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Ameliorating soil chemical properties of a hard setting subsoil layer in Coastal Plain USA with different designer biochars

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HIGHLIGHTS

- Biochar was used to ameliorate chemical properties of Norfolk soils.
- Additions of designer biochars have variable effects on soil chemical properties.
- Designer biochars did improve chemical properties of hard-setting Norfolk subsoil.

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ABSTRACT

Biochar application is an emerging management option to increase soil fertility. Biochars could improve chemical properties of soils with hard setting subsoil layer. However, biochar effect can be inconsistent because different biochars react differently in soils. We hypothesized that addition of designer biochars will have variable effects on improving the chemical properties of hard setting layers. The objective of this study was to investigate the effects of biochars on soil properties in Norfolk's soil with a hard setting subsoil layer grown with winter wheat (*Triticum aestivum* L.). All designer biochars were added at the rate of 40 Mg ha^{-1}. Feedstocks used for biochars production were: plant-based (pine chips, 100% PC); animal-based (poultry litter, 100% PL); 50:50 blend (50% PC:50% PL); 80:20 blend (80% PC:20% PL); and hardwood (100% HW). Higher nutrient availability was found after additions of biochars especially additions of 100% PL and 50:50 blend of PC and PL. On the average, applications of 100% PL and 50:50 blend of PC:PL had the greatest amount of soil total nitrogen with means of 1.94 ± 0.3% and 1.44 ± 0.3%, respectively. When compared with the control and other biochars, 50:50 blend of PC:PL additions resulted in increase of 669% for P, 830% for K, 307% for Ca, 687% for Mg and 2315% for Na while application of 100% PL increased the concentration of extractable P, K, Ca, Mg, and Na by 363%, 1349%, 152%, 363%, and 3152%, respectively. Overall, our results showed promising significance since biochars did improve chemical properties of a Norfolk's soil.

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1. Introduction

The rising global population growth combined with global food supply and security necessitates a major optimization in agricultural productivity. This will require preservation and replenishment of soil organic matter to sustain nutrient cycling, improve water- and nutrient-use efficiency and mitigate against climate change (Jones et al., 2012). The fertility of highly weathered Ultisols in the southeastern Coastal Plains region of United States is low. In this region, intensive crop production depletes soil nutrients and reduces soil organic carbon.

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 C contents. Extensive clay mineral weathering and clay eluviations along with intensive leaching of bases and high levels of exchangeable Al (Gamble and Daniels, 1974; Daniels et al., 1978) has promoted the formation of a hard setting subsoil layers. These soil characteristics severely limit fertility and crop productivity, which leaves few management options for improvements (Novak et al., 2009a).

Application of mulches, composts and manures have frequently been shown to increase soil fertility but because of hot and humid conditions, organic matter is usually mineralized rapidly. As an alternate, biochar has been described as a possible means to improve soil fertility and sequester C (Lehmann et al.,

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2006, 2011; Sohi et al., 2010; Lehmann, 2007). An increase in soil fertility is the most frequently reported benefit linked to adding biochar to soils (Manya, 2012; Novak et al., 2014). The increase in the availability of major plant nutrients due to application of biochar was also reported by Glaser et al. (2002) and Lehmann et al. (2002).

The relationship between biochar properties and its potential to enhance soil fertility is still unclear and does not always allow the establishment of appropriate process conditions to produce a biochar with desired characteristics (Novak and Busscher, 2012; Manya, 2012; Keiluweit et al., 2010; Sanchez et al., 2009; Brewer et al., 2009; Hammes et al., 2008). The influence of biochar on soil properties and crop productivity is likely to vary significantly among biochars because biochar's effectiveness is governed by biomass sources and pyrolysis conditions (Chan et al., 2007, 2008; Gaskin et al., 2008; Chan and Xu, 2009; Nguyen et al., 2010). Gaskin et al. (2010) reported that N from biochar might not be available to plants. Other researchers reported that the increase of soil nutrients due to biochars may be short-lived, declining with plant uptake and leaching (Gaskin et al., 2010; Rondon et al., 2007; Steiner et al., 2007). Inconsistencies between reported effects of biochar derived from pyrolysis of crop biomass and those for other sources suggest additional research is needed.

