Journal of Environmental Quality

SPECIAL SECTION

ENVIRONMENTAL BENEFITS OF BIOCHAR

Switchgrass Biochar Affects Two Aridisols

J. A. Ippolito,* J. M. Novak, W. J. Busscher, M. Ahmedna, D. Rehrah, and D. W. Watts

The use of biochar has received growing attention because of its ability to improve the physicochemical properties of highly weathered Ultisols and Oxisols, yet very little research has focused on its effects in Aridisols. We investigated the effect of low or high temperature (250 or 500°C) pyrolyzed switchgrass (*Panicum virgatum* L.) biochar on two Aridisols. In a pot study, biochar was added at 2% w/w to a Declo loam (Xeric Haplocalcids) or to a Warden very fine sandy loam (Xeric Haplocambids) and incubated at 15% moisture content (by weight) for 127 d; a control (no biochar) was also included. Soils were leached with 1.2 to 1.3 pore volumes of deionized H_2O on Days 34, 62, 92, and 127, and cumulative leachate Ca, K, Mg, Na, P, Cu, Fe, Mn, Ni, Zn, NO_3–N, NO_2–N, and NH_4–N concentrations were quantified. On termination of the incubation, soils were destructively sampled for extractable Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Zn, NO_3–N, and NH_4–N, total C, inorganic C, organic C, and pH. Compared with 250°C, the 500°C pyrolysis temperature resulted in greater biochar surface area, elevated pH, higher ash content, and minimal total surface charge. For both soils, leachate Ca and Mg decreased with the 250°C switchgrass biochar, likely due to binding by biochar's functional group sites. Both biochars caused an increase in leachate K, whereas the 500°C biochar increased leachate P. Both biochars reduced leachate NO_3–N concentrations compared with the control; however, the 250°C biochar reduced NO_3–N concentrations to the greatest extent. Easily degradable C, associated with the 250°C biochar's structural make-up, likely stimulated microbial growth, which caused NO_3–N immobilization. Soil-extractable K, P, and NO_3–N followed a pattern similar to the leachate observations. Total soil C content increases were linked to an increase in organic C from the biochars. Cumulative results suggest that the use of switchgrass biochar prepared at 250°C could improve environmental quality in calcareous soil systems by reducing nutrient leaching potential.

The soil fertility benefits of charcoal application have been reported as early as 1847 (Allen, 1847), when Allen suggested that plant nutrients are sorbed within charcoal pores. More recently, increased attention has been given on the use of biochar (biomass-derived black carbon), a byproduct from the pyrolysis processing of organic feedstock (Antal and Grønli, 2003), as a beneficial soil conditioner.

Numerous researchers have noted that short- and long-term biochar applications to highly weathered, infertile Ultisols and Oxisols have resulted in fertility improvements (Lima et al., 2002; Lehmann et al., 2003; Glaser et al., 2004; Steiner et al., 2007; Kimetu et al., 2008; Asai et al., 2009; Novak et al., 2009b; Gaskin et al., 2010; Major et al., 2010a,b). However, studies on the effects of biochar application to alkaline soils are sparse. Asai et al. (2009) applied a teak/rosewood-derived biochar (0 and 8 Mg ha^{-1}; pH 7.5) to rice grown in an alkaline Laos soil and noted an increase in rice yield at two of three locations with the 8 Mg ha^{-1} biochar application, possibly due to biochar increasing plant-available P content. Van Zwieten et al. (2010) mixed 10 Mg ha^{-1} of two separate paper mill waste biochars into an Australian Aridisol. Other than an increase in total C content, the authors did not observe a change in extractable soil nutrients. This was speculated to be in response to the initial soil pH (7.7), free soil Ca^{2+} content (21.7 $cmol_c$ kg^{-1}), and alkaline pH of both biochars (8.2 and 9.4).

Elevated biochar pH values, as observed by Van Zwieten et al. (2010), are typically a function of higher pyrolysis temperatures (Novak et al., 2009b). Greater pyrolysis temperatures (e.g., >500°C) can also create biochars that contain higher ash content and greater surface area yet minimal total surface charge as compared with biochars created at lower temperatures (e.g., <400°C) (Novak et al., 2009b). Antal and Grønli (2003) suggested that low pyrolysis temperatures can create torrified-like biochars that contain semi-degraded cellulose and hemi-cellulose compounds because 300 to 400°C is the critical temperature range for their structural breakdown. Compared with 500°C, biochars created at 250°C probably contain more COOH and C-OH functional groups, which may act as nutrient retention sites (Glaser et al., 2002); the potential exists for

J. Environ. Qual. 41
doi:10.2134/jeq2011.0100
Received 18 Mar. 2011.
*Corresponding author (jim.ippolito@ars.usda.gov).
© ASA, CSSA, SSSA
5585 Guilford Rd., Madison, WI 53711 USA

J.A. Ippolito, USDA–ARS, Northwest Irrigation and Soils Research Lab., 3793N 3600E, Kimberly, ID 83341; J.M. Novak, W.J. Busscher, and D.W. Watts, USDA–ARS, Coastal Plains Research Center, Florence, SC 29501; M. Ahmedna, Dep. of Human Environment and Family Sciences, North Carolina Agriculture and Technical State Univ., Greensboro, NC 27411; D. Rehrah, Dep. of Human Environment and Family Sciences, North Carolina Agriculture and Technical State Univ., Greensboro, NC 27411. Assigned to Associate Editor David Laird.

Abbreviations: DTPA, diethylenetriaminepentaacetic acid; ICP, inductively coupled plasma–optical emission spectroscopy.

greater soil nutrient retention with biochars created at lower versus higher pyrolysis temperatures. Furthermore, biochars designed for greater nutrient retention in aridic settings could possibly reduce nutrient transport losses, thus benefitting environmental quality.

A void exists in the literature in terms of biochar (created at low or high temperature) environmental effects in aridic soil environments. Improvements in fertility levels of Aridisols are important because these soils are used extensively for and can be very productive in agronomic settings (Missouri Cooperative Soil Survey, 2010). Thus, the objective of the current research was to identify changes in aridic soil fertility status and nutrient leaching with a low pH biochar produced at relatively low temperatures as compared with a high pH biochar produced at high temperatures.

