Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil

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Abstract: Agricultural soils in the southeastern U.S. Coastal Plain region have meager soil fertility characteristics because of their sandy textures, acidic pH values, kaolinitic clays, low cation exchange capacities, and diminutive soil organic carbon contents. We hypothesized that biochar additions will help ameliorate some of these fertility problems. The study objectives were to determine the impact of pecan shell–based biochar additions on soil fertility characteristics and water leachate chemistry for a Norfolk loamy sand (fine-loamy, kaolinitic, thermic typic Kandiudults). Soil columns containing 0, 0.5, 1.0, and 2.0% (wt/wt) biochar were incubated at 10% (wt/wt) moisture for 67 days. On days 25 and 67, the columns were leached with 1.2 to 1.4 pore volumes of deionized H_2O, and the leachate chemical composition determined. On days 0 and 67, soil samples were collected and analyzed for fertility. The biochar had a pH of 7.6, contained 834.2 and 3.41 g kg^{-1} of C and N, respectively, and was dominated by aromatic C (58%). After 67 days and two leaching events, biochar additions to the Norfolk soil increased soil pH, soil organic carbon, Ca, K, Mn, and P and decreased exchangeable acidity, S, and Zn. Biochar additions did not significantly increase soil cation exchange capacity. Leachates contained increasing electrical conductivity and K and Na concentrations, but decreasing levels of Ca, P, Mn, and Zn. These effects reflect the addition of elements and the higher sorption capacity of biochar for selective nutrients (especially Ca, P, Zn, and Mn). Biochar additions to the Norfolk soil caused significant fertility improvements.

Key words: Biochar, coastal plain soil, fertility, GRACEnet, leachate

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For more than 150 years, sandy soils of the southeastern U.S. Coastal Plain region have been cultivated for row crops, particularly corn and cotton (Gray, 1933; Trimble, 1974). Most of these agricultural soils are Ultisols (Buol, 1973; Gardner, 1981) formed in fluvial and marine sediments (Daniels et al., 1999) deposited 0.5 to 5 million years before present during the Pliocene to early Pleistocene periods (Daniels et al., 1970; 1978). The warm, humid climate and long time for pedogenesis have created distinct soil profile, mineralogical, and chemical characteristics. Extensive clay eluviation has created shallow A horizons (0–0.20 m thick); well-developed E horizons (0.2–1 m thick) that have sand, loamy sand, or sandy loam textures; and relatively thick Bt horizons (1.0–3.0 m thick) with sandy clay to clay textures (Daniels et al., 1970; Shaw et al., 2004). Intensive leaching of bases has resulted in low soil pH values, extensive clay mineral weathering, low cation exchange capacity (CEC) values (2–8 $cmol_c$ kg^{-1}), and high levels of exchangeable Al (Gamble and Daniels, 1974; Daniels et al., 1978). These soil characteristics severely limit soil fertility and agricultural management options.

For instance, sandy soils exhibit high N leaching after fertilizer or manure application (Trindale et al., 1997; Ritter et al., 1998; Zotarelli et al., 2007). Moreover, Ultisols in the Coastal Plain region have low soil organic carbon (SOC) contents in the surface 0- to 15-cm depth (6.3–9.2 g kg^{-1}; Hunt et al., 1996; Novak et al., 2007a) because of rapid residue oxidation, which is further accelerated by inversion tillage for row crop production (Bauer et al., 2006). The physical and chemical problems discussed above severely limit soil fertility and hence crop productivity on the Ultisols of the southeastern U.S. Coastal Plain.

Fertility problems associated with southeastern Coastal Plain Ultisols are similar to those of Oxisols in intertropical regions (Eswaran and Tavernier, 1980), which also have low pH, SOC, and CEC values (Tiessen et al., 1994; Lehmann et al., 2003). Poor soil fertility raises concerns about the sustainability of agriculture in regions dominated by Oxisols and has spurred the development of management practices to restore or improve their fertility status (Glaser et al., 2002). Applications of mulches, composts, and manures increase soil fertility; however, under tropical conditions, the increase is short term because the added organic matter is quickly oxidized and added bases are rapidly leached (Tiessen et al., 1994).

On the other hand, application of biochar (charcoal produced by pyrolysis of biomass feedstock) to infertile Oxisols has been shown to provide longer-lasting improvements in soil fertility (Glaser et al., 2002; Lehmann et al., 2003; Steiner et al., 2007). Biochar composed primarily of single and condensed ring aromatic C (Lehmann, 2007) has both a high surface area per unit mass and a high charge density. Because of these properties, biochar is both more recalcitrant in tropical soils and contributes a higher capacity to sorb cations per unit mass than does biogenic soil organic matter (Sombroek et al., 2003; Liang et al., 2006).

Biochar application to soils is not a new concept (Mann, 2005). For example, in the Amazon basin, anthropogenic dark earth soils (referred to as Terra Preta) contain large amounts of charred materials most likely added by pre-Columbian farmers who practiced a form of slash and char agriculture (Sombroek et al., 2003) along with disposal of charcoal remains from hearths (Glaser et al., 2002). In these soils, the biochar acts as a soil conditioner, improving soil physical properties and nutrient use efficiency, thereby increasing plant growth. Today, 500 years after cessation of the practices that created these soils, the Terra Preta soils are highly valued for agricultural and horticultural use in the Amazon basin (Glaser et al., 2002; Lehmann and Rondon, 2006).