Biochar 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. 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 fertility and tilth of soils 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 improving the chemical conditions of this soil layer. The objective of this study was to investigate the contrasting effects of multiple designer biochars on ameliorating chemical properties in hard setting subsoil layer grown with winter wheat in the Coastal Plain regions of the southeastern USA.

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. Particle size analyses were carried out using the hydrometer method (Gee and Bauder, 1986). 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 summarizes some selected soil physical and chemical properties of the soil used in the study.

Table 1
Selected physical and chemical properties of the hardsetting Norfolk subsoil used in the study.

Soil properties	Norfolk soil
1. Physical	
Sand (%)	80.7
Silt (%)	16.7
Clay (%)	2.6
Soil texture	Loamy sand
Bulk density (Mg m^{-3})	1.5
Porosity (%)	44
Penetration resistance (MPa)	1.1
2. Chemical	
pH	5.93
C (%)	5.81
N (%)	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
CEC (cmol kg^{-1})[a]	2.5

[a] *Source:* Busscher et al. (2010). Soil Science. Volume 175:10–14.

2.2. Feedstock description, biochar production, and characterization

The three feedstocks consisted of pine chips (PC), poultry litter (PL) and hardwood (HW). The blending, pelletilization and pyrolysis procedures that were followed in this study were reported in the early papers 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 500 °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 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. Experimental design and set-up

The experimental treatments consisted of a 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 plant available P and other salts potentially causing nutrient imbalances and resulting 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). Each pot was planted with 14 wheat seeds (Pioneer, Variety: 26R20) following

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 (%)	78.6	51.1	63.6	75.7	66.2
N (%)	0.38	3.85	3.42	1.30	0.30
C:N ratio	207:1	13:1	19:1	58:1	221:1
Na (mg kg^{-1})	150.8	21620.0	10414.0	4117.0	480.0
Mg (mg kg^{-1})	1252.0	15030.0	7680.0	3628.0	741.0
Al (mg kg^{-1})	365.0	1098.0	708.0	435.0	420.0
Si (mg kg^{-1})	300.0	920.0	930.0	646.0	–
P (mg kg^{-1})	592.0	315.7	17074.0	6275.0	200.0
K (mg kg^{-1})	3014.0	69380.0	33971.0	14434.0	6237.0
Ca (mg kg^{-1})	3621.0	49366.0	23080.0	13829.0	5164.0
Mn (mg kg^{-1})	110.7	1072.0	559.0	264.6	113.0
Fe (mg kg^{-1})	623.0	3290.0	1622.0	2407.0	2046.0
Cu (mg kg^{-1})	19.6	288.1	147.5	63.5	9.1
Zn (mg kg^{-1})	70.9	1253.0	563.5	251.1	6.7

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

the two rows in crossing pattern (7 seeds row^{-1}). For the first three days, each pot received about 0.32 cm of irrigation water day^{-1} using an automatic sprinkler system. 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 fungicide treatments (Tebustar[R]) were used at the rate of 0.3 L ha^{-1} on day 25 and day 40.

2.4. Soil sampling and soil analyses

After harvesting the winter wheat, soils containing the belowground biomass were removed carefully from each pot. Belowground biomass was separated from the soil by soaking the entire soil mass in a bucket of water followed by several washing to detach the soil mass from the roots. Separated soil mass were mixed together, air-dried for several days and sieved (2-mm mesh screen) prior to soil chemical analyses. Air-dried soil samples were extracted with double acid (0.025 N H_2SO_4 + 0.05 N HCl) extracting solution as described by Mehlich (1953) and analyzed for selected extractable nutrients (P, Ca, Mg, K, Na, Cu, Fe, Al, Mn, Cu and Zn) using an inductively coupled plasma spectrophotometer. Soil samples were also analyzed for total carbon (TC) and total nitrogen (TN) using a LECO Truspec analyzer (LECO Corp., St. Joseph, MI). Soil pH and electrical conductivity (EC) were determined by using 1:2 soils to water ratio (Thomas, 1996).