Materials and Methods

Soils

A soil from the 0- to 20-cm depth of the Declo series (coarse-loamy, mixed, superactive, mesic Xeric Haplocalcids) was obtained from a field at the University of Idaho Experimental Station in Aberdeen, Idaho. At this location, field crops were grown under irrigation and consisted of a 3-yr barley (*Hordenum vulgare* L.), wheat (*Triticum aestivum* L.), and potato (*Solanum tubersum* L.) rotation. The Warden series is also an Aridisol (coarse-silty, mixed, superactive, mesic Xeric Haplocambids) and was collected from the 0- to 20-cm depth in a field on the Washington State University Experimental Station at Prosser, Washington. Field crops were also grown under irrigation at this site, consisting of a 3-yr rotation of alfalfa (*Medicago sativa* L.), corn, and wheat.

The characteristics of both soils are presented in Table 1. Soil pH was determined on a 1:1 soil/deionized H_2O suspension (Thomas, 1996), total N and C were determined by the dry combustion method outlined by Nelson and Sommers (1996) using a Flash EA1112 Elemental Analyzer (CE Elantec, Inc., Lakewood, NJ), and inorganic C content was determined by a modified pressure-calcimeter method (Sherrod et al., 2002). Organic C contents were determined as difference between total C and inorganic C contents. Total S, P, Ca, Mg, K, Na, Fe, Mn, Ni, Zn, and Cu were determined via USEPA Method 3050b (USEPA, 1996a) and quantified using inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Soltanpour et al., 1996).

Biochar

Switchgrass feedstock was obtained from a field in its fourth year of growth at the Clemson University, Pee Dee Research and Education Center in Darlington, South Carolina (J.M. Novak, personal communication, 2010). Switchgrass was collected, air-dried, and ground to pass a 1- to 2-mm sieve. Different pyrolysis temperatures can be used to create variations in biochar structural and surface characteristics. Pyrolytic temperatures result in changes in biochar properties due to selective losses of plant structural compounds (Antal and Grønli, 2003). Thus, switchgrass biochar was made using a slow pyrolysis (1–3 h) procedure under a continual N_2 gas stream at 250 or 500°C. After pyrolysis, biochars were ground to pass a 0.25-mm sieve (J.M. Novak, unpublished data).

Biochar chemical characterization properties are presented in Table 1; a more detailed description of physical and chemical characteristics is presented by Novak et al. (2011). Briefly, biochar pH was determined in deionized H_2O from a 1% (w/v) mixture after shaking for 24 h. Surface area was determined from N_2 adsorption isotherms at 77°K using a Nova 2000 Surface Area Analyzer (Quantachrome Corp., Boynton Beach, FL). Total negative surface charge was determined based on the method outlined by Boehm (1994). Ash content and total

Table 1. Declo and Warden soil and switchgrass biochar characteristics produced at pyrolysis temperatures of 250 and 500°C. Total elemental composition expressed on a dry weight basis.

Characteristic	Declo soil	Warden soil	Switchgrass 250°C	Switchgrass 500°C
pH	8.1	7.3	5.4	8.0
Surface area, $m^2\ g^{-1}$	ND†	ND	0.40	62.2
Total negative surface charge, mmol H^+ eq g^{-1} C	ND	ND	1.19	0.82
Ash, %	ND	ND	2.6	7.8
Total C, %	1.8	0.4	55.3	84.4
Inorganic C, %	1.1	BD‡	ND	ND
Organic C, %	0.7	0.4	ND	ND
H, %	ND	ND	6.0	2.4
O, %	ND	ND	36	4.3
N, %	0.07	0.05	0.43	1.07
P, %	0.07	0.06	0.10	0.24
Ca, %	3.67	0.43	0.11	0.51
Mg, %	0.77	0.49	0.12	0.38
K, %	0.19	0.19	0.49	1.16
Fe, mg kg^{-1}	13,400	27,400	48.6	149
Mn, mg kg^{-1}	262	390	36.6	136
Ni, mg kg^{-1}	1.68	5.73	10.8	9.04
Zn, mg kg^{-1}	46.8	61.2	11.6	44.0
Cu, mg kg^{-1}	BD	6.25	5.16	11.4

† Not determined.

‡ Below detection.

C, H, O, N, and S were determined by Hazen Research, Inc. (Golden, CO) following ASTM D 3172 and 3176 standard methods (ASTM, 2006). Additional biochar elemental analyses were determined using USEPA Method 3052 (USEPA, 1996b) and quantified using ICP-OES.

Biochar Soil Incubation and Nutrient Leaching

Each biochar was mixed at 2% (w/w) into the Declo or Warden soil at a rate approximately equivalent to 24 Mg ha^{-1} assuming a 10 cm application depth and a bulk density of 1.2 g cm^{-3}; a control (i.e., no biochar application) was also included. Preincubated soils, with and without biochar, were analyzed for diethylenetriaminepentaacetic acid (DTPA)-extractable Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn (Lindsay and Norvell, 1978); Olsen-extractable P (Kuo, 1996); NO_3–N and NH_4–N using a 2 mol L^{-1} KCl extract (Mulvaney, 1996); total C (Nelson and Sommers, 1996); inorganic and organic C; and pH as previously described.

The soil mixtures (450 g total) were placed in 10.3-cm-diameter by 8.5-cm-tall pots with drain holes covered by nylon mesh. Each treatment was replicated three times. Soil moisture content was maintained at 15% (w/w; approximately field capacity) throughout the experiment via gravimetric adjustments two to three times per week. All pots were incubated at room temperature throughout the experiment.

Each pot was leached on Days 34, 62, 92, and 127 of the incubation using 1.2 to 1.3 pore volumes of deionized H_2O. Pore volume was determined by initially measuring soil bulk density and calculating pore space in the pots. The 20 to 30% extra deionized H_2O ensured that all soil pore spaces were flushed. Total leachate was collected within 30 h, and the total volume was recorded. The samples were filtered through a 0.45-μm membrane filter and analyzed for Ca, K, Mg, Na, P, Cu, Fe, Mn, Ni, and Zn using ICP-OES. Leachate NO_3–N, NO_2–N, NH_4–N, and orthophosphate were determined via automated colorimetric analysis. Mass of element leached after each event was determined by multiplying concentration by leachate volume. Cumulative element mass in leachate was determined by summing their weights after all four leaching events.

