Biochars Impact on Soil-Moisture Storage in an Ultisol and Two Aridisols

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Abstract: Biochar additions to soils can improve soil-water storage capability; however, there is sparse information identifying feedstocks and pyrolysis conditions that maximize this improvement. Nine biochars were pyrolyzed from five feedstocks at two temperatures, and their physical and chemical properties were characterized. Biochars were mixed at 2% wt wt^{-1} into a Norfolk loamy sand (Fine-loamy, kaolinitic, thermic Typic Kandiudult), a Declo silt loam (Coarse-loamy, mixed, superactive, mesic xeric Haplocalcid), or a Warden silt loam (Coarse-silty, mixed, superactive, mesic xeric Haplocambid). Untreated soils served as controls. Soils were laboratory incubated in pots for 127 days and were leached about every 30 days with deionized water. Soil bulk densities were measured before each leaching event. For 6 days thereafter, pot-holding capacities (PHC) for water were determined gravimetrically and were used as a surrogate for soil-moisture contents. Water tension curves were also measured on the biochar-treated and untreated Norfolk soil. Biochar surface area, surface tension, ash, C, and Si contents, in general, increased when produced under higher pyrolytic temperatures (≥500°C). Both switchgrass biochars caused the most significant water PHC improvements in the Norfolk, Declo, and Warden soils compared with the controls. Norfolk soil-water tension results at 5 and 60 kPa corroborated that biochar from switchgrass caused the most significant moisture storage improvements. Significant correlation occurred between the PHC for water with soil bulk densities. In general, biochar amendments enhanced the moisture storage capacity of Ultisols and Aridisols, but the effect varied with feedstock selection and pyrolysis temperature.

Key words: Aridisol, biochar, GRACEnet, soil moisture, Ultisol.

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Soil-water storage is often the most limiting factor to crop production in the arid Pacific Northwest and temperate Southeast regions of the United States. In the arid regions of Washington and Idaho, for example, rainfall totals are very low (<300 mm; Schillinger et al., 2010). Low rainfall in the arid to semiarid regions of these two states creates periods of drought resulting in crop moisture stress (Grulke, 2010). In contrast, annual rainfall in the temperate Coastal Plain region of South Carolina is much larger (1,321 mm; SC DNR, 2010) and is generally sufficient for crop water requirements (Sheridan et al., 1979). Despite ample rainfall totals, soil-water deficits still occur in the Coastal Plain region because of poorly distributed rainfall patterns combined with low soil-water storage capacities (Sadler and Camp, 1986; Busscher et al., 2010). Water deficits in both these regions may be reduced if soil-water storage can be increased.

The application of biochar to soil is considered a win-win strategy to increase soil C sequestration (Lehmann et al., 2006; Laird, 2008; Sohi et al., 2009) while also improving soil physical conditions that influence soil hydraulic parameters and water retention (Glaser et al., 2002; Kameyama et al., 2011). Biochar is a coproduct of the pyrolysis process for transforming lignocellulosic (Antal and Grønli, 2003) and animal manure (Cantrell et al., 2007; Cantrell et al., 2008; Ro et al., 2010) feedstocks into useful energy products (e.g., fuel gas, liquid bio-oil, biochar; Bridgewater, 2003; Mohan et al., 2006; Mullen et al., 2010). Raw feedstocks are pyrolyzed under anoxic conditions using a variety of production parameters that involve exposing feedstocks for either a few seconds or a few hours at temperatures ranging from 300°C to 700°C (Sohi et al., 2009). During the pyrolysis process, feedstocks undergo transformations through a series of dehydration, degassing, and carbonization reactions (Aiman and Stubington, 1993; Drummond and Drummond, 1996). These modifications contribute to differences in each biochar's physical (Downie et al., 2009) and chemical properties (Amonette and Joseph, 2009).

When biochar is present in a soil system, it can contribute to better water storage through modifying that portion of the soil pore size distribution associated with aggregation improvements (Downie et al., 2009) and by water storage in pores (Downie et al., 2009; Chen et al., 2010; Shackley and Sohi, 2010). Several studies have investigated the impact of biochars on soil-moisture storage. In an early study, Tryon (1948) reported that charcoal significantly increased the soil-moisture storage capacity of sand, whereas mixed results were achieved in a loam and a clay-textured forest soil. Glaser et al. (2002) reported that soil-water retention capacity was 18% greater than adjacent soils after biochar applications in the tropical Terra Preta region of Amazonia. Gaskin et al. (2007) reported improvements in soil-moisture storage after biochar was added at high rates (88 Mg ha^{-1}) to a sandy-texture Ultisol. More recently, Laird et al. (2010) applied biochar made from hardwoods to an Iowa Mollisol, and Karhu et al. (2011) applied biochar made from birch feedstock to a silt loam soil in Finland; both reported soil-moisture content improvements. In all these studies, however, there was no examination of relationships between structural and chemical characteristics of the biochar and changes in soil-moisture retention. Further work is needed to identify what physical and chemical characteristics of biochar can maximize improvements in soil-moisture storage.

Water may potentially react with inorganic constituents in the remaining biochar ash (Pierce et al., 1951). As an example, plants can accumulate Si from 0.1% to 10% of shoot dry weight (Takahashi et al., 1990; Hodson et al., 2005). Once taken up by the plant, Si reacts with water molecules in polymerizations reactions causing phytolith or silica hydrogel formations, which are essential structures used in plant biochemical and biophysical reactions (Simpson and Volcani, 1981; Currie and Perry, 2007)). If biochar is produced from Si-enriched raw feedstocks, phytoliths, Si hydrogels, or other silica gel, the resulting biochar may express the same tendency to react with soil water by physically adhering water molecules (Pandis et al., 2011) or trapping water vapor in internal pores (Khan and Shah, 2007). Assuming that water-binding pathways of Si-enriched biochars operate in soils, then the Si content of biochars may be an important characteristic to improve soil-water storage.

In the present work, we hypothesized that biochars having different chemical characteristics and surface properties would lead to dissimilar soil-moisture storage capacity improvements. Soil-moisture contents can be easily expressed on a gravimetric weight basis or through soil tension measurements. Monitoring soil-moisture characteristics in soil treated with biochars using conventional pressure plate techniques is problematic because of using disturbed soil cores (Dane and Hopmans, 2002) and by biochar potentially plugging micropores on the ceramic plates. To avoid these method issues, we chose to approximate the gravimetric soil-moisture content by developing a pot-holding capacity (PHC) for water convention. The PHC for water conveniently allows us to evaluate multiple biochars incubated in several soils. In addition, we evaluated water retention curves in an Ultisol generated from a ku-pF instrument, allowing for determination of water contents by weight at two different tensions. The specific objectives of this study were to (i) examine the effects of nine biochars on PHC for water in a sandy Ultisol and two fine-textured Aridisols, (ii)) conduct soil-water retention curves on a Norfolk loamy sand treated with nine biochars, and (iii) determine if predictable relationships exist between the PHC for water with chemical and physical properties of biochars and with changes in soil bulk density.

