Chemosphere 142 (2016) 176–183

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Efficacies of designer biochars in improving biomass and nutrient uptake of winter wheat grown in a hard setting subsoil layer

G.C. Sigua [a,*], J.M. Novak [a], D.W. Watts [a], M.G. Johnson [b], K. Spokas [c]

[a] United States Department of Agriculture, Agricultural Research Service, Coastal Plains Soil, Water, and Plant Research Center, Florence, SC 29501, USA
[b] United States Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Western Ecology Division, 200 Southwest 35th Street, Corvallis, OR 97333, USA
[c] United States Department of Agriculture, Agricultural Research Service, St. Paul, MN, USA

HIGHLIGHTS

- Biochar was used to provide alternative recalcitrant carbon source in the soils.
- Additions of different designer biochars may have variable effects on biomass and nutrient uptake of winter wheat.
- Designer biochars did improve both aboveground and belowground biomass and uptake of winter wheat.

ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form 29 May 2015
Accepted 8 June 2015
Available online 22 June 2015

Keywords:
Designer biochars
Belowground biomass
Aboveground biomass
Hard setting subsoil

ABSTRACT

In the Coastal Plains region of the United States, the hard setting subsoil layer of Norfolk soils results in low water holding capacity and nutrient retention, which often limits root development. In this region, the Norfolk soils are under intensive crop production that further depletes nutrients and reduces organic carbon (C). Incorporation of pyrolyzed organic residues or "biochars" can provide an alternative recalcitrant C source. However, biochar quality and effect can be inconsistent and different biochars react differently in soils. We hypothesized that addition of different designer biochars will have variable effects on biomass and nutrient uptake of winter wheat. The objective of this study was to investigate the effects of designer biochars on biomass productivity and nutrient uptake of winter wheat (*Triticum aestivum* L.) in a Norfolk's hard setting subsoil layer. Biochars were added to Norfolk's hard setting subsoil layer at the rate of 40 Mg ha^{-1}. The different sources of biochars were: plant-based (pine chips, PC); animal-based (poultry litter, PL); 50:50 blend (50% PC:50% PL); 80:20 blend (80% PC:20% PL); and hardwood (HW). Aboveground and belowground biomass and nutrient uptake of winter wheat varied significantly ($p \leqslant 0.0001$) with the different designer biochar applications. The greatest increase in the belowground biomass of winter wheat over the control was from 80:20 blend of PC:PL (81%) followed by HW (76%), PC (59%) and 50:50 blend of PC:PL (9%). However, application of PL resulted in significant reduction of belowground biomass by about 82% when compared to the control plants. The average uptake of P, K, Ca, Mg, Na, Al, Fe, Cu and Zn in both the aboveground and belowground biomass of winter wheat varied remarkably with biochar treatments. Overall, our results showed promising significance for the treatment of a Norfolk's hard setting subsoil layer since designer biochars did improve both aboveground/belowground biomass and nutrient uptake of winter wheat.

Published by Elsevier Ltd.

1. Introduction

Norfolk soils in the southeastern U.S. Coastal Plain region have meager soil fertility characteristics because of their sandy textures, acidic pH values, kaolinitic clays and with depleted organic carbon contents. For more than 150 years, Norfolk soils of the southeastern U.S. have been cultivated for row crops, particularly winter wheat, corn and cotton (Novak et al., 2009a,b; Gray, 1933). Most of these agricultural soils are highly weathered Ultisols (Boul, 1973; Gardner, 1981). Extensive clay mineral weathering and clay eluviations along with intensive leaching of bases and high levels of exchangeable Al (Daniels et al., 1978; Gamble and Daniels,

* Corresponding author at: USDA-ARS-CPSWPRC, 2611 West Lucas St., Florence, SC 29501, USA.
E-mail address: gilbert.sigua@ars.usda.gov (G.C. Sigua).

http://dx.doi.org/10.1016/j.chemosphere.2015.06.015
0045-6535/Published by Elsevier Ltd.

1974) has promoted the formation of a hard setting subsoil layers (E horizon). These soil characteristics severely limit fertility and crop productivity, which leaves few management options for improvements (Novak et al., 2009a).

An additional issue with farming in the sandy Coastal Plain is the formation of a hard setting subsoil layer. In the Norfolk soil series, for example, the hard setting subsoil layer results in low water holding capacity that impedes root development. According to Mullins et al. (1990), hard setting soils are soils that are hard, structureless mass during drying and are thereafter difficult or impossible to cultivate until the profile is rewetted. There are at least three agronomic limitations of hard setting subsoil layer in the Norfolk soils: difficulty in producing a good tilth; constraints to seedling emergence; and constraints to root growth. It is generally accepted that compaction restricts root growth and crop production. Oussible et al. (1992) have shown that root penetration in deep soil layers was hampered by subsurface compaction. Excessive soil compaction impedes root growth and therefore limits the amount of soil explored by roots (Ahmad et al., 2009).

As a counter measure to these soil limitations, the Natural Resource Conservation Service and the Agricultural Research Service have developed soil and water conservation management practices (i.e., deep tillage, deep disruption, etc.) for these soils that promote productivity (Novak and Busscher, 2012). Unfortunately, the beneficial effects of tillage are temporary; deep disruption must be done annually (Busscher et al., 2000; Carter et al., 1996). It has been postulated that increasing the organic C content of the hard setting subsoil layer may promote soil aggregation and root penetration. The soil organic C levels are concentrated at the surface or deteriorate in the hot, wet weather (Wang et al., 2000; Parton et al., 1987). An ideal organic carbon-enriched amendment for these soils would be one that is long-lasting and increases aggregation, fertility and water retention (Novak and Busscher, 2012). Recently, Laird (2008) described how a long-lasting technology could be adopted as a management strategy to revitalize soils. In South America, pre Columbian Amazonian inhabitants improved their infertile soils by applying biochars (Lehmann et al., 2006; Glaser et al., 2002). Carbon in the form of biochar is resistant to degradation, having remained in tropical Amazonian soils for centuries (Steiner et al., 2007).