After the last leaching event, soils were allowed to dry to between 1 and 2% moisture content (wt. basis). Soils were removed from the pots, ground to pass a 2-mm sieve, and analyzed for the same chemical constituents as described for the preincubated soils.

Statistical Analysis

An ANOVA was performed to compare the effects of biochar type on leachate and soil chemical characteristics using Proc GLM in SAS version 9.2 (SAS Institute, Inc., 2008). Differences were examined at a significance level (α) of 0.05, with mean separation determined using Fisher's protected LSD procedure for each soil separately.

Results and Discussion

Biochar Characteristics

As shown in Table 1 and described by Novak et al. (2009b) and Singh et al. (2010a), higher pyrolysis temperatures produce biochars with greater surface area, elevated pH, higher ash content, and minimal total surface charge. Pyrolysis, or more correctly torrification, at 250°C created a biochar that contained semi-degraded cellulose and hemi-cellulose compounds because 300 to 400°C is the critical temperature range for their structural breakdown (Antal and Grønli, 2003). As compared with 500°C, biochar created at 250°C probably contained more COOH and C-OH functional groups, which may act as nutrient retention sites (Glaser et al., 2002); thus, the potential exists for greater soil nutrient retention with biochars created at lower versus higher pyrolysis temperatures. In general, lower pyrolysis temperatures result in biochars containing lower elemental concentrations (Singh et al., 2010a).

Nutrient Leaching

The Declo and Warden soil mean leachate masses of Ca, K, Mg, Na, P, and NO_3–N for each leaching event, and cumulative mass leached over all leaching events, are presented in Tables 2 and 3, respectively. Leachate NO_2–N, NH_4–N, and orthophosphate were all below detection limits. Results for both soils were similar based on the observed cumulative mass of elements leached; Cu, Fe, Mn, Ni, and Zn concentrations in the Declo and Warden leachate were all below detection. A decrease in leachate Ca and Mg content associated with 250°C switchgrass biochar was likely due to increasing the amount of negative exchange sites present in the soils because the 250°C switchgrass biochar contained a greater total negative surface charge as compared with the 500°C switchgrass biochar (Table 1). The decrease in leachate Ca and Mg content associated with the 250°C biochar also supports the contention of Glaser et al. (2002) that low-temperature biochars contain more surface functional groups, which can act as nutrient retention sites.

The addition of 250 and 500°C biochar in the Declo soil and the 500°C biochar in the Warden soil caused an increase in leachate K content likely due to the biochar's high K content and the fact that 2.4 times more K was present in the 500°C versus the 250°C biochar (Table 1). Elevated biochar K concentrations can be attributed to higher pyrolysis temperatures, which result in greater biochar pH values due to the hydrolysis of K salts (Singh et al., 2010a). The increase in leachate K could also have been due to biochar-borne K being in a readily soluble form. In addition, increased K in leachate may be further explained by biochar exchange sites being preferentially occupied by Ca and Mg. According to the lyotropic series, Ca^{2+} and Mg^{2+} have a stronger affinity for surface exchange sites as compared with K^+ (Bohn et al., 1985). Novak et al. (2009a) speculated a similar conclusion after applying increasing pecan shell biochar at rates of 0, 0.5, 1.0, and 2.0% (by weight) to a Norfolk loamy sand (Kandiudults). After a 25-d incubation and ensuing deionized H_2O leaching, Ca and Mg leachate concentrations decreased, whereas K leachate concentrations increased, with greater biochar rates.

The leachate P content increased two- to threefold with the 500°C switchgrass biochar as compared with the 250°C biochar treatment or the control. This was related to the elevated P concentration in the 500°C as compared with the 250°C biochar (Table 1); the 500°C biochar contained two to three times more P as the 250°C biochar. Novak et al. (2009a) observed a decrease in leachate P concentrations with pecan shell biochar addition to a Norfolk loamy sand. They suggested that

Table 2. Mean leachate Ca, Mg, K, P, and NO_3–N from the Declo soil treated without biochar (control) and with low (250°C) or high temperature (500°C) switchgrass biochar (n = 3).

Treatment	Ca	Mg	K	P	NO_3–N
	mg kg^{-1}				
First leaching					
Control	43.9 (5.40)† a‡	10.7 (1.30) a	3.20 (0.37) c	0.14 (0.02) a	27.8 (3.85) a
Switchgrass (250°C)	32.4 (1.47) b	8.36 (0.27) b	5.06 (0.37) b	0.16 (0.02) a	4.29 (0.33) c
Switchgrass (500°C)	47.7 (2.15) a	12.2 (0.60) a	6.57 (0.22) a	0.16 (0.01) a	17.0 (0.21) b
Second leaching					
Control	14.8 (1.11) a	3.88 (0.34) a	2.36 (0.14) b	0.15 (0.03) a	3.17 (0.32)
Switchgrass (250°C)	9.51 (1.70) b	2.33 (0.50) b	2.95 (0.50) b	0.16 (0.02) a	BD§
Switchgrass (500°C)	13.6 (0.41) a	3.57 (0.11) a	6.31 (0.25) a	0.21 (0.01) a	3.74 (0.42)
Third leaching					
Control	15.5 (1.46) a	3.61 (0.32) a	2.10 (0.10) c	0.08 (0.01) b	4.93 (0.37)
Switchgrass (250°C)	10.6 (0.99) b	2.37 (0.29) b	2.97 (0.31) b	0.11 (0.02) b	BD
Switchgrass (500°C)	13.5 (0.75) a	3.22 (0.19) a	6.60 (0.21) a	0.15 (0.01) a	4.12 (0.21)
Fourth leaching					
Control	13.5 (0.26) a	3.22 (0.04) a	1.88 (0.04) b	0.02 (0.02) b	1.04 (0.22)
Switchgrass (250°C)	11.9 (2.06) a	2.68 (0.56) a	3.07 (0.46) b	0.08 (0.01) ab	BD
Switchgrass (500°C)	11.4 (1.52) a	2.50 (0.30) a	6.00 (1.18) a	0.15 (0.08) a	BD
Cumulative					
Control	87.7 (6.59) a	21.4 (1.61) a	9.54 (0.44) c	0.39 (0.07) b	36.9 (3.73) a
Switchgrass (250°C)	64.5 (3.32) b	15.7 (1.09) b	14.0 (1.60) b	0.51 (0.03) b	4.29 (0.33) c
Switchgrass (500°C)	91.6 (10.5) a	21.5 (0.60) a	25.5 (1.53) a	0.67 (0.06) a	24.9 (0.51) b

† Different letters within a column for a particular leaching event indicate significance between treatments at α = 0.05 according to Fisher's protected LSD test.