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To predict the reactivity as well as stability of biochar when used as a soil amendment, it is important to know the biochars organic structural composition. Biochar from Terra Preta soils analyzed using solid-state nuclear magnetic resonance (NMR) analysis was shown to be composed of a highly heterogeneous mixture of organic structures (Novotny et al., 2007). The structural form of C in biochar depends on the biogeochemistry of the biomass feedstock and the conditions under which it was pyrolyzed (Kramer et al., 2004; Lehmann, 2007). Biochars composed primarily of condensed aromatic C are known to persist in soil environments for millennia, whereas biochars with higher levels of single-ring aromatic and aliphatic C will mineralize more rapidly (Lehmann, 2007; Novotny et al., 2007). Surface area and surface charge density of biochar will have a large influence on soil CEC and the ability of biochar additions to ameliorate soil fertility problems.

We hypothesize that biochar additions to the sandy, Coastal Plain soils of the southeastern United States would increase the SOC content and CEC and improve the fertility status. The specific objectives of this investigation were to determine the 1) chemistry of biochar derived from pyrolysis of pecan shells, a locally abundant source of feedstock; 2) effects of biochar additions on fertility characteristics of a Norfolk soil; and 3) effects of biochar additions on the chemical composition of leachate collected from a Norfolk soil.

MATERIALS AND METHODS

Production and Characterization of Pecan Shell–Based Biochar

Pecan shells were obtained from a supplier in Lumberton, NC. They were ground using a Retsch Mixer Mill (SR-2000; Cole-Palmer, Vernon Hills, IL) to pass through a 2-mm sieve. Per each pyrolysis batch, approximately 1000 to 2000 g of shells were placed into a crucible (25 cm wide × 10 cm deep) and were inserted into a Lindberg box programmable furnace equipped with an airtight retort (model 5116HR; Lindberg, Watertown, WI). The furnace retort atmosphere was purged with N_2 using a flow rate of 0.1 $m^3\ h^{-1}$. The furnace was controlled with a multiple-step pyrolysis temperature program. The furnace was initially heated to 40 °C; temperature was ramped to 170 °C at 5 °C min^{-1} and was maintained at this temperature for 30 min. The temperature was then ramped to 700° C at 5 °C min^{-1}, and the pecan shells were subjected to pyrolysis for 1 h. The biochar was cooled in the oven under the N_2 atmosphere overnight. After cooling, the biochar was ground to pass through a 0.25-mm sieve.

The sieved biochar moisture percent (wt/wt) content was measured by oven drying a 2-g portion overnight at 80 °C. Biochar pH was measured according to Ahmedna et al. (1998). The method consisted of preparing a 1% (wt/wt) suspension of biochar in deionized water. The suspension was heated to about 90 °C and stirred for 20 min to allow dissolution of the soluble biochar components. After cooling to room temperature, the pH of the biochar suspension was measured using a Corning pH meter (Acton, MA). The biochar percent ash content (wt/wt) was determined by dry combustion at 760 °C in air for 6 h using an Isotemp laboratory muffle furnace (Fisher Scientific, Pittsburgh, PA). Biochar percent moisture was 1.4%, pH was 7.5, and ash content was 3.8% (wt/wt).

A sample of the biochar was analyzed for total C, H, N, S, and O (by difference) determination using ASTM D 3176 method (ASTM, 2006). For total elemental analyses, the biochar was redried and then digested using the EPA method 3052 microwave-assisted acid digestion method (USEPA, 2008). The elemental concentrations (Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Si, and Zn expressed on a dry, wt/wt, ash-free basis) in the biochar digests were measured using an Elan DRC-II (Perkin-Elmer, Shelton, CT) inductively coupled plasma mass spectrometer. Analytical operating conditions and element detection limits are available at EBG-SWES-UA (2008).

Solid-state cross-polarization magic angle-spinning total-sideband suppression ^{13}C NMR spectral pattern of the biochar was obtained using a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at a ^{13}C frequency of 75.5 MHz. Additional technical parameters to acquire the spectra have been described by Wang et al. (2007). The chemical shift region assignments were as follows: 0 to 50 ppm, aliphatic C; 50 to 109 ppm, O-alkyl C; 109 to 163 ppm, aromatic C; and 163 to 190 ppm, carboxylic C. The percent C distribution was determined by estimating the area in these chemical shift regions as a percentage of the total area under the spectral curve.