MATERIALS AND METHODS

Selection of Soils and their Characteristics

Assessment of biochar influence on soil properties was determined in two separate laboratory experiments. In the first experiment, Norfolk soil was incubated with nine biochars. In a second experiment, switchgrass biochars were incubated in Declo and Warden soils.

The Norfolk soil chemical and physical properties, along with agricultural management history of the collection site were reported by Novak et al. (2009). Briefly, the Norfolk soil formed in marine sediments in the middle coastal plain physiographic region of South Carolina. This region has an annual precipitation total of between 1,130 to 1,321 mm, although it experiences extended periods of drought lasting up to several weeks (Busscher et al., 2010). The Norfolk soil was collected from the 0- to 15-cm surface layer in cropped field at the Clemson University Pee Dee research and Education Center, Florence, South Carolina. The field has a long history (20 years) of row-crop production including corn (*Zea mays* L.), cotton (*Gossypium hirsutum* L.), soybeans (*Glycine max* [L.] Merr.), and wheat (*Triticum aestivum* L.). The soil was air dried and 2-mm sieved before use.

The Norfolk soil was confirmed as a loamy sand (Table 1; sedimentation method: Soil Characterization Lab, The Ohio State University, Columbus, OH). This soil also has a low SOC content and an acidic pH (4.8). X-ray diffraction analyses revealed that it is an extensively weathered Ultisol because its mineralogy is composed mostly of quartz and kaolinitic clays (Novak et al., 2009).

The two Aridisols used in the experiment were chosen based on their textural differences from the loamy sand, arid location, and their need for improved water-holding capacities. A soil sample from the Ap horizon (0- to 20-cm depth) of the Declo series was obtained from a field at the University of Idaho Experimental Station in Aberdeen, Idaho. Field crops were historically grown under irrigation and consisted of a 3-year barley (*Hordeum vulgare* L.), wheat, and potato (*Solanum tubersum* L.) rotation. The Declo soil has a silt loam texture because it is composed of 190, 515, and 295 mg kg^{-1} sand, silt, and clay, respectively (sedimentation method, Gee and Bauder, 1986; Table 1). The Warden soil was also confirmed a silt loam because it contains 240, 515, and 245 g kg^{-1} of sand, silt, and clay, respectively (sedimentation method, Gee and Bauder, 1986; Table 1). The Warden silt loam was collected from the Ap horizon (0–20 cm deep) in a field on the Washington State University Experimental Station at Prosser, Washington. The crops in this field were also grown under irrigation and have historically consisted of a 3-year rotation of alfalfa (*Medicago sativa* L.), corn, and wheat. Both soils were air dried and then ground to pass through a 2-mm sieve.

Feedstock Selection and Biochar Pyrolysis Conditions

Raw feedstocks for this study were chosen based on their common occurrence as a biofuel crop, as an available agricultural by-product, or as an industrial wood-waste product (Table 2). These included peanut hulls from Georgia, pecan shells from North Carolina, poultry litter from Mississippi, switchgrass from South Carolina, and hardwood waste products from Canada. All raw feedstocks required considerable processing before pyrolysis including air drying, grinding, and sieving to pass a 1- to 2-mm sieve. These biochars were produced at four facilities: peanut hull biochar at University of Georgia; poultry litter biochar at the USDA-ARS Southern Regional Research Center, New Orleans, Louisiana; pecan shell and switch grass biochars at North Carolina Agricultural and Technical State University; and hardwood biochar at Dynamotive Energy Systems (Vancouver, British Columbia, Canada).

The pyrolysis procedure for raw feedstock conversion into biochars at these four locations varied according to their respective

TABLE 1. Characteristics of Soils

	Soil Texture ($g\ kg^{-1}$)				Carbon Content ($g\ kg^{-1}$)		
Series	Sand	Silt	Clay	pH	Organic	Inorganic	Total
Norfolk	730	250	20	4.8	16.8	—	16.8
Declo	190	515	295	8.1	6.9	11	17.9
Warden	240	515	245	7.3	4.4	—	4.4

TABLE 2. Raw Feedstocks, Collection Location, and Pyrolysis Conditions for Biochar Manufacture

Feedstock	location	Pyrolysis (°C)	Furnace	Residence Time†	Method Reference
Hardwood	Canada	≈500	Fluidized-bed kiln	5 sec	T. Bouchard‡
Peanut hull (*Archis hypogaea*)	Georgia	400	Heated rotary drum	1–2 h	Gaskin et al., 2008
		500		1–2 h	
Pecan shell (*Carya illinoensis*)	North Carolina	350	Lindberg Electric box with retort	1–2 h	Novak et al., 2009
		700		1–2 h	
Poultry litter (*Gallus domesticus*)	Mississippi	350	Lindberg Electric bench with retort	1–2 h	Lima and Marshall, 2005
		700		1–2 h	
Switchgrass (*Panicum virgatum*)	South Carolina	250	Lindberg Electric box with retort	8 h	Toles et al., 1998
		500		1–2 h	

†Feedstock pyrolysis time.
‡Personal communication.

methods (Table 2). Briefly, the biochars from peanut hulls, pecan shells, poultry litter, and switchgrass were made using a slow (1–2 h long) pyrolysis residence time under a continual stream of N_2 gas (Table 2). These feedstocks were pyrolyzed either at a low (<400°C) or a high (>500°C) temperature to yield different structural and surface characteristics (Novak et al., 2009). Specifically, peanut hulls were pyrolyzed at 400°C and 500°C, pecan shells at 350°C and 500°C, and poultry litter biochar at 350°C and 700°C. Biochar from switchgrass was made at 500°C, but also at 250°C. Switchgrass biochar produce at 250°C required a longer residence time (8 h) in the Lindberg furnace, allowing sufficient time for carbonization to occur (Table 2). This lower temperature and longer residence provided a torrified-like product that would be expected to contain semidegraded cellulose and hemicellulose compounds, because 300°C to 400°C is the critical temperature for their structural breakdown (Antal and Grønli, 2003). Biochar from hardwood was made from wood wastes using a fast pyrolysis system consisting of a 1- to 2-sec exposure to ≈500°C (Tom Bourchard, oral communication, 2011). After recovery from the pyrolyzer, all biochars were initially ground to pass a 0.42-mm sieve using a Wiley Mini Mill (Thomas Scientific, Swedesboro, NJ). The 0.42-mm-sieved biochars were then further ground by hand using a mortar and pestle to pass through a 0.25-mm sieve and stored in a dessicator until use.

