Geoderma 158 (2010) 443–449

Contents lists available at ScienceDirect

Geoderma

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

Impact of biochar amendments on the quality of a typical Midwestern agricultural soil

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ARTICLE INFO

Article history:
Received 19 November 2009
Received in revised form 13 May 2010
Accepted 24 May 2010
Available online 26 June 2010

Keywords:
Biochar
Charcoal
Black carbon
Soil quality
Manure

ABSTRACT

Biochar, a co-product of thermochemical conversion of lignocellulosic materials into advanced biofuels, may be used as a soil amendment to enhance the sustainability of biomass harvesting. We investigated the impact of biochar amendments (0, 5, 10, and 20 g-biochar kg^{-1} soil) on the quality of a Clarion soil (Mesic Typic Hapludolls), collected (0–15 cm) in Boone County, Iowa. Repacked soil columns were incubated for 500 days at 25 °C and 80% relative humidity. On week 12, 5 g of dried and ground swine manure was incorporated into the upper 3 cm of soil for half of the columns. Once each week, all columns were leached with 200 mL of 0.001 M $CaCl_2$. Soil bulk density increased with time for all columns and was significantly lower for biochar amended soils relative to the un-amended soils. The biochar amended soils retained more water at gravity drained equilibrium (up to 15%), had greater water retention at −1 and −5 bars soil water matric potential, (13 and 10% greater, respectively), larger specific surface areas (up to 18%), higher cation exchange capacities (up to 20%), and pH values (up to 1 pH unit) relative to the un-amended controls. No effect of biochar on saturated hydraulic conductivity was detected. The biochar amendments significantly increased total N (up to 7%), organic C (up to 69%), and Mehlich III extractable P, K, Mg and Ca but had no effect on Mehlich III extractable S, Cu, and Zn. The results indicate that biochar amendments have the potential to substantially improve the quality and fertility status of Midwestern agricultural soils.

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1. Introduction

The emerging cellulosic bioenergy industry has been promoted as a means of simultaneously improving energy security, improving weak rural economies, and helping to mitigate the threat of global climate change. Concerns, however, have been raised that the harvesting of crop residues for the production of bioenergy could have adverse impacts on soil and environmental quality (Lal, 2004; Wilhelm et al., 2004; Lal and Pimentel, 2007). The harvesting of crop residue removes substantial amounts of plant nutrients from soil agro-ecosystems. Unless these nutrients are replaced by the addition of synthetic fertilizers, manure, or other soil amendments the productivity of the soil will decline. Even if synthetic fertilizers are added to replace the removed nutrients, the sustained removal of crop residues without compensating organic amendments will cause a decline in levels of soil organic matter, which will lead to degradation of soil structure, a decline in cation exchange capacity, a decline in the capacity of soils to hold nutrients and water, and ultimately a decline in soil productivity (Wilhelm et al., 1986).

The loss of soil organic matter also indicates the loss of soil organic C to the atmosphere as CO_2, and hence the necessity of discounting any C offset credits accrued from biofuels displacing fossil fuels. Furthermore, the removal of above ground residue leaves the soil surface vulnerable to raindrop impact, which increases surface crusting, restricts infiltration of water, and increases surface runoff and erosion (Blanco-Canqui and Lal, 2009). Runoff, erosion and the leaching of nutrients not only degrade soil quality but also adversely impact the quality of water in streams and reservoirs. Thus the emerging cellulosic bioenergy industry will not be sustainable unless new agronomic systems are also deployed that enhance the amount of C that is retained by the soils from which biomass feedstock is harvested.