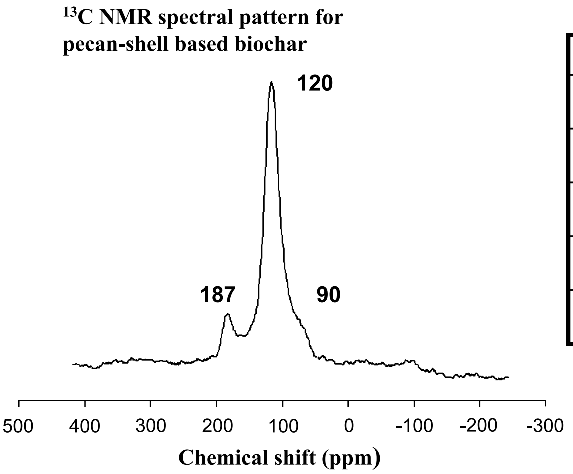
Norfolk Soil Collection and Analyses

A bulk sample of a Norfolk soil from the Ap horizon (0–15 cm deep) was collected from a field contiguous to the USDA-ARS–Coastal Plain Research Center, Florence, SC. The field is nearly level (1–2% slopes) and has a 30-year history of row crop production (Sojka et al., 1984). The soil was collected using a shovel in mid-April, approximately 1 week after fertilization with 49 kg N ha^{-1} of 28-0-0 UAN (urea + NH_4NO_3) for an upcoming corn crop. The soil was air dried and 2-mm sieved. The Ap horizon is a loamy sand with a particle size distribution of 730, 250, and 20 g kg^{-1}, respectively, of sand, silt, and clay (sedimentation method; Soil Characterization Lab, Ohio State University, Columbus, OH). X-ray diffraction analysis of the clay fraction revealed a preponderance of kaolinite, with minor amounts of hydroxy (Fe and Al) interlayered chlorite (X-ray diffraction method; Soil Characterization Lab, Ohio State University). The pH of the untreated Norfolk Ap soil was 4.8, as measured in a 1:1 soil-to-deionized water mixture (Novak et al., 2007a). The total C and total combustible nitrogen (TCN) contents were determined using a LECO TruSpec CN analyzer (LECO Corp., St Joseph, MI). Soil C was assumed to be organic in nature because the low soil pH precluded carbonates.

Biochar Incubation in Norfolk Ap Soil

The biochar incubation experiment was conducted in open-top, 10-cm-diameter, 17-cm-tall schedule-40 PVC columns. Column bottoms were sealed using a nylon mesh fabric to support the soil bed and minimize soil loss. Sufficient amounts of 0.25-mm sieved biochar was mixed into 750-g of air-dried, 2-mm-sieved Ap horizon soil to create 0, 0.5, 1.0, and 2.0% (wt/wt) biochar treatments. These biochar rates equated to field applications of approximately 0, 10, 20, and 40 metric tons ha^{-1}. Each treatment was set up in triplicate. Deionized H_2O was then mixed into each treatment to obtain a soil-moisture content of 10% (wt/wt), representing the upper range (between 5 and 10%) of field capacity for a typical Norfolk Ap soil horizon. The moist soil treatments were then placed into columns, and they were tamped down by hand to obtain a bulk density of 1.2 g cm^{-3}. This created a headspace above the soil of 8 to 10 cm for adding water. The columns were laboratory incubated for 67 days at 10% soil moisture. The laboratory room temperature and percent relative humidity, respectively, throughout the incubation ranged between 17 and 27 °C and 23 and 61%.

On days 25 and 67, each column was leached with 1.2 to 1.4 pore volumes of deionized water; the leachate was collected and weighed. The leachates were analyzed for total organic carbon (TOC) concentrations using a Shimadzu TOC-Vcs (Shimadzu



%C distribution in pecan-shell based biochar		
ppm	**structural group**	**%C**
0 to 50	**aliphatic**	**0**
50 to 109	**O-alkyl**	**29**
109 to 163	**aromatic**	**58**
163 to 190	**carboxyl**	**13**

FIGURE 1. ^{13}C NMR spectral pattern for pecan shell–based biochar (%C distribution for structural groups determined as described by Wang et al. (2007).

Corp., Columbia, MD), and for Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn concentrations with a Varian ICP-OES (Varian Inc., Palo Alto, CA). The ICP detection limit for this suite of 11 elements was a conservative 0.05 mg L^{-1}. The leachate pH and electrical conductivity (EC) were measured using a standard pH and a conductivity meter.

Samples of the biochar-treated Norfolk Ap soil were collected on incubation days 0 and 67 for analysis of plant available nutrients using Mehlich 1 (diluted HCl and H_2SO_4) extractant. Measurements of Mehlich 1–extractable Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn and exchangeable acidity values were conducted by the Clemson University Soil Testing Laboratory using ICP. The pH and EC of the biochar-treated Norfolk Ap soil were measured using the methods of Novak et al. (2007a).

Statistics

The mean values of SOC and TCN contents between the treatments, sorted by incubation day, were tested using a one-way analysis of variance (ANOVA) with a $P < 0.05$ level of significance. The soil fertility characteristics and chemical composition of the deionized water leachates were sorted and tested in a similar manner. All statistical tests were performed using SigmaStat v. 3.5 software (SSPS Corp., Chicago, IL).