Biochar Characterization and Interaction With Water

All biochar samples were characterized for their physical and chemical properties as shown in Table 3. The pH of each biochar was measured in triplicate using a 1% (wt vol^{-1}) biochar:deionized water mixture after shaking for 200 revolutions per minute for 24 h. Surface area (SA) characteristics were obtained from duplicate N_2 adsorption isotherms at 77°K using a Nova 2000 Surface area analyzer (Quantachrome Corp., Boynton Beach, FL) with results fitted using the Brunauer, Emmett, and Teller equation.

Each biochar surface tension (ST) was measured by determining their water repellency characteristics using the molarity of ethanol drop (MED) method of Roy and McGill (2002). A detailed description of the MED method including thermodynamic relationships between solid, liquid, and gas phases and equations describing how these phases influence tension or interfacial free energy is available (Roy and McGill, 2002).

Briefly, in the MED test procedure, a quantity of each biochar was weighed that sufficiently covered the bottom of an

TABLE 3. Chemical and Physical Properties of Biochars

Biochar (°C)†	pH	SA‡ ($m^2\ g^{-1}$)	ST ($mN\ m^{-1}$)	Ash‡	C‡	H‡	O‡	N‡	Si
				g kg^{-1}					
Hardwood (500)	5.7	1.28	54	89	726	28	152	3.4	1.4
Peanut hull (400)	7.9	0.52	47	82	748	45	89	27	9
Peanut hull (500)	9.9	1.22	61	93	818	29	20	27	13
Pecan shell (350)	4.6	1.01	42	24	645	53	275	3.0	0.2
Pecan shell (700)	9.1	222	71	52	912	15	18	2.6	0.3
Poultry litter (350)	7.7	1.10	45	359	461	37	76	50	17
Poultry litter (700)	9.6	9.00	39	524	420	2.5	0.3	28	25
Switchgrass (250)	6.4	0.4	36	26	553	60	351	4.3	6
Switchgrass (500)	9.2	62.2	55	78	844	24	29	11	14

†Pyrolysis temperature used to carbonize raw feedstock.
‡Source: Novak et al. (2009).
SA: surface area, ST: surface tension.

aluminum weighing dish to a depth of at least 6 mm. Next, a 3 *M* ethanol droplet was dispensed on the biochar surface. If the droplet took longer than 10 sec to enter the surface, then the test was repeated on a new area of the biochar using a higher strength ethanol solution (up to 6 *M*). If the time of entry was less than 10 sec, the test was repeated on a new area of the biochar using a lower-strength ethanol solution (down to 0 *M*). Testing continued until a value between 5 and 10 sec was recorded. A value for γ_c (ST, as mN m^{-1}) was then calculated by the following equation after Roy and McGill (2002).

$$\gamma_c = 61.05 - 14.75 \ \ln(C_{EtOH} + 0.5) \qquad (1)$$

where C_{EtOH} is the ethanol concentration as mol L^{-1} in the solution yielding uptake within 5 to 10 sec. The tests were run in duplicate, and mean values reported (Table 3). The resolution of this MED method was 1 mN m^{-1}.

For each biochar sample, a single estimate of ash and elemental (C, H, O, and N) content was determined on an oven dry-weight basis by Hazen Research, Inc. (Golden, CO), following the ASTM D 3172 and 3176 standard method (ASTM, 2006). In this method, the O content was determined by difference. For the total Si content, a single measurement on each biochar was determined using ASTM D 2795-86 (ASTM, 2006) by initially fusing the biochar $NaHO_2$ in a Zr crucible, followed by dissolution in dilute HCl. The prepared liquid was then analyzed for total Si using a Perkin-Elmer AAnalyst 300 atomic absorption spectrophotometer (Perkin Elmer, Waltham, MA).

Biochar Incubation and Leaching of Norfolk Loamy Sand

The Norfolk loamy sand and biochar incubation experimental procedure and water leaching protocols were previously described in Novak et al. (2009). Similar procedures were used in this experiment except that the incubation period was extended to 118 days, and three additional deionized water leaching events occurred. Briefly, each biochar (0.25-mm sieved) sample was mixed at 2% (wt wt^{-1}) into the Norfolk loamy sand. After placement of soil and biochar into each pot, the pots were gently tapped to a bulk density of between 1.2 to 1.3 g cm^{-3}. The biochar additions corresponded to a field application rate of about 45 Mg ha^{-1}. Untreated Norfolk loamy sand served as controls (i.e., no biochar added). Four representatives were established per the biochar-treated and untreated Norfolk loamy sand. All pots were laboratory incubated at a PHC for water of 10% (wt wt^{-1}), and the PHC was readjusted to 10% twice weekly. As noted earlier, the PHC for water was used as a surrogate value for each soil's moisture content.

A total of four leaching events were carried out after 28, 63, 90, and 118 days of incubation. Before each leaching event, the bulk density of each pot was determined by measuring soil surface height differences at four locations that were referenced to a level plane across each pot rim. A mean value from these four measurements was calculated, and the bulk density determined using a polynomial equation that considered each pot's volume with soil height differences from the rim. Before leaching on day 28 of incubation, each pot was weighed for an initial (day 0) PHC for water, then immediately leached using 1.2 to 1.3 pore volumes of deionized water. The leachate was collected until free drainage had ceased, usually within 30 h. Each leachate weight was recorded, and the percentage of water retained by each pot was calculated. Thereafter, the pots were weighed on the second and sixth day after each leaching event, and the PHC for water on a wt wt^{-1} basis was calculated.

Switchgrass Biochar Incubation and Leaching in Declo and Warden Silt Loams

The biochar laboratory incubation and leaching experiment was repeated with minor modifications using the two fine-textured Aridisols that were only incubated with the 250°C and 500°C switchgrass biochar. The switchgrass biochar was chosen for use in these silt loams because it caused the greatest response in the Norfolk loamy sand. Other modifications included analyzing the treatments in triplicate and maintaining PHC for water between leaching events at 15% (wt wt^{-1}). The treatments involving Declo and Warden silt loams plus switchgrass biochar were incubated at a greater PHC for water to reflect more water storage at field capacity in the silt loam soils (Table 1). Leaching events were conducted on days 34, 62, 92, and 127 of incubation. Before each of these events, bulk density was estimated using the previously described methods.

Norfolk Soil Water Tension Measurements

Soil-water tension results at 5 and 60 kPa, and the difference between the two results, were evaluated on triplicate samples for the Norfolk soil using a ku-pF Apparatus (UGT GmbH, Müncheberg, Germany). Both biochar-treated and untreated (control) Norfolk soils (295 g, air dried) was placed into a 245-cm^{-3} cylindrical sample holder and were gently tapped to a bulk density of 1.2 g cm^{-3}. Samples were saturated in a deionized water bath and placed on the ku-pF an apparatus. After several weeks of monitoring, the soil-water tension readings from embedded tensiometers and water contents by weight were automatically recorded at 10-min intervals. Weight changes of the cylindrical vessels as a function of time along with the water tension data were processed according to the method of Schindler (1980). Mean water tension values along with their S.D. were then computed. Water tension values for the two silt loams soils (Declo and Warden) were not determined.