‡ Values within parentheses represent 1 SD of the mean.

§ Below detection.

Table 3. Mean leachate Ca, Mg, K, P, and NO_3–N from the Warden soil treated without biochar (control) and with low (250°C) or high temperature (500°C) switchgrass biochar (n = 3).

Treatment	Ca	Mg	K	P	NO_3–N
	mg kg^{-1}				
First leaching					
Control	23.2 (1.71)† a‡	5.85 (0.42) a	3.79 (0.10) b	0.23 (0.01) b	22.2 (1.52) a
Switchgrass (250°C)	17.9 (0.83) b	4.89 (0.21) b	3.59 (0.05) b	0.22 (0.02) b	7.49 (0.25) c
Switchgrass (500°C)	23.8 (0.52) a	6.19 (0.12) a	5.55 (0.29) a	0.33 (0.01) a	10.4 (0.36) b
Second leaching					
Control	7.82 (1.20) a	1.98 (0.36) a	2.59 (0.27) b	0.32 (0.02) b	1.78 (1.30)
Switchgrass (250°C)	2.83 (0.39) b	0.74 (0.11) b	2.29 (0.20) b	0.46 (0.08) b	BD§
Switchgrass (500°C)	7.37 (3.16) ab	2.52 (0.14) a	6.61 (0.35) a	0.65 (0.07) a	3.65 (0.32)
Third leaching					
Control	5.48 (0.47) a	1.37 (0.11) a	2.15 (0.10) b	0.36 (0.02) b	2.48 (0.29)
Switchgrass (250°C)	3.21 (0.43) b	0.83 (0.11) b	2.62 (0.24) b	0.49 (0.02) b	BD
Switchgrass (500°C)	5.87 (0.72) a	1.51 (0.19) a	5.35 (0.72) a	0.98 (0.14) a	2.52 (0.83)
Fourth leaching					
Control	4.33 (0.06) a	1.09 (0.01) a	1.80 (0.04) c	0.41 (0.04) b	BD
Switchgrass (250°C)	3.96 (0.28) a	0.99 (0.06) a	2.74 (0.07) b	0.52 (0.02) b	BD
Switchgrass (500°C)	4.15 (0.46) a	1.07 (0.12) a	4.23 (0.26) a	1.34 (0.12) a	BD
Cumulative					
Control	40.8 (0.56) a	10.3 (0.03) b	10.3 (0.23) b	1.31 (0.02) b	26.5 (0.37) a
Switchgrass (250°C)	27.9 (0.42) b	7.46 (0.08) c	11.2 (0.26) b	1.69 (0.10) b	7.49 (0.25) c
Switchgrass (500°C)	41.2 (2.68) a	11.3 (0.29) a	21.7 (1.22) a	3.30 (0.30) a	16.6 (0.85) b

† Values within parentheses represent 1 SD of the mean.

‡ Different letters within a column, for a particular leaching event, indicate significance between treatments at α = 0.05 according to Fisher's protected LSD test.

§ Below detection.

the declines in P concentration were probably due to retention of biochar surface functional groups, adsorption by Fe and Al (hydr)oxides, and precipitation as Ca and Mg phosphates. Apparently, in the Declo and Warden soils, these reactions have not occurred to the extent necessary to reduce leachate P concentrations associated with the 500°C biochar treatment. This suggests that the 500°C switchgrass biochar P was present in a readily available and leachable form or did not immediately react with biochar sorption sites or soil phases or that the addition of this biochar caused the soils to reach the maximum P sorption capacity.

In both soils, the 500°C switchgrass biochar reduced NO_3–N leaching as compared with the control; even greater NO_3–N leaching reductions were observed with the 250°C switchgrass biochar application. By adding a C source, biochar application likely stimulated microbial growth, the microbial population expanded, and NO_3–N immobilization occurred. The marked difference between the 250 and 500°C biochars was likely due to the ease at which microorganisms could utilize the added C source. High-temperature biochars are primarily composed of single and condensed ring aromatic C (Lehmann, 2007), which are relatively resistant to microbial degradation. On the other hand, low-temperature biochars likely contain more easily degradable anhydrocellulose, polysaccharides, alcohols, aliphatic compounds, and OH-containing C structures (Antal and Grønli, 2003; Gonzalez-Perez et al., 2004). Easily degradable biochar C sources would stimulate the microbial population to a greater degree, as observed by Hamer et al. (2004), and thus an increase in N immobilization would be observed. Biochar N immobilization has also been suggested by other researchers (Lehmann et al., 2003; Steiner et al., 2008; Novak et al., 2010). Biochar NO_3–N sorption was not considered to play a major role in the reduction of leachate NO_3–N. Biochars have limited anion exchange capacity, which decreases rapidly on their oxidation in soil, and thus biochars are likely to adsorb only small amounts of NO_3–N (Singh et al., 2010b).