RESULTS AND DISCUSSION

Biochar and Soil Compositional Analyses

The ^{13}C NMR spectral pattern of the pecan biochar (Fig. 1) revealed two prominent peaks at 120 and 187 ppm and a shoulder near 90 ppm. These peaks indicate that most of this biochar is distributed in aromatic structures (58%), with less amounts of C having single bonds to O (29%) and in carboxyl (13%) groups. The lack of a distinct peak near 75 ppm suggests little carbohydrate C; rather, the shoulder near 90 ppm is more characteristic of acetal C (Wershaw, 1985). The pecan shells used as feedstock for preparation of the biochar are composed primarily of lignin and cellulose (47%, acid-detergent lignin; Ramirez et al., 1986). Charring of lignin and cellulose at temperatures of 500 °C was reported to cause loss of their aliphatic components along with a conversion of ring structures into aromatic compounds (Rutherford et al., 2004). During pyrolysis at 700 °C in this study, it was suspected that a similar decomposition of cellulose and lignin and structural rearrangement of ring compounds to form condensed and single-ring aromatic structures of the biochar. This speculation has merit because the high pyrolysis temperature explains the lack of alkyl C (0–50 ppm) as volatile material such as oils, fatty acids, and alkyl alcohols would be lost (Antal and Grønli, 2003). Carboxyl-containing structures were present in the NMR spectra possibly because of their structural decomposition resistance during pyrolysis. Alternatively, their presence could be due to water sorption during handling and grinding. The biochar percent moisture after grinding and before total elemental analyses was less than 2% and 4%, respectively. Consequently, single-ring aromatic and some heterocyclic compounds could have been reoxidized, forming carboxylic and acetyl OH groups as evident

TABLE 1. Total elemental analyses of pecan shell–based biochar and Norfolk Ap soil[†] (data sorted into macroelement, microelement pools)

	Biochar	Norfolk Ap soil
Macroelement (g kg^{-1})		
Al	0.22	5.1
C	834.2	16.8
Ca	3.64	0.49
Fe	0.07	2.91
H	10.3	—
K	4.15	0.38
N	3.41	1.26
O	19.8	—
Si	104.9	424.8
Microelements (mg kg^{-1})		
Cu	14	4.6
Cr	0.31	23
Mg	698	445
Mn	78	55
Na	218	951
Ni	0.5	2
P	263	185
S	95	2
Zn	7	43

[†] Determined on biochar and soil using EPA 3052 method (HNO_3 + HF).

TABLE 2. SOC and TCN contents of Norfolk Ap soil and soil + percent biochar mixtures on 0- and 67-day incubations

Norfolk Ap soil + % biochar	SOC (g kg^{-1})[†]		TCN (g kg^{-1})	
	0 d	67 d	0 d	67 d
0	17.0^{a}	17.4^{a}	1.26^{a}	1.24^{a}
0.5	18.1^{a}	18.3^{a}	1.14^{a}	1.28^{a}
1.0	22.2^{b}	21.9^{b}	1.25^{a}	1.09^{b}
2.0	31.2^{c}	29.2^{c}	1.49^{b}	1.21^{a}

[†] Means compared within a column followed by a different letter are significantly different at $P < 0.05$ using a one-way ANOVA (multiple comparisons vs. Norfolk Ap soil + 0% biochar as a control).

in the ^{13}C NMR spectra (Fig. 1). The NMR spectra indicate that this pecan shell–based biochar is composed of a mixture of organic structural groups reflecting the chemistry of the feedstock and reactions occurring during both pyrolysis and after pyrolysis on exposure of the biochar to oxygen and water. These findings are similar to reports for black C isolated from dark earth soils (Schmidt and Noack, 2000; Novotny et al., 2007).

The total elemental analyses of the pecan shell biochar and the Norfolk Ap soil were quite dissimilar (Table 1). The biochar was enriched in C, Ca, K, Mg, N, and Si compared with soil, whereas the Norfolk Ap soil was enriched in Al, Fe, Na, and Si. Pyrolysis of organic feedstock's from 400 to 700 °C results in a concentration of C but a reduction of O and H due to evaporation of sorbed H_2O and driving off of $^{-}$OH functional groups (Antal and Grønli, 2003). The N-containing structures in the biochar, such as amino acids, amines, and amino sugars during the high-temperature pyrolysis (700 °C) process were probably condensed to form N-heterocyclic aromatic structures (Koutcheiko et al., 2007). Thus, much of the residual N in the biochar (Table 1) was likely present as recalcitrant heterocyclic N rather than the more bioavailable amine N.

The elemental composition (C, H, O, N, and S) of biochar was similar to values reported for other carbonized charcoals (Antal and Grønli, 2003). The Norfolk Ap soil elemental composition was Al-, Fe-, and Si-enriched; these elements are predominant in the chemical structure of aluminosilicates in the sand-size fraction (Smith et al., 1976), and Fe-oxides and hydroxides in the clay-size fraction (Shaw et al., 2004).

Changes in Soil Organic Carbon Content and Fertility Characteristics

The Norfolk Ap soil treatments with 1 and 2% biochar addition on day 0 had significantly greater mean SOC contents than the control (Table 2); mean SOC content was increased between 5.1 and 14.2 g kg^{-1}. Similar SOC concentrations were present in the soil after 67 days of incubation, indicating no significant loss of biochar C during the incubation. The biochar contained some N (3.41 mg kg^{-1}; Table 1); however, mixing 0.5 to 1.0% biochar had no detectable effect on TCN of the Norfolk Ap horizon. Adding 2% biochar significantly increased the soil mean TCN content, but only by 0.23 g kg^{-1}. This trend was not observed after 67 days of incubation. Mean TCN contents in treatments after 67 days of incubation (except 1.0% biochar) were similar to the control (0% biochar).