Statistical Analysis

The mean PHC for water (wt wt^{-1}) for the biochar-treated and untreated Norfolk loamy sand (n = 4) on day 0 (before leaching commenced) and then on days 2 and 6 after each leaching event was initially tested using a one-way analysis of variance to establish if a significant difference existed among samples. Next, a Holm-Sidek pairwise multiple-comparisons procedure was used to determine significant differences among biochar-treated and untreated Norfolk soils samples at a P = 0.05 level of rejection. A similar statistical analysis was used to compare PHC for water (wt wt^{-1}) for the Declo and Warden silt loams. These statistical tests were performed using SigmaStat v. 3.5 software (SSPS Corp., Chicago, IL).

Water tension values for the biochar-treated and untreated Norfolk soil were analyzed using a generalized linear mixed (PROC GLMMIX) model with amendment as a fixed effect and replicate as a random effect (Jones and Huddleston, 2009). Means were separated with a least squares mean separation procedure.

All mean soil bulk density values measured before the first (L1) and fourth leaching (L4) events were compared using a t test. This comparison allowed for an assessment of whether soil bulk density increases after 127 days of incubation were significant and identified which biochar was more successful at reducing soil compaction. In addition, a Holm-Sidek pairwise multiple-comparisons procedure was used to compare mean bulk density values of biochar-treated and untreated soils measured within the L1 and then L4 treatments, thus allowing for an assessment among biochars. An overall pooled mean was calculated by grouping all values ($n = 36$, except the controls) by leaching event. These grouped mean soil bulk density values sorted by leaching event were compared using the Holm-Sidek pairwise comparison (L1 vs. L4) to determine if overall biochars could modify soil compaction.

The biochars SA, ST, pH, ash, C, H, O, N, and Si contents were regressed against water PHC for the Norfolk loamy sand on days 2 and 6 after the first leaching event. In addition, regression relationships between mean bulk density and mean % PHC were examined by pooling day 2 and then day 6 treatment values ($n = 40$). The bulk density regression relationship was repeated for the pooled Declo and Warden silt loams ($n = 12$).

RESULTS AND DISCUSSION

Soil Characteristics

The Norfolk soil used in this study was dominated by sand, had the greatest SOC content among the three soil types, and an acidic pH (Table 1). The Declo and Warden soils had a silt loam texture and low SOC contents and had an alkaline pH. Only the

TABLE 4. Mean Percent Pot-Holding Capacity for Water Measured in the Norfolk Soil Containing 0 and 2% (wt wt^{-1}) Biochars on Days 0, 2, and 6 After All Four Leaching Events (S.D. Values Are in Parentheses; $n = 4$)

Leaching Event/Day of Study	Biochar (°C)	Pot-Holding Capacity for Water (wt wt^{-1})		
		Day 0	Day 2†	Day 6†
First leaching on day 28	Control	2.87 (0.05)	19.54 (0.52)a	9.57 (0.91)a
	Peanut hull (400)	3.97 (0.24)	23.49 (0.14)bc	13.34 (0.62)bd
	Peanut hull (500)	4.26 (0.66)	22.50 (1.52)b	12.23 (1.46)b
	Pecan shell (350)	3.30 (0.17)	21.11 (0.59)ab	11.64 (0.69)abc
	Pecan shell (700)	3.61 (0.04)	22.00 (1.32)ab	12.19 (1.18)bc
	Poultry litter (350)	4.56 (0.15)	21.60 (0.36)ab	12.49 (0.41)bc
	Poultry litter (700)	4.51 (0.17)	20.11 (0.29)a	10.42 (0.56)ab
	Switchgrass (250)	3.37 (0.23)	24.52 (1.23)c	14.31 (0.94)cd
	Switchgrass (500)	4.29 (0.13)	29.92 (1.65)d	19.90 (1.52)e
	Hardwood	4.10 (0.28)	24.46 (1.82)c	14.19 (1.54)c
Second leaching on day 63	Control	7.68 (1.05)	15.42 (0.27)a	5.25 (0.5)a
	Peanut hull (400)	8.08 (0.02)	19.41 (0.93)b	8.58 (1.62)bd
	Peanut hull (500)	8.12 (0.04)	17.37 (0.90)b	6.23 (1.00)ab
	Pecan shell (350)	7.78 (0.16)	17.74 (0.79)b	7.47 (1.01)b
	Pecan shell (700)	8.08 (0.14)	18.66 (0.43)b	7.97 (0.55)b
	Poultry litter (350)	8.23 (0.08)	18.18 (0.34)b	7.68 (0.42)b
	Poultry litter (700)	8.21 (0.20)	19.23 (2.68)b	7.37 (1.19)b
	Switchgrass (250)	7.73 (0.10)	21.06 (2.55)bc	10.05 (2.14)c
	Switchgrass (500)	8.12 (0.14)	21.48 (0.59)c	10.45 (0.47)c
	Hardwood	8.20 (0.10)	21.75 (1.36)c	11.39 (1.49)cd
Third leaching on day 90	Control	8.14 (0.08)	14.36 (0.68)a	6.63 (0.23)a
	Peanut hull (400)	8.59 (0.12)	17.99 (0.03)b	10.18 (1.19)b
	Peanut hull (500)	8.64 (0.06)	16.35 (0.95)c	8.37 (0.81)b
	Pecan shell (350)	8.27 (0.07)	16.67 (0.62)c	8.79 (0.64)b
	Pecan shell (700)	8.30 (0.08)	17.48 (0.25)b	9.32 (0.36)b
	Poultry litter (350)	8.62 (0.05)	17.57 (0.81)b	9.79 (0.71)b
	Poultry litter (700)	8.64 (0.04)	15.74 (0.92)ac	8.28 (0.90)b
	Switchgrass (250)	8.14 (0.17)	20.52 (2.52)d	11.78 (2.20)bc
	Switchgrass (500)	8.35 (0.06)	20.23 (0.67)d	11.95 (0.40)c
	Hardwood	8.65 (0.11)	21.14 (0.50)d	13.48 (0.39)c
Fourth leaching on day 118	Control	7.71 (0.12)	14.31 (0.07)a	5.83 (0.23)a
	Peanut hull (400)	8.22 (0.01)	17.68 (0.89)b	9.25 (0.89)b
	Peanut hull (500)	8.47 (0.18)	15.50 (0.76)ab	7.23 (0.69)bc
	Pecan shell (350)	8.03 (0.17)	16.25 (0.69)ab	8.01 (0.85)b
	Pecan shell (700)	8.03 (0.09)	16.22 (0.36)ab	7.69 (0.29)bc
	Poultry litter (350)	8.31 (0.08)	16.44 (0.65)ab	9.32 (1.19)b
	Poultry litter (700)	8.26 (0.11)	14.71 (0.88)ab	6.28 (0.98)ac
	Switchgrass (250)	7.70 (0.11)	19.96 (2.30)c	11.08 (1.75)d
	Switchgrass (500)	8.12 (0.10)	20.07 (90.58)c	11.89 (0.62)d
	Hardwood	8.29 (0.15)	19.96 (0.38)c	11.53 (0.44)d

†Mean values within a column sorted by leaching event and followed by a different letter are significantly different using a Holm-Sidek multiple-comparisons procedure at $P = 0.05$ level of significance.

