-N) sorption and retention during soil N transformation to $NH_3$ due to its high surface area (82 $m^2$ $g^{-1}$) and high CEC (46.9 cmol $kg^{-1}$). Previous research documented that the potential for $NH_3$ volatilization loss was enhanced in soil with pH above 7.5 (Fan and Machenzie, 1993; Kissel et al., 2008). The addition of coal char has a potential to increase soil pH because the char pH is around or higher than 7.5. The soil with low $H^+$ buffering capacities has a potential for $NH_3$ volatilization as the soil pH increased when added dry urea dissolves and hydrolyzes (Ferguson et al., 1984).

Char is one of the C rich organic amendments. Char not only has high C content properties that make it a suitable material to enhance or recover soil C, but it also contains some nutrients that are essential for plant growth. Adding C rich materials can hasten the process in increasing soil organic C, and improving soil properties and crop yields in semi-arid regions such as in agricultural landscapes of western Nebraska (Blanco-Canqui et al., 2020). It is worth noting that although there was a reduction in $NH_3$ volatilization due to the sorption properties of char in previous study (Panday et al., 2020), determining effects of char on urea hydrolysis itself and soil pH would provide understanding on how char is affecting soil processes to reduce $NH_3$ volatilization. Hence, the objective of this study was to determine the effects of char addition on soil pH, urea-N transformation to $NH_3$ over 21-day laboratory incubation under adequate environmental conditions. We hypothesis that char would affect soil pH and processes that control urea hydrolysis and $NH_3$ volatilization in fertilized treatments and conserve soil N from lost to the atmosphere.

## Materials and methods

A 21-day laboratory study was conducted on Tripp fine sandy loam soil (coarse-silty, mixed, superactive, mesic Aridic Haplustolls, 0-3% slope) located at the Panhandle Research and Extension Center, Scottsbluff, NE at the University of Nebraska-Lincoln. In 2019, soil was collected from 0 to 20 cm depth from a nearby field, which had a 7.9 pH, 19 g $kg^{-1}$ organic matter, 15.0 mg $kg^{-1}$ initial extractable N ($NH_4$–N and $NO_3$–N) and 12.8 cmol $kg^{-1}$ 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 beaker 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 and then urea-N was applied to the soil surface and left there in each beaker. Char properties used in this study (Appendix 1- 2) is similar to the char used in Panday et al. (2020).

The current study was arranged in randomized complete block design with four replications (replication was considered as block factor). The char was added at two rates that corresponded to 0 and 13.4 Mg C $ha^{-1}$ (equivalent to 0 and 44.6 Mg char $ha^{-1}$). The urea was also added at two rates that corresponded to 0 and 200 kg N $ha^{-1}$. The amounts of char and urea added represent the amount of char and urea added in the field study for average yield production. The two rates of char and urea were mixed to generate four fertilizer treatment combinations as follow: 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). The fertilizer treatments were mixed with soil in beakers at four replications. The total number of treatments was 176 (4 treatment × 4 replications × 11 set).

The beakers containing soil and different treatments were closed with a lid and consider as Day 0. The beakers were placed in a constant room temperature (25 °C) which was maintained during the entire 21-day experiment. On every other day, beaker's lids were opened for 15 min for air circulation and to avoid $CO_2$ gas accumulation inside the beaker. There were 11 sets of all treatment combinations and each treatment was analyzed for pH, $NH_3$ volatilization and residual N (urea, $NH_4$ and $NO_3$) on every other day (Day 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20). Additional 11 beakers were containing only soil were used for the water losses with the beakers contacting treatments.

Ammonia volatilization loss was measured with each treatment combination using acid trap method. A sponge of 2 cm diameter 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 acid trap was installed on Day 0 and each acid trap was exchanged with fresh ones every other day as the treatments were sampled (Day 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20. Acid traps were removed from the beaker and rinsed with a 2M KCl solution and squeezed multiple times to extract the solution.

After removing the acid trap, 10 mL deionized water was added to soil in beakers to adjust for water losses during the venting process. At each sampling date, one set of treatments were used for multiple analysis. The analysis consisted of soil pH which was determined by a glass electrode (soil to water ratio, 1:1). The urea-N, $NH_4$-N, and $NO_3$-N were evaluated by extraction using 2M KCl-PMA solution (Potassium Chloride-Phenyl Mercuric Acetate) 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 2M KCl (Douglas and Bremner, 1970). Each beaker containing soil suspension (10 g soil) was placed in a shaker for 15 minutes 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 et al., 2015). Ammonia trapped in acid trap solution, as well as $NH_4$-N and $NO_3$-N present in soil solutions, were determined by using a flow analyzer (AA3 SEAL analytical, Germany).

Cumulative $NH_3$ loss was calculated by summing $NH_4$-N across all collection dates. To estimate the cumulative $NH_3$ volatilization loss per applied N in fertilized soil (%), 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 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, 2015) with treatment as fixed effect and replication as random effect. The analysis of variance (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 $P < 0.05$ was considered significant unless otherwise indicated.

## Results

### Ammonia volatilization

Most of the $NH_3$ volatilization (about 70% of total $NH_3$ volatilization in fertilized treatment) occurred within the first week of the experiment with the addition of 200 kg N $ha^{-1}$ (Figure 2-1). The highest peak of daily $NH_3$ volatilization loss was observed on Day 4 following treatment application. There was a significant effect of treatment on daily $NH_3$ volatilization loss up to Day 8 (Figure 2-1). The daily $NH_3$ volatilization loss in the treatment C0N1 was greater than C1N1 only on Day 6. Both fertilized treatments (with and without char) had greater daily $NH_3$ loss than the unfertilized on Days 2, 4, and 6. The C0N1 treatment exhibit the highest $NH_3$ volatilization than any other treatment. Cumulative $NH_3$ volatilization loss across treatments ranged from 0.006 to 0.042 mg $g^{-1}$ N in this 21-day laboratory study. There was a significant treatment effect on cumulative $NH_3$ volatilization loss (Table 2-1). Both fertilized treatments (C1N1 and C0N1) had a greater cumulative $NH_3$ loss than unfertilized. Char application in C1N1 reduced cumulative $NH_3$ loss in the fertilized treatment by 15.3% compared with similar N-rate with no char addition in C0N1. However, char addition exhibited no $NH_3$ volatilization when urea was not added in C0N0 and C1N0.

## Soil pH

There was a significant effect of treatment on soil pH throughout the study period (Figure 2-2). At the beginning of experiment, soil pH increased to around 8.0 in the treatment C0N1 (Figure 2-2). The same treatment continued to have the highest soil pH among all treatments until Day 6 and then observed a drop in pH by 0.5 units. Soil pH was consistently lower in the treatment C1N1 than C0N1 until Day 10, except on Day 8. On and after Day 10, soil pH with the C0N1 was $\leq 7.1$ and with the C1N1 between 7.1 and 7.3. Between unfertilized treatments, soil pH was around 7.8 in the beginning and starting from Day 8, it dropped to and stayed at 7.7 for C0N0 and around 7.5 for the treatment C1N0.

## Soil residual nitrogen (urea, ammonium, and nitrate)

Soil residual urea-N and $NH_4$-N were higher in fertilized treatments with or without char (were not different from each other) compared to unfertilized treatments until Day 6 and Day 10, respectively (Figure 2-3 and Figure 2-4). Soil residual urea-N did not differ with the addition of char between the C0N1 and C1N1 in the first 4 days. Soil residual $NH_4$-N exhibited similar behavior in both fertilized treatments on Days 0, 2, 8 and 10, but in different magnitude. The C1N1 treatment had a greater $NH_4$-N than C0N1 on Days 4 and 6. The addition of char did not influence soil residual $NH_4$-N when urea was not added (C1N0). There was a significant treatment effect on soil residual $NO_3$-N throughout the study period (Figure 2-5). Both fertilized treatments had higher soil residual $NO_3$-N compared to unfertilized treatments from Day 6 to the end of the study period. Soil residual $NO_3$-N in the C1N1 was higher than C0N1 on Days 8, 10, 14, 16 and 18.

## Soil total nitrogen

Soil used in the study had 0.015 mg $g^{-1}$ residual inorganic N ($NH_4$–N and $NO_3$–N) and 0.1 mg $g^{-1}$ urea-N was added to fertilized treatments. Total-N ($NH_4$–N and $NO_3$–N) in glass beaker ranged from 0.013 to 0.022 mg $g^{-1}$ N in unfertilized treatments and 0.703 to 0.122 mg $g^{-1}$ N in fertilized treatments (Figure 2-6). Total-N was always greater in fertilized than unfertilized treatments (Figure 2-6). Both fertilized treatments had 0.075 mg $g^{-1}$ N on Day 0 compared to other days which had a total N of > 0.10 mg $g^{-1}$.

## Discussion

Fertilizer is the primary source for $NH_3$ volatilization which can increase with increasing N application rate, especially with surface broadcast compared to sub-surface banding or deep placement (Cai et al., 2002; Jantalia et al., 2012). Sommer et al. (2004) and Reichmann et al. (2013) demonstrated that $NH_3$ volatilization is dependent on urea hydrolysis as influenced by soil temperature and moisture which may raise $NH_4$/ $NO_3$ 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 32 to 35% water-filled pore space throughout the experiment period allowed for considerable $NH_3$ volatilization loss (up to 37.80% of applied N). These losses aligned with other studies that reported $NH_3$ loss of 15 to 64% of applied N from a surface applied urea-N fertilizer (Vaio et al., 2008; San Francisco et al., 2011; Siddique et al., 2019).

Cation exchange capacity and N fixation capacity can affect soil $NH_3$ volatilization, likely because these soil properties control the amount of available total applied N near soil surface (Ferguson et al., 1984). Clay minerals are capable of fixing total applied N in soil, which can reduce the pool of available N for $NH_3$ volatilization (Pelster et al., 2018). The reduction in $NH_3$ volatilization in char addition fertilized treatment by 15.3% compared to no char addition fertilized treatment was probably related to increased char sorption N because of high surface area and CEC associated with char compared to soil. Our observation agreed with previous research that documented a reduction with $NH_3$ volatilization with char addition in fertilized treatment due to increased sorption of N related to high char surface area and CEC (Wang and Alva, 2000; Panday et al., 2020).

Ammonium ($NH_4$) is the predominant form at pH below 7.5 (Fan et al., 1993; Sherlock et al., 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 was 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). The dilution effect of fly ash, another coal combustion residue such as char used in this experiment, on pH has been reported by Lai et al. (1999).

Reduction in $NH_3$ loss in char fertilized treatment coincided with greater residual $NH_4$-N in that treatment than in no char fertilized treatment on Days 4 and 6. Prolonged and higher presence of $NH_4$-N can eventually lead to a greater $NH_3$ emission (Peng et al., 2015; Zaman et al., 2008). However, it is important to note that KCl-extractable $NH_4$-N does not directly correlate with $NH_3$ emissions because it includes the proportion of free $NH_4$-N in solution and bound $NH_4$-N in CEC pools (Pelster et al. 2018). Those $NH_4$-N bound to CEC pools are only moderately available and most of the $NH_3$ volatilization loss would derive from free $NH_4$-N in soil solution (Witter et al., 1989; Pelster et al., 2018). Therefore, a greater $NH_4$-N in char fertilized 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 two weeks of urea application despite the presence of KCl-extractable $NH_4$-N in soil.

The residual $NH_4$-N was higher in char fertilized treatment compared to no char fertilized treatment on Day 4 and 6. Besides, char properties of increased sorption N, addition of char with pH 7.6 which was less than the soil pH of 7.9 helps in reducing the char fertilized treatment pH to 7.3 compared to no char fertilized treatment pH to 7.8 on Day 6, thus reducing $NH_3$ volatilization. This explains why there was lower daily $NH_3$ volatilization in char fertilized treatment compared to no char fertilized treatment 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; Sherlock et al., 1994; Panday et al., 2020).

When compared to char and no char fertilized treatments, a reduction in $NH_3$ loss coincided with a trend of reduction in residual $NH_4$-N and increase in residual $NO_3$-N after Day 4. This trend also coincided with reduction in soil pH of char and no char fertilized treatments from Day 6. However, there was no significant difference in total N (sum of $NH_4$–N and $NO_3$–N) between char and no char fertilized treatments, which means only N was converted from one form to another form. When $NO_3$-N form becomes dominant, then $NH_3$ volatilization is minimum or absent. Microbial processes are involved in $NO_3$-N reducing mechanism in soil which are responsible for loss $NO_3$-N and production of potential greenhouse gas, nitrous oxide ($N_2O$) (Giles et al., 2012).

Total inorganic N in 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 beginning of the experiment (soil mineral N present and added) could be due to soil N mineralization (Robertson and Groffman, 2007; Anderson et al., 2010). Maximum N mineralization occurs when soil temperatures are between 25 and 35°C (Stark and Firestone, 1996) and soil moisture is near field capacity (Stanford and Epstein, 1974; Cassman and Munns, 1980). A 28-day laboratory study reported a 3.5 mg N $kg^{-1}$ mineralization in sandy loam soil (Knoepp and Swank, 2002). Another study reported an approximately 310 mg N $kg^{-1}$ mineralization in a 312-day incubation experiment under Waimea sandy loam soil (Deenik, 2006).

## Conclusion

Char rate at 13.4 Mg C $ha^{-1}$ was effective in reducing $NH_3$ volatilization from fertilized soil by lowering soil pH. In addition to its properties of high surface area, CEC and total C content, char's 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 other soil N cycle processes as well. Further research is warranted to evaluate the potential use of char in farmland to reduce $NH_3$ losses and enhance N use efficiency (NUE) for crop production.

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**Table 2-1.** Mean cumulative $NH_3$ volatilized as affected by treatment.

| **Treatment**[†] | **Cumulative $NH_3$ volatilized,** mg N g$^{-1}$ |
|---|---|
| C0N0 | 0.012 c[‡] |
| C0N1 | 0.039 a |
| C1N0 | 0.010 c |
| C1N1 | 0.033 b |

[†] 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 in a column followed by same lowercase letter are not significantly different.

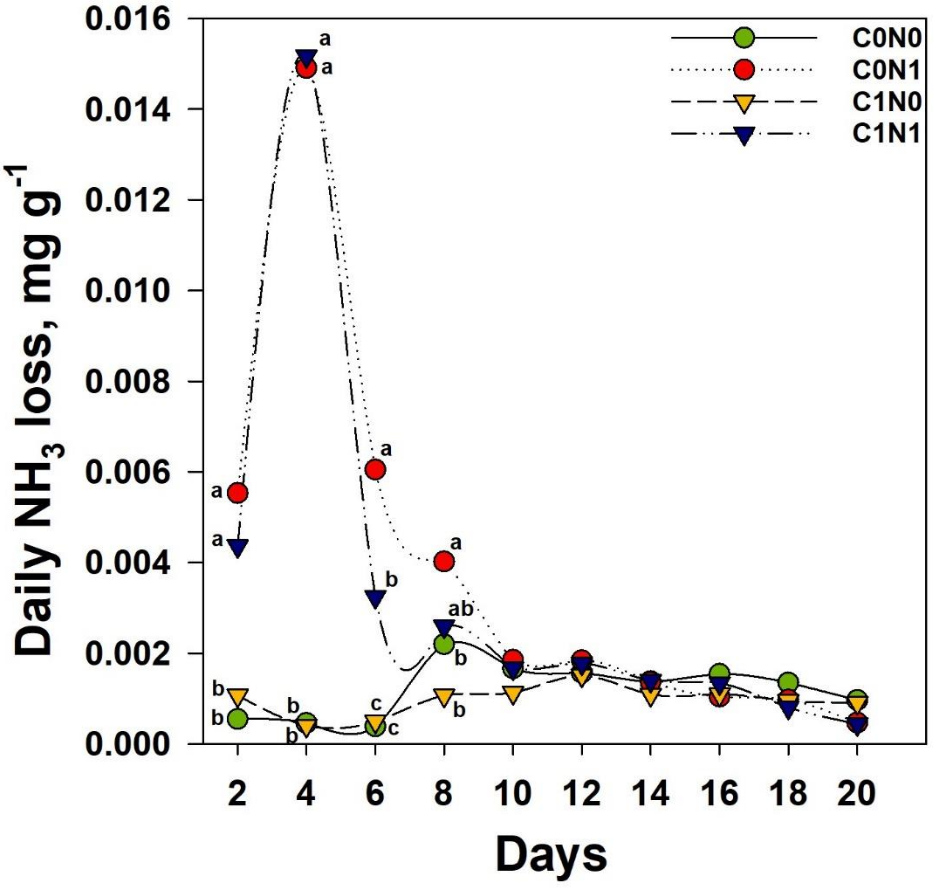

**Figure 2-1.** Daily $NH_3$ volatilization losses under different treatments. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha$^{-1}$ with no char (C0N1), char at 13.4 Mg C ha$^{-1}$ with no fertilizer (C1N0) and char at 13.4 Mg C ha$^{-1}$ with urea at 200 kg N ha$^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