2.5. Statistical analysis

To determine the effect of the different designer biochars in ameliorating chemical properties of a Norfolk soil 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. Soil pH and electrical conductivity

Soil pH and electrical conductivity (EC) of a Norfolk's hard-setting subsoil layer varied significantly ($p \leqslant 0.001$) with the application of the different designer biochars (Table 3). Soils that were treated with 50:50 blend of PC:PL and 100% PL had the greatest soil pH with means of 8.42 ± 0.23 and 8.28 ± 0.07, respectively. These two designer biochars also had the two greatest EC readings with means of 295.0 ± 19.0 *u*Siemen cm^{-1} and 220.5 ± 79.8 *u*Siemen cm^{-1}, respectively.

Results have shown the beneficial effect of designer biochars on enhancing soil pH of highly weathered Norfolk soil in Coastal Plain region. Applications of the different designer biochars resulted in significantly higher soil pH than in the control soils (Table 3). The order of soil pH is as follows: 50:50 blend of PC:PL (8.42 ± 0.23) = 100% PL (8.28 ± 0.07) > 80:20 blend of PC:PL (7.05 ± 0.18) > HW (6.28 ± 0.04) = 100% PC (6.22 ± 0.11) > control (4.95 ± 0.33). As shown in Fig. 1, the two greatest percent increase in soil pH relative to the control treatment were from soils treated with 50:50 blend of PC:PL (70%) and 100% PL (67%) followed by 80:20 blend of PC:PL (42%), HW (27%) and 100% PC (26%).

With the exception of 100% PC (−9%), application of the other designer biochars to a highly weathered Norfolk soil resulted in

Table 3
Changes in pH, EC, TN and TC of a hard setting subsoil layer as affected by designer biochars.

Biochar treatments	pH	EC (*uSiemen* cm^{-1})	TN (%)	TC (%)
Control	4.95 ± 0.33d[A]	19.5 ± 4.6c	1.42 ± 0.18b	42.6 ± 2.8a
Hardwood	6.28 ± 0.04c	30.8 ± 7.9c	1.04 ± 0.06c	43.9 ± 0.2a
50:50 Blend (PC:PL)	8.42 ± 0.23a	295.0 ± 19.0a	1.44 ± 0.32b	42.3 ± 0.5a
80:20 Blend (PC:PL)	7.05 ± 0.18b	135.5 ± 39.4b	1.37 ± 0.12b	42.7 ± 1.1a
100% Pine chips (PC)	6.22 ± 0.11c	17.7 ± 4.1c	1.37 ± 0.15b	44.1 ± 0.6a
100% Poultry litters (PL)	8.28 ± 0.07a	220.5 ± 79.8ab	1.94 ± 0.31a	39.8 ± 6.2a
$LSD_{0.05}$	0.28	90.3	0.32	0.42
F-values	197.09***[B]	15.04***	7.31**	1.18^{ns}

[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] *** – Significant at $p \leqslant 0.0001$, ** – significant at $p \leqslant 0.001$, ^{ns} – not significant.

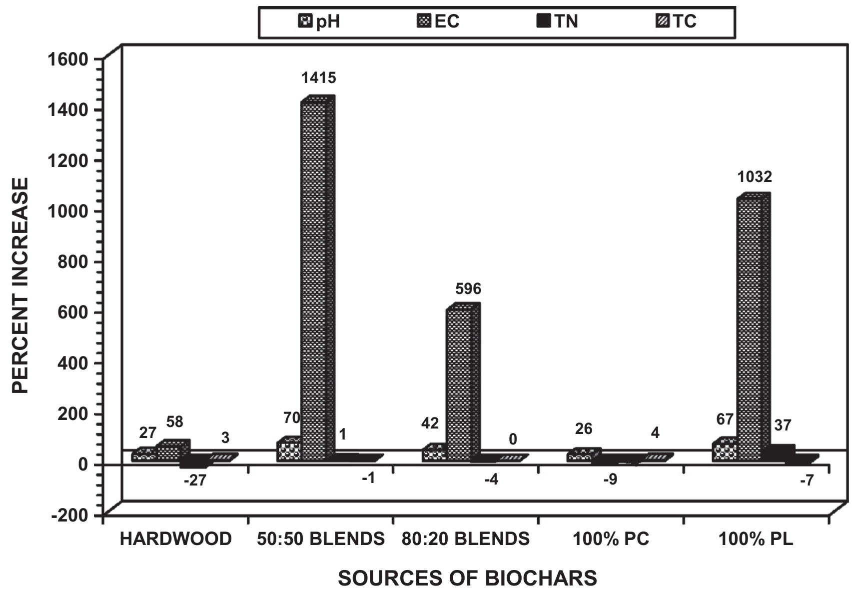

Fig. 1. Calculated percent change on soil pH, EC, TN and TC of Norfolk's soil with hard setting layer when compared with the control.

significantly higher soil EC than the control soil (Table 3). As shown in Fig. 1, the order of percent increase in soil EC over the control is as follows: 50:50: blend of PC:PL (1415%) > 100% PL (1032%) > 80:20 blend of PC:PL (596%) > HW (58%). The average soil EC of the control was 19.5 ± 4.6 *u*Siemen cm^{-1}.