Biochar Amended Soil Characteristics

Only one replicate of each soil was chemically characterized immediately after biochar addition; they represented conditions a few hours (1–3 h) before being incubated. Biochar-treated and untreated soils (*n* = 3) were then incubated for 127 d, with four leaching events occurring during this time period. At termination, the soils were air-dried and chemically extracted for available plant nutrients. Soil DTPA-extractable K, Mn, and Ni and Olsen-extractable P are presented in Fig. 1. Soil DTPA-extractable K concentrations were greatest in the 500°C switchgrass biochar treatment, intermediate in the 250°C biochar treatment, and lowest in the control (Fig. 1A) because the 500 and 250°C biochars contributed readily available K to the soil. This corresponded with the observed increase in leachate K concentration when proceeding from the control to the 250 and 500°C biochar treatments. It appeared that biochar application immediately affected readily extractable K as observed in the prestudy soil DTPA-extractable K concentrations. Van Zwieten et al. (2010) reported comparable K results after mixing 10 Mg ha^{-1} of a wood waste chip biochar pyrolyzed at 550°C to an Australian calcareous soil. Similarly, Gaskin et al. (2010) observed a linear increase in soil-extractable K content after mixing peanut hull biochar into a Tifton sand. However, in the second year of the study, the K effect diminished, suggesting that biochar served only as a temporary source of K or that the soil failed to retain K.

Declo and Warden soil DTPA-extractable Mn (Fig. 1B) and Ni (Fig. 1C) concentrations were greatest with the 250°C biochar treatment. This result was interesting given that Mn concentrations were 3.5 times greater in the 500°C switchgrass, whereas Ni concentrations were similar between the two biochars (Table 1). Increasing pyrolysis temperature from 250 to 500°C could have increased biochar carbonate formation, as shown by Yuan et al. (2011), and in turn could have caused the precipitation of Mn or Ni carbonates that were less extractable with DTPA. In support of this conclusion, Cao et al. (2009) showed that Pb sorption was attributed to Pb-carbonate formation as biochar pyrolysis temperature was increased from 200 to 350°C.

Perhaps Mn and Ni were selectively sorbed by exchange sites on the 250°C biochar, and the number of these particular exchange sites was reduced when the switchgrass was pyrolyzed at 500°C. This contention is supported by the greater total negative surface charge present at 250°C as compared with 500°C (Table 1). Novak et al. (2009a) also suggested that Mn was selectively sorbed on pecan-shell biochar exchange sites when a reduction in leachate Mn with increasing biochar applications to a Norfolk loamy sand was observed. In agreement with our study, Namgay et al. (2010) suggested that cation exchange reactions contribute to metal cation sorption on biochar. However, Uchimiya et al. (2010) proposed that heavy metal retention by biochar could be due to specific metal-ligand complexation involving surface functional groups (e.g., oxygen, phosphorus, sulfur, and nitrogen functional groups) that may or may not involve cation exchange. As compared with the initial soil Mn and Ni concentrations, the postleaching soil Mn and Ni concentrations were lower. This finding suggests that, given time, more stable Mn and Ni organic complexes were formed.

Olsen-extractable soil P concentration was greatest with the 500°C switchgrass biochar treatment (Fig. 1D). This was likely due to the elevated P concentration in the 500°C as compared with the 250°C biochar, supporting the leachate P observations. Novak et al. (2009b) added 2% (by wt.) of the same switchgrass biochar as used in the current study, pyrolyzed at 250 or 500°C, to a Norfolk loamy sand. The soils were incubated for 1 to 2 h and air dried, and the Mehlich-1 P content was measured. Similar to the current study, the authors noted an increase in extractable P with the 500°C biochar–treated soil as compared with the lower-temperature biochar. In soils with low P test concentrations, the 500°C switchgrass biochar could be a source of plant-available P. However, the 250°C switchgrass biochar would be favored in areas sensitive to off-site P movement.

The 250°C switchgrass biochar reduced Declo soil pH (8.1 ± 0.0) as compared with the control (8.3 ± 0.0) and the 500°C biochar treatment (8.3 ± 0.0). In the Warden soil, the 250°C switchgrass biochar treatment lowered soil pH (7.2 ± 0.0), whereas the 500°C biochar treatment raised soil pH (7.7 ± 0.0) as compared with the control (7.4 ± 0.1). Changes in other soil constituents, such as DTPA-extractable Mg, Cr,