Application of biochar, a co-product of the pyrolysis platform for transforming lignocelluloses biomass into liquid energy products, to the soils from which biomass was harvested has been proposed as a key component of a potentially sustainable integrated agronomic-biomass–bioenergy production system (Fowles 2007; Lehmann 2007; Laird 2008). During pyrolysis most of the Ca, Mg, K, P, and plant micronutrients, and about half of the N and S in the biomass feedstock are partitioned into the biochar fraction. Thus using the biochar as a soil

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0016-7061/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.geoderma.2010.05.013

amendment returns most of those nutrients to the soils from which they came. Biochar also increases the capacity of soils to adsorb plant nutrients (Liang et al., 2006; Cheng et al., 2008) thereby reducing leaching losses of nutrients. Biochar has been shown to decrease soil bulk density, and increase cation exchange capacity, nutrient cycling, and the ability of soils to retain plant available water. Thus the use of biochar as a soil amendment is anticipated to increase both nutrient and water use efficiency and thereby crop productivity (Glaser et al., 2001; Liang et al., 2006). Indeed several reports indicate that soil biochar applications increase crop yields (Iswaran et al., 1980; Kishimoto and Sugiura, 1985; Marjenah, 1994; Yamato et al., 2006).

The C content of biochar varies from <1 to >80%, depending on the nature of the feedstock and the thermal–chemical process employed (Antal and Grnli, 2003; Spokas and Reicosky, 2009). In general, the C in biochar is very stable in soil environments (Schmidt et al., 1999; Glaser et al., 2002; Kuzyakov et al., 2009; and Lehmann et al., 2009). Radio C dates of naturally occurring wildfire chars in soils are often measured in 1000 s y.b.p. (Skjemstad et al., 1998; Pessenda et al., 2001; Swift, 2001; Preston and Schmidt, 2006). By contrast, the half-life of C in plant and animal residues if returned directly to the soil is measured in weeks or months. Thus the transformation of biomass C into stable forms of biochar coupled with soil application of the biochar is a system that effectively removes CO_2 from the atmosphere through photosynthesis and sequesters the C in soils for millennia. Furthermore, there are several reports indicating that soil biochar applications reduce emissions of N_2O and CH_4 from soils either by preventing the formation of these potent greenhouse gasses or by enhancing their oxidation after the gasses have formed (Yanai et al., 2007; Spokas and Reicosky, 2009).

A key advantage of soil biochar applications is that C offset credits can be easily and accurately quantified based on the amount of biochar C applied to the soil and the stability of the biochar C. Soil biochar applications may also qualify for less easily quantified C offset credits based on reductions in N_2O and CH_4 emissions, increase crop productivity and/or reductions in agricultural inputs due to increased fertilizer and water use efficiency (Laird et al., 2009). Because of C offset credits accrued through soil biochar applications, bioenergy produced through an integrated biomass–bioenergy–biochar platform, may be viewed as C-negative energy and there is a potential for such a system to result in agrading soil quality rather than degrading soil quality.

Much of the previous work on the impact of biochar on soil quality has been conducted in the tropics. The highly weathered Oxisols and Ultisols of the tropics intrinsically have low nutrient retention capacity due to a dominance of Fe- and Al-oxides and 1:1 phyllosilicates in the clay fraction. By contrast, Midwestern Mollisols are typically dominated by 2:1 phyllosilicates clays, have higher levels of soil organic matter, and higher nutrient and water holding capacities. Here we test the hypothesis that soil biochar amendments will enhance the quality of a typical Midwestern Mollisol by quantifying the impact of biochar and manure amendments on various soil quality indicators using a soil column leaching/incubation study. A companion paper (Laird et al., 2010) reports the leaching of nutrients from the same soil columns.

2. Materials and methods

2.1. Soil and charcoal

Surface (0 to 15 cm) soil (Clarion, fine-loamy, mixed, superactive, Mesic Typic Hapludolls) was collected from a fallow strip between field plots on the Iowa State University Agronomy and Agricultural Engineering Research Farm in Boone County Iowa. The soil was stored at field moisture content in plastic buckets with tight closing lids until it could be used within one month of collection.