TABLE 5. Mean Water Content in the Norfolk Soil at 5 and 60 kPa After 0% and 2% Biochar Additions (S.D. Values Are in Parentheses; n = 3)

Norfolk + Biochar (°C)	Water Content (wt wt^{-1})†
At 5 kPa	
Switchgrass (500)	0.226 (0.0220)a
Switchgrass (250)	0.197 (0.017)b
Hardwood (500)	0.180 (0.033)cb
Peanut hull (500)	0.177 (0.016)cb
Poultry litter (350)	0.170 (0.009)cd
Pecan shell (700)	0.167 (0.009)cd
Pecan shell (350)	0.166 (0.027)cd
Peanut hull (400)	0.164 (0.019)cd
Poultry litter (700)	0.177 (0.016)cd
Control	0.149 (0.022)d
At 60 kPa	
Switchgrass (500)	0.088 (0.003)a
Pecan shell (700)	0.082 (0.006)ba
Switchgrass (250)	0.081 (0.005)bc
Hardwood (500)	0.080 (0.004)bc
Poultry litter (350)	0.080 (0.001)bc
Poultry litter (700)	0.079 (0.002)bc
Peanut hull (500)	0.078 (0.003)bc
Pecan shell (350)	0.077 (0.004)bc
Peanut hull (400)	0.075 (0.004)c
Control	0.074 (0.003)c
Difference between 5 and 60 kPa	
Switchgrass (500)	0.137 (0.020)a
Switchgrass (250)	0.117 (0.012)ba
Peanut hull (500)	0.099 (0.014)bc
Hardwood (500)	0.099 (0.030)bc
Poultry litter (350)	0.089 (0.009)dc
Peanut hull (400)	0.088 (0.020)dc
Pecan shell (350)	0.088 (0.023)dc
Poultry litter (700)	0.085 (0.007)dc
Pecan shell (700)	0.084 (0.007)dc
Control	0.075 (0.020)d

†Means sorted by kPa were analyzed using a generalized linear mixed (PROC GLMMIX) model with significant differences between means tested with a least-squares mean separation procedure.

Declo silt loam, among the three series, contained carbonates causing the highest measured pH value of 8.1.

Physical and Chemical Characteristics of Biochars

Feedstock selection and pyrolysis conditions for biochar production are presented in Table 2. Six of the nine biochars were pyrolyzed using a Lindberg electric furnace equipped with a retort. The remaining three biochars were pyrolyzed using either a heated rotary drum or a fluidized bed kiln (Table 2). More procedural information concerning the pyrolysis conditions for these biochars is available (see citations in Table 2).

The biochars were characterized for various chemical and physical properties (Table 3). Biochars produced at higher pyrolysis temperatures (≥500°C) were characterized by having alkaline pHs, higher ash contents, larger SA values, and greater C concentrations. The quantity of H and O, in the biochars, on the other hand, declined at the higher pyrolysis temperatures because of dehydration of hydroxyl groups and thermal degradation of ligno-cellulosic structures into volatile compounds (Spokas et al., 2011). Feedstock selection also influenced biochar characteristics. The highest Si contents occurred in the switchgrass biochars (184–200 g kg^{-1}), whereas hardwood biochar contained the least (3.4 g kg^{-1}). The large variation in total silica content among the biochars should be expected because plant Si accumulation varies greatly between species (Currie and Perry, 2007). Biochar produced from poultry litter had the highest pH, N, and ash contents probably because of salts from unassimilated inorganic nutrients, treatment with amendments to minimize NH_3 volatilization (Novak et al., 2009), and the presence of uric acid and undigested proteins in the litter (Nahm, 2003).

Surface tension values among the biochars ranged from 36 to 71 mN m^{-1} implying differences in their water repellency (Table 3). Biochars pyrolyzed at higher temperatures (except poultry litter) had greater ST values and thus were more hydrophilic. Pecan shell biochar produced at 700°C had the greatest ST and should have the greatest affinity for attracting water. The range in ST values obtained with the MED method suggests that the biochar surfaces differ in their relative proportions of hydrophilic and hydrophobic functional groups. This is not unexpected because Amonette and Joseph (2009) reported that feedstock selection and pyrolysis condition differences will influence the carbonization processes resulting in compositional variations among organic structures. Compositional differences on biochar surfaces will cause the formation of domains with differing degrees of water repellency.

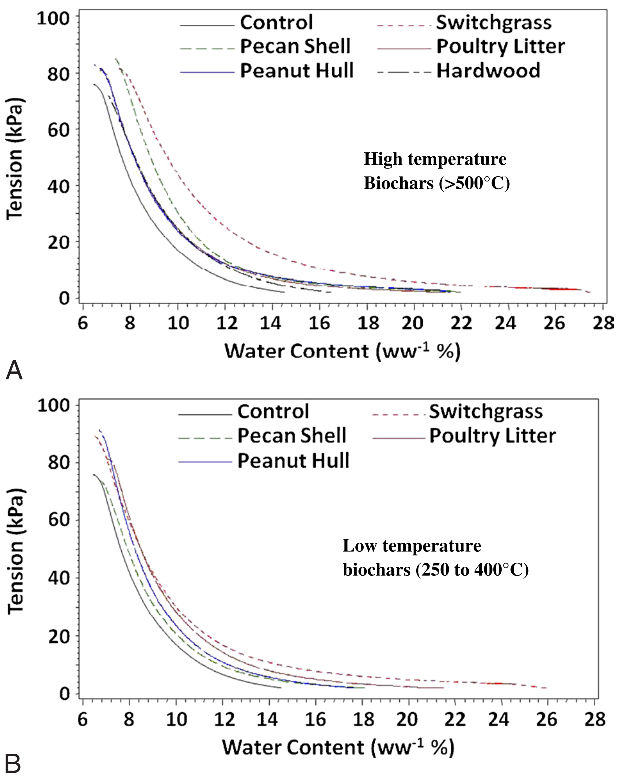

FIG. 1. Norfolk soil-water contents after mixing in (A) high-temperature and (B) low-temperature biochars (2% biochar [wt wt^{-1}]; results are from one representative sample).

PHC for Water in the Norfolk Loamy Sand

Following the first leaching event, the largest improvement in % PHC for water on day 2 in the Norfolk loamy sand occurred in the switchgrass biochar (500°C) treatment (Table 4). In the same leaching event, biochar produced from switchgrass (250°C) and hardwood also significantly improved the % PHC for water relative to the control (Table 4). Mixed results were observed for the remaining biochar treatments.