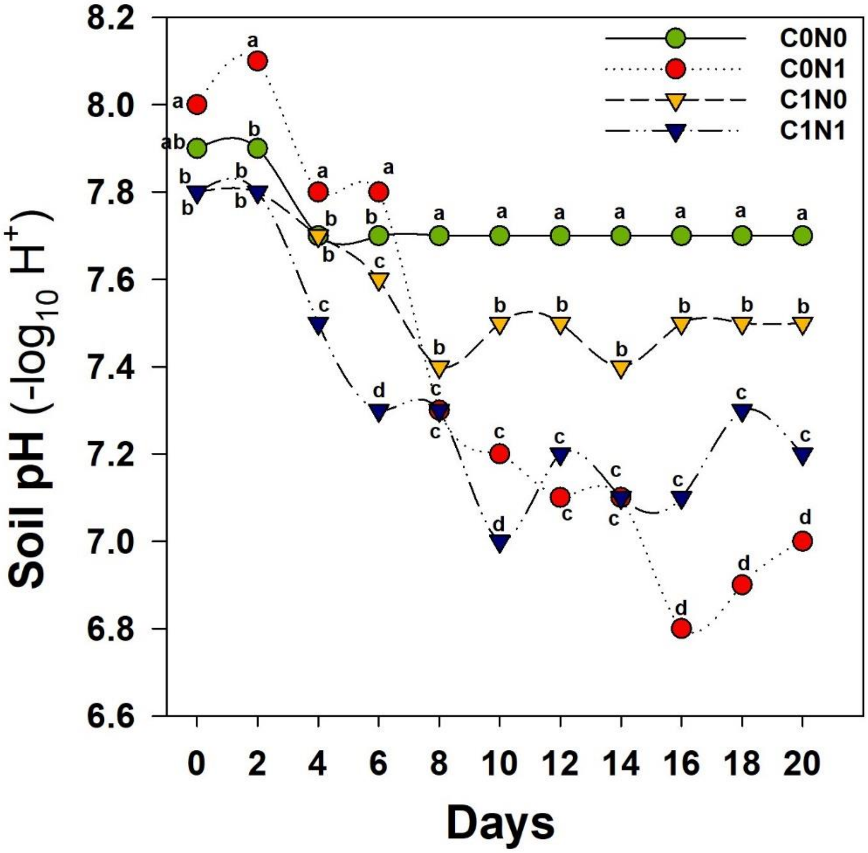

**Figure 2-2.** Daily soil pH under different treatments. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha$^{-1}$ with no char (C0N1), char at 13.4 Mg C ha$^{-1}$ with no fertilizer (C1N0) and char at 13.4 Mg C ha$^{-1}$ with urea at 200 kg N ha$^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

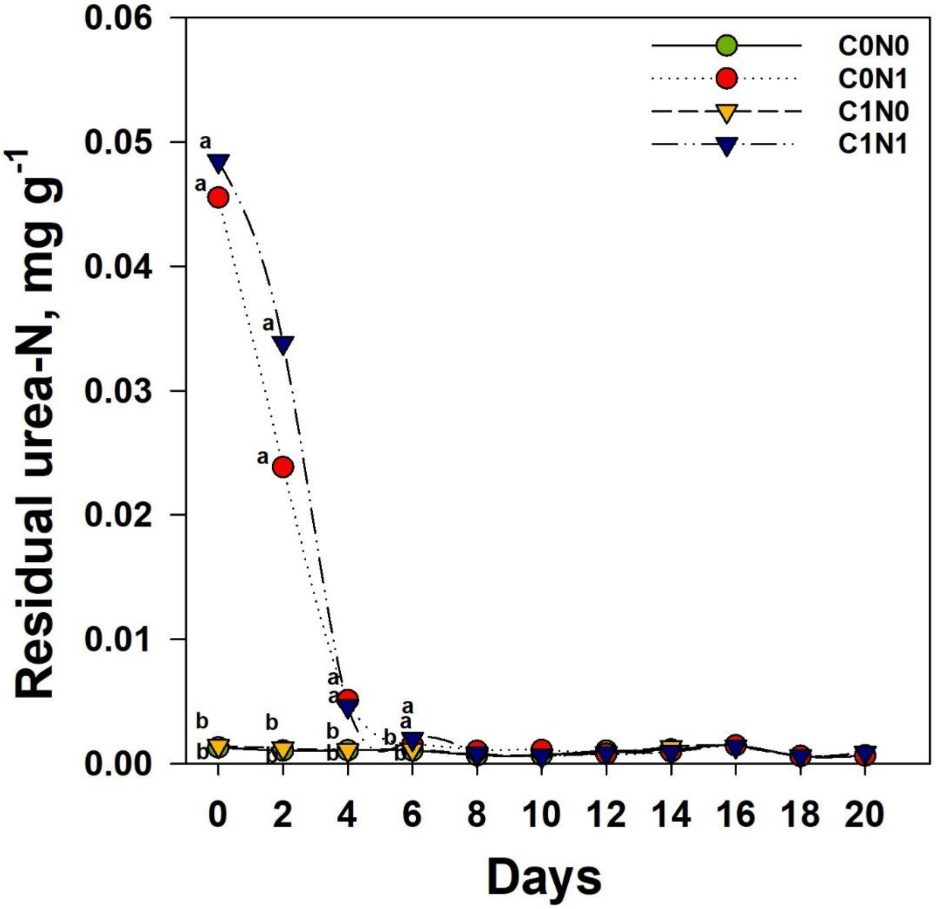

**Figure 2-3.** Daily soil residual urea-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha$^{-1}$ with no char (C0N1), char at 13.4 Mg C ha$^{-11}$ with no fertilizer (C1N0) and char at 13.4 Mg C ha$^{-1}$ with urea at 200 kg N ha$^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

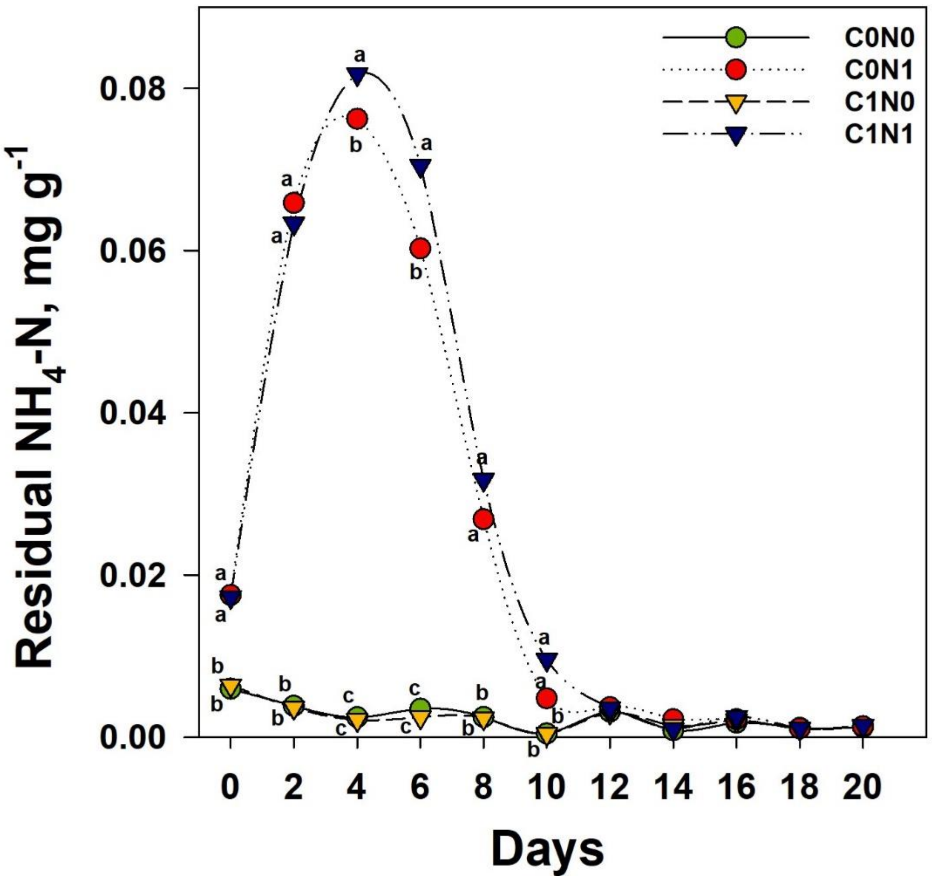

**Figure 2-4.** Daily soil residual $NH_4$-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N $ha^{-1}$ with no char (C0N1), char at 13.4 Mg C $ha^{-1}$ with no fertilizer (C1N0) and char at 13.4 Mg C $ha^{-1}$ with urea at 200 kg N $ha^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

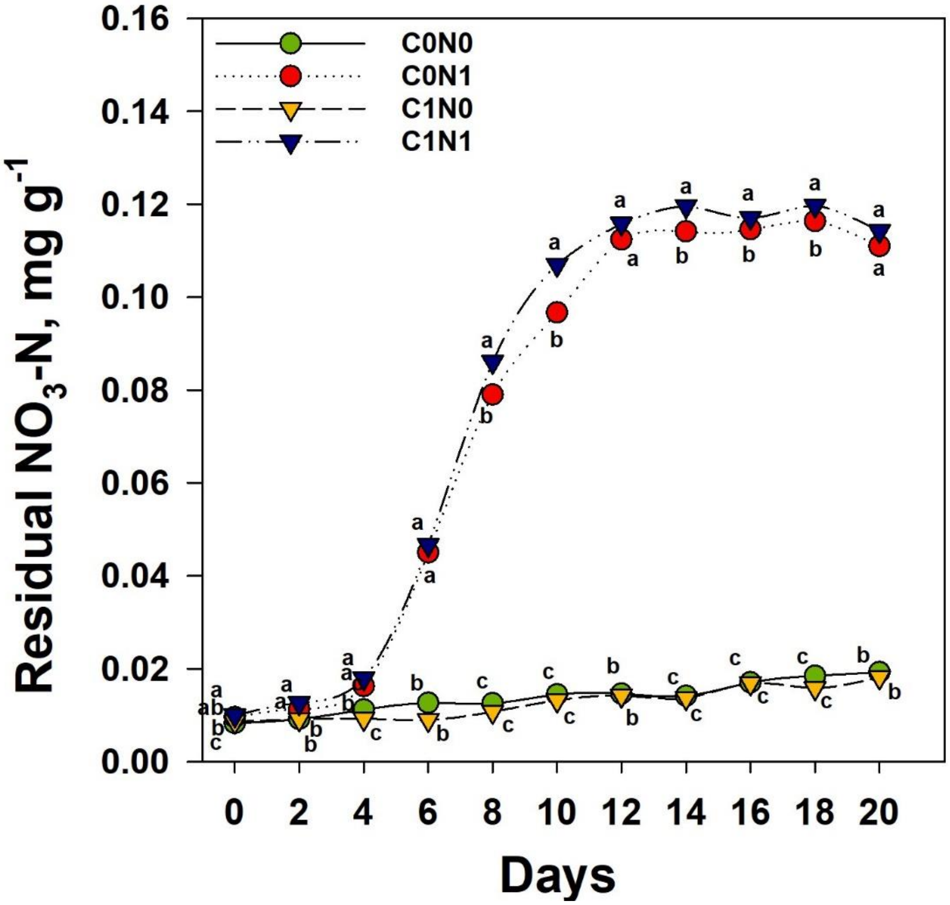

**Figure 2-5.** Daily soil residual $NO_3$-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N $ha^{-1}$ with no char (C0N1), char at 13.4 Mg C $ha^{-1}$ with no fertilizer (C1N0) and char at 13.4 Mg C $ha^{-1}$ with urea at 200 kg N $ha^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

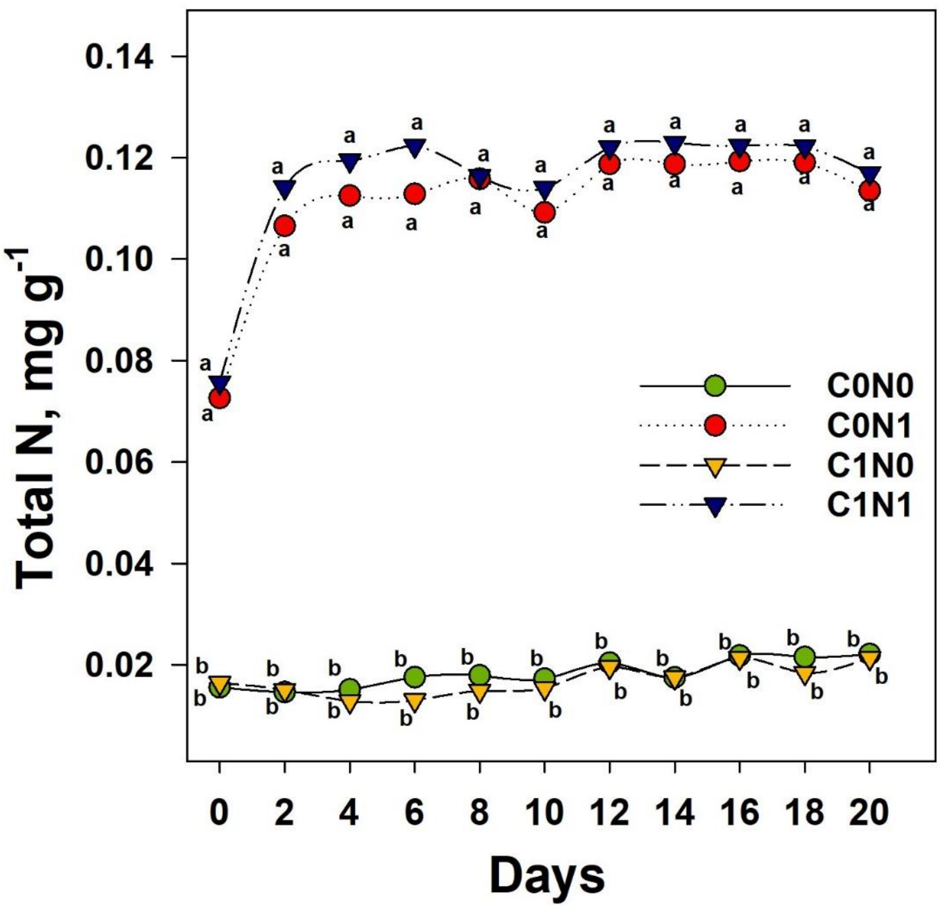

**Figure 2-6.** Daily soil total-N under different treatment. Treatments included control with no char or urea (C0N0), urea fertilizer at 200 kg N ha$^{-1}$ with no char (C0N1), char at 13.4 Mg C ha$^{-1}$ with no fertilizer (C1N0) and char at 13.4 Mg C ha$^{-1}$ with urea at 200 kg N ha$^{-1}$ (C1N1). Means with different letters across treatments on a given sampling day are significantly different at $P < 0.05$.

# CHAPTER 3- POTENTIAL AMENDMENTS FOR IMPROVING PRODUCTIVITY OF A LOW CARBON SEMI-ARID SOIL

## Abstract

Applying soil amendments with high C content can potentially improve soil properties and increase crop yields. This strategy could be particularly valuable in semi-arid regions such as western Nebraska with low C soils because of intensive tillage, erosion, high pH and frequent droughts. Thus, the objective of this 3-yr (2017-2019) field study was to evaluate the effects of organic amendments such as char, biochar, composted manure, and municipal compost on soil C, soil chemical properties, crop nutrient uptake, and crop yields in a low C (7 g $kg^{-1}$ organic C) sandy loam soil with limited productivity near Scottsbluff, NE. The field was planted to dry bean (*Phaseolus vulgaris*) in 2017, maize (*Zea mays* L.) in 2018, and sugar beet (*Beta vulgaris* L.) in 2019. Char (22.3, 44.6, 66.9, 89.2, and 133.8 Mg $ha^{-1}$; equivalent to 6.7, 13.4, 20.1, 26.8, and 40.2 Mg C $ha^{-1}$), biochar (5.6 and 11.2 Mg $ha^{-1}$), composted manure (33.6 and 67.2 Mg $ha^{-1}$), and municipal compost (33.6 and 67.2 Mg $ha^{-1}$) were applied and incorporated. Char at 22.3, 44.6 and 133.8 Mg $ha^{-1}$ and municipal compost rate at 67.2 Mg $ha^{-1}$ increased soil organic C (SOC) concentration compared to the control. Char at all rates and biochar at 11.2 Mg $ha^{-1}$ increased uptake of Fe in maize in the second year and char at 133.8 Mg $ha^{-1}$ increased Fe in sugar beet leaf tissues in the third year. Maize yield was higher by 10.7 to 30.6% at all char rates except with the lowest rate. Municipal compost and composted manure at 67.2 Mg $ha^{-1}$ also increased maize yield by 18.0 to 24.7%. Since biochar was applied at much lower rates on soil than other amendments, biochar had small or no effects. Results

suggest that locally available products such as char, municipal compost, or compost manure can be potential soil amendments to increase soil productivity in low C soils.

## Introduction

Soil degradation, nutrient depletion, and declining in crop productivity are major constraints, particularly in semi-arid region of the Great Plains, United States of America (MacCarthy et al., 2010; Rajashekhara Rao et al., 2012; Mikha et al., 2017). This region of the USA was exposed to the historic Dust Bowl of the 1930's as the cropland lost its top productive surface rich with organic material and decreased land productivity (Tanaka and Aase, 1989; Stewart, 2004; Larney et al., 2012). The recovery of crop land from soil top losses and decline in productivity may require long period of time (Pimentel and Burgess, 2013). Previous research documented that the Dust Bowl caused some cropland to loss approximately 27-30 cm of the top soil and decline in land productivity both of which are not yet recovered (Mikha et al., 2014 and 2017). Pimentel and Burgess (2013) also documented that the losses of 1 mm thickness from one hectare of cropland could be equivalent to 15 t $ha^{-1}$ of soil surface and nutrients that could require about 20 years to be recovered in cropland production. The soils in the Great Plains region of the USA are characterized by low soil organic C (SOC) and low productivity due to intensive tillage, low precipitation, wind erosion, and frequent droughts (Nielsen and Calderon, 2011; Mikha et al., 2013; He et al., 2017). Hence it is important to improve soil properties for enhancing soil productivity and optimizing the benefits of inputs in semi-arid region of the Great Plains.

Organic amendments can be alternative and/or complement to inorganic fertilizer for enhancing soil productivity (Uzoma et al., 2011). Extensive use of inorganic fertilizers in semi-arid regions is not favored due to soil with low crop yield potential and subsequent reduced return on input cost (Wang et al., 2016). In contrast, organic amendments could supply essential plant nutrients as well as C to improve soil properties and productivity (Sanderman et al., 2009). For instance, composted manure was reported to improve soil physical and chemical properties and increase crop yield (Hergert and Nielsen, 2010; Hepperly et al., 2013; Maharjan and Hergert, 2019). However, in some cases, its benefits can be minimal due to their bulky nature and supply low amounts of nutrients and organic matter (Lentz et al., 2014; Schulz et al., 2014). Municipal compost, which is prepared under controlled aerobic microbial process to decompose organic matter present in municipal solid waste, is another potential organic amendment that was found to benefit soil, crop, and environment (Rodd et al., 2002; Hosseinpur et al., 2012; Mbarki et al., 2018). It can be particularly beneficial to restore degraded soils of semi-arid regions by promoting the activity of microbial communities in the soil (Jedidi et al., 2004; Bouzaiane et al., 2007).