Biochars have been produced from a wide variety of organic materials including forestry and crop residues, paper mill sludge and poultry waste (Chan and Xu, 2009). The influence of biochar on soil properties and crop productivity is likely to vary significantly among biochars because biochar's effectiveness are governed by biomass sources and pyrolysis conditions (Chan et al., 2007, 2008; Gaskin et al., 2008; Chan and Xu, 2009; Nguyen et al., 2010). Accordingly, biochars quality can be variable and different biochars react differently in soils (Sigua et al., 2014; Novak and Busscher, 2012). Novak et al. (2009b) recognized that biochars could be designed with specific chemical and physical properties to target specific soil deficiencies. He perceived that a biochar could be designed to improve the tilth of a hard setting subsoil layer. Since one biochar type will not resolve all issues in all soils, there is a need to conduct additional research on the efficacy of designer biochars in improving biomass and nutrient uptake of crops grown in soils especially with hard setting subsoil layer. We hypothesized that the addition of different designer biochars to a hard setting subsoil layer will have variable effects on biomass and nutrient uptake of winter wheat. The objective of this study was to investigate the effects of multiple designer biochars on biomass and nutrient uptake of winter wheat (*Triticum aestivum* L.) grown in Norfolk soil with hard setting subsoil layer.

2. Materials and methods

2.1. Soil and site description

The Norfolk soil series (fine loamy, kaolinitic, thermic, Typic Kandiudult) was used in the study. This soil is classified as an Ultisols order (US Soil Taxonomy) that formed in extensively weathered Coastal Plain marine sediments with the clay fraction dominated by kaolinite. The Norfolk is a well drained soil located in upland landscapes (Daniels et al., 1978). This soil was collected from the Clemson University, Pee Dee Research and Education Center, Darlington, South Carolina. The collection site has a long history of row crop production (>30 yrs), which in 2007, was converted to switchgrass (*Panicum virgatum*) production.

The hard setting subsoil layer of the Norfolk was collected by removing the top 0–15 cm Ap horizon using a front-end loader. Using a shovel, soils were collected between 15 and 40 cm soil depths. The soil samples were air-dried; and then passed through a 2 mm sieve to remove plant material and large aggregates. Particle size analyses were carried out using the hydrometer method (Soil Characterization Laboratory, The Ohio State University, Columbus, Ohio). The organic carbon (SOC) and total nitrogen (TN) contents of Norfolk subsoil were measured using a LECO Truspec analyzer (LECO Corp., St. Joseph, Michigan). Table 1 summarized some selected soil physical and chemical properties of the soil used in the study.

2.2. Feedstock description, biochar production, and characterization

The three feedstocks were consisted of pine chips (PC), poultry litters (PL) and hardwoods (HW). The blending, pelletilization and pyrolysis procedures that were followed in this study were reported in the early paper of Sigua et al. (2014) and Novak et al. (2014). Biochars were produced from each of the pelletized feedstocks using a slow pyrolysis procedure at 350 °C (Cantrell and Martin, 2012). Each pelletized biochar particle had a length of between 10–20 mm and diameter of about 6–8 mm.

Hardwood biochar was also used in this study for comparison. The HW biochar was processed to <0.5 mm particle size to test if smaller size biochar was more effective at improving the hard setting subsoil layer. The HW biochar was manufactured from oak and

Table 1
Selected soil chemical and mineralogical properties of the soil used in the study.

Soil properties	Norfolk soil
1. Physical	
Sand (g kg^{-1})	807
Silt (g kg^{-1})	167
Clay (g kg^{-1})	26
Soil texture	Loamy sand
Bulk density (Mg m^{-3})	1.5
Porosity (%)	44
Penetration resistance (MPa)	1.1
2. Chemical	
pH	5.93
C (g kg^{-1})	5.81
N (g kg^{-1})	0.82
P (mg kg^{-1})	20.3
K (mg kg^{-1})	121.5
Ca (mg kg^{-1})	244.5
Mg (mg kg^{-1})	54.7
Na (mg kg^{-1})	29.6
Al (mg kg^{-1})	83.0
Fe (mg kg^{-1})	10.7
Cu (mg kg^{-1})	0.18
Zn (mg kg^{-1})	3.8

hickory hardwood sawdust using fast pyrolysis at 500 °C. It had a 14% ash content, an O:C ratio of 0.22, and a surface area of 0.75 $m^2 g^{-1}$. The pH was determined in a 2:1 (water:solid) ratio using distilled water after stirring for 24 h. Ash content of the biochar was determined using ASTM methods for wood charcoal (600 °C). Selected chemical properties of the biochars used in the study are presented in Table 2.

2.3. Scanning Electron Microscopic (SEM) Imaging and Energy Dispersive Spectroscopy (EDS) of Biochar Samples

The PL was suspected to contain excessive plant nutrients and salts (Novak et al., 2014), thus images were collected from its surface using a scanning electron microscope (SEM) (JEOL 6500; Tokyo, Japan) at the University of Minnesota-Surface Characterization Laboratory. The biochar was attached to the SEM mount by an adhesive pad (PELCO Tabs™, Ted Pella, Inc. Redding, CA), and then dried at 105 °C for 24 h to remove trapped water vapor. The PL biochar was then stored under vacuum until analysis. The EDS data was collected from the observed surface precipitated salts to assess their qualitative chemical composition (Thermo-Noran Vantage system). There was no surface coating used for this imaging.

2.4. Experimental design and experimental set-up

Experimental treatments consisted of control, 50:50 blend of pine chips (PC) and poultry litters (PL); 80:20 blend of PC and PL; PL (100%); and PC (100%). The blending ratios of the PC:PL were chosen to reduce the amount of nutrients and other salts potentially causing burns to the wheat plants (Novak et al., 2014). The treatments were replicated four times using pots that were arranged in a completely randomized block design. Biochars were added to Norfolk's hard setting subsoil layer at the rate of 40 Mg ha^{-1}. Each pot also received blanket applications of 45 kg N ha^{-1}, 60 kg P ha^{-1} and 80 kg K ha^{-1} before planting. This application rate was chosen because previously published work identified it as suitable rate for obtaining significant improvement in fertility characteristics of a Norfolk's Ap horizon (Novak et al., 2009a,b). Each pot was planted with 14 wheat seeds (Pioneer, Variety: 26R20) following the two rows in crossing pattern (7 seeds row^{-1}). Each pot received about 0.32 cm of irrigation water day^{-1} using an automatic sprinkler system for the first three days. To account for warmer seasonal temperature, the irrigation rate was gradually increased to about 0.64 cm after five days and further increased to about 1.1 cm of irrigation water per day thereafter. Half of the required irrigation water was delivered in the morning (9 am) and the remaining half amount was delivered in the afternoon (2 pm). Greenhouse temperature and relative humidity were measured daily in order to monitor the need for any supplemental irrigation if needed. Downy mildew occurred on some plants, so fungicides treatments (Tebustar®) were used at the rate of 0.3 L ha^{-1} on day 25 and on day 40.

Table 2
Selected chemical properties of the different designer biochars that were used in the study.