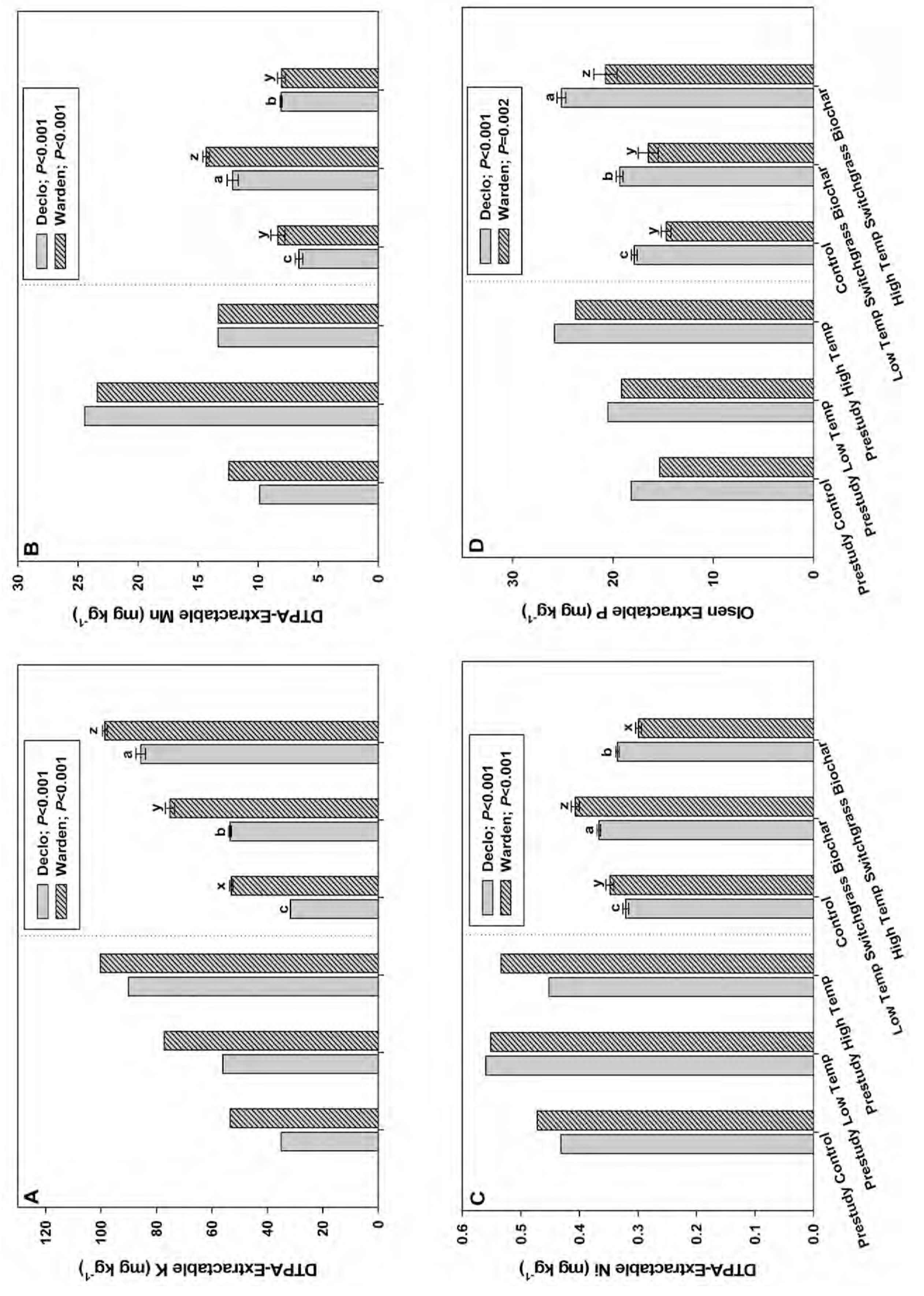

Fig. 1. Pre- (n = 1) and post- (n = 3) 127 d incubation soil diethylenetriaminepentaacetic acid (DTPA)-extractable K (A), DTPA-extractable Mn (B), DTPA-extractable Ni (C), and Olsen-extractable P (D) associated with control (no biochar), low temperature (250°C), and high temperature (500°C) switchgrass biochar application (2% w/w). Different letters within a soil series (a,b, or c for Declo; x, y, or z for Warden) represent significant differences at α = 0.05 as determined by the Fisher's protected LSD procedure. Error bars represent 1 SD of the mean.

Cu, Zn, Fe, and NH_4–N and total N content, were negligible (data not shown).

Declo and Warden soil NO_3–N concentrations are shown in Fig. 2A. As with the leaching results, soil NO_3–N concentrations were lowest with the 250°C switchgrass biochar treatment, supporting the contention that microbial immobilization occurred to a greater extent with the readily available C source. This emphasizes the fact that biochar structural properties could be altered, through manipulating the pyrolysis process, to reduce excess soil NO$_3$–N and thus lower the risk of downward NO$_3$–N transport. To create a biochar that promotes microbial immobilization or the sorption of excess soil NO$_3$–N, low pyrolysis temperatures, a feedstock with easily mineralizable compounds, or a biochar with a high anion exchange capacity could be created.

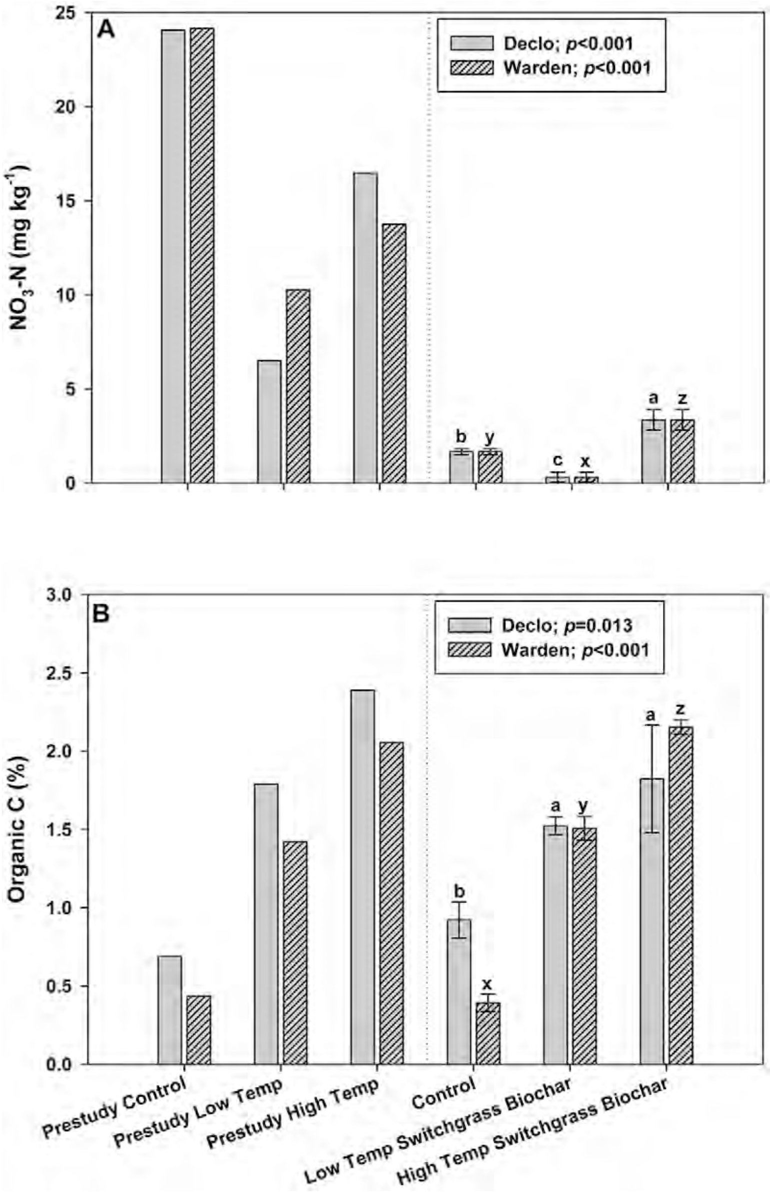

Fig. 2. Pre- (n = 1) and post- (n = 3) 127 d incubation soil NO$_3$–N (A) and organic C (B) associated with control (no biochar), low-temperature (250°C), and high-temperature (500°C) switchgrass biochar application (2% w/w). Different letters within a soil series (a, b, or c for Declo; x, y, or z for Warden) represent significant differences at α = 0.05 as determined by the Fisher's protected LSD procedure. Error bars represent 1 SD of the mean.