Furthermore, adding C-enriched materials such as char and biochar that contain more C compared to composted manure or municipal compost could be a more effective strategy to increase soil C, improve other soil chemical properties and, thus enhance soil productivity. For example, char, which is the residue from the inefficient burning of coal, contains up to 293 g $kg^{-1}$ C and its application at optimal levels to fertilized soils can reduce ammonia volatilization loss (Panday et al., 2020). Blanco-Canqui et al. (2020) also found that char application increased SOC although it benefits on soil properties or crop yields appeared to be limited. Also, interest in using biochar for sequestering C, reducing greenhouse gas emissions, improving soil properties, and increasing crop yields is increasing (Filiberto and Gaunt, 2013; Smith, 2016; Kätterer et al., 2019).

There is a caveat in using some of potential soil amendments as they can contain toxic compounds, such as heavy metals and pesticides, particularly in industrial by-products such as char (Mantovi et al., 2003; Wuana and Okieimen, 2011). When such amendments are incorporated into soil, it may have toxic effects on microorganisms, crops, and human health (Antonious, 2016; Mahar et al., 2016). This warrant should be given special attention to determine any potential accumulation of toxic constituents from soil amendment in soil, plant tissue or grains before use in agricultural soils.

The objective of this study were to evaluate the effects of biochar, char, composted manure, and municipal compost on SOC, soil chemical properties, crop nutrient uptake, and crop yield in a low yielding soil at the semi-arid region of western NE. We hypothesized that application of organic amendment improves SOC, soil chemical properties, crop nutrient uptake, and crop yield.

## Materials and methods

A field trial was conducted at a grower's field in Scottsbluff, NE in 2017-2019. The soil at the study site is a Tripp very fine sandy loam (Coarse-silty, mixed, superactive, mesic Aridic Haplustolls) with <1% slopes. Soil pH was 8.2 and SOC was equivalent to 7 g kg$^{-1}$. The hills in the farmer's field were leveled for easy management. This levelling exposed the sub-surface soil to the surface and moved the surface soil to the lower section of the field. The study site fall within the area that lost the surface soil for levelling and the sub-surface soil was exposed. The chosen study site exhibit low productivity and high alkaline soil property. Monthly weather data for the entire trial period and long term (1981-2010) weather data were collected from a nearby weather station associated with High Plains Regional Climate Center (HPRCC, 2019).

The experimental design was a randomized complete block with four replications, resulting in 48 plots in total. Each plot size was 6.1 × 6.1 $m^2$. The treatment included:

1) no amendment, or control,
2) five levels of char: 22.3, 44.6, 66.9, 89.2, and 133.8 Mg $ha^{-1}$ (equivalent to 6.7, 13.4, 20.1, 26.8, and 40.2 Mg C $ha^{-1}$),
3) two levels of biochar: 5.6 and 11.2 Mg $ha^{-1}$,
4) two levels of composted manure: 33.6 and 67.2 Mg $ha^{-1}$,
5) two levels of municipal compost: 33.6 and 67.2 Mg $ha^{-1}$.

Char used in this field study was the same coal combustion residue from a sugar factory in Scottsbluff, NE, where it was passed through an 8 mm sieve to remove foreign materials before to spread in field. Additional details about char is given in Appendix 1- 2. Properties of char that was used in the experiment. Char rates were selected up to 133.8 Mg $ha^{-1}$ as the highest end, mainly for economic, i.e., cost associated with transport and field application and an effort to simulate on-farm practices. Biochar, prepared from pine trees, was obtained from High Plains Biochar LLC, WY. Composted manure was obtained from a local feedlot and municipal compost from the City of Scottsbluff. The chemical properties of the amendments is in Table 3-1. All treatments were applied relatively uniform to the plots through manual distribution and incorporated into 0-15 cm soil depth immediately with the disc harrow in the spring of 2017 (only one time application). Tillage operations were carried out for land preparation every year.

The treatment plots were planted to dry bean (*Phaseolus vulgaris*) in 2017, maize (*Zea mays* L.) in 2018 and sugar beet (*Beta vulgaris* L.) in 2019. Dry bean was planted on 1st June 2017. Maize was planted on 4th May 2018 and sugar beet on 6th May 2019. Except for treatment application and crop harvest, all other management practices, including fertilizer application followed typical farming practices of the producer. Those fertilizers were ammonium nitrate (34-0-0), triple superphosphate (0-20-0), and muriate of potash (0-0-50) and applied to all plots to ensure optimal level for crop performance. No micronutrients were added to experimental plots.

During the growing season, aerial imagery was taken early in the season (after emergence) to observe visual color differences due to applied treatments in 2017. In 2018, soil samples from the top 20 cm were collected from all 48 treatment plots before maize planting. Each sample consisted of a composite of 6 cores collected with a 3 cm diameter probe. Collected soil samples were analyzed for $pH_{1:1}$, organic C, N, P, K, Ca, Mg, S, Fe, B, Zn and CEC. Crop tissue samples from recently matured maize and sugar beet leaves were collected for nutrient analysis in 2018 and 2019. Twenty recently matured leaves below the whorl from 20 maize plants per plot were collected in 2018 whereas four recently matured leaves from four plants per plot were collected for sugar beet crop tissue samples in 2019.

Dry bean and maize were hand-harvested from the middle two rows of 1.5 m each from all treatment plots on 27th September 2017 (dry bean) and 22nd October 2018 (maize). Sugar beet was harvested from middle two rows of 1.5 m each using a single row digger (Kodiak Manufacturing., Inc. Charleston, TN) on 3rd October 2019. Dry bean and maize grain associated with char amendment treatment plots were analyzed for selected heavy metals.

The effects of amendment types and rates on parameters studied (SOC, soil chemical properties, crop nutrients uptake, and yields) were tested using PROC GLIMMIX procedure in SAS software v. 9.4 (SAS, 2015) with amendments, year and their interaction were considered as fixed effects. The replications were considered as random effects. The relative yield was calculated by dividing yield for each treatment by the highest yield in the block each year. When main or interaction effects were significant, means were separated by the least square means (LSD) test (Littell et al., 2006). A paired t test was conducted to determine SOC in amendment treatments relative to the control treatment. Statistical significance was evaluated at $P < 0.05$ unless otherwise stated.

## Results

### Weather

The average annual temperatures at the study site were 9.8 °C in 2017, 8.9 °C in 2018 and 5.4 °C in 2019 compared to 9.4 °C in a 30-year average (1981-2010) (Figure 3-1). The average annual precipitation was 439 mm in 2017, 539 in 2018, and 557 in 2019. The annual precipitation throughout the study period (2017-2019) exhibited at least 10% greater annual precipitation than a 30-year average (Figure 3-1). During the growing season (May to October), average ambient temperatures throughout the study period were within 1.0 to 1.5 °C of the 30-year average. Occasionally, the ambient temperatures were greater that the 30-year average such as in May of 2017 by 1.6 °C, in October of 2018 by 1.7 °C and in 2019 during May by 4.5 °C and October by 4.8 °C. Growing season precipitation from May to October varied by year. Compared to 30-year average, the growing season precipitation was 2.5% less in 2017, 54.1% higher in 2018, and 37.4% higher in 2019 (Figure 3-1). In addition to the precipitation variability, the hail on 15th August of 2019 damaged sugar beet crop and affected its ripening stage. Throughout the growing season, 2019 was cooler followed by 2017 than 2018, resulting a slower rate of growing degree days accumulation (Appendix 3- 1).

### Crop leaf tissue

The dry bean in 2017 and the maize in 2018, crop tissues exhibited chlorotic symptoms in early spring with all treatments except for the treatment that received char (Figure 3-2). In 2018 crop nutrient concentrations such as N, Fe, and B in maize leaf tissue were among the highest tissue uptake, particularly char at the highest addition rates (66.9, 89.2, and 133.8 Mg $ha^{-1}$) compared to the other amendments and the control treatment (Table 3-2). Greater Fe uptake in sugar beet leaf tissue was observed in amendment treatments at the high rates compared with low rates and compared to control in 2019 (Table 3-3). In 2018, N concentration in maize leaf tissue was 2.5-5.5% higher while B concentration was 32.2-35.3% higher when char was applied at rates $\geq$ 66.9 Mg $ha^{-1}$ compared to control (Table 3-2). Also, Fe concentration in maize leaf tissue linearly increased ($r^2$= 0.96; $P$= 0.001) with increasing char rates. In 2019, Fe concentrations in sugar beet leaf tissue were 117.8%

higher with char applied at 133.8 Mg ha$^{-1}$. Biochar did not have large effects but increased Fe concentration by 45% when applied at 11.2 Mg ha$^{-1}$ compared to control treatment.

### Crop yield

Crop yield across the amendment treatments ranged from 1.18 to 3.43 Mg ha$^{-1}$ for dry bean in 2017, 11.30 to 17.08 Mg ha$^{-1}$ for maize in 2018 and 8.70 to 16.06 Mg ha$^{-1}$ for sugar beet in 2019 (Table 3-4). Dry beans and sugar beet crops were not influenced by amendments types and rates. Maize crop production was highly influenced by char amendments especially at 133.8 and 66.9 Mg ha$^{-1}$ and with municipal compost at the rate of 67.2 Mg ha$^{-1}$. In 2018, maize yield increased by 5.2 to 30.1% with char, 1.4 to 6.7% with biochar, 4.3 to 17.1% with composted manure, and 12.2 to 24.6% with municipal compost. All char treatments with the exception of the lowest char rate (22.3 Mg ha$^{-1}$) increased maize yield compared to the control treatment. Maize yield increased ($r^2$= 0.97; $P$= 0.001) with increasing rates of char (Appendix 3- 2). Both application rates (33.6 and 67.2 Mg ha$^{-1}$) of municipal compost increased maize yield, but only the high rate of composted manure (67.2 Mg ha$^{-1}$) increased maize yield. The high application rate of composted manure and municipal compost increased maize yield by 11.1 to 12.6% relative to the low rate of application (33.6 Mg ha$^{-1}$) for both amendments.

Although statistical differences were not significant, soil amendments tended to increase dry bean yield in 2017 and sugar beet yield in 2019. For example, dry bean yield increased by 12.2 to 52.4% with char, 13.1 to 16.4% with biochar, 2.0 to 14.1% with composted manure, and 14.4% with municipal compost (for both rates) compared with control treatment. Similarly, sugar beet yield increased by 1.8 to 11.5% with char, 5.6 to 9.6% with biochar, 2.4 to 4.0% with composted manure, and 6.5 to 9.6% with municipal compost compared with control treatment.

The relative yield was influenced by amendments ($P < 0.05$) and year ($P = 0.001$), but not by amendments x year interaction (Table 3-5). Relative yield was higher with maize in 2018 within a block compared to the highest yielded block of dry bean in 2017 or sugar beet in 2019. Char applied at ≥ 89.2 Mg ha$^{-1}$ increased yield by more than 12.5% compared to control treatment. The high rate of municipal compost had similar a higher relative yield compared to control. Biochar, composted manure, and the low rate of municipal compost did not affect relative yield. In 2017 and 2018, harvested grain samples from the char treatments (≥ 44.6 Mg ha$^{-1}$) and control analyzed for any potential trace metal accumulation showed no significant difference in metal concentrations (Appendix 3- 3).

**Soil chemical properties**

In a year, soil amendments increased organic C level by 7 to 60% in this low C soil (Table 3-6). Char treatments at 22.3, 44.6, 89.2, 133.8 Mg ha$^{-1}$ and municipal compost at 67.2 Mg ha$^{-1}$ had significant increases in soil organic C compared to the control. Amendments also had a significant effect on pH and Ca concentrations (Appendix 3- 4). Soil pH increased in the municipal compost at 33.6 Mg ha$^{-1}$ compared to control. Char applied at 89.2 Mg ha$^{-1}$ and biochar at 5.6 Mg ha$^{-1}$ also increased Ca level in soil solution compared to control. There was no effect of soil amendments on N, P, K Mg, S, Fe, B, Zn, and CEC concentrations. Addition of composted manure or municipal compost did not significantly change level of P or K in soil.

## Discussion

Blanco-Canqui et al. (2020) reported char at > 67.3 Mg ha$^{-1}$ increased soil C where the initial soil organic C was > 10 g kg$^{-1}$. In contrast, the current study soil had a much lower initial organic C (7 g kg$^{-1}$) and char as low as 22.3 Mg ha$^{-1}$ increased soil C compared to the control. Amendments such as char and biochar may need more time (> 3 years) to interact with soil and become a C substrate for microbes under favorable conditions of humidity and temperature (Fernández et al., 2007; Kammann et al., 2011). Biochar contained a high C concentration (85.4%) and often improves soil properties (Blanco-Canqui, 2017). Limited or no effect of biochar in the present study may be due to the low rate of application (up to 11.2 Mg ha$^{-1}$) (Blanco-Canqui et al., 2019) and slightly alkaline nature of the study soil. Previous studies found positive effects of biochar on degraded and coarse-textured soils under high rates of application ≥ 50 Mg ha$^{-1}$ in (Chan et al., 2008; Kammann et al., 2011). Most positive results on biochar were reported from acidic soils due to the potential liming effect of biochar on crop yields (Liu et al., 2012; Burell et al., 2016). Compost materials are well recognized to improve soil properties and crop yield over time. Thus, in this study, we expect that these materials can have broader impacts on soil chemical properties and crop yields in the long-term (> 3 years).

Our previous study suggested that char might enhance soil fertility through greater nutrient availability (Panday et al., 2020). The reduction in N loss via volatilization following char application (up to 13.4 Mg C ha$^{–1}$ in fertilized loam and 10.1 Mg C ha$^{–1}$ in fertilized sandy loam soils) due to its considerably high surface area (82 m$^{2}$ g$^{-1}$) and cation exchange capacity of 46.9 cmol kg$^{-1}$ that jointly increase its sorption capacity (Jamieson et al., 2014). However, no significant gain in yield following application of composted manure and municipal compost at 33.6 Mg ha$^{-1}$, which had low C:N ratios; 11:1 and 12:1, suggests that additional N input or availability from the soil amendments applied was minimal under low rates of application. Under sub-optimal N supply where crop N uptake depends on soil N availability, N uptake under ample supply largely depends on vegetative growth rate that involves many factors affecting crop growth and development including C assimilation of crop (Gastal and Lemaire, 2001) and micronutrient uptake (Joseph et al., 2013).

In the current study, macronutrients were not a limiting factor since farmer applied NPK fertilizer on the top of soil amendments. Thus, enhanced micronutrients uptake might have contributed to yield gain in maize in 2018 with rates of char application and sufficient moisture availability. This result aligns with a report by Joseph et al. (2013) where improved canola and wheat yields were observed due to increased Fe and Zn uptake with pyrite amendment with sulfur oxidizing bacteria. Iron chlorosis is common in calcareous soil particularly early in the spring when there is a considerable amount of precipitation. In the current study, soil had a pH of 8.2 and there was > 230 mm precipitation in May alone in 2018 (30-yr average 65 mm, 2017; 101 mm, 2019; 129 mm). Chlorotic symptoms due to Fe deficiency were visible in plots other than char plots in 2017 and 2018. Although chlorotic symptoms often disappear in the later stage of growth, amendments that increase Fe concentration could reduce chlorosis and increase crop yields as was the case in 2018 (Naeve, 2006).

Increased nutrient concentrations such as N, Fe, Mn, and B in leaf tissue for crops in selected amended plots suggest that crops were able to adsorb these nutrients more than the crops without amendment. Release of essential nutrients at initial crop establishment stage depends upon source and composition of soil amendment and therefore, different amendments might differently promote crop growth (Gonzalez et al., 2001; Pandey et al., 2009; Dumroese et al., 2011).

Any yield benefit observed with municipal compost and higher rate of composted manure would imply that these amendments might have improved soil properties and processes and subsequently affected yield. Compared to other amendments, biochar was applied at much lower rates and that could have masked yield benefits from biochar application. Besides its source and manufacturing conditions, beneficial effects of biochar on soil and crop productivity will depend on amount of its application (Kammann et al., 2011).

There was no heavy metal accumulation in harvested grains under different rates of char. However, there may be other limitations such as an increase in salt content (which could affect the growth of sensitive crops) and adverse effects of herbicide/pesticide sorption (Herrera et al., 2008; Singh and Ghoshal, 2010). Study shows that some biochar products may be toxic depending upon the source materials (Kookana et al., 2011). Composted manure and municipal compost often contain pathogens and high levels of dissolved salts in soil (Nicholson et al., 2003).

In the current study, all amendments except biochar were locally and abundantly available. However, it is important to account for added cost to operations for any amendment depending on source, availability, and transport cost. Every year, more than 31,820 Mg of char is produced in Scottsbluff, Nebraska by Western Sugar Cooperative (WSC) and its equivalent value would be around \$71 million at the most current market price of biochar at \$2.5 kg$^{-1}$. Compared to production volume as well as the application of the equivalent amount of biochar in agricultural fields would be much expensive to char, which is currently available at no cost. Currently, three states (Nebraska, Colorado, and Wyoming) have declared char as a safe material to use in the agricultural field and WSC has similar plants in Colorado, Wyoming and Montana for possible expansion of char as soil amendment in those states. In contrast, when char will be a new soil amendment for the farmer, it also may bear the burden of blame for a poor crop year, whether or not it was the responsible factor for field application. Therefore, economics will be another important factor to consider before deciding on amendments.

## Conclusion

Our results suggest that locally available amendments including char, municipal compost or composted manure can increase productivity of low organic C (7 g kg$^{-1}$) soils in semi-arid regions. Increased maize yield following char application and high rate of municipal compost in this low C soil can be potentially due to increased micronutrient uptake and improved soil properties including soil organic C. Biochar appears to have limited effect on crop yields if rates of application are low (<11.2 Mg ha$^{-1}$). Further studies are needed to corroborate our study findings before recommending an extensive use of these amendments to farmlands.