Lump charcoal >1 cm was obtained from a commercial producer who uses mixed hardwood [primarily oak (*Quercus* spp.) and hickory (*Carya* spp.)] and slow pyrolysis (traditional kilns) to produce high C charcoal that is used primarily in the steel industry. The lump charcoal was ground in a hammer-mill and the <0.5 mm fraction (here after referred to as biochar) was separated by dry sieving. Basic properties of the biochar (moisture, volatiles, fixed carbon and ash content) were determined by proximate analysis (ASTM standard 1762-84(2007)). Total C and N in the biochar and freeze-dried swine manure were determined by dry combustion using a Carlo Erba NA1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ). Elemental composition of biochar and manure was determined by ashing the samples at 700 °C, digesting the ash in aqua regia, and analyzing the elemental composition of the digest by inductively coupled plasma-atomic emission spectroscopy. Calcium carbonate equivalent was determined by gradually titrating a biochar suspension to neutrality with 0.5 M HCl over a period of 39 days. The long period was required because the slurry pH would drop immediately when an aliquot of acid was added but then slowly increase over the next 24 h.

2.2. Preparation of soil columns

Batches (15 kg) of field moist soil were tumbled in a rotary cement mixer for 20 min. During the tumbling treatment a predetermined amount of the biochar was slowly added to the soil to bring the final biochar content to 0, 5, 10, or 20 g kg^{-1} of oven dry soil. The tumbling treatments produced roughly spherical soil aggregates ~1 cm diameter.

Soil columns (7.7 cm id by 25 cm length = 1164 cm^3 volume) were constructed of PVC tubing and fitted with PVC end caps on the bottoms. A hole was drilled through the end caps and drain tubes (3 mm i.d.) were attached to the bottom of each column. A small amount of fiberglass was inserted into the drain opening at the base of the columns and then 100 g of coarse sand (2–5 mm) was placed in the bottom of each column. The sand filled the concave portion of the end cap which protruded below the base of the PVC column. The soil columns were packed with 1 kg (oven dry weight equivalent) of moist soil by tamping the columns as the soil was added. All columns were packed to an initial bulk density of 1.1 g cm^{-3}.

2.3. Soil column incubation and leaching

The columns were incubated in a constant temperature room (25 °C and 80% relative humidity) for the duration of the study. On week 12 of the incubation 5 g of dried and ground swine manure was added to half of the columns. The manure was incorporated into the top 3 cm of the soil in the columns using a laboratory spatula. Control columns not receiving manure were also tilled in a similar manner. Once each week during the incubations, all columns were leached with 200 mL of 0.001 M $CaCl_2$. The leachate was introduced on the top of each column using a slow (~1 h) dripping technique with the aid of a syringe barrel and flow restricting needle mounted above the middle of each column. A 25 mm fiberglass filter paper was placed in the middle of each column to help disperse water drops as they impacted on the upper surface of the soil in the columns.

2.4. Analysis of soil column properties

Soil bulk density was determined periodically during the incubation by measuring the distance from the soil surface to the top of the column. From this measurement we determined the volume of headspace above the soil in the column and by difference the soil volume. Soil bulk density was then determined by dividing the known mass of soil added to the columns by the soil volume. This method of determining bulk density yields an average bulk density for the entire column and assumes no change in soil mass through the incubation.

Gravity drained equilibrium water content and saturated hydraulic conductivity were determined at the end of the leaching-incubation experiment. Drain tubes on the bottom of each column were connected to a common water (0.001 M $CaCl_2$) source, and the water content of the

columns was slowly increased to saturation by raising the water source until the head height was slightly above the upper surface of the soil in the columns. Saturated hydraulic conductivity was then measured by the constant head method (Klute, 1965). Water retention at gravity drained equilibrium was determined by allowing the saturated columns to freely drain for 48 h and then measuring the gross weight of each column. The mass of water retained by the soil was determined by subtracting the PVC column, sand, and oven dry soil weights from the gross column weights.

2.5. Analysis of soil properties

After the saturated hydraulic conductivity and gravity drained equilibrium water content determinations were completed, the intact soil cores were removed from the columns with the aid of high pressure Ar gas line attached to the drain holes in the bottom of the columns. The soil cores where then sectioned to separate soil samples for the 0–3 cm, 3–6 cm, and 6 cm–bottom depth increments. Soil samples were dried on the laboratory bench for two weeks and then stored in sealed plastic bags until analyzed.