3.2. Total carbon and total nitrogen

Overall, designer biochar treatments had significantly affected the levels of soil TN (Table 3). However, the level of soil TC was not affected by designer biochar (Table 3). On the average, application of 100% PL (1.94 ± 0.3%) had the greatest amount of TN while the least amount of TN in soil was from HW treatment (1.04 ± 0.06%). Application of 100% PC 1.37 ± 0.15%), 80:20 blend of PC:PL (1.37 ± 0.12%) and 50:50 blend of PC:PL (1.44 ± 0.32%) were superior over the application of HW (1.04 ± 0.06%) in increasing the levels of TN in the soil. Application of 100% PL was superior over all designer biochars and the control in terms of percent increase in TN. This designer biochar increased TN by about 37% when compared to the TN level in the control (Fig. 1). This shows the beneficial effect of designer biochars on enhancing soil TN in a typical highly weathered Norfolk soil.

3.3. Mehlich extractable P, K, Ca, Mg and Na

Concentrations of Mehlich extractable P, Ca, K and Mg varied significantly ($p \leqslant 0.0001$) with designer biochars (Table 4). In general, incorporation of all the designer biochars increased the P, Ca, K and Mg contents. There was a much greater increase in the concentrations of Mehlich extractable soil P, Ca, K and Mg for treatments with 50:50 blend of PC:PL and 100% PL compared with the control soils (Fig. 2). When compared with the control and other designer biochars, 50:50 blend of PC:PL and 100% PL had the highest Mehlich extractable P, K, Ca, Mg and Na concentrations. Application of 50:50 blend of PC:PL resulted in increase of 669% for P, 830% for K, 307% for Ca, 687% for Mg and 2,315% for Na over the control. Application of 100% PL increased the concentration of Mehlich extractable P, K, Ca, Mg, and Na by 363%, 1349%, 152%, 363%, and 3152% when compared with the control treatment (Fig. 2).

Application of 100% PC had a negative increase in the concentration of Mehlich extractable P (−21%) and K (−11%) when compared with the control treatment. This designer biochar had the least amount of increase in the concentration of Mehlich extractable Ca (36%), Mg (5%), and Na (−3%) when compared with the control treatments (Fig. 2). Overall, our results had shown the beneficial effect of designer biochar on enhancing concentrations of Mehlich extractable P, K, Ca, Mg and Na of Norfolk's soil with hard setting subsoil layer in Coastal Plain region.

3.4. Mehlich extractable Al, Fe, Mn, Cu and Zn

Designer biochars had significantly ($p \leqslant 0.0001$) affected the concentrations of Mehlich extractable Al, Fe, Mn, Cu and Zn

Table 4
Changes in P, K, Ca, Mg and Na of a hard setting subsoil layer as affected by designer biochars.

Biochar treatments	P (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	Na (mg kg^{-1})
Control	15.4 ± 1.5c[A]	46.5 ± 9.9c	42.5 ± 7.4c	8.2 ± 0.7c	4.8 ± 0.7c
Hardwood	11.3 ± 1.6c	80.2 ± 7.8c	68.7 ± 2.3bc	9.2 ± 0.3c	5.1 ± 0.2c
50:50 Blend (PC:PL)	118.9 ± 32.6a	439.4 ± 15.9b	172.7 ± 48.8a	64.7 ± 18.7a	115.2 ± 33.7b
80:20 Blend (PC:PL)	37.2 ± 7.9c	154.4 ± 12.4c	81.9 ± 16.0bc	21.2 ± 4.1c	29.9 ± 4.7c
100% Pine chips (PC)	12.3 ± 1.1c	41.2 ± 2.4c	57.9 ± 6.9c	8.6 ± 0.3c	4.6 ± 0.2c
100% Poultry litters (PL)	66.8 ± 31.2b	673.2 ± 149.6a	106.9 ± 48.3b	38.1 ± 13.1b	155.2 ± 37.3a
$LSD_{0.05}$	27.8	115.3	43.2	14.1	30.6
F-values	20.6***[B]	44.4***	10.3***	22.8***	40.9***

[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] *** – Significant at $p \leqslant 0.001$, ** – significant at $p \leqslant 0.01$, ns – not significant.