Properties[a]	Biochars sources				
	Pine chips (PC)	Poultry litter (PL)	50:50 Blend (PC:PL)	80:20 Blend (PC:PL)	Hardwood
C (g kg^{-1})	786	511	636	757	662
N (g kg^{-1})	3.8	38.5	34.2	13.0	3.0
C:N Ratio	207:1	13:1	19:1	58:1	221:1
Na (μg g^{-1})	150.8	21620.0	10414.0	4117.0	480.0
Mg (μg g^{-1})	1252.0	15030.0	7680.0	3628.0	741.0
Al (μg g^{-1})	365.0	1098.0	708.0	435.0	420.0
Si (μg g^{-1})	300.0	920.0	930.0	646.0	–
P (μg g^{-1})	592.0	315.7	17074.0	6275.0	200.0
K (μg g^{-1})	3014.0	69380.0	33971.0	14434.0	6237.0
Ca (μg g^{-1})	3621.0	49366.0	23080.0	13829.0	5164.0
Mn (μg g^{-1})	110.7	1072.0	559.0	264.6	113.0
Fe (μg g^{-1})	623.0	3290.0	1622.0	2407.0	2046.0
Cu (μg g^{-1})	19.6	288.1	147.5	63.5	9.1
Zn (μg g^{-1})	70.9	1253.0	563.5	251.1	6.7
Surface area ($m^2 g^{-1}$)	47.5	25.9	69.3	16.8	–

[a] Data reported in this table were first reported by Novak et al. (2009a,b).

2.5. Weekly growth and harvesting of aboveground and belowground biomass

Growth measurements of winter wheat were taken weekly by measuring height of the plants. Plants were harvested by cutting the aboveground biomass from the surface of the soil. Freshly cut aboveground biomass was oven-dried at 60 °C for about 48 h. Belowground was separated from the soil by soaking the entire pot in a bucket of water followed by several washing to detach the soil from roots. The belowground biomass was also oven-dried at 60 °C for about 48 h. Both the aboveground and belowground biomass were weighed and prepared for tissue analyses as described below.

2.6. Tissue analyses of aboveground and belowground biomass

Both the aboveground and belowground biomass was ground to pass through 1-mm mesh screen in a Wiley mill. Ground samples were digested in an auto-block using a mixture of nitric and perchloric acid and were analyzed for tissue P, K, Ca, Mg, Cu, Fe, Al, and Mo concentrations using an Inductively Coupled Plasma (ICP) spectroscopy. Nutrient uptake of winter wheat tissues was calculated using Eq. (1) for the aboveground uptake and Eq. (2) for the belowground uptake.

$$NU_{N,\,P,\,K,\,Ca,\,Mg,\,Cu,\,Fe,\,Al\text{ and }Mo} = [CN_{N,\,P,\,K,\,Ca,\,Mg,\,Cu,\,Fe,\,Al\text{ and }Mo}] \times DMY_{Aboveground} \quad (1)$$

where NU = nutrient uptake (kg ha^{-1}); CN = concentration of nutrients (%); $DMY_{Aboveground}$ = dry matter yield (kg ha^{-1}).

$$NU_{N,\,P,\,K,\,Ca,\,Mg,\,Cu,\,Fe,\,Al\text{ and }Mo} = [CN_{N,\,P,\,K,\,Ca,\,Mg,\,Cu,\,Fe,\,Al\text{ and }Mo}] \times DMY_{Belowground} \quad (2)$$

where NU = nutrient uptake (kg ha^{-1}); CN = concentration of nutrients (%); $DMY_{Belowground}$ = dry matter yield (kg ha^{-1}).

2.7. Statistical analysis

To determine the effect of the different designer biochars on biomass and nutrient uptake of winter wheat grown in soils with hard setting subsoil layer, data were analyzed with a one-way ANOVA using PROC GLM (SAS Institute, 2000). For this study, *F*-test indicated a significant ($p \leqslant 0.05$) effect, so means of the different designer biochars were separated following the procedures of Least Significance Differences (LSD) test, using appropriate mean squares (SAS Institute, 2000).

3. Results

3.1. Aboveground and belowground biomass

Aboveground biomass and belowground biomass of winter wheat are shown in Fig. 1. These biomass components of winter

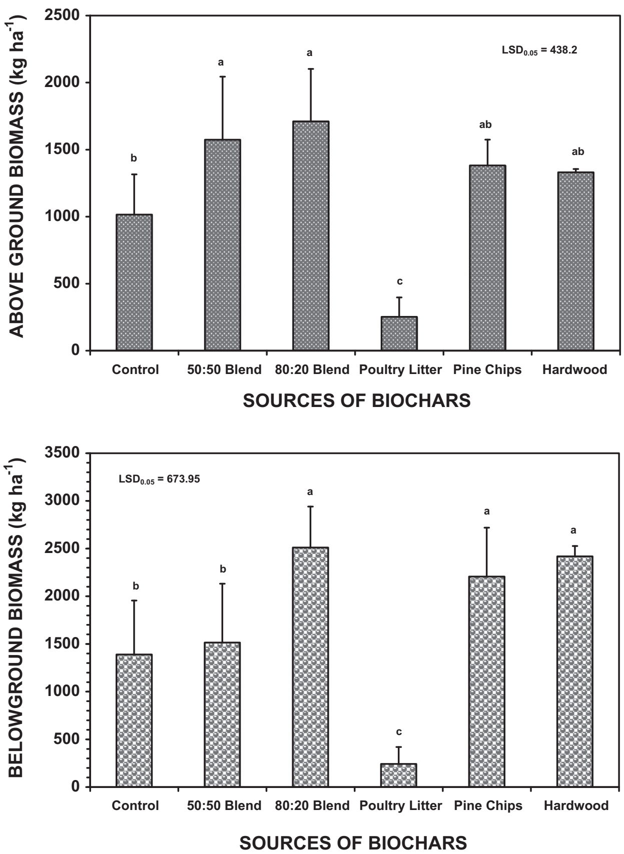

Fig. 1. Average aboveground biomass and belowground biomass of winter wheat as affected by the different designer biochars. Means of aboveground biomass are significantly different ($p \leqslant 0.05$) when superscripts located at top bars are different.

wheat varied significantly ($p \leqslant 0.0001$) with the different designer biochar applications. Application of 80:20 blend of PC and PL produced the greatest aboveground biomass (1711 kg ha^{-1}), belowground biomass (2511 kg ha^{-1}) and total biomass (4222 kg ha^{-1}) of winter wheat. The least amount of aboveground biomass (252 kg ha^{-1}), belowground biomass (243 kg ha^{-1}) and total biomass (496 kg ha^{-1}) were all observed from winter wheat that was fertilized with 100% PL.