Improvement in % PHC for water among the nine biochar treatments was best observed after addition of 2% switchgrass (500°C) biochar. This biochar caused the greatest increase in % PHC for water of 9.9% and 10.3 on days 2 and 6, respectively, relative to the controls. This translates to 1.5 to 1.7 cm more water in a 15-cm soil depth compared with the Norfolk control. Incorporating other biochars, especially on day 6 after the first leaching event, showed mixed % PHC for water improvements relative to the control regardless of pyrolysis temperature and feedstock choice (Table 4).

The three additional leaching events on days 63, 90, and 118 tested the biochars' ability to repeat changes in the % PHC for water (Tables 3). After the second leaching event on days 2 and 6, most biochars continued to significantly improve the % PHC for water. Both switchgrass (250°C and 500°C) and the hardwood biochar, after the second leaching event on days 2 and 6, repeated their % PHC for water improvements. This is an important finding because it implies that these biochars can repeat their service of improving moisture storage. The relative increase in % PHC for water with these three biochars relative to the control, unfortunately, was not as large as that obtained after the first leaching event (e.g., ≈6.3% vs. ≈10.3%). The % PHC for water on day 6 after the second leaching event in the Norfolk loamy sand treated with pecan shell and poultry litter biochars declined to 2.1% to 2.7% relative to the controls. Although significant increases in the % PHC for water was apparent after incorporating most biochars, repeated leaching revealed that their ability to improvement water storage diminished.

Even after the third and fourth leaching event, both switchgrass and hardwood biochar continued to exhibit the largest positive effect on the % PHC for water (Table 4). Their improvement on day 2 ranged from about a 5.6% to 6.7% increase in the PHC for water than the control; the increase on day 6 also was also between 5% and 6.8%. Again, the % PHC for water in the Norfolk loamy sand treated with the six remaining biochars on days 2 and 6 after the third and fourth leaching event showed mixed results. Overall, conducting multiple leaching events in the Norfolk loamy sand revealed that biochars pyrolyzed from switchgrass and hardwoods had the most repeatable impact on improving the % PHC for water. For the remaining biochars, multiple leaching revealed that there was smaller to essentially no significant improvement in the % PHC for water.

TABLE 6. Mean Percentage Pot-Holding Capacity for Water Measured in the Declo and Warden Soils Treated With 0% and 2% Switchgrass Biochars on Days 0, 2, and 6 After Individual Leaching Events (S.D. Values Are in Parentheses, $n = 4$)

		% Mean Pot-Holding Capacity for Water (wt wt^{-1})		
Declo Soil	**Biochar (C°)**	**Day 0**	**Day 2[†]**	**Day 6**
1st leaching on day 34	Control	5.37 (0.13)	30.53 (1.29)a	14.18 (0.30)a
	Switchgrass (250)	5.54 (0.41)	33.53 (0.70)b	15.97 (0.18)a
	Switchgrass (500)	5.58 (0.10)	37.09 (0.89)c	17.58 (3.60)a
2nd leaching on day 62	Control	11.99 (0.03)	26.97 (0.99)a	14.34 (1.00)a
	Switchgrass (250)	11.99 (<0.01)	30.94 (1.50)b	17.80 (1.22)b
	Switchgrass (500)	12.10 (0.09)	31.94 (1.09)b	18.12 (1.51)b
3rd leaching on day 92	Control	12.44 (0.08)	22.86 (0.53)a	11.82 (0.28)a
	Switchgrass (250)	12.28 (0.14)	28.29 (0.21)b	16.46 (0.33)b
	Switchgrass (500)	12.25 (0.11)	28.14 (0.46)b	15.70 (0.96)b
4th leaching on day 127	Control	12.50 (0.18)	22.63 (0.47)a	12.49 (0.51)a
	Switchgrass (250)	11.95 (0.12)	28.04 (0.82)b	17.21 (0.69)b
	Switchgrass (500)	11.92 (0.07)	27.96 (0.72)b	16.63 (1.02)b
Warden soil				
First leaching on day 34	Control	5.10 (0.27)	32.12 (0.48)a	16.22 (1.47)a
	Switchgrass (250)	5.38 (0.11)	38.66 (0.33)b	16.52 (1.13)a
	Switchgrass (500)	5.48 (1.22)	38.19 (1.22)b	20.53 (0.46)b
Second leaching on day 62	Control	12.14 (0.11)	27.37 (1.94)a	16.38 (0.48)a
	Switchgrass (250)	12.23 (0.11)	32.79 (0.87)a	19.19 (0.91)b
	Switchgrass (500)	12.06 (0.13)	31.84 (0.38)b	17.54 (0.37)a
Third leaching on day 92	Control	12.51 (0.15)	23.62 (0.41)a	12.49 (0.46)a
	Switchgrass (250)	12.29 (0.04)	29.99 (0.50)b	17.82 (0.71)b
	Switchgrass (500)	12.11 (0.30)	29.42 (0.40)b	14.64 (1.64)c
Fourth leaching on day 127	Control	12.26 (0.15)	23.57 (0.77)a	13.54 (0.73)a
	Switchgrass (250)	12.06 (0.11)	29.19 (0.17)b	18.62 (0.22)b
	Switchgrass (500)	11.68 (0.29)	29.86 (0.48)b	17.54 (0.42)c

[†]Mean values within a column sorted by soil and followed by a different letter are significantly different using a Holm-Sidek pairwise multiple-comparisons procedure at a $P = 0.05$ level of significance.

Water Contents at Different Tension in the Norfolk Loamy Sand

Mean soil-water contents at 5 and 60 kPa and the water content difference between these two tension points are presented in Table 5. Treating the Norfolk loamy sand with the higher temperature (500°C) switchgrass biochar resulted in the most significant soil-moisture improvement at 5 and 60 kPa. In fact, additions of switchgrass (500°C) biochar caused the Norfolk loamy sand to contain 0.137 g of water per gram of soil (difference between tensions) compared with the calculated difference (0.075) in the control. This is an almost a twofold water storage improvement in the Norfolk loamy sand between these two tension points. Significant moisture content improvements in the Norfolk loamy sand at 5 kPa also occurred after mixing in switchgrass (250°C), hardwood (500°C), and peanut hull (500°C) biochars relative to the control. Mixed results occurred in Norfolk soil treated with the remaining biochars at 60 kPa, with only the switchgrass (500°C) and pecan shell (700°C) remaining significantly different than the control.