The C:N ratio of the pecan biochar is 244:1. Nitrogen immobilization typically occurs when organic residues possessing a C:N ratio of greater than 32:1 are added to soils (Alexander, 1977; Thompson and Troeh, 1978). The wide C:N ratio, in association with its aromaticity, will cause slow biochar decomposition (Lehmann, 2007). Although biochars/soil black carbon will undergo slow chemical and microbial decomposition (Schmidt and Noack, 2000), the rate of decomposition is so slow that even large additions of biochar to soil will probably not significantly immobilize N.

The high stability of biochar in soil environments is beneficial with respect to C sequestration because C added to the soil as biochar will be removed from the atmosphere for 1000 years or more. German (2003) reported that biochar in soils is stable and resistant to microbial attack; one site in the Amazonian Black Earth region had biochar dated to 6850 years old. In comparison, the mean residence time of soil organic matter has been estimated as between 250 and 3280 years (Stevenson, 1994). In hind sight, we suggest that the SOC dated in those presented in Stevenson (1994) likely contained significant amounts of black C, which would make the average age of the total SOC pool much older than the age of the biogenic SOC fraction. Laird et al. (2008) physically separated biogenic humic material from black C from an Iowa Mollisol and reported modern radio C dates for

TABLE 3. Fertility characteristics of Norfolk Ap soil + percent biochar mixtures on 0- and 67-day incubations (Mehlich 1 extractant)[†]

Norfolk Ap soil + % biochar	Incubation day	Fertility characteristics[‡]											
		pH[§]	CEC	Exch. acid	Ca	Cu	K	Mg	Mn	Na	P	S	Zn
		cmol$_c$ kg^{-1}			mg kg^{-1}								
0	0	4.8^{a}	5.7^{a}	2.4^{a}	437^{a}	0.6^{a}	35^{a}	117^{a}	12^{a}	5^{a}	30.5^{a}	8.67^{a}	13^{a}
0.5	0	5.1^{b}	5.3^{a}	2.0^{a}	470^{b}	0.7^{a}	49^{b}	98^{b}	7^{b}	5^{a}	30.8^{a}	7.67^{a}	12^{a}
1.0	0	5.5^{c}	5.4^{a}	1.9^{a}	516^{c}	0.7^{a}	66^{c}	90^{c}	15^{c}	6^{a}	31.2^{a}	7.83^{a}	11^{a}
2.0	0	6.3^{d}	5.9^{a}	1.2^{b}	720^{d}	0.8^{a}	111^{d}	91^{d}	10^{d}	7^{b}	35.2^{b}	8.50^{a}	11^{a}
0	67	5.2^{a}	5.2^{a}	2.4^{a}	392^{a}	0.6^{a}	26^{a}	93^{a}	7^{a}	3^{a}	28.7^{a}	6.33^{a}	12^{a}
0.5	67	5.6^{b}	5.4^{a}	2.1^{a}	462^{b}	0.7^{a}	47^{b}	91^{a}	6^{a}	5^{b}	31.7^{b}	5.16^{a}	11^{b}
1.0	67	5.9^{c}	5.6^{a}	2.0^{a}	537^{c}	0.7^{a}	49^{c}	92^{a}	16^{b}	4^{a}	31.7^{c}	4.00^{b}	11^{b}
2.0	67	6.4^{d}	5.9^{a}	1.5^{b}	692^{d}	0.8^{a}	69^{d}	89^{a}	10^{c}	4^{a}	33.3^{d}	3.17^{c}	10^{c}

[†] Extracted with H_2SO_4 + HCl.

[‡] Mean values sorted by incubation day were compared using a one-way ANOVA for multiple-comparisons tests vs. a control (Norfolk Ap soil + 0% biochar).

[§] Means followed by a different letter are significantly different at $P < 0.05$.

the biogenic humic material and much older dates for the black C fraction. Therefore, soil applied biochar has the potential to increase the recalcitrant pool of soil C and will persist in soil environments much longer than C added in the form of residues or biogenic soil organic matter.

Biochar additions to soils are reported to improve soil fertility by raising soil CEC (Liang et al., 2006). Soil CEC increases are due to carboxylate groups on the surfaces of the biochar itself and to exposed carboxylate groups of organic acids sorbed by the biochar, both of which contribute negative surface charge to biochar particles (Liang et al., 2006). Biochar in this experiment contained some carboxyl characteristics (13%; Fig. 1); yet, the ability of biochar additions to increase the soil CEC even at 2% biochar addition was negligible (Table 3). One might expect after a 67-day incubation that additional carboxylate groups would form because of oxidation of the biochar surfaces (Schmidt and Noack, 2000). However, differences in Norfolk Ap CEC values for the day-0 and day-67 samples were negligible (Table 3).