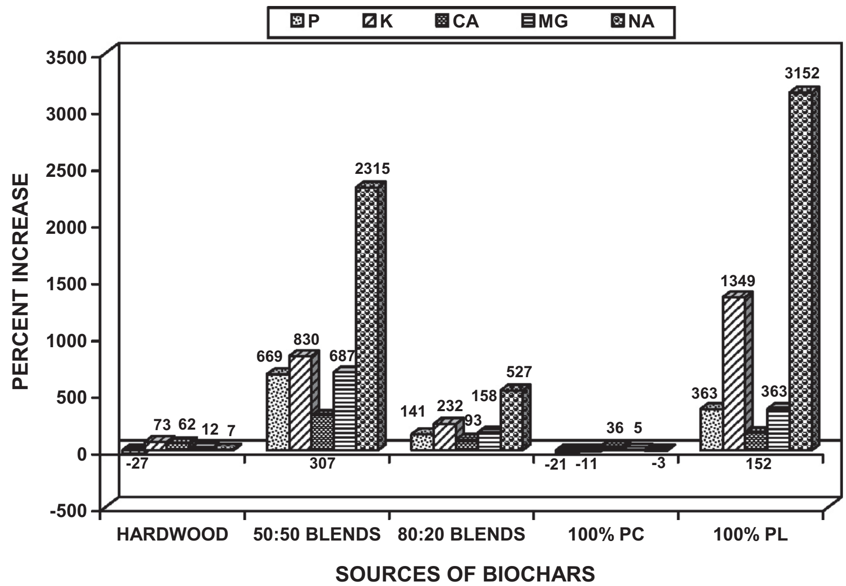

Fig. 2. Calculated percent change on Mehlich extractable P, K, Ca, Mg and Na of Norfolk's soil with hard setting layer when compared with the control.

Table 5
Changes in Al, Fe, Mn, Cu and Zn of a hard setting subsoil layer as affected by designer biochars.

Biochar treatments	Al (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
Control	80.9 ± 5.5b[A]	7.5 ± 0.8c	5.3 ± 0.3de	0.43 ± 0.03 cd	2.4 ± 0.3bc
Hardwood	60.3 ± 5.4c	10.3 ± 0.7ab	6.9 ± 0.4bc	0.54 ± 0.02b	1.2 ± 0.4d
50:50 Blend (PC:PL)	106.6 ± 17.9a	11.1 ± 1.7a	9.4 ± 0.9a	0.57 ± 0.06b	5.1 ± 0.9a
80:20 Blend (PC:PL)	79.2 ± 6.2b	8.0 ± 0.8c	5.8 ± 0.5 cd	0.43 ± 0.02d	2.6 ± 0.5bc
100% Pine Chips (PC)	67.5 ± 2.1bc	5.7 ± 0.3d	4.1 ± 0.1e	0.52 ± 0.03bc	1.8 ± 0.2 cd
100% Poultry Litters (PL)	121.1 ± 17.2a	8.9 ± 1.8bc	7.8 ± 1.9b	0.72 ± 0.12a	7.8 ± 1.9b
$LSD_{0.05}$	16.3	1.7	1.4	0.09	0.8
F-values	18.2***[B]	11.46***	15.5***	11.9***	23.2***

[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] *** – Significant at $p \leqslant 0.001$, ** – significant at $p \leqslant 0.001$, ns – not significant.