Plotting the % soil-moisture contents as a function of tension further emphasizes the fact that more water was stored in the Norfolk loamy sand after mixing in the switchgrass (500°C) biochar (Fig. 1A). Comparing the amount of water present at 33 kPa among the treatments confirmed that about 2% more water was stored in the Norfolk loamy sand after mixing in the switchgrass (500°C) relative to the control. Smaller (≤1%) increases in water storage occurred at this tension in the Norfolk loamy sand after mixing the other four high temperature biochars (Fig. 1A). The lower temperature biochars (250°C–400°C; Fig. 1B) also positively impacted water storage at 33 kPa, but the magnitude of the increase was lower than the higher temperature (≥500°C) biochars. These results corroborate the % PHC for water results (Table 4) that mixing 2% switchgrass biochars into the Norfolk loamy sand had the most significant improvement in soil-moisture storage. Biochar pyrolyzed from hardwood, pecan shell, and peanut hull feedstock also showed modest improvements in soil-moisture storage.

PHC for Water in the Declo and Warden Silt Loams

Tryon (1948) reported that increases in moisture content after adding two different charcoals (0 to 45% vol vol^{-1}) made from hardwood and conifer feedstocks to three forest soils were soil texture dependent, with sand showing the most significant improvement. In that study, incubated fine-textured soils amended with charcoals had minimal increases in their soil-moisture content.

In contrast to Tryon's (1948) work, adding 2% switchgrass biochars (250°C–500°C) to the Declo and Warden silt loams soils resulted in % PHC of water ranging from almost 3% to 7% relative to the controls (Table 6). Similar to the trends observed with the Norfolk loamy sand, the most significant increase in % PHC for water was obtained after the first leaching event. On day 2 after the first leaching event, the Declo and Warden soil-moisture contents were improved between 0.5 and 0.8 cm of water per 15-cm soil compared with their controls. Similar to the Norfolk loamy sand, the % PHC for water values declined in these two silt loams after three additional leaching events.

Regardless of declines in % PHC for water, even after the fourth leaching event, the values associated with 2% switchgrass biochar application were still 5% to 7% greater than the controls. Thus, biochars added to finer-textured Aridisols did increase their ability to retain water even after multiple leaching events. Either a low- or high-pyrolysis-temperature switchgrass biochar will increase water retention in these fine-textured soils.

Soil Bulk Density Changes After Incubation

Soil bulk density values sorted by soil series were compared between the L1 and L4 leaching events (Table 7). In all treatments, the bulk density values in the Norfolk loamy sand measured before L4 (after 127 days of incubation) were significantly higher than values measured before L1. Pooling soil bulk densities for the Norfolk loamy sands treated with biochars (n = 36) also showed a significant increase between leaching events. The increase in bulk density was attributed to recompaction by particles settling with leaching water.

Comparing Norfolk loamy sand bulk density results within a leaching event revealed mixed results among the biochar treatments (Table 7). Before the first leaching event, Norfolk loamy sand treated with poultry litter biochar (700°C) had the highest bulk density, whereas soil treated with biochar made from switchgrass and hardwood had the lowest values. By the fourth leaching event, the highest bulk density again occurred in the Norfolk loamy sand treated with poultry litter biochar (700°C), whereas the lowest bulk density occurred in soil treated with switchgrass biochar (250°C). By the end of this experiment, low-temperature switchgrass biochar (250°C) had the most significant impact at minimizing soil recompaction (Table 6; 1.32 vs. 1.43 g cm^{-3}).

TABLE 7. Mean Soil Bulk Densities Measured in the Norfolk, Declo, and Warden Soil Containing 0% or 2% (wt wt^{-1}) Biochar Before the First (L1) and Fourth (L4) Leaching Events (S.D. Values Are in Parentheses)

		Soil Bulk Density (g cm^{-3})	
Soil + Biochar	**Pyrolysis (°C)**	**L1†‡**	**L4**
Norfolk (n = 4)			
Control	NA	1.41 (0.02)a,a	1.57 (0.02)b,a
Peanut hull	400	1.38 (0.01)a,b	1.55 (0.06)b,a
	500	1.38 (0.02)a,b	1.61 (0.04)b,ab
Pecan shell	350	1.39 (0.03)a,b	1.51 (0.03)b,ac
	700	1.49 (0.03)a,a	1.56 (0.04)b,a
Poultry litter	350	1.38 (0.02)a,b	1.57 (0.05)b,a
	700	1.40 (0.01)a,a	1.63 (0.03)b,db
Switchgrass	250	1.32 (0.02)a,c	1.43 (0.01)b,e
	500	1.26 (0.02)a,d	1.50 (0.03)b,af
Hardwood	Fast	1.34 (0.02)a,ec	1.51 (0.06)b,af
	Pooled§	1.36 (0.05)a	1.54 (0.07)b
Declo (n = 3)			
Control	NA	1.17 (0.01)a,a	1.29 (0.01)b,a
Switchgrass	250	1.16 (0.02)a,a	1.19 (0.02)a,b
	500	1.11 (0.01)a,b	1.22 (0.02)b,b
	Pooled	1.13 (0.03)a	1.21 (0.02)b
Warden (n = 3)			
Control	NA	1.16 (0.02)a,a	1.28 (0.03)b,a
Switchgrass	250	1.09 (0.01)a,b	1.21 (0.02)b,a
	500	1.08 (0.01)a,b	1.23 (0.04)b,a
	Pooled	1.08 (0.01)a	1.22 (0.03)b

†Means between columns sorted by soil series were tested for significant differences using a t test with first letter noting significant differences at P = 0.05.

‡Means within a column sorted by soil series were tested using a Holm-Sidek pairwise multiple-comparisons procedure with second group of letters noting significant differences at P = 0.05.

§Pooled means were calculated by grouping results within columns except for control values.

In the Declo silt loam, the low temperature (250°C) switchgrass biochar maintained the bulk density during the experiment, but the high temperature (500°C) did not. Before the fourth leaching event, addition of both of these biochars to the Declo silt loam resulted in significantly lower soil bulk densities compared with the control (Table 7). The switchgrass biochars also decreased soil bulk density values before the first leaching in the Warden silt loam. Before the fourth leaching, however, the biochar did not affect the bulk density compared with the control. These results imply that, if mixed into loamy sand and silt loam soils, biochars pyrolyzed from switchgrass at low temperatures (250°C) could help minimize potential increases in soil bulk density.

Linking Biochar and Soil Properties With Changes in Moisture Content

One of our objectives was to relate modification in the PHC for water to the biochars chemical and physical properties and with changes in soil bulk densities. We focused on the biochars SA and ST characteristics since the literature reported that biochars with high SA contain macropores and fissures that could physically entrap water molecules (Downie et al., 2009) and contain hydrophobic domains causing a low propensity to interact with water molecules (Roy and McGill, 2002). In addition, we examined relations between the biochars' elemental composition analyses (pH, ash, C, O, H, N, and Si content) and possible retention of water to structural groups containing these elements (Major et al., 2009). Declines in PHC for water may also be related to soil reconsolidation (i.e., increasing bulk density) after multiple leaching resulting in less pore space for water retention (Thompson and Troeh, 1978).