For each soil sample, total C and N were determined by high temperature combustion using a Carlo Erba NA1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ). Effective cation exchange capacity was determined using the method of Sumner and Miller (1996). Plant available nutrients were extracted using the Mehlich 3 method and analyzed by inductively coupled plasma-atomic emission spectroscopy (Mehlich, 1984). Soil pH was determined using the method described by Thomas (1996). Specific surface area was determined using the EGME method (Carter et al., 1986), and water retention was measured at −33, −100, −500, and −1500 kPa soil water matric potential using a pressure plate apparatus (Dane and Hopmans, 2002). Water retention measurements were determined on soil samples collected from the 6 cm-bottom depth increment for the no-manure control columns only.

2.6. Statistical analysis

The overall experimental design included 4 biochar rates, 2 manure treatments, and 6 replications (48 columns) and soil samples collected from three depth increments for each column. The treatments were randomly assigned to columns arranged on two tables each holding 24 columns within the same constant temperature room. Blocking by table was not significant and thus a completely randomized design was used for all statistical analyses. A three-way analysis of variance was used to determine significance of the overall model, biochar, manure, depth and interaction terms for total C, N, ECEC, pH, and Mehlich 3 extractable nutrients. A two-way analysis of variance was used for gravity drained equilibrium water content and bulk density, which were measured on whole columns and therefore did not include a depth variable. A one-way analysis of variance was used to evaluate biochar treatment effects for moisture retention and specific surface as these were measured only for the 0–6 cm depth increment of the control (no-manure) columns. Tukey's Studentized Range test (alpha 0.05) was used to distinguish differences among treatment means. All statistical analyses were conducted using SAS 9.1 for Windows.

3. Results and discussion

The biochar used in this study contained 71.5% total C and 0.72% total N by mass, and 63.8% fixed C, 19.7% volatiles, 13.9% ash and 2.6% moisture by proximate analysis. The pH of the biochar was 7.6 when first placed in deionized water but increased to 8.2 after 7 days. The swine manure was 41.3% C and 3.51% N on a dry weight basis. Amounts of N, P, Ca, K, Mg, Si, Na, Cu, Mn, and Zn added to the columns by the various biochar and manure treatments are given in Table 1 of the companion manuscript (Laird et al., 2010).

Total soil organic C is one of several key indicators of soil quality (Andrews et al., 2004). Here the addition of biochar to the soil without manure significantly increased the total C content measured after the 500-day incubation by 17.6, 37.6 and 68.8%, respectively, for the 5, 10, and 20 g kg^{-1} biochar treatments relative to the 0 g kg^{-1} biochar controls (Tables 1 and 2). Based on the known C content of the biochar and mass balance analysis, there was no detectable loss of the biochar C during the 500-day incubation. By contrast, the manure treatments did not have a significant effect on the total C content of the whole column soils. The manure treatments, however, were only incorporated to a depth of 3 cm, and analysis of the C content for the 0–3 cm depth increment revealed a small increase (average 6.4%) in C content for the manure treated columns relative to the no-manure controls. Based on mass balance analysis of C for the 0–3 cm depth increment only, less than 20% of the manure C was recovered at the end of the 500-day incubation. The results demonstrate a critical difference in the relative stability of C in biochar, which is highly stable in soil environments, and the C in manure or other biological sources, which is subject to relatively rapid mineralization in soil environments.

Total N content of the soil in the no-manure control columns significantly increased by 0.6, 4.7 and 6.9% respectively for the 5, 10, and 20 g kg^{-1} biochar treatments (Tables 1 and 2). Total N in the soil of the manure treated columns averaged only 2% higher than the total N in the soil of the no-manure control columns, and this difference was not statistically significant. More N was added to the columns with the manure (195 mg N per column) than with the biochar (144 mg N for the 20 g kg^{-1} biochar treatment). Thus the results suggest that N in the biochar is present in a more stable form than the N in the manure. During pyrolysis a significant fraction of the N in proteins and peptides is transformed into N heteroaromatic compounds (Knicker et al., 2008), which may be resistant to microbial degradation.