The high pyrolysis temperature (700 °C) may have contributed to the relatively low level of surface oxidation of the pecan shell biochar and hence the lack of a significant impact of biochar additions on the CEC of the Norfolk Ap horizon soil. Higher pyrolysis temperatures generally cause greater condensation of aromatic structures and even the formation of graphitic cores (Antal and Grønli, 2003). Such highly condensed aromatic C has less surface area and fewer oxidizable surface functional groups than more open (less condensed) aromatic C structures. High-temperature biochars are also more resistant to chemical oxidation and microbial degradation and hence have a longer half-life in soil environments than soil organic matter. The recalcitrant characteristics of high-temperature biochar, however, would be a desirable property if the primary goal was to remove atmospheric CO_2 and sequester C in soil for millennia (Laird, 2008). On the other hand, if the primary goal was to increase soil CEC values, then the addition of biochar prepared by pyrolysis of feedstocks at lower temperatures (400–500 °C) or under different moisture and pressures conditions (Antal and Grønli, 2003) may be more desirable. Low-temperature biochars will most likely also increase soil C sequestration, but they will probably more rapidly change soil fertility characteristics when compared with using high-temperature biochars.

Some microbial oxidizable compounds such as anhydrocellulose (dehydrated forms of cellulose), polysaccharides, alcohols, and so on, should exist in biochars prepared by pyrolysis of feedstocks at lower temperatures (Antal and Grønli, 2003). Baldock and Smernik (2002) and Hamer et al. (2004) both reported a relationship between biochar pyrolysis temperature and resistance to soil microbial decomposition. Hamer et al. (2004) found that biochars produced from maize and rye at 350 °C were more prone to soil microbial degradation than biochar made from oak wood pyrolyzed at 800 °C. The authors attributed differences in biochar decomposition because of their C:N ratios; higher pyrolysis temperatures caused wider C:N ratios in the oak wood biochar because of loss of N and concentration of C (Hamer et al., 2004).

Upon decomposition and oxidation by soil microbial communities, these organic carbon structures should produce byproducts containing a higher density of carboxylate and other O-containing functional groups (i.e., ^{-}OH, ^{-}OR, etc.) capable of serving as sites for cation exchange (Stevenson, 1994). Therefore, when creating biochars for use as a soil fertility amendment, the biomass pyrolysis conditions could be designed to carbonize the material under moist conditions and at lower temperatures.

Research has shown that soil pH is more influenced by monomeric Al species on exchange sites than by H^{+1} (Sparks, 1995). Aqueous monomeric hexahydronium $[Al(H_2O)_6]^{+3}$ species act as pH buffers because they can undergo rapid and reversible hydrolysis reactions influencing solution pH values by liberating or accepting H^{+1} (Sparks, 1995). For soil pH to change, the biochar itself or a cation in the biochar must react with the soluble monomeric Al species or displace it from exchange surfaces on clays or soil organic matter. At pH 4.8, the Norfolk soil with no biochar had 42% (2.4 $cmol_c$ exchangeable acidity $kg^{-1} \div 5.7$ $cmol_c$ CEC $kg^{-1} \times 100$; Table 3) of the total soil CEC sites occupied by $[Al(H_2O)_5]^{+2}$. This would be the dominant monomeric Al species in the Norfolk Ap soil + 0% biochar at pH 4.8 (Sparks, 1995). Additions of 0.5 and 1% biochar to the Norfolk soil did not significantly modify the exchangeable acidity values, although soil pH values significantly increased by 0.7 U (Table 3). With the addition of 2% biochar, the pH increased from 4.8 to 6.3, and exchangeable acidity was reduced by 50% ($\Delta 1.2$ $cmol_c$ kg^{-1}; Table 3). Thus, biochar was an effective liming agent, neutralizing solution pH and reducing exchangeable acidity values. However, substantial additions of biochar (2% or 40 metric tons ha^{-1}) were required to obtain increases in pH and reductions in exchangeable acidity.

During pyrolysis, cations (primarily K, Ca, Si, and Mg) present in the pecan shells formed metal oxides (e.g., ash) that were admixed with the biochar. Once in the soil environment, these oxides can react with H^{+1} and monomeric Al species, modifying soil pH and exchangeable acidity values. Because the biochar contained a high Ca concentration (3.64 mg kg^{-1}; Table 1), Reaction (1) involving CaO exemplifies the liming ability of the ash associated with the biochar:

$$2\mathrm{Al} - \mathrm{soil} + 3\mathrm{CaO} + 3\mathrm{H_2O} \rightarrow 3\mathrm{Ca} - \mathrm{soil} + 2\,\mathrm{Al(OH)_3} \quad (1)$$

During this reaction, Ca replaces the monomeric Al species on soil mineral or soil organic matter CEC sites. Accompanying this reaction is an increase in soil solution pH caused by the depletion of the readily hydrolysable monomeric Al and the formation of the more neutral $[Al(OH)_3]^0$ species (Sparks, 1995). This general reaction explains the decline in exchangeable acidity for the Norfolk Ap soil and the increase in solution pH and Ca on CEC sites (Table 3). The pH increase and exchangeable acidity decrease were similar for the day-0 and day-67 samples. This suggests that the liming effect of biochar occurred rapidly and was sustainable on equilibration.