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**Table 3-1.** Chemical properties of the organic amendments (char, biochar, composted manure, and municipal compost) used in the study.

| **Parameter** (dry weight basis, %) | **Char** | **Biochar** | **Composted manure** | **Municipal compost** |
|---|---|---|---|---|
| Moisture | 2.1 | 2.6 | 10.0 | 62.0 |
| pH[†] | 7.6 | 7.0 | 7.0 | 7.3 |
| Total C | 29.3 | 85.4 | 12.5 | 18.2 |
| Total N | 0.4 | 0.7 | 1.1 | 1.5 |
| P as $P_2O_5$ | 0.2 | nd | 1.6 | 1.0 |
| K as $K_2O$ | 0.2 | nd | 1.6 | 0.7 |
| Ca | 4.8 | nd | nd | 5.4 |
| Mg | 1.1 | nd | nd | 0.4 |
| S | 0.5 | nd | 0.3 | nd |
| Fe | 1.3 | nd | 0.7 | nd |
| B | <0.1 | nd | nd | nd |
| Zn | <0.1 | nd | <0.1 | nd |
| Ash | nd | 6.2 | nd | nd |
| Trace metals[†] | Yes | nd | nd | Yes |

Char and municipal compost contain trace metals (As, Cd, Cr, Pb, Hg, and Se). However, those concentrations are below the phytotoxicity limits for heavy metal soil contamination or n soil (Cameron, 1992)

[†]unitless; nd-not detected (below detection limit)

**Table 3-2.** Amendment effect on the concentration of different nutrient in leaf tissue in maize in 2018.

| Treatment | Rate | N | P | K | Ca | Mg | S | Zn | Fe | Mn | Cu | B | Mo |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg ha$^{-1}$ | % | | | | | | mg kg$^{-1}$ | | | | | |
| Control | - | 3.1 bc[†] | 0.4 | 3.4 | 0.5 | 0.2 | 0.3 | 36.0 | 41.0 c | 97.0 ab | 11.6 | 13.2 cd | 0.8 |
| Char | 22.3 | 3.0 c | 0.4 | 3.3 | 0.5 | 0.2 | 0.3 | 34.5 | 66.7 ab | 89.5 bcd | 10.7 | 15.7 abc | 0.7 |
| | 44.6 | 3.1 bc | 0.4 | 3.4 | 0.5 | 0.2 | 0.3 | 34.5 | 61.7 ab | 95.0 abc | 11.5 | 16.1 abc | 0.7 |
| | 66.9 | 3.2 a | 0.3 | 3.3 | 0.6 | 0.2 | 0.3 | 38.5 | 68.3 ab | 94.3 abc | 12.1 | 17.9 a | 0.8 |
| | 89.2 | 3.1 ab | 0.3 | 3.3 | 0.5 | 0.2 | 0.3 | 36.3 | 73.7 a | 91.0 abcd | 11.6 | 17.4 ab | 0.7 |
| | 133.8 | 3.2 a | 0.3 | 3.1 | 0.5 | 0.2 | 0.3 | 35.5 | 71.8 a | 84.0 d | 11.3 | 17.7 a | 0.9 |
| Biochar | 5.6 | 3.1 bc | 0.4 | 3.4 | 0.5 | 0.2 | 0.4 | 38.0 | 53.0 bc | 96.3 ab | 11.9 | 12.5 d | 0.3 |
| | 11.2 | 3.1 abc | 0.4 | 3.2 | 0.5 | 0.2 | 0.4 | 33.3 | 59.7 ab | 98.0 a | 11.2 | 12.3 d | 0.8 |
| Composted manure | 33.6 | 3.1 bc | 0.4 | 3.3 | 0.5 | 0.2 | 0.3 | 36.0 | 50.3 bc | 88.0 cd | 10.9 | 14.6 bcd | 1.0 |
| | 67.2 | 3.1 bc | 0.4 | 3.3 | 0.5 | 0.2 | 0.3 | 37.5 | 55.7 bc | 91.8 abc | 10.8 | 15.0 abcd | 0.7 |
| Municipal compost | 33.6 | 3.1 bc | 0.3 | 3.3 | 0.5 | 0.2 | 0.4 | 36.5 | 52.7 bc | 91.2 abcd | 11.2 | 12.4 d | 1.1 |
| | 67.2 | 3.1 abc | 0.4 | 3.3 | 0.6 | 0.2 | 0.3 | 34.8 | 52.3 bc | 89.8bcd | 11.5 | 14.0 cd | 0.8 |
| Significance | | * | NS | NS | NS | NS | NS | NS | ** | * | NS | *** | NS |

[†] Means for each nutrient followed by same lowercase letters are not significantly different.

****$P < 0.001$, **$P < 0.01$, *$P < 0.05$, NS = not significant.

Char rates 22.3, 44.6, 66.9, 89.2 and 133.8 Mg ha$^{-1}$ were equivalent to 6.7, 13.4, 20.1, 26.8 and 40.1 Mg C ha$^{-1}$, respectively.

**Table 3-3.** Amendment effect on the concentration of different nutrients in leaf tissue in sugar beet in 2019.

| Treatment | Rate | N | P | K | Ca | Mg | S | Zn | Fe | Mn | Cu | B | Mo |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg ha$^{-1}$ | % | | | | | | mg kg$^{-1}$ | | | | | |
| Control | - | 4.4 | 0.3 | 4.5 | 1.0 | 0.8 | 0.3 | 24.0 | 377.0 bc[†] | 73.3 | 6.7 | 28.6 | 0.3 |
| Char | 22.3 | 4.5 | 0.4 | 4.2 | 1.0 | 0.7 | 0.3 | 23.3 | 622.5 abc | 78.3 | 7.0 | 26.5 | 0.2 |
| | 44.6 | 4.5 | 0.3 | 4.4 | 1.1 | 0.7 | 0.3 | 26.0 | 480.2 bc | 76.3 | 6.8 | 28.7 | 0.2 |
| | 66.9 | 4.4 | 0.4 | 4.4 | 1.0 | 0.7 | 0.3 | 24.5 | 475.0 bc | 72.8 | 6.8 | 29.1 | 0.3 |
| | 89.2 | 4.3 | 0.3 | 4.0 | 1.1 | 0.8 | 0.3 | 22.5 | 673.8 ab | 77.3 | 6.5 | 29.6 | 0.3 |
| | 133.8 | 4.4 | 0.4 | 4.1 | 1.1 | 0.7 | 0.3 | 21.8 | 820.5 a | 73.0 | 8.2 | 26.9 | 0.4 |
| Biochar | 5.6 | 4.6 | 0.3 | 4.6 | 1.0 | 0.8 | 0.3 | 24.5 | 321.5 c | 74.0 | 6.4 | 28.5 | 0.2 |
| | 11.2 | 4.5 | 0.3 | 4.2 | 1.1 | 0.8 | 0.3 | 26.3 | 545.5 abc | 80.8 | 6.8 | 28.1 | 0.3 |
| Composted manure | 33.6 | 4.6 | 0.4 | 4.3 | 0.9 | 0.8 | 0.3 | 20.5 | 416.5 bc | 76.8 | 7.7 | 28.5 | 0.3 |
| | 67.2 | 4.4 | 0.3 | 4.3 | 1.1 | 0.7 | 0.3 | 21.3 | 583.0 abc | 69.5 | 6.2 | 26.7 | 0.2 |
| Municipal compost | 33.6 | 4.4 | 0.4 | 4.2 | 1.0 | 0.7 | 0.3 | 23.3 | 444.0 bc | 70.0 | 7.6 | 29.3 | 0.3 |
| | 67.2 | 4.2 | 0.3 | 4.0 | 1.0 | 0.8 | 0.3 | 21.8 | 677.8 ab | 76.3 | 6.3 | 27.5 | 0.3 |
| Significance | | NS | NS | NS | NS | NS | NS | NS | * | NS | NS | NS | NS |

[†] Means for each nutrient followed by same lowercase letters are not significantly different.

****$P < 0.001$, **$P < 0.01$, *$P < 0.05$, NS = not significant.

Char rates 22.3, 44.6, 66.9, 89.2 and 133.8 Mg ha$^{-1}$ were equivalent to 6.7, 13.4, 20.1, 26.8 and 40.1 Mg C ha$^{-1}$, respectively.

**Table 3-4.** Mean crop yields as affected by the different treatments.

| **Treatment** | **Rate** | **Yield** | | |
|---|---|---|---|---|
| | | Dry bean (2017) | Maize (2018) | Sugar beet (2019) |
| | | Mg ha$^{-1}$ | | |
| Control | - | 1.79 | 12.41 e[†] | 10.62 |
| Char | 22.3 | 2.37 | 13.12 de | 10.81 |
| | 44.6 | 2.13 | 13.74 cd | 10.84 |
| | 66.9 | 2.02 | 15.12 ab | 10.94 |
| | 89.2 | 2.13 | 14.89 bc | 12.41 |
| | 133.8 | 2.73 | 16.21 a | 11.84 |
| Biochar | 5.6 | 2.04 | 12.30 e | 11.21 |
| | 11.2 | 2.08 | 13.24 de | 11.64 |
| Composted manure | 33.6 | 2.05 | 13.01 de | 10.87 |
| | 67.2 | 1.75 | 14.65 bc | 11.04 |
| Municipal compost | 33.6 | 2.05 | 13.94 cd | 11.31 |
| | 67.2 | 2.05 | 15.48 ab | 11.64 |
| Significance | | NS | *** | NS |

[†] Means for each variable followed by same lowercase letters for each crop are not significantly different.

Char rates 22.3, 44.6, 66.9, 89.2 and 133.8 Mg ha$^{-1}$ were equivalent to 6.7, 13.4, 20.1, 26.8 and 40.1 Mg C ha$^{-1}$, respectively.***$P < 0.001$ and NS = not significant.

**Table 3-5.** Mean relative yields as affected by treatment, year, and their interaction.

| **Treatment** | **Rate**, Mg $ha^{-1}$ | **Relative Yield** |
|---|---|---|
| Control | - | 0.64 c[†] |
| Char | 22.3 | 0.70 bc |
| | 44.6 | 0.70 bc |
| | 66.9 | 0.72 bc |
| | 89.2 | 0.75 ab |
| | 133.8 | 0.82 a |
| Biochar | 5.6 | 0.66 bc |
| | 11.2 | 0.70 bc |
| Composted manure | 33.6 | 0.67 bc |
| | 67.2 | 0.67 bc |
| Municipal compost | 33.6 | 0.70 bc |
| | 67.2 | 0.74 ab |
| Significance | | * |
| **Year** | | |
| 2017 | | 0.70 b |
| 2018 | | 0.82 a |
| 2019 | | 0.61 c |
| Significance | | *** |
| Treatment x Year | | NS |

[†] Means in a column followed by same lowercase letter are not significantly different. Char rates 22.3, 44.6, 66.9, 89.2 and 133.8 Mg $ha^{-1}$ were equivalent to 6.7, 13.4, 20.1, 26.8 and 40.1 Mg C $ha^{-1}$, respectively.***$P < 0.001$, *$P < 0.05$ and NS = not significant.

**Table 3-6.** Pair-wise t test results comparing soil organic C under amendment treatments against the control.

| Treatment | **Rate** (Mg ha$^{-1}$) | **Soil C** (g kg$^{-1}$) | **p-value** |
|---|---|---|---|
| Control | - | 7.3 | - |
| Char | 22.3 | 10.2 | 0.01 |
| | 44.6 | 11.7 | 0.01 |
| | 66.9 | 9.0 | 0.37 |
| | 89.2 | 11.4 | 0.01 |
| | 133.8 | 10.7 | 0.02 |
| Biochar | 5.6 | 9.5 | 0.22 |
| | 11.2 | 9.9 | 0.11 |
| Composted manure | 33.6 | 7.8 | 0.87 |
| | 67.2 | 10.1 | 0.13 |
| Municipal compost | 33.6 | 8.0 | 0.54 |
| | 67.2 | 10.0 | 0.04 |

Char rates 22.3, 44.6, 66.9, 89.2 and 133.8 Mg ha$^{-1}$ were equivalent to 6.7, 13.4, 20.1, 26.8 and 40.1 Mg C ha$^{-1}$, respectively.

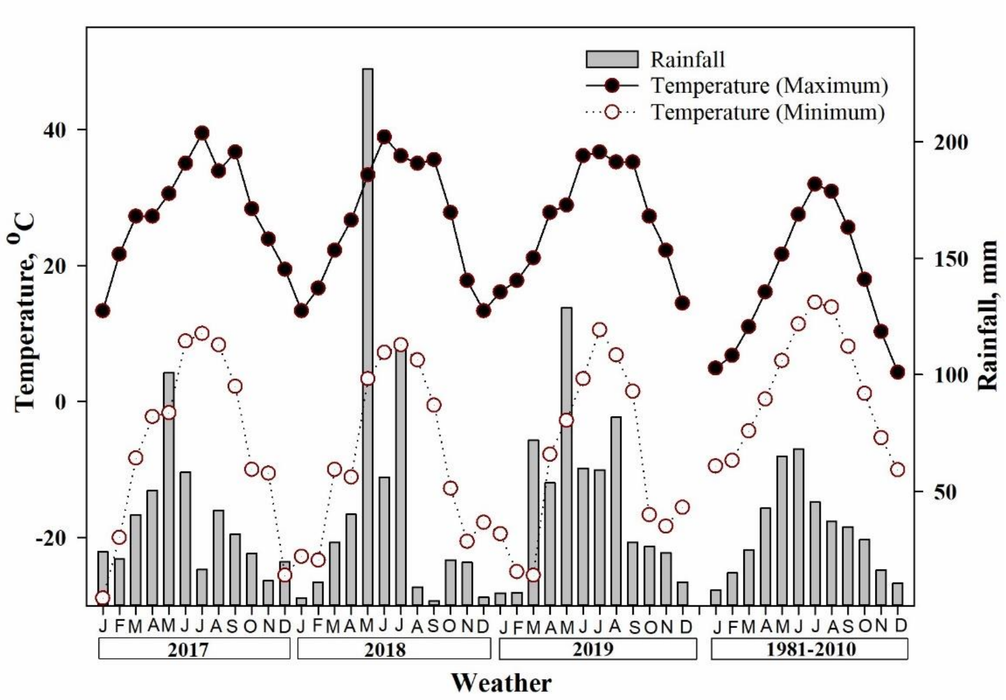

**Figure 3-1.** Monthly cumulative rainfall and average maximum and minimum air temperature in 2017, 2018, 2019 and a 30-year average (1981-2010) in Scottsbluff, NE.

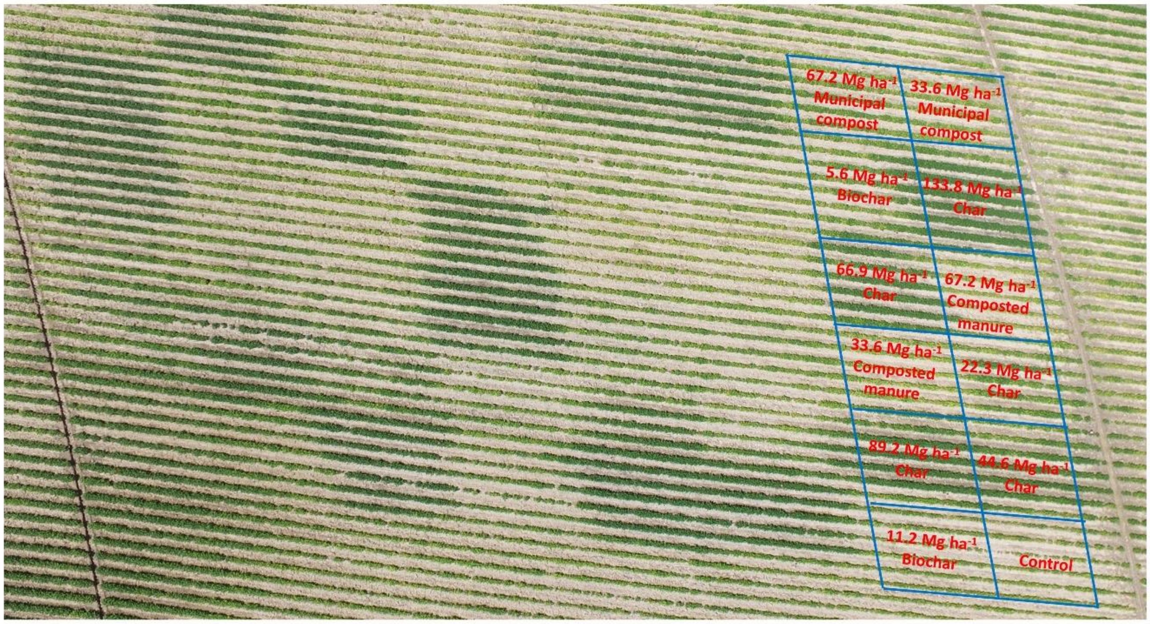

**Figure 3-2.** Aerial imagery showing visual color differences due to applied treatments in dry bean plot in 2017. A set of 12 blue colored polygons represent one block of the experiment where each polygon corresponds to different treatments. Treatments included no amendment or control, five levels of char: 22.3, 44.6, 66.9, 89.2, and 133.8 Mg ha$^{-1}$, two levels of biochar: 5.6 and 11.2 Mg ha$^{-1}$, two levels of composted manure: 33.6 and 67.2 Mg ha$^{-1}$ and two levels of municipal compost: 33.6 and 67.2 Mg ha$^{-1}$.

# CHAPTER 4 - DOES APPLICATION OF COAL CHAR WITH UREA OR COMPOSTED MANURE IMPROVE SOIL AND CROP YIELDS IN SEMI-ARID REGION?