The relatively large standard deviations associated with C and N determinations of soils by thermal combustion obscure any biochar by manure interactions that may influence the recovery of manure C or N. However, because C and N were determined simultaneously for the same sample, the C:N ratios have much greater precision than either C or N alone. This is so because errors associated with measuring the sample weights, moisture content, and certain instrument errors cancel out when C:N ratios are calculated. Our analysis of C:N ratios for the whole column soils still failed to detect a manure by biochar interaction (Table 1), however our analysis of C:N ratios for the 0–3 cm depth increment revealed a significant manure by biochar interaction ($P>F=0.0037$). Furthermore, our analysis showed that the amount of leachate N attributed to the manure from these columns during the first 45 weeks of the incubation decreased significantly from 60 to 40% with increasing biochar additions (Laird et al., 2010). Combined, these results suggest that biochar helped stabilize some of the N that was added with the manure.

The capacity of soils to retain plant available water is another key indicator of soil quality (Andrews et al., 2004). Here we measured

Table 1
Analysis of variance showing significance ($P>F$) for the effect of biochar, manure and depth on soil quality indicators measured after the 500-day incubation of soil columns with weekly leaching. Mean values for these soil quality indicators are given in Table 2.

Source	DF	C	N	C:N	ECEC	pH
Model	23	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Biochar	3	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Depth	2	<0.0001	<0.0001	0.0012	<0.0001	<0.0001
Manure	1	0.0026	<0.0001	<0.0001	0.12	<0.0001
Biochar*depth	6	0.25	0.82	0.75	0.063	0.33
Biochar*manure	3	0.82	0.99	0.54	0.0002	0.069
Depth*manure	2	0.0003	<0.0001	<0.0001	0.20	0.0001
Biochar*depth*manure	6	0.16	0.33	0.12	0.49	0.53

Table 2
Mean values ($n=6$) for soil quality indicators measured after the 500-day incubation of soil columns with weekly leaching. Biochar treatments, C0, C5, C10, and C20 include amendment of 0, 5, 10, and 20 g-biochar kg^{-1}, respectively. The "M" in the treatment name indicates incorporation of 5 g of dried swine manure into the top 3 cm of soil on week 12 of the incubation. Minimum significant (alpha 0.05) differences between any two means are based on the Tukey Studentized Range test. Analysis of variance for these data is presented in Table 1.

Soil property and depth	Biochar treatments without manure				Biochar treatments with manure				Tukey minimum significant difference
	C0	C5	C10	C20	C0M	C5M	C10M	C20M	
C (%)									
0–3 cm	1.99	2.38	2.73	3.51	2.15	2.52	2.92	3.63	0.224
3–6 cm	2.00	2.32	2.67	3.44	2.01	2.38	2.78	3.35	
6 cm–bottom	2.00	2.35	2.79	3.31	1.95	2.34	2.71	3.39	
N (%)									
0–3 cm	0.168	0.170	0.178	0.180	0.193	0.193	0.200	0.208	0.017
3–6 cm	0.167	0.168	0.170	0.180	0.177	0.175	0.182	0.180	
6 cm–bottom	0.168	0.170	0.178	0.178	0.163	0.170	0.172	0.178	
C:N									
0–3 cm	11.9	14.0	15.3	19.5	11.1	13.1	14.6	17.4	1.30
3–6 cm	12.0	13.8	15.7	19.1	11.4	13.6	15.3	18.6	
6 cm–bottom	11.9	13.8	15.7	18.6	12.0	13.8	15.8	19.0	
ECEC (cmol/kg)									
0–3 cm	17.1	19.8	20.7	20.8	17.5	17.8	19.2	21.6	2.44
3–6 cm	16.3	19.0	19.8	19.6	16.3	17.4	18.8	20.2	
6 cm–bottom	17.6	18.0	18.3	19.4	17.1	17.5	18.3	21.0	
pH									
0–3 cm	6.40	6.42	6.90	7.13	5.95	6.07	6.45	6.75	0.476
3–6 cm	6.33	6.55	6.88	7.23	6.03	6.42	6.82	7.08	
6 cm–bottom	6.60	6.57	7.03	7.25	6.32	6.85	7.05	7.17	