(Table 5). Application of 50:50 blend of PC:PL produced the greatest concentration of Mehlich extractable Al (106.6 ± 17.9 mg kg^{-1}), Fe (11.1 ± 1.7 mg kg^{-1}), Mn (9.4 ± 0.9 mg kg^{-1}) and Zn (5.1 ± 0.9 mg kg^{-1}) while application of 100% PL had the greatest concentration of Cu (0.72 ± 0.12 mg kg^{-1}). Overall, application of 50:50 blend of PC:PL and 100% PL resulted in significant increase in the concentrations of Mehlich extractable Al, Fe, Mn, Cu and Zn when compared with the control treatment. The percent increase in the concentration of Al, Fe, Mn, Cu and Zn over the control treatment due to the application of 50:50 blend of PC:PL were 32%, 48%, 76%, 33% and 110%, respectively. Application of 100% PL resulted in increase of 50% for Al, 19% for Fe, 46% for Mn, 68% for Cu and 32% for Zn. Modifications in the Mehlich extractable Al, Fe, Mn, Cu and Zn concentrations among the designer biochars treatments was quite variable (Table 5).

Soils that were treated with 100% PC had negative percent increase in the concentration of Mehlich extractable Al (−17%), Fe (−25%) Mn (−23%) and Zn (−24%) when compared with the control treatment (Fig. 2). Similarly, application of HW resulted in negative increase in the concentration of Al (−26%) and Zn (−49%) relative to the control treatment. Moderate increase in the concentration of Mehlich Al, Fe, Mn, Cu and Zn were noted from soils treated with 80:20 blend of PC:PL and 100% HW when compared with the control treatment. Again, our results have shown favorable effect of designer biochars on improving the concentrations of Mehlich extractable Al, Fe, Mn, Cu and Zn in Norfolk's soil layer.

4. Discussion

Results of our study have demonstrated the favorable and beneficial effects of added designer biochars on chemical properties of the Norfolk soil with hard setting subsoil layer. Results from this study support our hypothesis that addition of different designer biochars will have variable effects on the changes in soil chemical properties. Biochars quality can be variable and different biochars react differently in soils (Novak and Busscher, 2012). A positive outcome from our results suggests that biochars can be designed to match soil conditions to enhance and/or improve soil fertility (Sigua et al., 2014). From these results, we can conclude that designer biochars may not only act as a soil conditioner which can increase cation capacity of the soil, but may also act as a low-grade fertilizer itself. Novak et al. (2009a) 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, the use of different designer biochars could be beneficial in improving fertility of soils particularly with a hard setting subsoil layer. Results of our study were similar to the findings of Yamato et al. (2006) who reported that charred bark induced changes in soil chemical properties by increasing the soil pH, total N, available phosphorus and amounts of exchangeable cations and base saturation. Ash accumulation from applied biochars and its effect on soil pH is well-documented liming mechanisms for improving soil fertility

(Sanchez et al., 1983). The addition of coal ash at the rate of 110 Mg ha^{-1} was shown to increase the pH of soils with various textures by up to 1.2 pH units (Mbagwu et al., 1991).

The higher magnitude of pH change in soils treated with biochar was generally attributed to ash residues in 50:50 blend (PC:PL) and 100% PL generally dominated by carbonates of alkali and alkaline earth metals and plant nutrients mostly bases such as Ca, Mg and K. Furthermore, the increased in soil pH could be associated with the decarboxylation of organic anions (Yan et al., 1996), ligand exchange and addition of basic cations (Bessho and Bell, 1992). In agreement with our results, Arocena and Opio (2003) also reported the capacity of ashes to neutralize the acidic soils. The increase in soil pH has rendered Ca, K, Mg and Na more soluble. The high Ca, K, Mg and Na contents of ash can increase the pH of the soil by displacing the H and Al ions adsorbed on the negative charge of soil colloids. A similar influence was observed after application of charcoal, which increased the pH and decreases the Al saturation of acid soils (Glaser et al., 2002). The higher pH values for soils amended with 50:50 blend (PC:PL) would favor hydrolysis reactions for Ca and Mg which increase the plant availability of these two nutrients. Biochar contains some alkaline materials and has relatively higher pH (Gaskin et al., 2008; Steiner et al., 2007) and, thus can neutralize soil acidity and increase the pH of acid soils.