The biochar significantly increased some important plant macronutrients. Mehlich 1–extractable Ca, K, and P all increased with the level of biochar additions (Table 3). However, the P increase was significant only at the highest level of biochar addition. By contrast, Mehlich 1–extractable Mg decreased with increasing biochar addition at day 0, suggesting that the Mg was strongly retained by the biochar. Extractable S and Zn concentrations also decreased slightly with increasing biochar additions, but the trend was significant only for the day-67 samples. Copper concentrations were not significantly affected by biochar additions, and Mn concentrations were variable. The observed variations in Mehlich 1–extractable plant nutrient concentrations, at days 0 and 67, reflected the combined effects of fertilization (nutrients added with the biochar), leaching of nutrients, and nutrient adsorption by the soil and added biochar. No plants were grown in these soils, and hence, plant uptake was not a variable in this study. In general, biochar additions increased the levels of plant macronutrients and had little effect on micronutrients.

Chemical Composition of the Water Leachates

It is important to examine the chemical composition of a deionized water extract of an amended soil; in some cases, the amendment can release elements that may cause plant growth

TABLE 4. Chemical composition of deionized water leachates from Norfolk Ap soil + percent biochar mixtures after 25- and 67-day incubation[†]

Norfolk Ap soil + % biochar	Incubation day	pH[§]	EC	TOC	Ca	Cu	K	Mg	Mn	Na	P	S	Zn
		Leachate chemical composition[‡]											
			μS cm^{-1}	mg L^{-1}									
0	25	5.7^{a}	364^{a}	76^{a}	189^{a}	—	32^{a}	113^{a}	5.4^{a}	8.2^{a}	2.0^{a}	25^{a}	1.3^{a}
0.5	25	6.0^{a}	382^{a}	65^{b}	175^{a}	—	58^{b}	82^{b}	1.1^{b}	11.0^{b}	1.4^{b}	22^{a}	0.7^{a}
1.0	25	6.0^{a}	439^{a}	70^{a}	136^{b}	—	72^{c}	63^{c}	0.3^{c}	11.9^{c}	1.5^{c}	23^{a}	0.4^{a}
2.0	25	6.0^{a}	559^{a}	82^{a}	99^{c}	—	99^{d}	34^{d}	0.2^{d}	14.0^{d}	1.2^{d}	26^{a}	0.1^{b}
0	67	5.8^{a}	364^{a}	45^{a}	31^{a}	—	9^{a}	18.6^{a}	0.1	2.80^{a}	2.20^{a}	9.5^{a}	0.27^{a}
0.5	67	5.9^{a}	387^{a}	38^{a}	32^{a}	—	17^{a}	17.1^{a}	—	3.02^{a}	1.26^{b}	8.9^{a}	0.12^{b}
1.0	67	5.7^{a}	502^{a}	48^{a}	37^{a}	—	25^{b}	17.1^{a}	0.1	4.02^{a}	1.40^{c}	10^{a}	0.13^{c}
2.0	67	6.0^{a}	571^{a}	68^{a}	46^{a}	—	52^{c}	15.9^{a}	—	5.90^{b}	1.42^{d}	11^{a}	0.06^{d}

[†] A dash line indicates mean value was below detection limit (0.05 mg L^{-1}).

[‡] Mean values sorted by incubation day were compared using a one-way ANOVA for multiple comparisons vs. a control (Norfolk Ap soil + 0% biochar, significant digits varied because of low mean element concentrations on day 67).

[§] Means followed by a different letter are significantly different at $P < 0.05$.

issues (Novak et al., 2007b). For the 25- and 67-day leachates, pH, EC values, and TOC concentrations (except 0.5% on day 25) were similar for the biochar-treated soils and control soils (Table 4).

The cation concentrations in the 25- and 67-day leachates seem to be influenced by cation valency. For instance, the monovalent cation (K and Na) concentrations in both the 25- and 67-day leachates increase with the level of biochar addition to the Norfolk Ap soil, whereas concentrations of multivalent cations (Ca, Mg, Mn, and Zn) all decreased for the day-27 leachates and either decreased or were not significantly different for the day-67 leachates with increasing levels of biochar addition. The strength of cation retention or repulsion from negatively charged surfaces increases with increasing ion charge and with distance between the charged surface and either the source of charge or the soluble ion (basis of diffuse double layer theory; Bohn et al., 1979). Consequently, multivalent cations were preferentially adsorbed over monovalent cations on exchange sites, and hence, the monovalent K and Na cations would be more available for movement with the leachate.

The decrease in concentration of multivalent cations in the leachates with increasing levels of biochar addition (Table 4) is particularity interesting in light of the fact that substantial amounts of Ca and Mg and less amounts of Mn and Zn were present in the biochar (Table 1). Much of the Ca added with the biochar probably replaced monomeric Al species on clays and/or soil organic matter exchange sites [see Reaction (1)]. This hypothesis is supported by increasing levels of Mehlich 1–extractable Ca with higher levels of biochar addition (Table 3). An explanation for the decrease in Mg, Mn, and Zn concentrations in day-27 leachates is a bit more complex, because their Mehlich 1–extractable concentrations of these elements either decreased or did not show substantial changes with increasing biochar additions. These observations suggest that the Mg, Mn, and Zn were either specifically adsorbed or very highly selectively adsorbed by exchange sites associated with the biochar.