moisture retention in two ways. First, the amount of water retained by soil in the columns at gravity drained equilibrium was respectively 10, 12, and 15% greater for the 5, 10, and 20 g kg^{-1} biochar treatments than the water retained by the 0 g kg^{-1} biochar control columns (Fig. 1). By contrast, the manure treatments did not have a significant effect on water retention at gravity drained equilibrium. Second, soil samples excavated from the 6 cm-bottom depth increment of columns not receiving manure retained 13% and 10% more water at −1 and −5 bars of soil water matric potential for the 20 g kg^{-1} biochar treatments relative to the 0 g kg^{-1} biochar treatments (Fig. 2). No effect of biochar on moisture retention at −0.33 and −15 bar soil water matric potential was detected. No significant effects of biochar or manure were detected on saturated hydraulic conductivity; hence the data are not reported here. The ability of biochar to increase the moisture retention capacity of soils has the potential to increase crop yields for crops exposed to water stress during critical periods of the growing season.

Farmers periodically invest in agricultural lime applications to counter the acidifying effects of ammoniacal fertilizers. Pyrolysis partitions acids into the bio-oil fraction and bases into the biochar, as such some forms of biochar are liming agents. The biochar used in this study had a pH of 8.2 in deionized water. After the 500-day incubation, the soil pH significantly increased by almost 1 pH unit for the 20 g kg^{-1} biochar treatments (Tables 1 and 2). The calcium carbonate equivalent (CCE) value for the biochar, determine by acid titration was 8.8, indicating that the hardwood biochar used in this study was a relatively weak liming agent. Biochars produced from pyrolysis of maize and wheat stover will likely have higher CCE values due to higher ash content.

Bulk density is an important indicator of the physical condition of the soil. The soils in the columns were initially packed to a bulk density of 1.1 g cm^{-3}. During the 500-day incubation/leaching experiment the soil consolidated due to the effects of gravity and leaching water application impacts. For all 6 dates during the incubations on which bulk

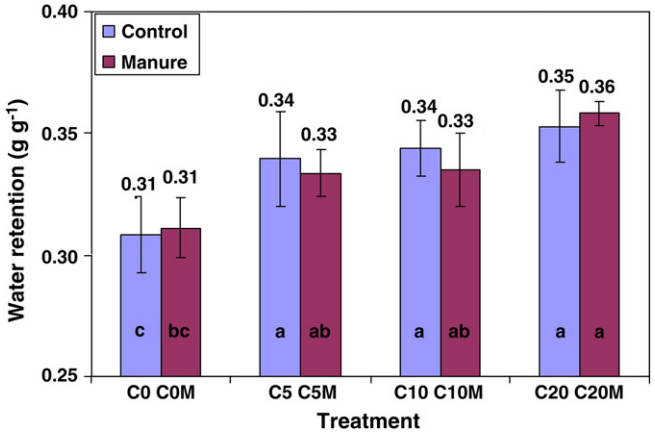

Fig. 1. Water content at gravity drained equilibrium in the soil columns (water remaining after 48 hr of free drainage). Error bars show standard deviations and treatment means with different letters are significantly different (alpha 0.05) by the Tukey Studentized Range test.

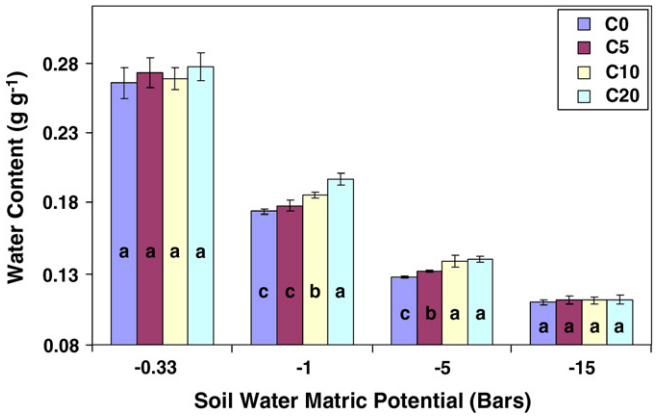

Fig. 2. Water retention for soil excavated from the 6 cm - bottom depth increment of the control (no manure) columns. Error bars show standard deviations and treatment means with different letters are significantly different (alpha 0.05) by the Tukey Studentized Range test.