Biochar, especially manure-based like poultry litter (100% PL) typically has higher pH than soil and it can act as a liming agent resulting in an increase in soil pH (Glaser et al., 2002; Lehmann et al., 2006). Higher soil pH increases nutrients availability and decrease the proportion of Al^{+3} and H^{+} ions in the cation exchange site, which effectively increases base saturation (Brady and Weill, 2004). The results of our soil pH response to additions of biochars were similar to the results reported by Yuan and Xu (2012). They have chosen six biochars for an investigation on their effects on the chemical properties of three acid soils in China. Incorporation of biochars increased the pH of the Ultisols and Oxisols. At the end of incubation, soil pH had increased by 0.72, 0.73, 0.55, 0.11 and 0.33 with the biochars from straws of mungbean, peanut, faba bean, wheat, and rice chaff compared with the control, respectively. Other authors also measured rises in soil pH when biochar was applied to soil (Chan et al., 2008; Laird et al., 2010; Peng et al., 2011; Van Zwieten et al., 2010).

Soil EC in our study underwent similar change as a consequence of biochar application because of the resulting soil pH that rendered Ca, K, Mg and Na more soluble. Application of 100% PL and 50:50 blend of PC and PL in Norfolk's hard setting subsoil layer resulted in greater EC values relative to the control. It is possible that the increased of soil EC is due to the high application rate (40 Mg ha^{-1}) of biochars. Application of 100% PL has increased soil EC by 1032% over the control while application of 50:50 blend of PC:PL has increased soil EC by 1415% over the control.

Application of the different designer biochars to this highly weathered Ultisols with hard setting subsoil layer could have added chemically active surfaces into the soils capable of modifying soil processes responsible for chemical, physical and microbiological properties. The ability of the added designer biochars to alter the nutrient status of the soil in our study appears to be a direct result of the nutrients available in the designer biochars themselves. Our results was highly supported by the early findings of Chan et al. (2007) who reported that the magnitude of changes in the range of soil chemical properties was roughly proportional to the rate of biochar application (i.e., increases with increasing rate of biochar application). The chemical composition of the designer biochar was responsible for the alteration of the nutrient status of each treated soil. Tyron (1948) also found increasing amount of exchangeable bases after additions of 45% hardwood and conifer charcoals to sandy and loamy sands.

A key physical feature of most biochars is their highly porous structure and large surface area. Pyrolyzed feedstocks can enhance surface area of the soil based on early studies of Liang et al. (2006). The porous structure of biochars can provide refugia for beneficial soil microorganisms, such as mycorrhizae and bacteria. Nutrient turnover reactions associated with those soil microorganisms can increase the binding and the availability of macronutrients such as N and P. Changes in soil chemical properties and soil quality reported in our study were supported by the findings of other researchers (Major et al., 2010; Lehmann et al., 2002) who have also reported that utilization of organic residues, as biochar feedstocks will alter the availability of key macronutrients such as N, P, Ca and Mg. Results of our study have shown that higher pH values may well reduce the availability of Al, Mn, Cu, and Fe due to formation of insoluble compounds.

Overall, designer biochar treatments had significantly affected the levels of soil TN. On the average, application of 100% PL had the greatest amount of TN while the least amount of TN in soil was from 100% HW treatment.

A number of factors could have affected the C mineralization of biochars in our study. The rapidity and stability with which given biochars are oxidized in the soil will depend on biochars' physical and chemical composition and the physical and chemical conditions of the surrounding soil environment (Stevenson, 1999). In addition, the C:N ratio of the biochars, age of the feedstocks and the degree of disintegration or particle size of the biochars govern the rate of their decomposition. It is well known that biochars produced from manure-based feedstocks (100% PL) have higher pH values and greater ash and N contents than lignocellulosic-based (100% PC) biochars (Cantrell and Martin, 2012; Spokas et al., 2012; Novak et al., 2009c). Biochars produced from lignocellulosic feedstocks have higher C:N ratio than manure-based biochars. The C:N ratios of the different designer biochars used in the study are as follows: 100% PC (2017:1) > 100% HW (221:1) > 80:20 blend of PC:PL (58:1) > 50:50 blend of PC:PL (19:1) > 100% PL (13:1). The profound difference in the C:N ratio of these biochars can explain the striking difference in the decomposition rates of designer biochars. Pine chip biochar with wide C:N ratio and low nitrogen content is associated with slow decay while PL biochar with narrow C:N ratio and containing high nitrogen content may undergo rapid mineralization. In comparing with the early work of Sigua et al. (2014), our results have also demonstrated that manure-based biochars (PL) with narrow C:N ratio had greater mineralization rates than lignocellulosic-based biochars with wide C:N ratio (100% PC and 100% HW).