Winter wheat that was treated with different designer biochars resulted in significant ($p \leqslant 0.001$) increase in the aboveground biomass over the control except for the application of 100% PL. The percent increase of aboveground biomass is as follows (Fig. 1): 80:20 blend of PC:PL (68%) > 50:50 blend of PC:PL (55%) > PC (36%) > Hardwood (31%). Application of PL biochar at 40 Mg ha^{-1} had reduced the aboveground biomass of winter wheat by 75% when compared with the untreated winter wheat (Fig. 1). Overall, the aboveground biomass of winter wheat did not vary among the 80:20 blend of PC:PL (1711 kg ha^{-1}), 50:50 blend of PC:PL (1574 kg ha^{-1}) and HW (1331 kg ha^{-1}), but were statistically different from the control (1016 kg ha^{-1}). Quite interestingly, our results have shown that all the biochar treatments, including the control had significantly higher aboveground biomass over the application of PL to winter wheat (Fig. 1).

The greatest percent increase in the belowground biomass of winter wheat was from 80:20 blend of PC:PL (81%) followed by HW (76%), PC (59%) and 50:50 blend of PC:PL (9%). Application of PL resulted in a significant reduction of belowground biomass by about 82% when compared to the control plants (Fig. 1). The belowground biomass of winter wheat did not vary among the application of 80:20 blend of PC:PL (2511 kg ha^{-1}), PC (2207 kg ha^{-1}) and hardwood (2418 kg ha^{-1}). However, the aboveground biomass production from these three biochars were significantly higher when compared with the application of 50:50 blend of PC:PL (1515 kg ha^{-1}), PL (243 kg ha^{-1}) and the control (1389 kg ha^{-1}). Overall, our results have shown the favorable effect of different designer biochars on the aboveground biomass of winter wheat grown in Norfolk's hard setting subsoil layer (Fig. 1).

The total biomass of winter wheat did not vary significantly among 80:20 blend of PC:PL (4222 kg ha^{-1}), HW (3749 kg ha^{-1}) and PC (3589 kg ha^{-1}). Application of different designer biochars except for PL had favorably increased total biomass of winter wheat over the control. Percent increased in total biomass as shown in Fig. 1 is as follows: 80:20 blend (76%) > HW (56%) > PC (49%) > 50:50 blend (28%). Application of PL at 40 Mg ha^{-1}had reduced the total biomass production of winter wheat by about 79% (Fig. 1). The average total biomass production of winter wheat without biochar treatment was about 2405 kg ha^{-1} while the average total biomass of winter wheat treated with PL was about 496 kg ha^{-1}. Except for the negative effect of PL, results again have shown the favorable effect of applying designer biochars in improving the total biomass of winter wheat grown in soils with hard setting subsoil layer.

3.2. Aboveground and belowground nutrient uptake

Table 3 shows the average nutrient uptake of winter wheat's aboveground and belowground biomass. Overall, the nutrient uptake in wheat's aboveground and belowground biomass varied widely among the different biochar treatments ($p \leqslant 0.001$). The average uptake of P, K, Ca, Mg, Na, Al, Fe, Cu and Zn in both the aboveground and belowground biomass of winter wheat also varied remarkably with biochar treatments.

Winter wheat treated with 80:20 blend of PC and PL had the overall greatest aboveground and belowground nutrient uptake. This application had improved the aboveground uptake of winter wheat for P, K, Mg, Na, Cu and Zn by 462%, 119%, 76%, 228%, 65% and 9%, respectively when compared with the uptake of winter wheat without biochar treatment. Application of 80:20 blend of PC and PL had improved the belowground uptake of winter wheat for P, K, Ca, Mg, Na, and Cu by 180%, 106%, 118%, 165%, 70%, and 550%, respectively when compared with the uptake of winter wheat without biochar treatment. Overall, our results have shown the favorable effect of using blended feedstocks for biochar application in enhancing nutrient uptake of winter wheat (Table 3).

4. Discussion

Results of our study have demonstrated the favorable and beneficial effects of added biochars on biomass productivity and nutrient uptake of winter wheat grown in Norfolk soil with hard setting subsoil layer. Our results support our hypothesis that addition of different designer biochars will have variable effects on biomass and nutrient uptake of winter wheat. The huge variability in physical structures and chemical compositions of the different biochar materials (100% PC, 100% PL, 80:20 PC:PL, 50:50 PC:PL and 100% HW) in our study may have had led to quite different effects on biomass productivity and nutrient uptake of winter wheat. Our results also suggest favorable effects of blending the different biochar feedstocks to form different designer biochars. Blending of 80% PC and 20% PL has shown promise for tuning the physiochemical characteristics of biochar from a mix of feedstocks (Jassal et al., 2015). Biochars quality can be variable and different biochars react differently in soils (Novak and Busscher, 2012). Therefore, we acknowledge that biochars can be designed to match soil conditions to enhance and/or improve soil fertility while increasing soil

Table 3
Aboveground and belowground nutrient uptake of winter wheat grown in Norfolk's hard setting subsoil amended with different sources of biochars.