Organic C content in the Declo and Warden soils is presented in Fig. 2B. Increases in total soil C content were entirely attributable to the increase in organic C content supplied with biochar application because inorganic soil C content was not affected by biochar application (not shown). The organic C increase was expected because the 250 and 500°C switchgrass biochars contained 55 and 84% total C, respectively (Table 1). Increasing the organic C content of these Aridisols, which initially contained ~0.5% organic C, is important for soil pedological processes such as soil structure development that improve tilth as well as for increasing soil water storage. Novak et al. (2011) monitored changes in soil water content after adding 2% (by weight) 250 or 500°C switchgrass biochar to the Declo and Warden soils. The authors observed an increase in moisture content by 3 to 7% relative to control soils. Based on evapotranspiration rates of Aberdeen, Idaho and Prosser, Washington, this could lead to an additional 0.4 to 2.5 d of available water for crop growth. Others have also reported increases in soil water retention with the use of biochar (e.g., Glaser et al., 2002; Chan et al., 2007).

The increased organic C content has implications as related to global climate change, removal of atmospheric CO$_2$, and long-term soil C sequestration. The increase in soil organic C content associated with both biochar applications might be expected to be maintained for decades or centuries depending on the half-life of the materials. As compared with nonpyrolyzed biomass, charring increases the stability of C against microbial decay (Baldock and Smernik, 2002), as is evident in the elevated soil organic C content of Amazonian Anthrosols. Supporting the concept that soil C pools would remain elevated for long periods of time, Steiner et al. (2007) observed, over 20 mo, only a 4% decrease in soil C loss associated with an 11 Mg ha^{-1} biochar application as compared with a 25% reduction in soil C from control soils. Similar research is required in other systems, such as arid environments, to quantify changes over time in soil C as well as nutrient pools associated with biochar application. Nonetheless, increasing soil C sequestration in an arid environment is difficult, but biochar may be the best organic C–enriched supplement for these soils to help achieve a reduction in atmospheric CO$_2$.

Conclusions

Little research has been performed to quantify the effects of biochar designed to improve aridic soil fertility status. We compared the effects of 250 or 500°C switchgrass biochar application on nutrient leaching and the soil fertility levels of two Aridisols. Overall, the 250°C biochar resulted in decreased Ca and Mg leaching, increased K leaching, and increased Mn and Ni soil-extractable concentrations. These observations were likely due to greater total negative surface charge in the 250°C versus the 500°C biochar, favoring divalent cation sorption. In addition, NO$_3$–N leaching and soil concentrations were reduced to a greater extent with the 250°C biochar versus 500°C biochar, likely due to microbial immobilization.

Based on the results of this study, the use of switchgrass biochar produced at 250°C appears to be a practical material for improving Aridisol soil nutrient status while reducing nutrient leaching losses that could adversely affect environmental quality. However, further large-scale research in production systems is required to more fully understand the nutrient dynamics associated with biochar usage in aridic systems.

Acknowledgments

The authors thank Ms. Mary Ann Kay for project maintenance and analyses. Mention of a specific product or vendor does not constitute a guarantee or warranty of the product by the U.S. Dep. of Agriculture or imply its approval to the exclusion of other products that may be suitable.

References

Allen, R.L. 1847. A brief compend of American agriculture. Third ed. C.M. Saxton, New York.

Antal, M.J., and M. Grønli. 2003. The art, science, and technology of charcoal production. Ind. Eng. Chem. Res. 42:1619–1640. doi:10.1021/ie0207919

Asai, H., B.K. Samson, H.M. Stephan, K. Songyikhangsuthor, K. Homma, Y. Kiyono, Y. Inoue, T. Shiraiwa, and T. Horie. 2009. Biochar amendment techniques for upland rice production in Northern Laos: 1. Soil physical properties, leaf SPAD and grain yield. Field Crops Res. 111:81–84. doi:10.1016/j.fcr.2008.10.008

ASTM. 2006. Petroleum products, lubricants, and fossil fuels: Coal and coke. ASTM International, West Conshohocken, PA.

Baldock, J.A., and R.J. Smernik. 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Org. Geochem. 33:1093–1109. doi:10.1016/S0146-6380(02)00062-1

Boehm, H.P. 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32:759–769. doi:10.1016/0008-6223(94)90031-0

Bohn, H., B. McNeal, and G. O'Connor. 1985. Soil chemistry. 2nd ed. John Wiley & Sons, New York.

Cao, X., L. Ma, B. Gao, and W. Harris. 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 43:3285–3291. doi:10.1021/es803092k

Chan, K.Y., L. Van Zwieten, I. Meszaros, A. Downie, and S. Joseph. 2007. Agronomic values of greenwaste biochar as a soil amendment. Aust. J. Soil Res. 45:629–634. doi:10.1071/SR07109

Gaskin, J.W., R.A. Speir, K. Harris, K.C. Das, R.D. Lee, L.A. Morris, and D.S. Fisher. 2010. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agron. J. 102:623–633. doi:10.2134/agronj2009.0083

Glaser, B., G. Guggenberger, and W. Zech. 2004. Identifying the pre-Columbian anthropogenic input on present soil properties of Amazonian dark earths (Terra Preta). p. 145–158. *In* B. Glaser and W.I. Woods (ed.) Amazonian dark earths: Explorations in space and time. Springer, New York.

Glaser, B., J. Lehmann, and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: A review. Biol. Fertil. Soils 35:219–230. doi:10.1007/s00374-002-0466-4

Gonzalez-Perez, J.A., F.J. Gonzalez-Vila, G. Almendros, and H. Knicker. 2004. The effect of fire on soil organic matter: a review. Environ. Int. 30:855–870. doi:10.1016/j.envint.2004.02.003

Hamer, U., B. Marschner, S. Brodowski, and W. Amelung. 2004. Interactive priming of black carbon and glucose mineralisation. Org. Geochem. 35:823–830. doi:10.1016/j.orggeochem.2004.03.003

Kimetu, J.M., J. Lehmann, S.O. Ngoze, D.N. Mugendi, J.M. Kinyangi, S. Riha, L. Verchot, J.W. Recha, and A.N. Pell. 2008. Reversibility of soil productivity decline with organic matter of differing quality along a degradation gradient. Ecosystems 11:726–739. doi:10.1007/s10021-008-9154-z

Kuo, S. 1996. Phosphorus. p. 894–897. *In* D.L. Sparks (ed.) Methods of soil analysis, part 3: Chemical methods. SSSA, Madison, WI.