The P concentrations generally decreased with increasing biochar application in both 25- and 67-day leachates by approximately 40% (0 vs. 2% biochar addition; Table 4). The field from which the Norfolk soil was collected has a long history of row crop production; past P fertilizer applications were the likely source of much P in the soil. The declines in leachate P concentrations with increasing biochar additions are probably due to a combination of reactions such as retention of o-PO$_4^{-3}$ through ligand exchange reactions involving O-containing functional groups on the biochar surface, adsorption of o-PO$_4^{-3}$ by Fe and Al oxides and hydroxides, and by adsorption and precipitation by Ca, Mg-phosphates (Bohn et al., 1979). Regardless of sorption mechanisms, these results suggest that biochar has the potential to ameliorate P leaching in soils with sandy textures, a common problem in fields containing excess soil P concentrations as a result of overapplication of swine manure (Novak et al., 2000).

Net Norfolk Ap Soil Fertility Changes

The net soil fertility change to the biochar-treated Norfolk Ap soil is presented in Table 5. The results after adding 2% biochar were presented because this treatment caused the most significant soil fertility variations compared with the untreated soil. The treated Norfolk Ap soil pH was more basic after

TABLE 5. Changes in Norfolk Ap soil fertility characteristics with and without 2% biochar (after 67-day incubation and two deionized water leaching events)

Characteristic	Unit	0% Biochar	2% Biochar	Net change	Relative %[†]
pH	—	4.8	6.4	+1.6	+33
CEC	cmol$_c$ kg^{-1}	5.7	5.9	+0.2	+3.5
Exchange acidity	cmol$_c$ kg^{-1}	2.4	1.5	−0.9	−38
C	g kg^{-1}	17.4	29.2	+11.8	+68
Ca	mg kg^{-1}	437	692	+255	+58
Cu	mg kg^{-1}	0.6	0.8	+0.2	+33
K	mg kg^{-1}	35	69	+37	+106
Mg	mg kg^{-1}	117	89	−28	−24
Mn	mg kg^{-1}	12	10	−2	−17
N	g kg^{-1}	1.24	1.21	−0.03	−2.4
Na	mg kg^{-1}	5	4	−1	−20
P	mg kg^{-1}	31	34	+3	+10
S	mg kg^{-1}	9	4	−5	−56
Zn	mg kg^{-1}	13	10	−3	−23

[†] Percent change based on values in Norfolk Ap soil + 0% biochar.

biochar addition through a 38% reduction in monomeric Al species on exchange sites (lower exchangeable acidity values). Soil Ca and K concentrations had marked increases (+58 and + 106%, respectively) implying that biochar additions can increase these important plant macronutrients.

The Norfolk Ap horizon had an 11.8 g C kg^{-1} increase after mixing in 2% biochar, and there was no detectable loss of SOC during the 67-day incubation, suggesting that biochar additions may be an effective means of sequestering C; longer-term studies need to be quantified in terms of C sequestration. Two percent biochar application to field soil is approximately 40 tons biochar ha^{-1}. This is a large amount of biochar to apply to soil, but the benefits of long-term C sequestration coupled with additions of several plant nutrients, neutralizing soil acidity, and reduced nutrient leaching should not be overlooked. Although we observed decreased leaching of several plant nutrients with increasing biochar additions, we did not observe significant increases in CEC or EC for the Norfolk Ap soil. The influence of biochar additions on Mehlich 1–extractable micronutrient concentrations was minimal.

CONCLUSIONS

Biochar has been used as a fertility amendment in soils of tropical regions for thousands of years, although scientific investigations of the effects on soil fertility are few. This same technology may improve fertility-poor soils in the southeastern U.S. Coastal Plain region. A laboratory study was conducted where a pecan shell–based biochar was incubated in a sandy, acidic Norfolk Ap soil. Biochar additions increased the SOC content but did not significantly improve the soil N status. Biochar additions seem to potentially be an effective means of sequestering C in soils as no detectable loss of SOC occurred during the 67-day incubation. A goal of this study was to increase the Norfolk Ap soil CEC by adding biochar. For soil CEC to increase, surfaces of the biochar must be oxidized to produce negatively charged carboxylate groups. No increase in soil CEC after 67 days was obtained, implying that this high-temperature biochar was not suited for that purpose within the time frame of this study. Soil pH and three major plant nutrients (Ca, K, and P) concentrations, however, increased after applying this biochar. Most soil micronutrient concentrations were not influenced by the biochar additions. Water leaching of biochar-treated Norfolk Ap soil showed K enrichment but net sorption of P and most multivalent cations.

This biochar was highly recalcitrant because the pecan shells were pyrolyzed at a high temperature forming primarily condensed aromatic C structures. On one hand, the recalcitrant nature of biochar may be important if the key goal is to sequester C in the highly stable SOC pool. On the other hand, if the goals are to improve soil fertility and also increase C sequestration, then a biochar having more readily oxidizable structural groups and a low C:N ratio may be more appropriate. Eventually, the biochar will oxidize and soil pH will decrease and CEC increase. The conditions under which feedstocks are pyrolyzed can potentially be designed to produce biochars with single or dual targeted characteristics either as a C-sequestration amendment, a soil fertility correction, or both.

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