Treatment	P ($kg\ ha^{-1}$)	K($kg\ ha^{-1}$)	Ca ($kg\ ha^{-1}$)	Mg ($kg\ ha^{-1}$)	Na ($kg\ ha^{-1}$)	Al ($kg\ ha^{-1}$)	Fe ($kg\ ha^{-1}$)	Cu ($kg\ ha^{-1}$)	Zn ($kg\ ha^{-1}$)
Aboveground uptake									
Control	0.56 ± 0.19b[a]	5.36 ± 1.39b	0.89 ± 0.22b	0.29 ± 0.07b	0.07 ± 0.02c	0.09 ± 0.05b	0.06 ± 0.02ab	0.0017 ± 0.0007b	0.011 ± 0.002ab
50:50 Blend[b]	2.68 ± 0.42a	11.90 ± 1.69a	0.29 ± 0.07c	0.56 ± 0.13a	0.55 ± 0.14a	0.29 ± 0.03a	0.14 ± 0.09a	0.0018 ± 0.0003b	0.011 ± 0.003ab
80:20 Blend	3.15 ± 0.58a	11.72 ± 1.31a	0.68 ± 0.11b	0.51 ± 0.09a	0.23 ± 0.05b	0.36 ± 0.00a	0.10 ± 0.11ab	0.0028 ± 0.0005a	0.012 ± 0.003a
Poultry Litter	0.51 ± 0.53b	2.04 ± 1.89c	0.04 ± 0.03c	0.08 ± 0.07c	0.12 ± 0.08bc	0.04 ± 0.02b	0.03 ± 0.02b	0.0004 ± 0.0003c	0.002 ± 0.001c
Pine Chips	0.96 ± 0.28b	6.95 ± 0.42b	1.25 ± 0.36a	0.35 ± 0.08b	0.08 ± 0.009c	–	0.04 ± 0.01ab	0.0019 ± 0.0005b	0.011 ± 0.001ab
Hardwood	1.07 ± 0.08b	6.15 ± 0.19b	1.18 ± 0.12a	0.37 ± 0.03b	0.07 ± 0.005c	–	0.04 ± 0.01ab	0.0004 ± 0.0003b	0.008 ± 0.001b
$LSD_{0.05}$	0.59	1.95	0.28	0.13	0.10	0.10	0.09	0.0007	0.004
Belowground uptake									
Control	0.52 ± 0.19b	5.42 ± 2.04b	0.38 ± 0.13b	0.17 ± 0.06b	0.54 ± 0.22b	0.52 ± 0.31a	0.35 ± 0.18ab	0.004 ± 0.002d	0.078 ± 0.033ab
50:50 Blend	1.36 ± 0.58a	8.61 ± 3.54ab	0.38 ± 0.15b	0.39 ± 0.17a	0.97 ± 0.37a	0.42 ± 0.28ab	0.29 ± 0.20ab	0.006 ± 0.001 cd	0.031 ± 0.012c
80:20 Blend	1.46 ± 0.46a	11.14 ± 3.34a	0.83 ± 0.09a	0.45 ± 0.12a	0.92 ± 0.24a	0.68 ± 0.42a	0.48 ± 0.31a	0.026 ± 0.009b	0.068 ± 0.004b
Poultry Litter	0.29 ± 0.27b	1.37 ± 0.84c	0.06 ± 0.04c	0.08 ± 0.05b	0.19 ± 0.08c	0.12 ± 0.11b	0.09 ± 0.10b	0.001 ± 0.001d	0.005 ± 0.006c
Pine Chips	1.18 ± 0.36a	8.70 ± 1.86ab	0.84 ± 0.12a	0.39 ± 0.06a	0.38 ± 0.09bc	0.58 ± 0.18a	0.40 ± 0.14a	0.014 ± 0.006c	0.096 ± 0.020a
Hardwood	1.20 ± 0.07a	9.32 ± 0.57a	0.99 ± 0.04a	0.41 ± 0.02a	0.27 ± 0.04	0.56 ± 0.07a	0.44 ± 0.07a	0.036 ± 0.008a	0.076 ± 0.007ab
$LSD_{0.05}$	0.57	3.59	3.79	0.15	0.33	0.39	0.28	0.009	0.02

[a] Means in columns within each subheading followed by common letter(s) are not significantly different from each other at $p \leqslant 0.05$.
[b] Blend of Pine Chips and Poultry Litter.

C sequestration (Sigua et al., 2014). Novak et al. (2009b) pioneered the concept that biochars could be designed with specific chemical and physical properties through feedstock selection, pyrolytic temperature, and residence time manipulation. Since one biochar type will not resolve all issues in all soils, there is a need to conduct additional research on the efficacy of different designer biochars in improving biomass and nutrient uptake of crops grown in soils with hard setting subsoil layer. Improved winter wheat biomass and nutrient uptake as a result of biochar amendment can be attributed to its nutrient and several indirect effects, including the increased levels of soil organic C, available water storage and aggregate formation and potential alteration of soil microbial populations and function (Sigua et al., 2014; Kolton et al., 2011; Steiner et al., 2008; Warnock et al., 2007).

While application of 80:20 blend of PC and PL had the greatest biomass productivity, application of 100% PL at 40 $Mg\ ha^{-1}$ had reduced the total biomass production of winter wheat by about 79%. It may appear that the effects of 50:50 and 80:80 blend of PC:PL on aboveground, belowground and total biomass of wheat were similar to the effects of applied 100% PC and 100% HW as shown in Fig. 1, but not the results of average percent change of aboveground, belowground and total biomass over the control. The actual percent change over the control is showing a much better contrast on the effects of the different designer biochars with respect to the aboveground biomass, belowground biomass and total biomass of winter wheat. Application of 80:20 blend of PC and PL resulted in higher average increase of percent change in aboveground, belowground and total biomass when compared with the application of 50:50 blend of PC and PL, 100% PC and 100% HW, respectively (Fig. 1).

In addition to the potential benefits of blending biochar feedstock as described above, a number of factors could have had affected the outcome of our study. For instance, differences in the rapidity and stability with which given biochars are oxidized in the soil depends on biochars chemical composition along with the physical and chemical conditions of the surrounding soil environment. Application of blended biochars in our study resulted in favorable soil pH and soil EC along with reduced concentrations of soluble salts and heavy metals. The beneficial effects of 80:20 and 50:50 blend of PC and PL could be attributed to lower concentrations of Na, Al, Mn, Fe, Cu and Zn and higher concentrations of P in the biochar materials when compared with the chemical composition of 100% PL biochar. The concentration of P in 80:20 and 50:50 blend of PC and PL were 6275 and 17,074 $\mu g\ g^{-1}$, respectively as compared to 326 $\mu g\ g^{-1}$ of P in 100% PL. The concentration of Na in 100% PL was remarkably high (21,620 $\mu g\ g^{-1}$) when compared with the concentration of Na in 80:20 (4117 $\mu g\ g^{-1}$) and 50:50 (10,414 $\mu g\ g^{-1}$) blend of PC and PL.

The high concentrations of Na and other nutrients in 100% PL had resulted in large decrease of wheat biomass and substantial increased in soil electrical conductivity (EC) and soil pH. Application of 100% PL and 50:50 blend of PC and PL in Norfolk's hard setting subsoil layer resulted in greater soil pH and soil EC values relative to the control (Fig. 2). It is possible that the