## Abstract

The addition of soil amendments can potentially improve soil properties, particularly in degraded soil and increase crop yields. Soil amendments with high C content would be more important in semi-arid regions such as western Nebraska, where soils are characterized by low C due to disruption of soil aggregates and rapid C decomposition from intensive tillage, erosion, high pH, and an ever-present risk of drought. A field study was conducted in 2016-2018 with objectives to i) evaluate the effect of char on soil and crop yields in sandy loam fertilized with urea or composted manure and ii) evaluate the performance of an active crop sensor in determining in-season maize (*Zea mays* L.) N status in char-amended urea fertilized sandy loam under irrigated condition in western NE. Char, a coal combustion residue, is a potential amendment as it contains up to 293 g kg$^{-1}$ C and some other essential plant nutrients. The experiment was arranged in split-plot randomized complete block design in four replications with char as the main and N treatment as subplot factors. Char treatment included five rates of char (0, 6.7, 13.4, 20.1 and 26.8 Mg C ha$^{-1}$), and N treatment included four rates of urea (0, 90, 180, and 270 kg N ha$^{-1}$) and two rates of composted manure (33.6 and 67.2 Mg ha$^{-1}$). A handheld spectral sensor was used to determine normalized difference red edge (NDRE) values at four different growth stages (V6, V8, V10, and R1) in 2017 and 2018. In 2 years, char applied at 13.4 Mg C ha$^{-1}$ or higher increased soil organic C by ≥17.9% and both rates of composted manure increased the concentrations of soil P by two folds and K by four folds compared to control. Grain yield and NDRE were not significantly different by char alone or by char application with N treatments. There was a significant interaction effect of N treatment and year on grain yield. A positive maize yield response to urea-N plateaued at 156.9 kg N $ha^{-1}$ with the corresponding yield of 14.6 Mg $ha^{-1}$ in second year was observed. There was a significant interaction effect of year, urea-N and maize growth stage on NDRE. The active sensor was able to determine maize N variability at different urea-N rates and maize yield was strongly correlated with NDRE at V8 and V10 growth stages. These findings found no adverse effect of char and underscore the potential use of char as a soil amendment to restore/ enhance C depending upon soil condition in semi-arid regions.

## Introduction

Agricultural landscapes in semi-arid regions are characterized by low soil organic matter or soil C and precipitation that is low and has high spatial and temporal variability (Mikha et al., 2013; Janmohammadi et al., 2018). Western Nebraska located in the semi-arid Great Plains receives annual precipitation of 385.6 mm compared to 736.6 mm in eastern NE (USA average; 991.2 mm) (HPRCC, 2019). The cultivated soils in this region have lost 30-50% of the original C level due to disruption of soil aggregates and rapid C decomposition from increasing drought, erosion, high pH and intensive tillage (Mikha et al., 2013; He et al., 2018).

The availability of soil organic C (SOC) determines nutrient cycling in agroecosystems (Zhang et al., 2009; Dil et al., 2014). Adding C rich materials could be an effective strategy to increase SOC, improve soil properties, and crop yields.

High C products such biochar can be cost-prohibitive for their use in agriculture (Houben et al., 2013). When C rich products are locally available and with minimal cost, they could be considered for potential use as an amendment.

In western NE, coal derived char from a local factory that contains up to 293 g $kg^{-1}$ total C by weight as well as other essential plant mineral nutrients are available in a considerable quantity and at low cost. Addition of char at optimal rates (up to 13.4 Mg C $ha^{-1}$ for loam and 10.1 Mg C $ha^{-1}$ for sandy loam soils) reduced N losses by decreasing ammonia volatilization in fertilized soils in a laboratory setting (Panday et al., 2020). Our recently conducted char amended field study reported improvements in crop micronutrients (Fe and Zn) uptake, soil C and crop yield compared to control in low C soil (Panday et al., Chapter 3).

There is always a reduced response of crop yields to chemical fertilizers in semi-arid regions due to influence of water availability (Wang et al., 2016). Several studies indicate that the long-term inappropriate application of chemical fertilizers increases soil acidification and degradation of soil structure which results in a decline in soil fertility and disturb soil-ecosystem (Hartemink, 2003; Dong et al., 2012). Soil degradation depletes the SOC pool, which can be greater in semi-arid regions than in sub-tropical (Diacono and Montemurro, 2011).

Restoring the lost SOC is a high priority to sustain soil properties, productivity, and environmental quality (Blanco-Canqui et al., 2015). A wide range of management options are available to increase SOC (Chan, 2008), but the question remains with the period of how long it might take to observe such a significant improvement. Hence it has been suggested that a combination of chemical fertilizers with either organic amendment such as animal/ farmyard manure rather than application of chemical fertilizer alone is an optimal way to reduce dependency on chemical fertilizer and for hastening the improvement in soil fertility (Zhang et al., 2009).

For better improvement of soil fertility for instance to improve N use efficiency (NUE), sensor-based N management has been promoted in cropping systems (Solari et al., 2008; Krienke et al., 2015; Montealegre et al., 2019). Proximal canopy sensors (for example, active sensors, with their source of energy) can be used to estimate crop N status based on leaf chlorophyll concentration or leaf greenness (Tremblay et al., 2011). Without the collection of destructive samples, these sensing tools have potential to identify and correct N stress which has already occurred during the growing season for plant production (Ping et al., 2008; Tagarakis and Ketterings, 2017; Naser et al., 2020). Algorithms using crop canopy reflectance sensing, for example active crop sensor algorithms (Solari et al., 2010), are well calibrated to make a useful N recommendation for maize production. However, there are limited studies of crop canopy sensor technology in semi-arid region (Shaver et al., 2011; Ballester et al., 2017; Pinar and Erpul, 2019).

The objective of this study was to evaluate the effects of char applied together with urea or composted manure on soil properties such as pH, SOC, N, P, K, Ca, Mg, S, Fe, and Zn and crop yields in sandy loam soil. We hypothesize that char, when applied together with other amendments, may perform better than when used alone. Furthermore, this study evaluates the performance of an active crop sensor in determining in-season N status in maize under furrow irrigation in fertilized sandy loam soil following char application in western NE.

## Materials and methods

A field study was conducted under a continuous maize cropping system at the University of Nebraska-Lincoln Panhandle Research and Extension Center in Scottsbluff, NE in 2016- 2018. The soil on the site is a Tripp very fine sandy loam, <1% slopes with 7.7 pH and 15 g $kg^{-1}$ SOC. Tripp soil is very deep and well drained. Weather data were collected from a nearby weather station (HPRCC, 2019).

The experiment was arranged in a split-plot randomized complete block design with four replications, resulting in 120 plots in total. The main plot factor was char treatment that included five rates of char (measured in C equivalent): C0 through C4 received char at 0, 6.7, 13.4, 20.1 and 26.8 Mg C $ha^{-1}$ respectively. These treatments correspond to 0, 22.3, 44.6, 66.9 and 89.2 Mg $ha^{-1}$ of char. The subplot factor was N treatment that included four rates of urea (urea-N): N0 through N3 received urea at 0, 90, 180 and 270 kg N $ha^{-1}$ and two rates of composted manure: N4 and N5 received composted manure at 33.6 and 67.2 Mg $ha^{-1}$. Char rates were selected up to 89.2 Mg $ha^{-1}$ as the highest end, mainly for economic, i.e., cost associated with transport and field application and an effort to simulate on-farm practices. The amounts of urea and compost manure added to represent the amount of fertilizer required in the field study for average yield production in western NE.

All the rates of char and composted manure were applied only one time in the spring of 2016. Char used in this field study was the same coal combustion residue from a sugar factory in Scottsbluff, NE, where it was passed through an 8 mm sieve to remove foreign materials before to spread in field. The fine powder of char was distributed uniformly with a golf course spreader. Composted manure was distributed evenly with a tractor-drawn manure spreader and further distributed manually across plots. The composted manure used in Chapter 3 and Chapter 4 was from the same feedlot. Those treatments were incorporated in to 0-15 cm soil depth with a disc harrow. Urea-N treatments were applied each year before maize planting. Tillage operation were carried out for land preparation every year.

Pioneer hybrid (P8989LR, 2635 growing degree days to maturity) maize was planted on 6 May 2016, 23 April 2017 and 20 April 2018 at 13760 seeds ha$^{-1}$. Each plot was 2.2 x 7.0 m$^2$. Best management practice recommendations were followed for herbicide application. Irrigation was applied based upon soil moisture, evapotranspiration, and potential crop water use estimates using furrow irrigation.

Baseline 0-20 cm soil samples were collected before treatment application and maize planting in the spring of 2016. Similar soil samples from all treatment plots were collected in the spring of 2018 before maize planting. Each sample consisted of a composite of 6 cores collected with a 3 cm diameter probe to a 20-cm depth. Soil samples were analyzed for $pH_{1:1}$, SOC, N, P, K, Ca, Mg, S, Fe, B, and Zn. Besides, before maize planting in 2018, soil samples from 20-60 and 60-120 cm depth were collected from selected treatment plots that included C0N0, C0N1, C0N3, C0N5, C4N0, C0N1, C4N3, and C4N5 for the determination of soil residual $NO_3$-N. Soil pH was measured by 1:1 soil-water ratio, organic C was measured by dry combustion analysis after treating the soil with acid to eliminate the inorganic C, $NO_3$-N was measured using flow injection method, and P was measured as Olsen P. Similarly, soil K, Ca, and Mg were measured using ammonium acetate extraction and Fe and Zn were measured after extraction with diethylenetriaminepentaacetic acid (DTPA).

Maize growth stage was determined according to the collar method (Abendroth et al., 2011). A handheld active crop sensor, RapidScan CS-45 (Holland Scientific Inc., Lincoln, NE, USA) was used to obtain normalized difference red-edge (NDRE) values from maize canopies at different growth stages. Sensor readings were collected at V6, V8, V10 and R1 maize growth stages from each plot which received urea-N fertilizer in 2017 and 2018. Wavelengths used in NDRE calculation were 780 nm for near infra-red (NIR) and 730 nm for red-edge (RE) and NDRE was calculated based on sensor readings at those wavelengths as

$$NDRE = \frac{NIR - RE}{NIR + RE}$$

At maturity, the center two rows (3 m each) of each plot were hand harvested in 2016 and 2017 and middle two rows (7 m each) were harvested with a plot combine in 2018. Harvest occurred around the third week of October each year to measure maize grain yield. Maize grain yield values were adjusted to 155 g kg$^{-1}$ moisture level.

Total N present in two rates of composted manure (33.6 and 67.2 Mg ha$^{-1}$) was estimated assuming availability of 20% of total manure-N in the first and 15 and 5% of the original N in the second and third years after composted manure application (Eghball et al., 2002; Wortmann and Shapiro, 2012).

Statistical analysis was completed with SAS 9.4 using the PROC MIXED procedure (SAS, 2015). Effects of char and N treatments on dependent variables (NDRE in 2017-2018 and maize yield in 2016-2018) were tested with char and N treatments, year (as a repeated measure variable) and their interaction as the fixed effects and block as random effects. When main or interaction effects were significant, means were separated by the least square means (LSD) (Littell et al., 2006). PROC REG and PROC NLIN were used to investigate quadratic and quadratic-plateau regression fits for the yield response to N treatment. PROC REG was also used to determine the linear relationship between NDRE vs. yield or NDRE vs. N rate. The growth stage NDRE value was chosen as representative of the relationship when the coefficient of linear regression ($r^2$) and regression slope (m) had higher values. Statistical significance was evaluated at $P < 0.05$ unless otherwise stated.

## Results

### Weather

The average annual temperatures at the study site were 10.3 °C in 2016, 9.8 °C in 2017 and 8.9 °C in 2018 compared to 30-year average of 9.4 °C (1981-2010) (Figure 4-1). The average annual precipitation was 394.7 mm in 2016, 439.4 mm in 2017, and 539.0 mm in 2018 compared to 30-year average of 396.7 mm. Except in 2016, the other two years had at least 10% greater annual precipitation than a 30-year average (1981-2010) (Figure 4-1).

During the growing season (May to October), average temperatures in all years were within 1.0-1.8 °C of the 30-year average. However, temperatures were 3.3 and 2.6 °C greater in June and October of 2016, 1.6 °C greater in May of 2017 and 1.7 °C greater in October of 2018 than 30-year average. Growing season precipitation from May to October varied by years. Compared to 30-year average, growing season precipitation was 18.8% less in 2016, 2.5% less in 2017, and 54.1% higher in 2018

(Figure 4-1). Throughout the maize growing season, 2018 had a higher rate of growing degree days accumulation compared to 2017 and 2016 (Appendix 4- 1).

**Soil fertility**

After two years following treatment application, there was no significant interaction effect of char and N treatments on soil chemical properties (Table 4-1. Changes in soil chemical properties in two years following char application as affected by char and nitrogen treatments and their interaction. The main factor effect of char and N treatments was significant on some soil chemical properties. Char had a significant effect on pH, SOC, K Ca, Mg and Fe concentrations, whereas N treatment had significant effects on P and K. Char applied at 13.4 Mg C ha$^{-1}$ or lower rate decreased pH compared to the control and char at 20.1 Mg C ha$^{-1}$ or higher rate. Char applied at 13.4 Mg C ha$^{-1}$ or higher rates increased SOC by ≥17.9% compared to control. Soil P and K concentrations increased with char application only at 20.1 Mg C ha$^{-1}$ compared to control. Soil Fe concentration increased ($r^2$= 0.87; $P$= 0.049) with increasing rates of char. Similarly, soil P concentration increased by two times and K concentration by four times with composted manure at 33.6 and 67.2 Mg ha$^{-1}$ compared to control.

There were no differences in soil residual $NO_3$-N by char or interaction effect of char and N treatment (Appendix 4- 2. Mean soil residual nitrate-N at three different depths (0-20, 20-60 and 60-120 cm) affected by char, nitrogen, and their interaction.). Soil residual $NO_3$-N in the 20-60 cm depth was greater than at the 0-20 cm layer. At 20-60 cm depth, there was a significant effect of N treatment on soil residual $NO_3$-N (Figure 4-2). Urea-N treatment at 270 kg N ha$^{-1}$ had the highest residual $NO_3$-N compared to other rates at 20-60 cm depth. With increasing N rates, a trend of higher residual $NO_3$-N ($r^2$= 0.83; $P$= 0.097) was observed at 60-120 cm depth (Figure 4-2).

## Maize yield

Averaged across treatments, maize grain yield was higher in 2017 (14.13 Mg ha$^{-1}$) by 51.51% and in 2018 (12.20 Mg ha$^{-1}$) by 21.75% than 2016 (9.96 Mg ha$^{-1}$) (Figure 4-3). Maize grain yields across char and N treatments ranged from 5.24 to 14.11 Mg ha$^{-1}$ in 2016, 6.86 to 20.05 Mg ha$^{-1}$ in 2017 and 7.93 to 17.10 Mg ha$^{-1}$ in 2018. Addition of urea-N increased maize yield by 12.75 to 29.39% in 2016, 27.22 to 46.15% in 2017 and 12.75 to 29.39% in 2018. Addition of composted manure increased maize yield by 14.16 to 21.48% in 2016, 3.31 to 3.98% in 2017 and 14.16 to 21.48% in 2018.

There was a significant interaction effect of year and N on yield (Table 2). Maize yield at urea rates 180 and 270 kg N ha$^{-1}$ in 2017 was the highest across all N treatments and years (Figure 4-3). There was no significant difference in maize yield between urea rates at 180 and 270 kg N ha$^{-1}$ and between two manure rates across years. Application of urea-N consistently produced higher yields than control across years. Maize yield at control treatment was similar to low composted manure rate in 2017 and 2018 and similar to high composted manure rate in 2017 only. The control treatment in 2016 had the lowest grain yield of all.

## Yield response to N application

Maize grain yield response to urea-N significantly fitted to a quadratic-plateau model only in 2017 (Figure 4-4). Maize grain yield plateaued at 156.9 kg N ha$^{-1}$ with the corresponding yield of 14.60 Mg ha$^{-1}$. There were trends for maize yield response to urea-N treatment plateauing in other years (plateau at 298.3 kg N ha$^{-1}$, $P$= 0.152 in 2016 and 188.2 kg N ha$^{-1}$, $P$= 0.093 in 2018).

### Normalized difference red-edge (NDRE)

There were no main or interaction (including year, growth stage or N treatment) effects of char on NDRE. There was a significant interaction effect of year, N treatment, and growth stage on NDRE (Table 4-2). Urea rates at 180 and 270 kg N ha$^{-1}$ at V8 and R1 in 2018 and urea at 180 kg N ha$^{-1}$ in 2017 had the highest NDRE value across N rate, year or growth stage (Table 4-3). The urea-N treatments N2 and N3 had greater NDRE than the control at V6, V10, R1 in 2017 and V8, V10 and R1 in 2018. The urea-N treatment N1 had greater NDRE than the control only at R1 in 2017 and at V10 and R1 in 2018. In 2017, NDRE did not differ by N treatment at V10 and in 2018, at V6 growth stage.

Normalized difference red-edge values had a higher linear regression coefficient ($r^2$) and slope (m) with urea-N at the V8 ($r^2$= 0.79, m= 0.16 in 2017 and $r^2$= 0.96, m= 0.14 in 2018) and V10 ($r^2$= 0.68, m= 0.24 in 2017 and $r^2$= 0.97, m= 0.13 in 2018) growth stages (Table 4-4). In both years, linear relationship of NDRE with urea-N rates was lower at V6 and R1 growth stages (Table 4-4).

### In-season N status and maize yield

Normalized difference red-edge values had a higher linear regression coefficient and slope with maize grain yield at V8 ($r^2$= 0.82, m= 86.22 in 2017 and $r^2$= 0.78, m= 93.58 in 2018) and V10 ($r^2$= 0.74, m= 101.41 in 2017 and $r^2$= 0.77, m= 151.29 in 2018) growth stages (Table 4-4). In both years, NDRE linear relationship of NDRE with maize grain yield was lower at V6 and R1 growth stages (Table 4-4).

Overall, the maize yield was strongly correlated with NDRE at V8 and V10 growth stages under this semi-arid irrigated field condition.

## Discussion

### Soil fertility improvement

Char used in this study contained crop essential macro- and micronutrients and thereby increased their concentrations in soil samples collected two years following char application. In our previous field study, we documented increased Fe uptake by maize and sugar beet in char applied plots compared to control (Panday et al., Chapter 3). Joseph et al. (2014) reported improved yields (canola and wheat) due to increased Fe and Zn uptake when pyrite amendment was incorporated with bacterization under sandy loam soil.

The initial pH of sandy loam in the current study was 7.7 and char had a pH of 7.6, addition of char reduced soil pH at least by 0.2 unit in 2-year study period. Decrease in soil pH with addition of char up to 13.4 Mg C ha$^{-1}$ compared to control could be due to dilution effect (Thomas, 1996). Similar results were observed in our previously conducted lab study that reported reduction in soil pH with the char applied at 13.4 Mg C ha$^{-1}$ in urea fertilized sandy loam compared to no char treatments (Panday and Maharjan, Chapter 2). Lai et al. (1999) reported a dilution effect of fly ash, another coal combustion residue such as char used in this experiment, on soil pH. Besides this, the possible electrolyte effect and cation exchange due to addition of char (CEC, 46.9 cmol kg$^{-1}$) in calcareous soil may increase the solubility of $CaCO_3$ and their removal by leaching and thereby, reduce pH (Chorom and Rengasamy, 1997). In contrast, char also contained 190 g kg$^{-1}$ of

$CaCO_3$ (Panday et al., 2020). Addition of char at higher rates (20.1 and 26.8 Mg C $ha^{-1}$) can also aid in increasing soil alkalinity due to the presence of high $CaCO_3$ and therefore, no reduction in pH was observed under higher rates.