density was measured, the biochar treated columns had significantly lower bulk densities than the no-biochar controls (Fig. 3). The manure additions did not have a significant effect on bulk density. The magnitude of the biochar effect on bulk density was larger than can be explained by simple dilution of the soil with the low bulk density biochar, furthermore the effect of 5 g kg^{-1} biochar treatments was nearly as large as the effect of the 20 g kg^{-1} biochar treatments. The results confirm that biochar is an effective soil conditioner (Kishimoto and Sugiura, 1985).

Cation exchange capacity and specific surface area are indirect measures of the capacity of soils to retain water, nutrients, and various contaminants. Here specific surface area was measured by the EGME adsorption method for the 6 cm–bottom depth increment of the no-manure control columns only. The specific surface area increased from 130 to 153 m^2 g^{-1} as the biochar concentration increased from 0 to 20 g kg^{-1} (Fig. 4). This difference indicates that the effective surface area of the biochar after the 500-day incubation in the soil was 1150 m^2 g^{-1}. The biochar treatments significantly increased ECEC by 4 to 30% relative to the controls (Tables 1 and 2). Based on these results we estimate that the effective ECEC of the biochar used in this study was 187 cmol kg^{-1}. Here "effective surface area" and "effective ECEC" are defined as the surface area or ECEC of biochar treated soil minus the surface area or ECEC of the control soil divided by the relative mass of biochar added to the soil. As noted by Cheng et al. (2008) fresh biochar may have relatively low CEC values but the CEC increases on incubation in soil environments due to oxidation of the biochar surfaces and/or adsorption of organic acids by the biochar. Clearly, the 500-day incubations were sufficient for significant CEC to develop on the biochar. We observed a small but significant decrease in ECEC with soil depth for most treatments. The cause of this decrease in ECEC with depth cannot be determined from the available data; however we speculate that the effect is related to differences in the extent of surface oxidation. Although the columns were freely drained (at all times except during measurement of saturated hydraulic conductivity), differences in gravimetric potential with depth and the matrix potential difference between the soil and the coarse sand in the bottom of the columns probably cause relatively higher water contents and lower pO_2 values in the lower half of the columns. These differences could affect both the rate and the extent of surface oxidation on biochar particles. The manure additions did not have a significant effect on ECEC, however there was a significant biochar by manure interaction (Table 1) for which we have no explanation.

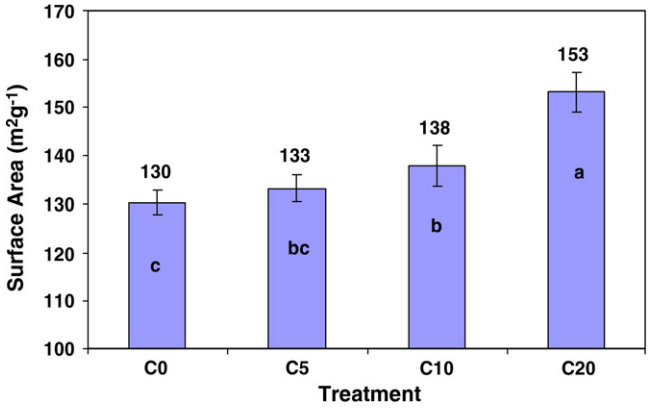

Fig. 4. Specific surface area determine by the EGME method for soil samples excavated from the 6 cm-bottom depth increment of the no-manure control columns. Biochar treatments, C0, C5, C10, and C20 include amendment of 0, 5, 10, and 20 g-biochar kg^{-1}, respectively. Error bars show standard deviations and treatment means with different letters are significantly different (alpha 0.05) by the Tukey Studentized Range test.