Based on these reports, the % PHC for water pooled on days 2 and 6 after the first leaching event was regressed with the soils bulk density values (Fig. 2). On days 2 and 6 after leaching for all three soils, there was a significant negative linear relationship between the % PHC for water with the soil bulk density. Although significant, the strength of the relationship between % PHC for water with soil bulk density revealed a modest relationship on day 2 (r^2 values between 0.49 and 0.76) and a weaker relationship on day 6 (r^2 values between 0.39 and 0.53; Fig. 2). These results suggest that the soil % PHC for water declines was modestly linked to increases in bulk density. Additional leaching caused the soil particles to pack more tightly, resulting in less pore space for water storage.

Results from the Norfolk loamy sand % PHC for water were regressed with each biochar's chemical and physical properties. None of the biochars chemical and physical characteristics examined in this study were found to be significant ($P > 0.05$). The lack of correlation may be related to the fact the biochar characteristics were measured before their incorporation into the soil. In the correlation analyses, it was assumed that these characteristics would remain constant throughout the incubation. However, the literature has shown that the structural and surface properties of biochar can be modified by abiotic

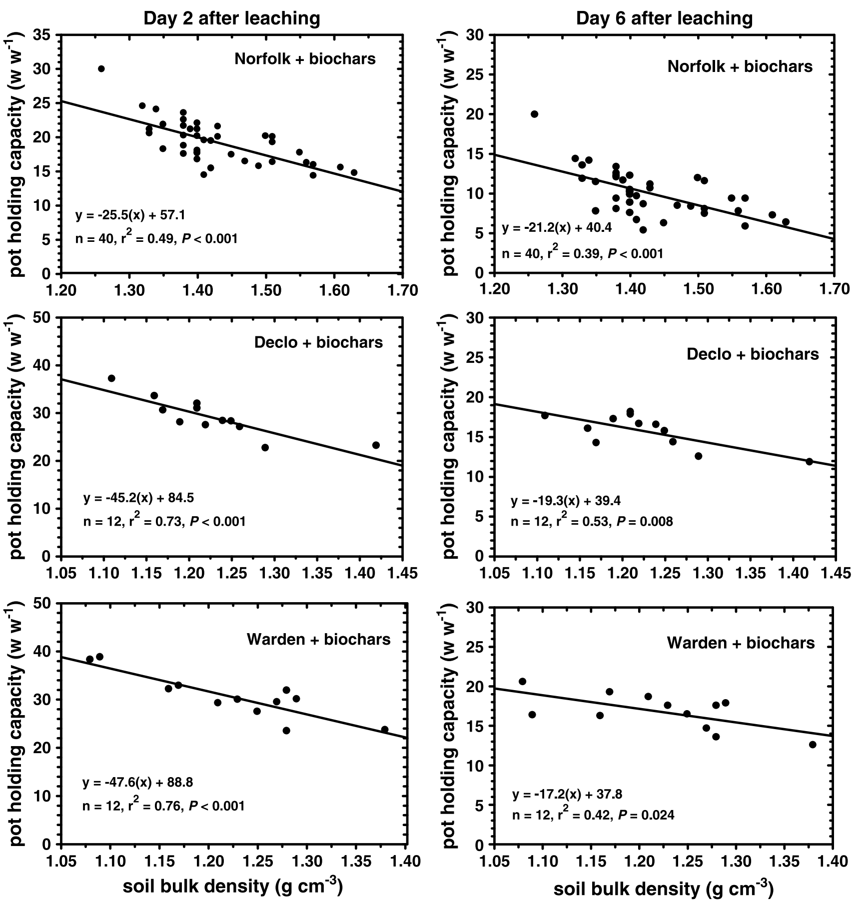

FIG. 2. Relationships between PHC for water and soil bulk densities for Norfolk, Declo, and Warden soils amended with 2% biochar (wt wt^{-1}).

and biotic processes within the time frame of the current study (Hamer et al., 2004; Liang et al., 2006; Cheng et al., 2006). If these changes were significant, then modification in the surface chemical properties could alter the extent of hydrophilic domains on the biochar surface. Loss of hydrophilic domains would cause the biochar interaction with water to be less favorable.

Others have shown that plant-derived Si can react with water molecules to form silica hydrogels (Simpson and Volcani, 1981; Currie and Perry, 2007). Therefore, if biochar is produced from Si-enriched raw feedstocks, the resulting biochar may physically attract water molecules (Pandis et al., 2011). Unfortunately, we did not observe this to be the case. Lack of correlation between the % PHC for water and the biochars Si content may be due to Si tetraethoxysilane being fully hydrated or that the total Si content was an improper characteristic to regress. Instead, the forms of biochar-borne Si, not the total biochar Si content, may play a role in retaining moisture. These hypotheses would require additional testing of biochar after isolation from soil through SEM inspection of biochar pores, measurement of pore volume and their diameters, reanalyses of ST, and by relating biochar Si forms to moisture binding using water adsorption measurements.

CONCLUSIONS

Sandy Ultisols in the Coastal Plain of South Carolina retain little water because of their coarse texture, which commonly creates crop moisture stress over the growing season. Several different biochars were incubated in a Norfolk loamy sand to evaluate their ability to improve soil-moisture retention. These biochars were made under different pyrolysis conditions, which should have caused diverse interactions between water and soil particles.

Among the nine biochars, additions of high- and low-temperature switchgrass and hardwood biochar to the Norfolk loamy sand caused significant increases in the PHC for water and water retained at different tensions. For the Norfolk loamy sand, these increases translated into an additional 1.5 cm of water per 15-cm soil depth. Additions of the other six biochars caused small increases in soil-moisture content, but their effects were less than those obtained with switchgrass and hardwood biochars. All treatments experienced an increase in soil bulk density during this experiment, which explained the noted declines in each soil-moisture storage capacity.

Switchgrass biochar added to the two silt loam Aridisols also improved the % PHC for water. Improvements in soil-moisture storage in these two silt loams ranged between 0.5 and 0.8 cm of water per 15-cm soil depth. This could be an appealing result for crop production in drier climates because these soils are located in a region of the United States that receives low (<300 mm) amounts of annual precipitation and has a heavy reliance on irrigation water.

Regression analyses revealed no significant relationships between SA, ST, and other biochars' chemical properties with changes in the Norfolk's % PHC for water. This was unexpected because the biochars exhibited varying degrees of SA, ST, and Si contents that implied differences in their potential to attract water molecules.

Results from this study suggest that certain feedstocks can be chosen and the pyrolysis conditions tailored to make designer biochars to maximize soil-water storage. Biochars made from switchgrass (high or low pyrolysis temperatures) and hardwood wastes (fast pyrolysis) caused the best moisture content improvements in sandy Ultisols, and biochars made from switchgrass also improved moisture-holding capacity in silt loam Aridisols.

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