Char applied at 20.1 Mg C $ha^{-1}$ or higher rates had a positive effect on SOC in the current study. A previous 2-year field study documented that a minimum application rate of 19.7 Mg C $ha^{-1}$ is required to significantly increase C concentration in soil (13.4 g $kg^{-1}$ organic C) (Blanco-Canqui et al., 2020). In contrast, our 3-yr field study reported char application even at rate of 6.7 Mg C $ha^{-1}$ increased soil C compared to the control in low C soil (7 g $kg^{-1}$ organic C) (Panday et al., Chapter 3). Summarizing these three findings, it appears that effect of char might vary by original soil C level as well. These pieces of evidence strongly support that char has potential to enhance/ restore depleted soil C in semi-arid regions.

Increase in soil P and K following application of composted manure is well documented (Johnson et al., 2006; Toth et al., 2006; Olsen et al., 2010). Though there were no significant effects of treatment on soil S concentration, continuous maize cultivation has shown a decrease in soil S. Currently, S deficiency is widespread in crops around the world. Besides natural biogenic sources of S availability to the environment, coal combustion in several industrial activities also contributed a substantial amount of S for plant needs by aerial deposition (Sabir et al., 2015). With the introduction of Clean Air Act Amendments, it restricts $SO_2$ emissions into the atmosphere from coal-fired facilities, if the coal contains appreciable amounts of S. To meet this requirement, most of the coal power plants use flue gas desulfurization process (Panday et al., 2018). Soil S depletion with crop harvest is further aggravated with the introduction of high-yield crop varieties with increased nutrient mining, including S from soils (Scherer, 2001). Addition of S to soil should be determined with consideration for organic matter content in soil, extractable S in soil, annual S removal with crop harvest, and S in irrigation water (Lamond, 1997).

The highest rate of urea-N fertilizer (270 kg N $ha^{-1}$) application led to substantial accumulation of residual $NO_3$-N in the soil profile. Variability in distribution of residual $NO_3$-N indicated that urea-N fertilizer leached from top 20 cm along with water. Soil texture and irrigation practice are main factors for downward movement of applied N-fertilizer in soil-based cropping systems (Thompson et al., 2005). Apart from $NO_3$ used by plants and other forms of losses to the environment, residual $NO_3$ stored in soil profile may or may not be taken up by plants in the following season. Ju et al. (2007) reported about 90% residual N ($NO_3$ + $NH_4$) could be immobilized in soil organic matter and reduce agricultural fertilizer input. Leaching of $NO_3$ also can pose a severe threat to the environment through groundwater contamination (Zhang et al., 2012).

### Maize yield improvement

Blanco-Canqui et al. (2020) reported no significant effect of char on crop yield in low C soil (12 g $kg^{-1}$ organic C). In contrast, we observed an increase in maize yield of 10.7 to 30.6% at all char rates except with the lowest rate (6.7 Mg C $ha^{-1}$) in a low C (7 g $kg^{-1}$ organic C) sandy loam soil (Panday et al., Chapter 3). In the current study, no yield benefit was observed with char. Yield benefit following char application was measurable in relatively low C and low-yielding soil (Panday et al., Chapter 3).

Maize planting was delayed by two weeks in 2016 and that considerably reduced yield potential (Boydston et al., 2006). Gunsolus (1990) reported that there could be a 7-13% maize yield loss at the delay of average two weeks from dates of planting. Maize grain yield plateaued at urea rate of 156.9 kg N ha$^{-1}$ in 2017, suggesting any additional N beyond this rate (agronomic optimum N rate) would not lead to significant yield increases (Maharjan and Hergert, 2019). Besides, if economic aspects of maize production that considers prices of grain and urea-N is incorporated in regression that would provide economically optimum N rates that would give producers most out of their input cost (Maharjan et al., 2016). Such agronomic and economic optimum N input rates would also minimize the environmental risk associated with agricultural N inputs (Sun et al., 2012).

Apart from urea fertilizer, composted manures are widely used as N sources in farming which provide soil nutrients, increase crop yields and potential for reduced nutrient losses during storage or after application (Larney et al., 2003; Hepperly et al., 2013). However, one of the disadvantages of manure management includes the unknowns regarding timing and amount of N mineralization (Tarkalson et al., 2012; Maharjan and Hergert, 2019). Applied organic N needs to go through one or more cycles of microbial immobilization and mineralization before crop N uptake occurs (Beegle et al., 2008). Manure can provide nutrients to crops for several years due to slow release of nutrients.

At the first three years of this study, N availability from applied composted manure was estimated to facilitate comparison with different urea-N rate treatments. Maize grain produced under composted manure at rates 33.6 (equivalent to 74.1 kg N

$ha^{-1}$) and 67.2 Mg $ha^{-1}$ (equivalent to 148.2 kg N $ha^{-1}$) was 9.7 and 10.3 Mg $ha^{-1}$ grain yield in the first year. Those yields with composted manure treatments were equivalent to yield with at least 90 kg N $ha^{-1}$ of urea in the same year. Similarly, maize grain produced from composted manure was equivalent to 55.6 and 111.1 kg N $ha^{-1}$ in the second year and 18.5 and 37.0 kg N $ha^{-1}$ in the third year. Those yields from estimated N present in composted manure were equivalent to < 90 kg N $ha^{-1}$ urea application in the second and third years. These observations show that N present in composted manure is comparable to urea-N and underscore the potential of sole dependence on composted manure to meet N requirement in maize production.

## NDRE and N recommendations

Normalized difference red-edge linear regression coefficient ($r^2$= 0.78-0.82 at V8 and 0.42-0.74 at V10) values with grain yield observed in this study aligned with other studies reported in the literature. Torino et al. (2014) found $r^2$ of 0.42 and 0.67 for NDRE with maize yield at V8 and V10 stages. Teal et al. (2006) found $r^2$ of 0.71-0.82 for red normalized difference vegetative index (NDVI) with maize yield at V8 stage. Normalized difference vegetative index is the most widely recognized vegetative index to quantity living biomass, originally proposed by Tucker (1979). However, NDRE is considered more useful in terms of estimating crop N status for high biomass crops because they are not subject to red waveband saturation as with NDVI (Gitelson et al., 2003; Thompson et al., 2015).

The current study suggests NDRE sensor reading with V8-10 growth stages can provide the highest yield potential predictability. The higher $r^2$ and m values observed with NDRE sensor reading under urea-N treatments conclude that there is linear relationships between NDRE and N rate at the V8-V10 growth stages in which management decisions based on crop sensor should be made under semi-arid furrow irrigated conditions.

## Conclusion

Char application at a rate of 13.4 Mg C ha$^{-1}$ and higher increased SOC compared to control in moderately productive soil. Char increased Fe concentrations, at lower rates also reduced pH and at higher rates increased K, and Mg in soil but did not affect crop yields. Char effect on crop yield might be soil condition specific or it might take several years before benefits of char on soil properties translate into crop yield. Active crop sensor performed well in the determination in-season N status and eventual crop yield in char-amended urea fertilized soil in semi-arid under irrigated field conditions. Further researches are needed to test the broader applicability of char across various agroecozones to influence adoption and use as a soil amendment in farmlands.

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**Table 4-1.** Changes in soil chemical properties in two years following char application as affected by char and nitrogen treatments and their interaction.

| | pH | SOC | N | P | K | Ca | Mg | S | Fe | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **Source of variation** | | mg kg$^{-1}$ | | | | | | | | |
| Char (C)[†] | | | | | | | | | | |
| C0 | -0.1 a[§] | 3.9 b | 3.5 | 11.1 | 3.0 b | 299.9 | 63.2 c | -3.0 | 0.41 b | 0.1 |
| C1 | -0.2 b | 4.2 b | 11.7 | 10.4 | 19.6 b | 56.6 | 63.8 bc | -1.8 | 0.97 a | 0.1 |
| C2 | -0.2 b | 5.1 a | 9.2 | 10.2 | 14.1 b | 40.8 | 73.2 bc | -1.7 | 1.17 a | 0.3 |
| C3 | -0.1 a | 5.3 a | 10.7 | 8.5 | 56.9 a | 386.6 | 95.9 a | -2.1 | 1.37 a | 0.0 |
| C4 | -0.1 a | 5.4 a | 2.5 | 10.8 | 35.3 ab | 181.2 | 81.6 ab | -2.0 | 1.26 a | 0.1 |
| Significance | *** | *** | NS | NS | * | NS | ** | NS | *** | NS |
| Nitrogen (N)[‡] | | | | | | | | | | |
| N0 | -0.1 | 4.4 | 4.9 | 9.2 b | 15.2 b | 92.9 | 78.0 | -2.5 | 1.2 | 0.1 |
| N1 | -0.2 | 4.6 | 12.3 | 6.8 b | 5.3 b | 219.6 | 72.6 | -2.1 | 0.8 | 0.0 |
| N2 | -0.1 | 4.6 | 5.6 | 5.7 b | 5.2 b | 232.3 | 73.2 | -2.6 | 0.9 | 0.1 |
| N3 | -0.2 | 4.1 | 6.6 | 5.8 b | 14.5 b | 115.1 | 65.5 | -2.4 | 1.0 | 0.1 |
| N4 | -0.1 | 5.5 | 6.1 | 18.3 a | 53.3 a | 264.3 | 88.0 | -1.7 | 1.3 | 0.3 |
| N5 | -0.1 | 5.0 | 9.6 | 15.3 a | 69.6 a | 136.0 | 80.9 | -1.4 | 1.0 | 0.2 |
| Significance | NS | NS | NS | *** | *** | NS | NS | NS | NS | NS |
| C x N | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |

[†] Char treatment included five rates of char (measured in C equivalent): C0 through C4 received char at 0, 6.7, 13.4, 20.1 and 26.8 Mg C ha$^{-1}$ respectively.

[‡] Nitrogen treatment included four rates of urea: N0 through N3 received urea at 0, 90, 180 and 270 kg N ha$^{-1}$ and two rates of composted manure: N4 and N5 received composted manure at 33.6 and 67.2 Mg ha$^{-1}$.

[§] Means for each variable are differences between 2018 and 2016 (negative value means decrease in means and vice-versa) and means followed by same lowercase letters are not significantly different.

**Table 4-2.** Summary of the mixed model repeated measures analysis of variance on crop yield (2016-2018) and normalized difference red-edge (NDRE) (2017-2018).

| **Source of variation** | **Yield** | **NDRE** |
|---|---|---|
| Year (Y) | | |
| 2016 | 9.96[§] | - |
| 2017 | 14.13 | 0.32 |
| 2018 | 12.20 | 0.34 |
| Significance | *** | *** |
| Char (C)[†] | | |
| C0 | 12.34 | 0.32 |
| C1 | 11.85 | 0.33 |
| C2 | 12.16 | 0.33 |
| C3 | 12.12 | 0.33 |
| C4 | 12.03 | 0.33 |
| Significance | NS | NS |
| Nitrogen (N)[‡] | | |
| N0 | 10.09 | 0.31 |
| N1 | 12.47 | 0.33 |
| N2 | 13.79 | 0.34 |
| N3 | 14.01 | 0.34 |
| N4 | 10.93 | - |
| N5 | 11.31 | - |
| Significance | *** | *** |
| Growth stage (G) | | |
| V6 | - | 0.25 |
| V8 | - | 0.35 |
| V10 | - | 0.37 |
| R1 | - | 0.34 |
| Significance | - | *** |
| Y x C | NS | NS |
| Y x N | ** | ** |
| Y x C x N | NS | NS |
| Y x G | - | *** |
| Y x C x G | - | NS |
| Y x N x G | - | *** |
| Y x C x N x G | - | NS |

[†] Char treatment included five rates of char (measured in C equivalent): C0 through C4 received char at 0, 6.7, 13.4, 20.1 and 26.8 Mg C ha$^{-1}$ respectively.

[‡] Nitrogen treatment included four rates of urea: N0 through N3 received urea at 0, 90, 180 and 270 kg N ha$^{-1}$ and two rates of composted manure: N4 and N5 received

composted manure at 33.6 and 67.2 Mg ha$^{-1}$ (N4 and N5 were not included in NDRE calculation).

[§]Although main factor was significant, lsd letters are not given when interaction effect involving that main factor was significant.

***$P < 0.001$, **$P < 0.01$ and NS = not significant.

**Table 4-3.** Normalized difference red-edge (NDRE) as affected by interactions of nitrogen, year and growth stage.

| | **NDRE** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 2017 | | | | 2018 | | | |
| **Nitrogen (N)[†]** | V6 | V8 | V10 | R1 | V6 | V8 | V10 | R1 |
| N0 | 0.22 j | 0.29 ghi | 0.30 gh | 0.34 de | 0.26 i | 0.35 cde | 0.31 fgh | 0.36 cd |
| N1 | 0.25 ij | 0.32 fg | 0.35 cde | 0.36 cd | 0.26 i | 0.37 bcd | 0.33 e | 0.38 ab |
| N2 | 0.26 i | 0.34 de | 0.38 ab | 0.36 cd | 0.25 ij | 0.38 ab | 0.35 cde | 0.39 a |
| N3 | 0.26 i | 0.33 e | 0.37 bcd | 0.36 cd | 0.26 i | 0.38 ab | 0.36 cd | 0.40 a |

[†]Nitrogen treatment included four rates of urea: N0 through N3 received urea at 0, 90, 180 and 270 kg N ha$^{-1}$.

[‡]Means for each variable followed by same lowercase letters are not significantly different.

**Table 4-4.** Coefficient of linear regression ($r^2$) and slope (m) for NDRE at various growth stages against applied urea-N and maize grain yield in 2017 and 2018.

| | **Urea-N** | | **Yield** | |
|---|---|---|---|---|
| **NDRE** | 2017 | 2018 | 2017 | 2018 |
| V6 | 0.85, 0.13[†] | 0.97, -0.03 | 0.73, 93.74 | 0.02[‡], -12.23 |
| V8 | 0.79, 0.16 | 0.96, 0.14 | 0.82, 86.22 | 0.78, 93.58 |
| V10 | 0.68, 0.24 | 0.97, 0.13 | 0.74, 101.41 | 0.77, 151.29 |
| R1 | 0.63, 0.05 | 0.83, 0.13 | 0.68, 49.07 | 0.33, 40.23 |

[†]$r^2$, m value

[‡]Except this one ($r^2$= 0.02) which had $P$ =0.12, all other $r^2$ values were significant at $P$ <0.01.

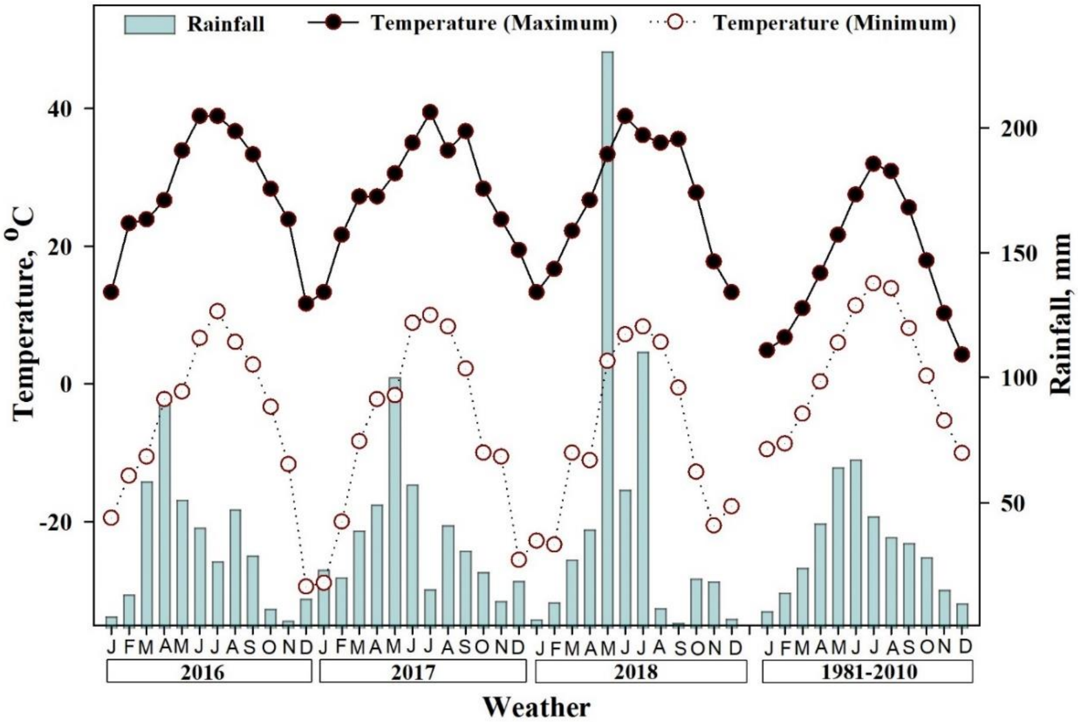


**Figure 4-1.** Monthly minimum and maximum air temperature and total rainfall in 2016-2018, and a 30-year long term average (1981-2010) in Scottsbluff, NE.