Unlike the significant effect of biochar application on soil TN, the concentration of TC in hard setting subsoil layer was not affected by the application of designer biochars. This result could be attributed to the size of biochar application. As described in the materials and methods section, biochars were produced from each of the pelletized feedstocks using a slow pyrolysis procedure at 500 °C. Each pelletized biochar particle had a length of between 10–20 mm and diameter of about 6–8 mm. Our present result was supported by the early findings of Sigua et al. (2014). From their research on C mineralization in two Ultisols amended with different sources and particle sizes of pyrolyzed biochar, they concluded that different particle sizes and sources of biochars as well as soil type influenced biochar stability in the soil. Earlier results of studies have shown that large charcoal particles originated from forest wildfires remained in soils for thousands of years (Gavin et al., 2003; Pessenda et al., 2001). For smaller particles as derived from grassland burning can hardly be detected in steppe ecosystems (Forbes et al., 2006). As noted previously, the particle size of biochars is an important characteristic for its ability to react with soil particles (Laird et al., 2009) and is believed to impact its resistance to microbial mineralization (Manya, 2012). In the case of dust-sized biochars, they have more finely divided or powdered solids that will normally produce a faster reaction than if the same mass is present as pelleted biochars. The powdered solid has a greater surface area than the pelleted biochar. When large, coarse organic materials are chopped or shredded, the decomposition process accelerates. Microbial accessibility to the finer organic materials is increased causing the materials to be quickly decomposed. The huge variability in physical structures and chemical composition of the different biochar materials may lead to quite different turnover times. Zimmerman et al. (2011) reported that both increased (positive priming) and decreased (negative priming) C mineralization has been observed following biochar additions to soils. The priming direction as observed in our study for C mineralization stimulation or suppression varied with soil, biochar types and biochar sizes.

Differences in the ameliorating effects of the applied biochars on chemical properties of soils with hard setting layers could be related to the varying carbon to nitrogen ratio among the different designer biochars. The C:N ratios of biochars used in the study vary widely between 13 and 211 with a mean of 64 (Table 2). This ratio is often used as an indicator of the ability of organic substrates to mineralize and release nutrients especially inorganic nitrogen when applied to soils. Generally, a C:N ratio of 20 is used as a critical limit above which immobilization of nitrogen by microorganism occurs, therefore the nitrogen applied of substrates is not available to plants (Leeper and Uren, 1993). According to the hypothesis of soil mineralization-immobilization turnover (MIT) processes, incorporation of different designer biochars in the soil may cause a rapid increased in the microbial biomass on and around the biochar particles, consequently the soil microbial biomass will act both as a sink for nutrients as a catalyst for decomposition (Jensen, 1997; Gilmour et al., 1985). Immediately after adding a C substrate to soil, the energy and growth substrates generated by heterotrophic metabolism will increase microbial biomass and hence the nitrogen demand of decomposer populations. The decomposition rate of organic materials added to soil is generally most rapid during the first weeks (Gilmour et al., 1985; Sorensen, 1981). Again, all things being equal, materials added to the soil with a C:N ratio greater than 20:1 will result in a temporary nitrogen deficit (immobilization), and those with a C:N ratio less than 24:1 will result in a temporary nitrogen surplus. As shown in our study, the two designer biochars with low C:N ratio such as PL (13:1) and 50:50 blend of PC:PL (19:1) had higher concentrations of N and extractable nutrients (P, K, Ca, Mg and Na) when compared with PC and HW. These two designer biochars have C:N ratios of over 200 (i.e., 207:1 for PC and 221:1 for HW).

5. Conclusions

Our results supported our hypothesis that addition of different designer biochars will have variable results in ameliorating soil chemical properties of a hard setting subsoil layer in Coastal Plain USA. Our study also demonstrated the favorable and beneficial effects of different designer biochars on improving soil chemical properties of Norfolk soils with hard setting subsoil layer. Application of 50:50 blend of PC and PL and 100% PL were found to be superior compared to other designer biochars because of their favorable effects on soil fertility. Overall, our results showed promising significance of designer biochars for improving soil fertility of an Ultisol's soil with hard setting subsoil layer in Coastal Plain, USA.

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