Lehmann, J. 2007. Bio-energy in the black. Front. Ecol. Environ 5:381–387. doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

Lehmann, J., J.P. da Silva, C. Steiner, T. Nehls, W. Zech, and B. Glaser. 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the central Amazon basin: Fertilizer, manure and charcoal amendments. Plant Soil 249:343–357. doi:10.1023/A:1022833116184

Lima, H.N., C.E.R. Schaefer, J.W.V. Mello, R.J. Gilkes, and J.C. Ker. 2002. Pedogenesis and pre-Colombian land us of "Terra Preta Anthrosols" ("Indian black earth") of Western Amazonia. Geoderma 110:1–17. doi:10.1016/S0016-7061(02)00141-6

Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42:421–428. doi:10.2136/sssaj1978.03615995004200030009x

Major, J., J. Lehmann, M. Rondon, and C. Goodale. 2010a. Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. Glob. Change Biol. 16:1366–1379. doi:10.1111/j.1365-2486.2009.02044.x

Major, J., M. Rondon, D. Molina, S.J. Riha, and J. Lehmann. 2010b. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333:117–128. doi:10.1007/s11104-010-0327-0

Missouri Cooperative Soil Survey. 2010. The cooperative soil survey. Available at http://soils.missouri.edu/tutorial/page4.asp (verified 14 Aug. 2011).

Mulvaney, R.L. 1996. Nitrogen: Inorganic forms. p. 1123–1184. *In* D.L. Sparks (ed.) Methods of soil analysis, part 3: Chemical methods. SSSA, Madison, WI.

Namgay, T., B. Singh, and B.P. Singh. 2010. Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (*Zea mays* L.). Aust. J. Soil Res. 48:638–647. doi:10.1071/SR10049

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 975–977. *In* D.L. Sparks (ed.) Methods of soil analysis, part 3: Chemical methods. SSSA, Madison, WI.

Novak, J.M., W.J. Busscher, D.L. Laird, M. Ahmedna, D.W. Watts, and M.A.S. Niandou. 2009a. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Sci. 174:105–112. doi:10.1097/SS.0b013e3181981d9a

Novak, J.M., W.J. Busscher, D.W. Watts, D.A. Laird, M.A. Ahmedna, and M.A.S. Niandou. 2010. Short-term CO_2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult. Geoderma 154:281–288. doi:10.1016/j.geoderma.2009.10.014

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

SAS Institute, Inc. 2008. SAS/STAT user's guide. Version 9.2. SAS Inst., Cary, NC.

Sherrod, L.A., G. Dunn, G.A. Peterson, and R.L. Kolberg. 2002. Inorganic carbon analysis by modified pressure-calcimeter method. Soil Sci. Soc. Am. J. 66:299–305. doi:10.2136/sssaj2002.0299

Singh, B., B.P. Singh, and A.L. Cowie. 2010a. Characterisation and evaluation of biochars for their application as a soil amendment. Aust. J. Soil Res. 48:516–525. doi:10.1071/SR10058

Singh, B.P., B.J. Hatton, B. Singh, A.J. Cowie, and A. Kathuria. 2010b. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. J. Environ. Qual. 39:1224–1235. doi:10.2134/jeq2009.0138

Soltanpour, P.N., G.W. Johnson, S.M. Workman, J.B. Jones, Jr., and R.O. Miller. 1996. Inductively coupled plasma emission spectrometry and inductively coupled plasma-mass spectrometry. p. 91–139. *In* D.L. Sparks (ed.) Methods of soil analysis, part 3: Chemical methods. SSSA, Madison, WI.

Steiner, C., B. Glaser, W.G. Teixeira, J. Lehmann, W.E.H. Blum, and W. Zech. 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonial Ferralsol amended with compost and charcoal. J. Plant Nutr. Soil Sci. 171:893–899. doi:10.1002/jpln.200625199

Steiner, C., W.G. Teixeria, J. Lehmann, T. Nehls, J.L. Vasconcelos deMacêdo, W.E.H. Blum, and W. Zech. 2007. Long term effects of manure, charcoal, and mineral fertilization on crop production and fertility on a highly weathered central Amazonian upland soil. Plant Soil 291:275–290. doi:10.1007/s11104-007-9193-9

Thomas, G.W. 1996. Soil pH and soil acidity. p. 475–490. *In* D.L. Sparks (ed.) Methods of soil analysis, part 3 Chemical Methods. SSSA, Madison, WI.

Uchimiya, M., I.M. Lima, K.T. Klasson, S. Chang, L.H. Wartelle, and J.E. Rodgers. 2010. Immobilization of heavy metal ions (Cu^{II}, Cd^{II}, Ni^{II}, and Pb^{II}) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58:5538–5544. doi:10.1021/jf9044217

USEPA. 1996a. Acid digestion of sediments, sludges, and soils. *In* Test methods for evaluating solid waste, physical/chemical methods. SW-846, USEPA, Washington, DC. Available at: http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3050b.pdf (verified 17 Aug. 2011).

USEPA. 1996b. Microwave assisted acid digestion of siliceous and organically based matrices. *In* Test methods for evaluating solid waste, physical/chemical methods. SW-846, USEPA, Washington, DC. Available at: http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3052.pdf (verified17 Aug. 2011).

Van Zwieten, L., S. Kimber, S. Morris, K.Y. Chan, A. Downie, J. Rust, S. Joseph, and A. Cowie. 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327:235–246. doi:10.1007/s11104-009-0050-x

Yuan, J.H., R.K. Xu, and H. Zhang. 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour. Technol. 102:3488–3497. doi:10.1016/j.biortech.2010.11.018