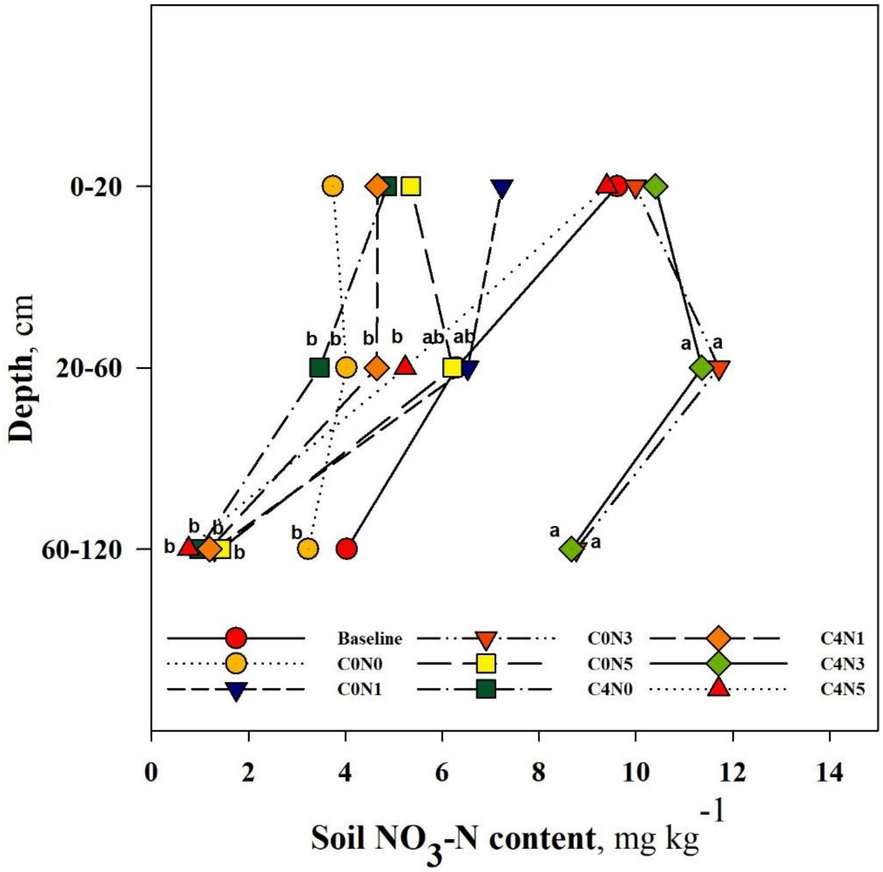


**Figure 4-2.** Soil residual nitrate-N content under different treatment that included C0N0; no char or urea, C0N1; no char and urea at 90 kg N ha$^{-1}$, C0N3; no char and urea at 270 kg N ha$^{-1}$, C0N5; no char and composted manure at 67.2 Mg ha$^{-1}$, C4N0; char at 26.8 Mg C ha$^{-1}$ and no urea, C4N1; char at 26.8 Mg C ha$^{-1}$ and urea at 90 kg N ha$^{-1}$, C4N3, char at 26.8 Mg C ha$^{-1}$ and urea at 270 kg N ha$^{-1}$, and C4N5; char at 26.8 Mg C ha$^{-1}$ and composted manure at 67.2 Mg ha$^{-1}$. Baseline samples were collected in spring of 2016 and treatment samples in spring of 2018. Means at 20-60 cm with different letters are significantly different at $P < 0.05$. Means at 60-120 cm with different letters are different at $P = 0.065$.

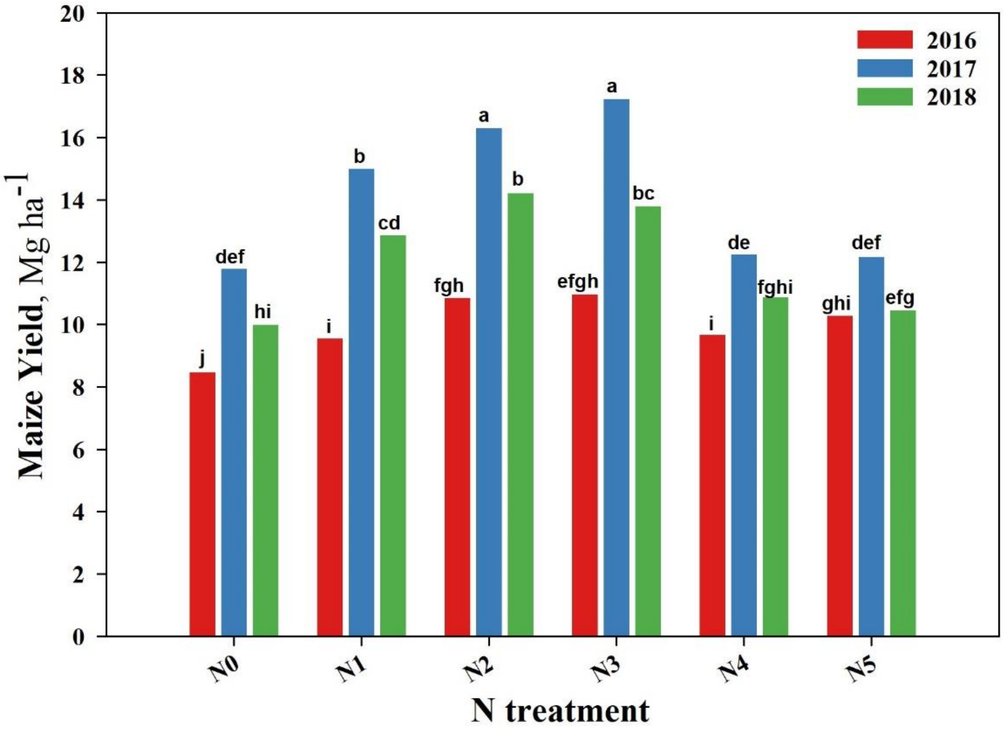


**Figure 4-3.** Maize yield as affected by interaction of nitrogen and year. Nitrogen treatments included four rates of urea: N0 through N3 received urea at 0, 90, 180 and 270 kg N ha$^{-1}$ and two rates of composted manure: N4 and N5 received composted manure at 33.6 and 67.2 Mg ha$^{-1}$. Means for each variable followed by same lowercase letters are not significantly different.

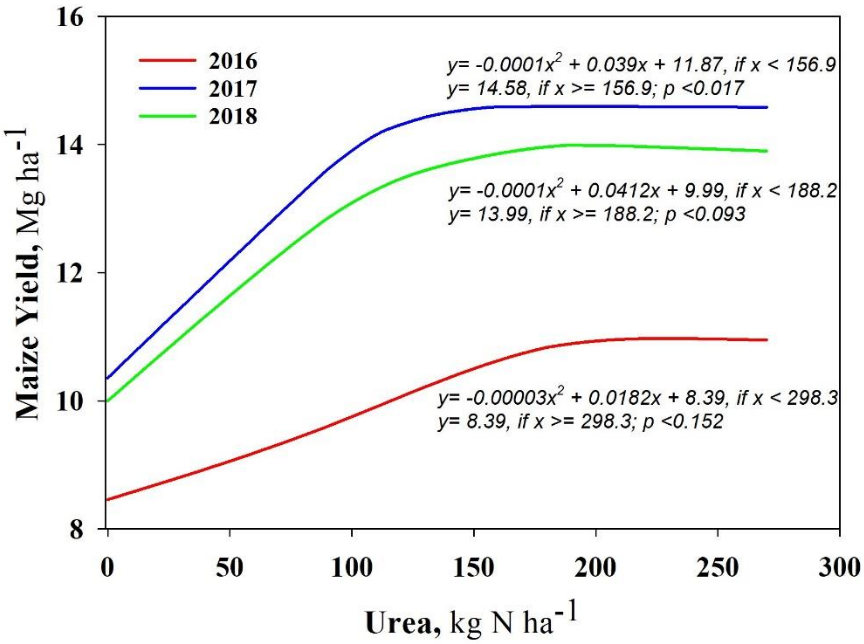


**Figure 4-4.** Means of maize yield at different urea-N rates in 2016, 2017 and 2018 and their quadratic-plateau regression. Lines represent fitted polynomial models where Y is the yield of grain (Mg ha$^{-1}$) and X is the rate of urea (kg N ha$^{-1}$).

# CONCLUSION

In this dissertation, C-rich coal combustion residue i.e., char was evaluated for its possible use as a beneficial soil amendment. Two laboratory and two field studies were conducted to assess the char effectiveness in reduction of environmental N losses and improve soil and crop yields in semi-arid region. Those studies were i) to evaluate effects of char on different forms soil N losses from fertilized loam and sandy loam soils, ii) to determine effects of char on soil pH, N transformations, and subsequent $NH_3$ volatilization in sandy loam soil, iii) to evaluate the effects of char and other amendments on soil C, soil fertility properties, crop nutrient uptake, and crop yields in a low C sandy loam soil with limited productivity, and iv) to evaluate the effects of char applied together with urea or composted manure on soil properties and crop yields in sandy loam soil. Furthermore, this study also evaluated the performance of active crop sensor in determining in-season N status under the given condition.

Our results show that char applied at 10.1 Mg C $ha^{-1}$ (or 33.6 Mg char $ha^{-1}$) in sandy loam and 13.4 Mg C $ha^{-1}$ (or 44.6 Mg char $ha^{-1}$) in loam soil can reduce ammonia volatilization in fertilized soil and subsequently reduce environmental N losses in a laboratory setting. Char application at 13.4 Mg C $ha^{-1}$ (or 44.6 Mg char $ha^{-1}$) can reduce pH in alkaline sandy loam soil. However, these recommendations are yet to validate from field trial. A minimum of 6.7 Mg C $ha^{-1}$ (or 22.5 Mg char $ha^{-1}$) of char is recommended to increase soil C for those soil which has an initial low C concentration. Char at a rate of 6.7 Mg C $ha^{-1}$ (or 22.5 Mg char $ha^{-1}$) is needed to increase the crop productivity under the same scenario. Application of char can increase Fe uptake in crop leaf tissue and possibly support to overcome Fe chlorosis problem in alkaline sandy loam soil. Similarly, a minimum of 12.2 Mg C $ha^{-1}$ (or 40.6 Mg char $ha^{-1}$) is recommended to increase soil C for moderately productive soil in semi-arid region. Active crop sensor can perform well in the determination of in-season N status and eventual crop yield in semi-arid soil under irrigated field conditions.

Overall, the current study provides evidence to consider a coal combustion residue to cropland. Char can reduce environmental N losses and contribute to soil sustainability and environmental safeguard. As with any soil amendment, there are risks to cropping systems if excessive amounts of char are applied. Hence, routine crop and soil monitoring should be conducted following the best management practices to ensure that crop and soil productivity is maintained.

If present trends continue, the amounts of char produced from coal-fired power plants in western NE will likely increase and more char will be available for agricultural use. However, the current study had some limitations, for example the nature of C present in char, char effect on N mineralization/ immobilization, possible adverse effects of pesticide sorption and trace metal accumulation following char application, etc. were not fully understood. Hence at first, the characterization of C present in char needs to be ascertained before extensive use of industrial waste product in a particular application.

The development of environmental and agronomic applications of char residue depends on a detailed knowledge of the speciation across a variety of conditions and physicochemical behavior of heavy metal ions and complexes as a function of composition and environment. To successfully transition char residue from a waste to be disposed of at cost (though currently, it is available at no cost), to a new product and create overall value, will require a detailed cost analysis of current residue storage practice including future liabilities. This should be undertaken for several generic refinery locations. Further studies are needed to identify which crops and soils will respond under what conditions in what percentage of years is required to aid in making economically rational decisions on where and how much char should be applied.

# Appendix

**Appendix 1- 1.** Char stockpiled at Western Sugar Cooperative in Scottsbluff, NE.

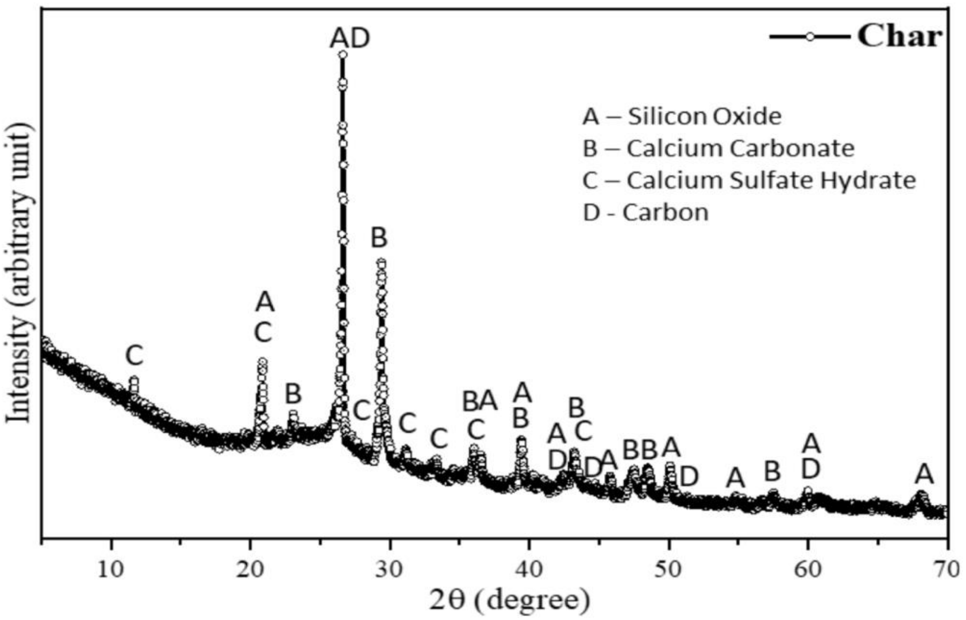
**Appendix 1- 2.** Properties of char that was used in the experiment.

| **Element** | **g kg$^{-1}$** |
|---|---|
| Total carbon | 293.0 |
| Nitrogen | 4.0 |
| Phosphorus | 2.0 |
| Potassium | 2.0 |
| Calcium | 48.0 |
| Magnesium | 11.0 |
| Sulfur | 5.0 |
| Iron | 12.7 |
| Chloride | 3.0 |
| Sodium | 2.0 |

| **Element** | **mg kg$^{-1}$** |
|---|---|
| Boron | 121.8 |
| Manganese | 121.0 |
| Copper | 64.6 |
| Zinc | 45.0 |
| Chromium | 14.4 |
| Lead | 8.8 |
| Molybdenum | 1.9 |
| Cadmium | 0.6 |
| Mercury | 0.3 |
| Selenium and Arsenic | nd |

| | |
|---|---|
| Particle size | |
| 0.05- 2 mm | 66.8% |
| 0.002- 0.05 mm | 11.2% |
| <0.002 mm | 22.0% |

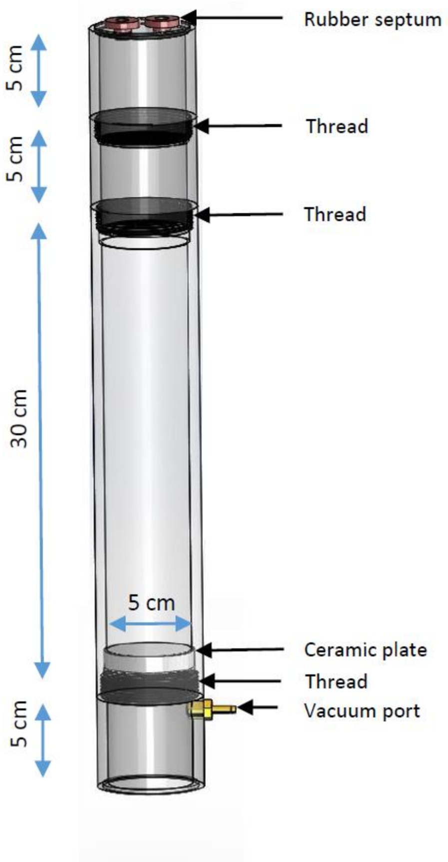
| | |
|---|---|
| pH | 7.6 |
| C:N | 79:1 |
| CEC | 46.9 cmol kg$^{-1}$ |
| Surface area | 82 m$^2$ g$^{-1}$ |



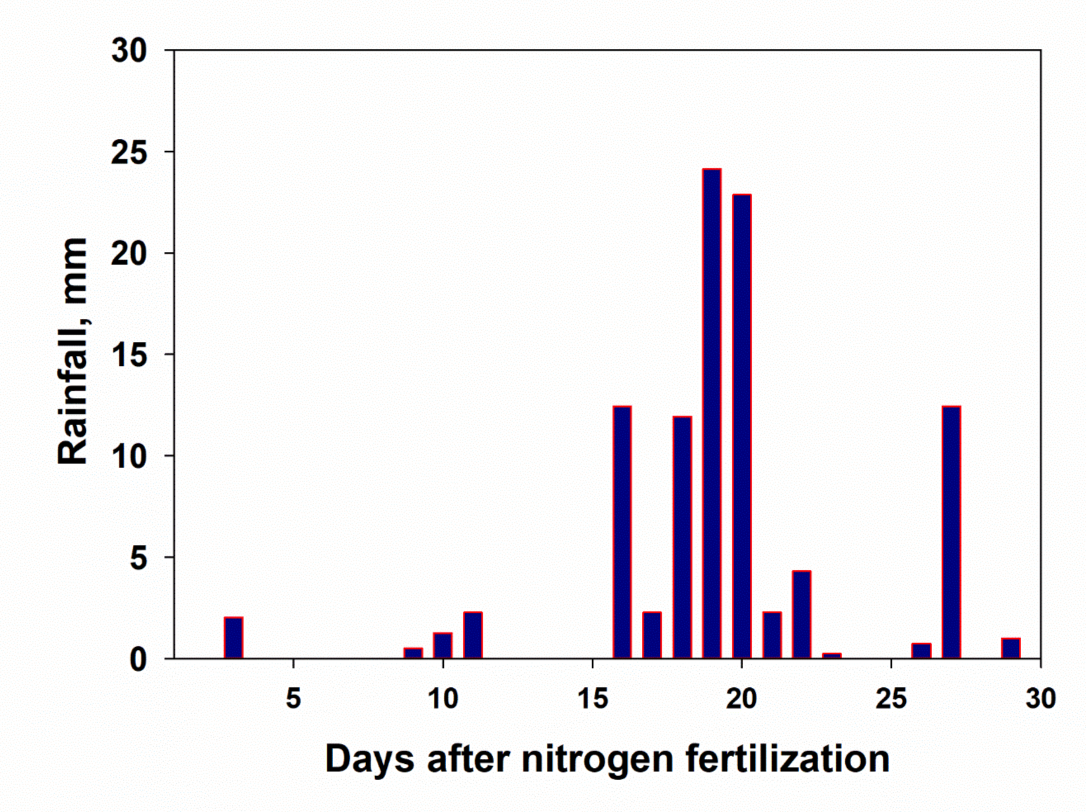
**Appendix 1- 3.** Powder x-ray diffraction pattern of the char.