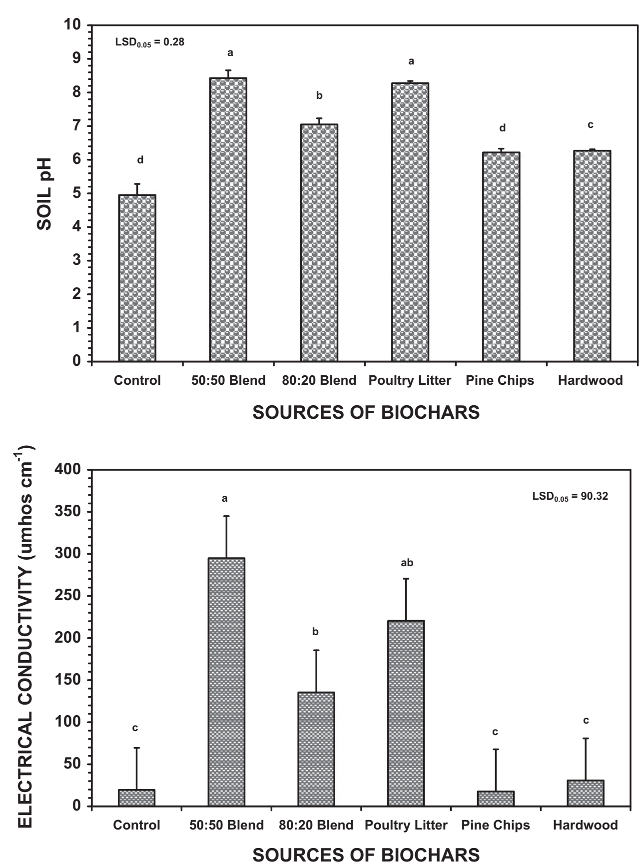

Fig. 2. Average pH and electrical conductivity of soils treated with the different designer biochars. Means of soil pH and soil electrical conductivity are significantly different ($p \leqslant 0.05$) when superscripts located at top bars are different.

increased in pH and increased amount of ions (as measured by EC) in the soils due to the high application rate (40 Mg ha^{-1}) of biochars benefited the plants with increased biomass productivity due to additional uptake of nutrients from the biochars. However, the application of biochar appears to have become a negative factor on plant growth and development of winter wheat as in the case of 100% PL and 50:50 blend of PC:PL. Application of 100% PL has increased soil pH and EC by 67% and 1032% over the control while application of 50:50 blend of PC:PL has increased soil pH and soil EC by 70% and 1415% over the control, respectively.

The negative effect of applied 100% PL on biomass productivity and nutrient uptake of winter wheat could be attributed to the pH and EC of soils as shown in Fig. 2. Excessively high EC can affect plants in the following ways: (1) specific toxicity of a particular ion, such as sodium; and (2) higher osmotic pressure around the roots prevents an efficient water absorption by the plant. The stress caused by high EC is a major challenge to non-halophytic higher plant like the winter wheat. The presence of salts and their elemental composition on the 100% PL biochar was confirmed using SEM/EDS analysis (Fig. 3). Poultry litter biochar had salt crystallized on the surface composed of KNO_3, KCl, and $Ca_3[PO_4]_2$ that are known to be soluble in water. The majority of the salts occurs on the surface of the biochar and not embedded in the biochar organic C matrix. As noted by the bright white colors across the surface, we speculate that the salts were easily dissolved in water because the anion is bound to a monovalent cation (Bohn et al., 1979). When exceeded and applied at high application rate (40 Mg ha^{-1}), these surface precipitated salts may cause serious limitations to agriculture by decreasing yield of various fruit, forage and field crops including wheat (Rausch et al., 1996; Sumaryati et al., 1992; Epstein et al., 1980; Richard, 1954).

Based on soil pH and soil EC, application of 100% PC and 100% HW biochars had minimal negative effect on biomass productivity and nutrient uptake of winter wheat (Fig. 2). The resulting pH of soils that were treated with 100% PC and 100% HW of 6.5 and 6.7, respectively were closed to the "ideal" soil pH. The average EC of soils treated with 100% PC and 100% HW were considerably low (Fig. 2). Although the average pH in soils with 100% PC and 100% HW were near neutral along with the low soil EC, their effects on winter wheat productivity and nutrient uptake were still significantly lower than the effect of 80:20 blend of PC and PL because they have low concentrations of nutrients (Table 2). The other factor could be the C:N ratio of these biochars (i.e. 207:1 for 100% PC and 221:1 for 100% HW). The profound differences in the C:N ratio of these biochars as compared with 100% PL (13:1), 50:50 blend of PC and PL (19:1) and 80:20 blend of PC and PL (58:1) can explain the striking difference in the decomposition rates. Similar results were obtained by Sigua et al. (2014). They reported that in Coxville soil with swine solid biochar had the greatest average amount of CO_2–C evolved while in Norfolk soil with pine chip biochar had the least average amount of CO_2–C evolved and these results could be related to the C:N ratio of the biochars. Pine chip biochar with wide C:N ratio and low nitrogen content is associated with slow decay while swine solid biochar with narrow C:N ratio and containing high nitrogen content may undergo rapid mineralization. Their results have demonstrated that manure-based biochars (poultry litter and swine solid) with narrow C:N ratio had greater mineralization rates than lignocellulosic-based biochars with wide C:N ratio (switchgrass biochar and pine chip biochar). The rates of mineralization in designer biochars may have had significant effect on biomass productivity and nutrient uptake of winter wheat.

Overall, the nutrient uptake in wheat's aboveground and belowground biomass varied widely among the different biochar treatments. The average uptake of P, K, Ca, Mg, Na, Al, Fe, Cu and Zn in both the aboveground and belowground biomass of winter wheat also varied remarkably with biochar treatments. Winter wheat treated with 80:20 blend of PC and PL had the overall greatest aboveground and belowground nutrient uptake. The beneficial effect of 80:20 blend of PC and PL on aboveground and belowground uptake could be related to the resulting soil pH and soil EC following its application because the availability of some plant nutrients is greatly affected by soil pH. The "ideal" soil pH is close to neutral, and neutral soils are considered to fall within a range from a slightly acidic pH of 6.5 to slightly alkaline pH of 7.5. The resulting pH of soils treated with 80:20 blend of PC and PL were fairly close to the "ideal" soil pH values (6.5–7.5). It has been determined that most plant nutrients are optimally available to plants within this 6.5–7.5 pH range, plus this range of pH is generally very compatible to plant root growth. At alkaline pH values, greater than pH 7.5 for example, phosphate ions tend to react quickly with calcium and magnesium to form less soluble compounds. At acidic pH values, phosphate ions react with aluminum and iron to again form less soluble compounds. Most of the other nutrients (especially micronutrients) tend to be less available when soil pH is above 7.5, and in fact are optimally available at a slightly acidic pH, e.g. 6.5–6.8. The exception is molybdenum, which appears to be less available under acidic pH and more available at moderately alkaline pH values. Addition of 80:20 blend of PC and PL resulted in higher soil pH than those soils without biochars. The higher pH values for soils would favor hydrolysis reactions for Ca and Mg which increase the plant availability of these two nutrients. Higher pH