**Appendix 1- 4.** Range for particle size and Brunauer, Emmett and Teller (BET) surface areas for char compared to reported values for sand, silt and clay particle classes (from Qi and Zhang, 2015).

| Sample | Particle size | BET surface area |
|---|---|---|
| | mm | $m^2 g^{-1}$ |
| Char | 2- 0.002 | 82.1 |
| Sand | 0.424-0.075 | 2.2 |
| Silt | 0.045-0.002 | 23.3 |
| Clay | 0.002-0.0009 | 52.2 |



**Appendix 1- 5.** Sketch of soil acrylic column used in the experiment.



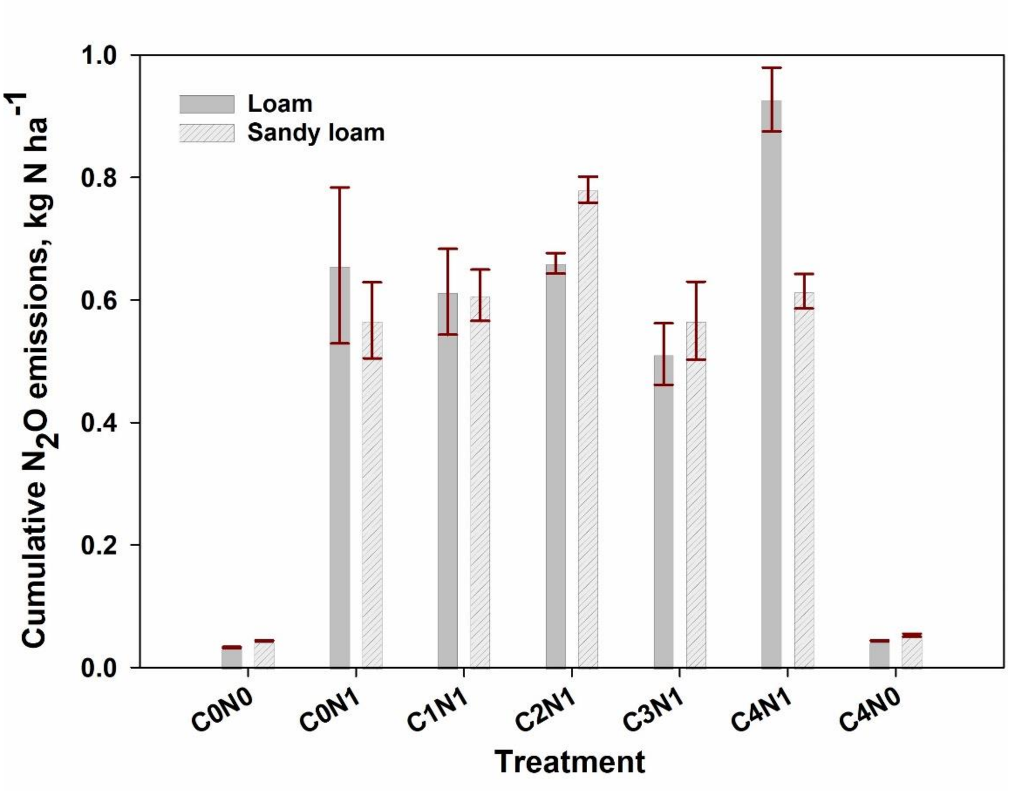
**Appendix 1- 6.** Amount of water added (equivalent to rainfall in May 2017 in Scottsbluff, NE) following days after nitrogen fertilization in soil column.

**Appendix 1- 7.** Laboratory calendar showing days of water addition and sample collection from soil column.

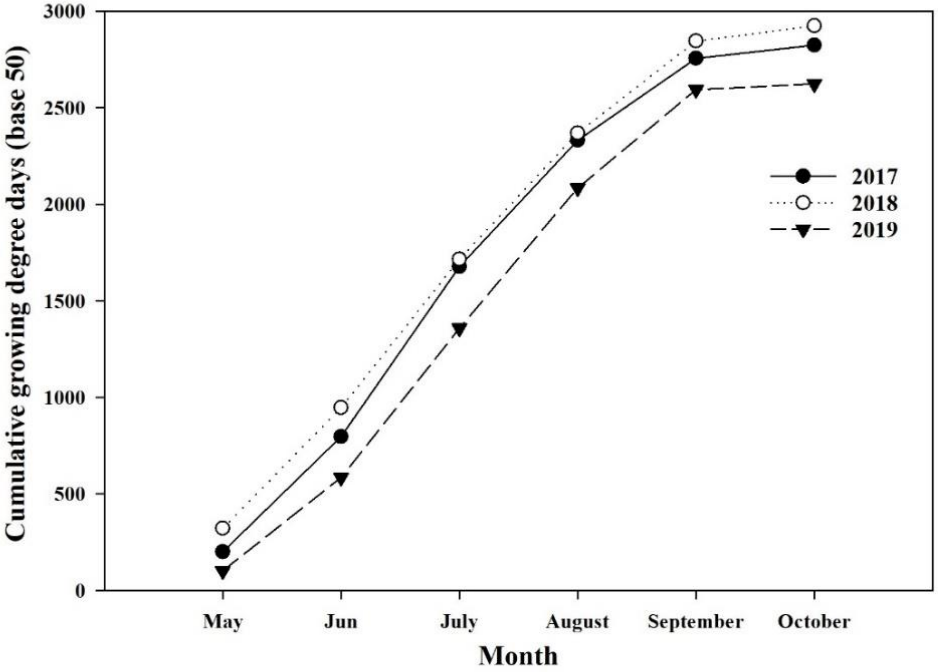
| **Activity\ Day**[†] | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water adeed[‡] | | | 3.9 | | | | | | 0.9 | 2.5 | 4.5 | | | | |
| Acid trap | ■ | ■ | ■ | | ■ | | ■ | | ■ | | ■ | | ■ | | |
| Gas sample | ■ | | ■ | | ■ | | ■ | | ■ | | ■ | | ■ | | ■ |
| Leachate sample | | | | | | | | | | | | | | | |
| Soil residual N | | | | | | | | | | | | | | | |
| **Activity\ Day** | **16** | **17** | **18** | **19** | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** | **28** | **29** | **30** |
| Water added | 24.5 | 4.5 | 23.4 | 47.4 | 44.9 | 4.5 | 8.5 | 0.5 | | | 1.5 | 24.5 | | 2 | |
| Acid trap | | ■ | | ■ | | ■ | | | | ■ | | | | ■ | |
| Gas sample | | ■ | | ■ | | ■ | | ■ | | ■ | | ■ | | ■ | |
| Leachate sample | | | | | ■ | ■ | | | | | | | ■ | | |
| Soil residual N | | | | | | | | | | | | | | | ■ |

[†] Prior to day 1, soil columns were prepared and the first acid trap was placed.

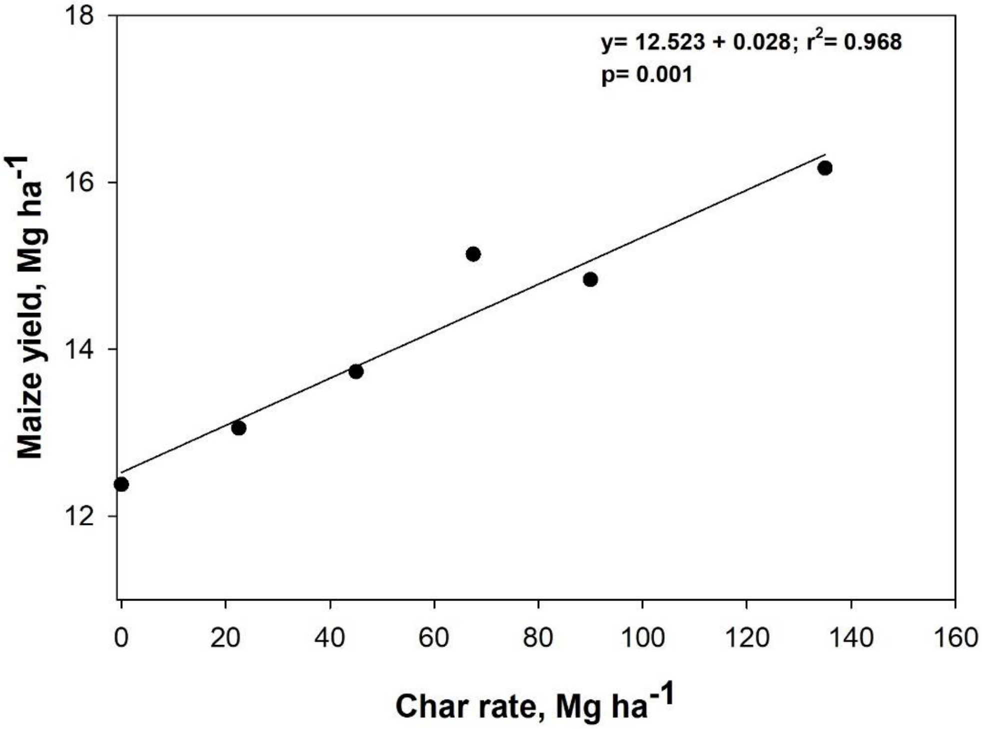
‡ Amount of water addition (mL) in soil column.



**Appendix 1- 8.** Cumulative $N_2O$ emissions (mean ± standard error; n=4) with different treatments in loam and sandy loam soils. C0N0, no char and no urea ammonium nitrate (UAN); C0N1–C4N1, UAN at 200 kg N ha$^{-1}$ and char at 0, 6.7, 10.1, 13.4, and 26.8 Mg C ha$^{-1}$, respectively; C4N0, 26.8 Mg C ha$^{-1}$ and no UAN.



**Appendix 3- 1.** Cumulative growing degree days for crop growing period of 2017, 2018 and 2019 in Scottsbluff, NE. Dry bean, maize and sugar beet were planted in 2017, 2018 and 2019, respectively.



**Appendix 3- 2.** Linear regression between maize yield per applied char rate in 2018.

**Appendix 3- 3.** Concentration of heavy metals (mg kg$^{-1}$) in maize and dry bean grains under five char treatments.

| | **Char**, Mg ha$^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Heavy Metal** | 0 | | 44.6 | | 66.9 | | 89.2 | | 133.8 | |
| | Dry bean | Maize | Dry bean | Maize | Dry bean | Maize | Dry bean | Maize | Dry bean | Maize |
| Aluminum (Al) | 23 | ND[†] | 21 | ND | 8 | ND | 5 | ND | 27 | ND |
| Antimony (Sb) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Arsenic (As) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Barium (Ba) | 1 | ND | ND | ND | 1 | ND | ND | ND | 2 | ND |
| Beryllium (Be) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Boron (B) | 10 | 2 | 9 | 2 | 10 | 2 | 12 | 2 | 11 | 2 |
| Cadmium (Cd) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Chromium (Cr) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Cobalt (Co) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Copper (Cu) | 9 | 1 | 9 | 1 | 10 | 1 | 12 | 1 | 9 | 1 |
| Iron (Fe) | 60 | 15 | 57 | 15 | 54 | 17 | 61 | 13 | 63 | 15 |
| Lead (Pb) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Manganese (Mn) | 4 | 15 | 4 | 13 | 4 | 16 | 4 | 14 | 4 | 14 |
| Mercury (Hg) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Nickel (Ni) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Selenium (Se) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Silver (Ag) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Thallium (Tl) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Vanadium (V) | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Zinc (Zn) | 25 | 14 | 24 | 14 | 27 | 15 | 32 | 14 | 24 | 15 |

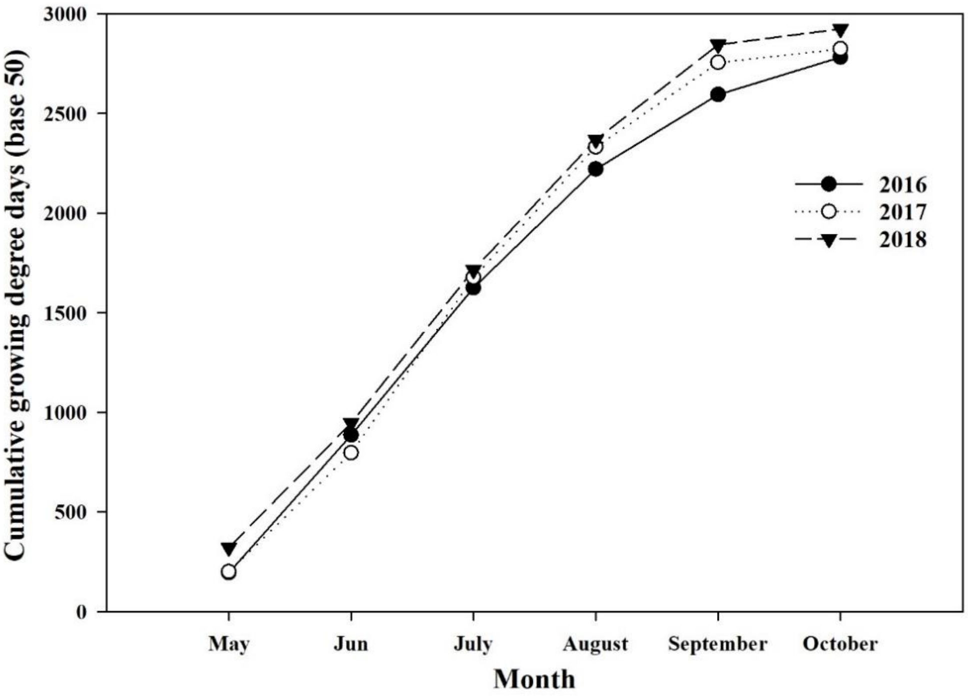
[†] Not detected.

**Appendix 3- 4.** Mean soil chemical properties as affected by the different treatments in 2018.

|  | **Rate** | **pH** | **N** | **P** | **K** | **Ca** | **Mg** | **S** | **Fe** | **B** | **Zn** | **CEC** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Treatment** | Mg ha$^{-1}$ |  | mg kg$^{-1}$ |  |  |  |  |  |  |  |  | cmol kg$^{-1}$ |
| Control |  | 8.3 b[†] | 13.6 | 29.1 | 686.0 | 4203.5 bc | 520.5 | 31.7 | 2.4 | 1.4 | 2.2 | 28.0 |
| Char | 22.3 | 8.4 ab | 12.1 | 26.4 | 693.0 | 4310.0 ab | 545.2 | 35.7 | 2.3 | 1.3 | 2.1 | 28.3 |
|  | 44.6 | 8.3 b | 15.2 | 28.3 | 719.8 | 4249.0 abc | 518.5 | 37.0 | 2.3 | 1.4 | 2.0 | 27.9 |
|  | 66.9 | 8.3 b | 16.4 | 57.8 | 798.8 | 4295.5 ab | 496.0 | 38.1 | 2.9 | 0.9 | 2.4 | 27.7 |
|  | 89.2 | 8.4 ab | 13.5 | 19.1 | 655.5 | 4387.8 a | 532.8 | 48.8 | 2.1 | 1.4 | 2.4 | 28.5 |
|  | 133.8 | 8.4 ab | 12.0 | 29.9 | 703.2 | 4275.0 abc | 528.8 | 24.0 | 2.3 | 1.2 | 2.0 | 28.0 |
| Biochar | 5.6 | 8.4 ab | 12.1 | 21.1 | 648.8 | 4379.8 a | 497.8 | 27.1 | 2.1 | 0.9 | 1.8 | 28.1 |
|  | 11.2 | 8.4 ab | 10.4 | 28.3 | 714.0 | 4213.5 bc | 486.0 | 30.6 | 2.3 | 0.9 | 2.0 | 27.4 |
| Composted manure | 33.6 | 8.4 ab | 15.6 | 43.7 | 750.8 | 4147.0 c | 513.2 | 29.2 | 2.4 | 1.1 | 2.2 | 27.4 |
|  | 67.2 | 8.3 b | 14.1 | 39.1 | 747.5 | 4250.8 abc | 536.5 | 38.0 | 2.4 | 1.6 | 2.2 | 28.2 |
| Municipal compost | 33.6 | 8.5 a | 11.8 | 24.8 | 638.7 | 4233.2 bc | 502.0 | 31.5 | 2.1 | 1.1 | 2.4 | 27.4 |
|  | 67.2 | 8.4 ab | 20.3 | 34.8 | 752.2 | 4261.8 abc | 499.5 | 37.4 | 2.2 | 1.3 | 2.2 | 27.8 |
| Significance |  | * | NS | NS | NS | * | NS | NS | NS | NS | NS | NS |

[†] Means in a column followed by same lowercase letter are not significantly different.

*$P < 0.05$ and NS = not significant.



**Appendix 4- 1.** Cumulative growing degree days for maize growing period of 2016, 2017 and 2018 in Scottsbluff, NE.

**Appendix 4- 2.** Mean soil residual nitrate-N at three different depths (0-20, 20-60 and 60-120 cm) affected by char, nitrogen, and their interaction.

| | Soil residual nitrate-N, mg kg$^{-1}$ | | |
|---|---|---|---|
| Source of variation | 0-20 cm | 20-60 cm | 60-120 cm |
| Char (C) [†] | | | |
| C0 | 6.57 | 7.11 | 3.23 |
| C4 | 7.33 | 6.17 | 1.19 |
| Significance | NS | NS | NS |
| Nitrogen (N) [‡] | | | |
| N0 | 4.30 | 3.74 b[§] | 3.23 |
| N1 | 5.94 | 6.55 ab | 1.23 |
| N3 | 10.19 | 11.54 a | 8.65 |
| N5 | 7.37 | 5.21 b | 1.36 |
| Significance | NS | ** | NS |
| C x N | NS | NS | NS |

[†] Char treatment included two rates of char (measured in C equivalent): C0 and C4 received char at 0 and 24.4 Mg C ha$^{-1}$ respectively.

[‡] Nitrogen treatment included three rates of urea: N0, N1 and N3 received urea at 0, 90, and 270 kg N ha$^{-1}$ and one rate of composted manure i.e., N5 at 67.2 Mg ha$^{-1}$.

[§] Means followed by same lowercase letters are not significantly different.

**$P < 0.01$ and NS = not significant.