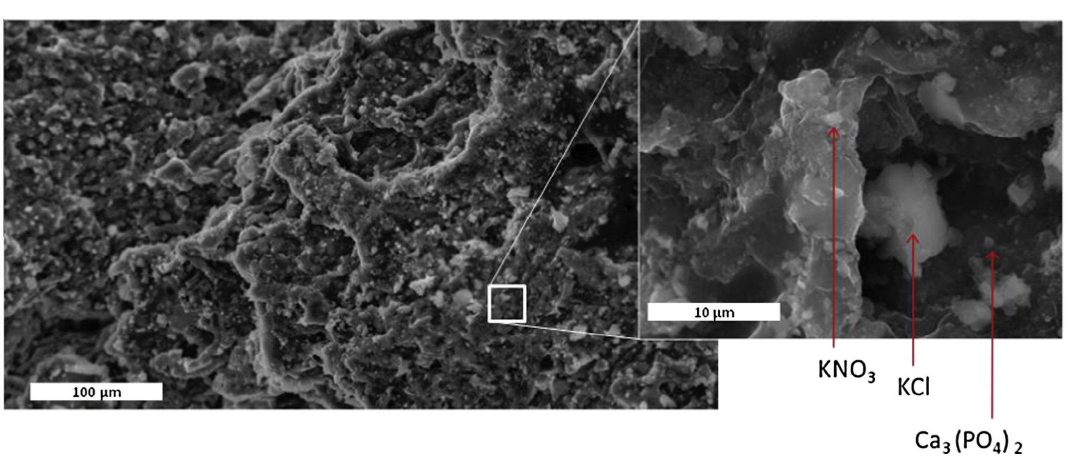

Fig. 3. Electron microscope (SEM) image of the poultry litter biochar, which clearly shows the present of numerous surface precipitated salts on the surface of the biochar. The inset shows a closer magnification along with tentative identification of the salt crystals achieved through EDS analyses.

Fig. 4. Comparison of early growth of winter wheat applied with 100% PL and winter wheat treated with 80:20 blend of PC:PL.

values may well inactivate Al, Mn, Cu, and Fe. Our results have shown that the availability of soil Mn, Cu, Fe, and Al were significantly lowered by the addition of blended biochars (Tisdale and Nelson, 1975). Perhaps the single direct benefit of neutral pH is the reduction in acidity and solubility of aluminum and manganese (Peevy et al., 1972). Some of the indirect benefits of having soil pH near the "ideal" pH in case of soils treated with 80:20 blend of PC and PL, among others would include: enhancing P and microelement availability; nitrification; nitrogen fixation; and improving soil physical conditions (Nelson, 1980; Tisdale and Nelson, 1975; Russell, 1973).

The resulting soil EC following application of 80:20 blend of PC and PL of 120 umhos cm^{-1} was relatively lower than the resulting EC of soils treated with 100% PL of about 230 umhos cm^{-1}. It is likely that there was a minimum interference with uptake of essential nutrients in soils with 80:20 blend of PC and PL compared with 100% PL. An imbalance in the salts content especially in soils applied with 100% PL may result in a competition between elements. This condition is called "antagonism", i.e. an excess of one ion limits the uptake of another ion. For example, excess of chloride reduces the uptake of nitrate, excess of phosphorus reduces the uptake of manganese, and excess of potassium limits the uptake of calcium. High salts concentration in soils with 100% PL may have had resulted in high osmotic potential of the soil solution, so the plant has to use more energy to absorb water. Under extreme high soil EC conditions, plants may be unable to absorb nutrients, water and will wilt, even when the surrounding soil is saturated. Fig. 4 shows the comparison of early growth between winter wheat applied with 100% PL and winter wheat treated with 80:20 blend of PC and PL.

5. Conclusions

Our results supported our hypothesis that addition of different designer biochars will have variable effects on biomass and nutrient uptake of winter wheat. Our study also demonstrated the favorable and beneficial effects of different designer biochars on biomass productivity and nutrient uptake of winter wheat grown in Norfolk soils with hard setting subsoil layer. Application of 80:20 blend of PC and PL was found to be superior over other blend because of its favorable effects on biomass productivity and nutrient uptake of winter wheat. Application of 100% PL resulted in significant reduction of aboveground biomass, belowground biomass and total biomass by about 75%, 82% and 79%, respectively when compared with the control plants. Overall, our results showed promising significance for improving soil fertility and tilth of Norfolk's hard setting subsoil layer since biochars did improve the aboveground, belowground and total biomass of winter wheat.

Disclaimer

Mention of a specific product or vendor does not constitute a guarantee or warranty of the product by the USDA or imply its approval to the exclusion of other products by the USDA or imply it approval to the exclusion of other products that may be suitable.

Acknowledgments

The information in this article has been funded through an Interagency Agreement between the United States Department of Agriculture-Agricultural Research Service (60-6657-1-204) and the United States Environmental Protection Agency (DE-12-92342301-1). It has been subject to review by scientists of the USDA-ARS-Coastal Plain Research Laboratory and by the National Health and Environment Effects Research Laboratory's Western Ecology Division and approved for journal submission. Approval does not signify that the contents reflect views of the US EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. We thank Cierra Buckman and Bree Williams for laboratory assistance and for the pine chips supplied by Dr. Carl Trettin of the USFS-Cordsville Station.

References

Ahmad, N., Hassan, F.U., Belford, R.K., 2009. Effects of soil compaction in the sub-humid cropping environment in Pakistan on uptake of NPK and grain yield in wheat. II. Alleviation. Field Crops Res. 110, 61–68.
Bohn, H.L, Brian, L., McNeal, B.L., George A. O'Connor, G.A., 1979. Soil Chemistry. Wiley-Interscience Publication, John Wiley and Sons.
Boul, S.W., 1973. Soils of the Southern states and Puerto Rico. So. Coop. Series Bull. 174. USDA, Washington, DC.
Busscher, W.J., Lipiec, J., Bauer, P.J., Carter Jr., T.E., 2000. Improved root penetration of soil hard layers by selected genotype. Comm. Soil Sci. Plant Anal. 31, 3089–3101.
Cantrell, K.B., Martin, J.H., 2012. Stochastic state-space temperature regulation of biochar production. J. Sci. Food Agric. 92, 481–489.
Carter, M.R., Holmstrom, D.A., Cochrane, L.A., Brento, P.C., Thomas, W.G., van Rocstel, J.A., Langile, D.R., 1996. Persistence of deep loosening of naturally compacted subsoils in Nova Scotia. Can. J. Soil Sci. 76, 541–547.
Chan, K.Y., Xu, Z., 2009. Biochar: nutrient properties and their enhancement. In: J. Lehmann, S. Joseph, (Eds.). 'Biochar for Environmental Management: Science and Technology. London, pp. 67–84.
Chan, K.Y., Van Zwieten, L., Meszaros, I.A., Downie, A., Joseph, S., 2007. Agronomic values of greenwaste biochar as a soil amendment. Austr. J. Soil Res. 45, 629–634.
Chan, K.Y., Van Zwieten, L., Meszaros, I.A., Downie, A., Joseph, S., 2008. Using poultry litter biochars as soil amendments. Austr. J. Soil Res. 46, 437–444.
Daniels, R.B., Gamble, E.E., Wheeler, W.H., 1978. Age of soil landscapes in the upper Coastal Plain of North Carolina. Soil Sci. Am. J. 42, 98–104.
Epstein, E., Norlyn, J.D., Rush, D.W., Kingsbury, R.W., Kelly, D.B., Cuningham, G.A., Wrona, A.F., 1980. Science 210, 399–403.
Gamble, E.E., Daniels, R.B., 1974. Parent materials of the upper- and middle-Coastal Plain soils in North Carolina. Soil Sci. Am. Proc. 38, 633–637.

Gardner, L.E., 1981. Element mass balance for South Carolina Coastal Plain watersheds. Water Air Soil Pollut. 15, 271–284.

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low temperature pyrolysis conditions on biochars for agricultural use. Trans. ASABE 51, 2061–2069.

Glaser, B.J., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. Biol. Fertil. Soils 35, 219–230.

Gray, L.C., 1933. History of Agriculture in the Southern United States to 1860. Carnegie Inst, Washington, DC.

Jassal, R.S., Johnson, J.S., Molodovskaya, M., Black, T.A., Jollymore, A., Sveinson, K., 2015. Nitrogen enrichment of biochar in relation to pyrolysis temperature and feedstock quality. J. Environ. Mgt. 152, 140–144.

Kolton, M., Harel, Y.M., Pasternak, Z., Graber, E.R., Elad, Y., Cytryn, E., 2011. Impact of biochar application to soil on the root-associated bacterial community structure of fully developed greenhouse pepper plants. Appl. Environ. Microbiol. 77, 4924–4930.

Laird, D.A., 2008. The charcoal vision: a win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100, 178–181.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitigat. Adapt. Strateg. Glob. Change 11, 403–427.

Mullins, C.E., MacLoead, D.A., Notthcote, K.H., Tisdall, J.M., Young, I.M. 1990. Hardsetting soils: behavior, occurrence and management. In: R. Lal, B.A. Stewart. Soil degradation. Advances in Soil Science, vol. 11. Springer-Verlag. New York. pp. 37–108.

Nelson, W.L. 1980. Agricultural liming: its effect on soil fertility, plant nutrition, and yields. In: Proc. 1st Natl. Conf. Agric. Limestone. Nashville, TN, pp. 34–39.

Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S., Masiello, C.A., 2010. Temperature sensitivity of black carbon decomposition and oxidation. Environ. Sci. Technol. 44, 3324–3331.

Novak, J.M., Busscher, W.J. 2012. Selection and use of designer biochars to improve characteristics of southeastern USA Coastal Plain degraded soils. In: J.W. Lee (Ed). Advanced Biofuels and Bioproducts. Springer Science media. USA, pp. 69–96.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmenda, M., Watts, D.W., Niandou, M.A.S., 2009a. Impact of biochar amendment on soil fertility of a southeastern Coastal Plain soil. Soil Sci. 174, 105–112.

Novak, J.M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., Das, K.C., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009b. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195–206.

Novak, J.M., Cantrell, K.B., Watts, D.W., Busscher, W.J., Johnson, M.G., 2014. Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks. J. Soils Sediments 14, 330–343.

Oussible, M., Crookston, R.K., Larson, W.E., 1992. Subsurface compaction reduces the root and shoot growth and grain yield of wheat. Agron. J. 84, 34–38.

Parton, W.J., Schimel, D., Cole, C.V., Ojima, D.S., 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Sci. AM. J. 51, 1173–1179.

Peevy, W.J., Brupbacher, R.H., Sedberry Jr., J.E., 1972. Effects of Some Liming Materials and Calcium Sulfate on Soil Reaction and Exchangeable Calcium and Magnesium. LSU Agr. Center, Baton Rouge, LA. p. 8.

Rausch, T., Matias, Kirch., Rainer, L., Lehr, A., Viereckj, L.R., Zhigang, A., 1996. Salt stress responses of higher plants: the role of proton pumps and Na^+/H^+-antiporters. J. Physiol. 48, 425–433.

Richard, L.A. 1954. Diagnosis and Improvement of Saline and Alkali Soils. Agricultural Handbook 60. USDA. Washington, DC. p. 160.

Russell, W.E., 1973. Soil Conditions and Plant Growth. William Clowes & Sons, Limited, London. p. 849.

SAS Institute. 2000. SAS/STAT User's Guide. Release 6.03. SAS Institute. Cary, NC.

Sigua, G.C., Novak, J.M., Watts, D.W., Cantrell, K.B., Shumaker, P.D., Szogi, A.A., Johnson, M.G., 2014. Carbon mineralization in two Ultisols amended with different sources and particle sizes of pyrolyzed biochar. Chemosphere 103, 313–321.

Steiner, C., Wenceslaus, G.T., Lehmann, J., Nehls, T., de Macedo, J.L., Blum, W.E., Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilizer on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant Soil 291, 275–290.

Steiner, C.K., Das, K.C., Garcia, M., Forster, B., Zech, W., 2008. Charcoal and smoke extract stimulate the soil microbial community in a highly weathered xanthic ferrasols. Pedobiologia 51, 359–366.

Sumaryati, S., Negrutiu, I., Jacobs, M., 1992. Characterization and regeneration of salt- and water-stress mutants from protoplast culture of *Nicotiana plumbaginifolia* (Viviani). Theor. Appl. Gen. 83, 613–619.

Tisdale, S.L., Nelson, W.L. 1975. Soil Fertility and Fertilizers. Macmillan Publishing Co., Inc., New York. p. 694.

Wang, Y., Admunson, R., Xu-Feng, N.V., 2000. Seasonal and altitudinal variation in decomposition and soil organic matter inferred from radiocarbon measurements of CO_2 flux. Global Biogeochem. Cycles 14, 199–211.

Warnock, D.D., Lehmann, J., Kuyper, T.W., Rillig, M.C., 2007. Mycorrhizal responses to biochar in soil-concepts and mechanisms. Plant Soil 300, 9–20.