Plant nutrients were present in the soil, added with the biochar and added with the manure. Leaching losses of plant nutrients from these columns were discussed by Laird et al. (2010). Here, we use the Mehlich 3 extraction to assess the levels of bioavailable nutrients that remained in the soils at the end of the 500-day leaching/incubation experiment. We observed significant increases in Mehlich 3 extractable P, K, Ca, and Mn with the amount of biochar added (Tables 3 and 4). The biochar treatments had no significant effect on Mehlich 3 extractable Mg, Cu, and Zn. The increases in Mehlich 3 extractable K, Ca, and Mn with increasing levels of biochar are most likely due to the presence of these nutrients in the biochar itself. Phosphorous on the other hand was present in relatively low concentrations in the biochar and relatively high concentrations in the manure, and the increase in Mehlich 3 extractable P with increasing biochar additions was primarily associated with the 0–3 cm depth

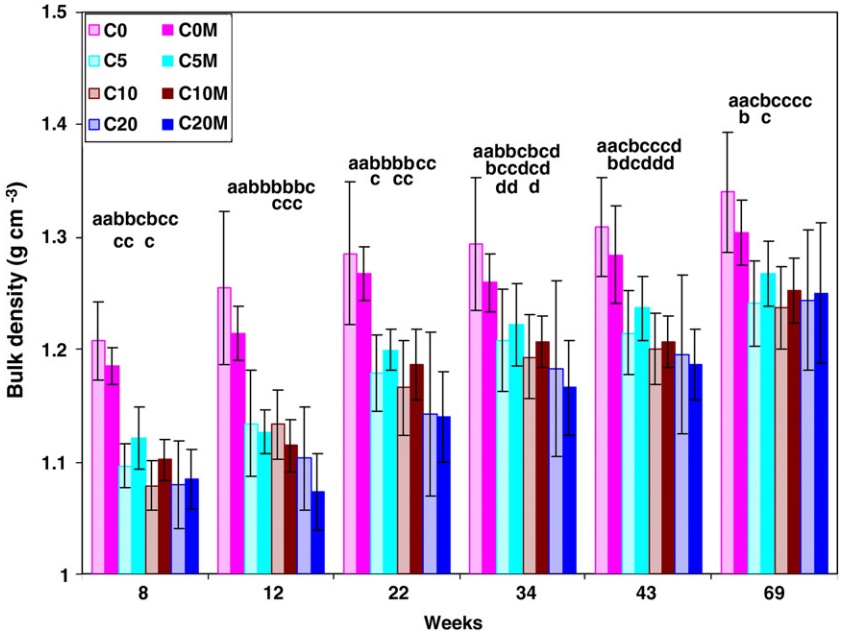

Fig. 3. Average bulk density for soil in the columns determined periodically during the incubation. Biochar treatments, C0, C5, C10, and C20 include amendment of 0, 5, 10, and 20 g-biochar kg^{-1} , respectively. The "M" in the treatment name indicates incorporation of 5 g of dried swine manure into the top 3 cm of soil on week 12 of the incubation. Error bars show standard deviations and treatment means with different letters are significantly different (alpha 0.05) by the Tukey Studentized Range test.

Table 3
Analysis of variance showing significance ($P>F$) of biochar, manure, and depth on Mehlich 3 extractable nutrients (mg kg^{-1}) measured after the 500-day incubation of soil columns with weekly leachings. Mean values for these analyses are given in Table 4.

Source	DF	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
Model	23	0.037	<0.0001	<0.0001	0.0023	<0.0001	<0.0001	0.038	<0.0001	<0.0001	<0.0001
Biochar	3	0.026	<0.0001	0.46	0.020	<0.0001	0.14	<0.0001	<0.0001	0.12	0.50
Manure	1	0.74	0.49	<0.0001	0.67	<0.0001	<0.0001	0.038	<0.0001	<0.0001	<0.0001
Depth	2	0.11	<0.0001	<0.0001	0.0067	<0.0001	<0.0001	0.22	<0.0001	<0.0001	<0.0001
Biochar*manure	3	0.0008	0.32	0.30	0.40	0.11	0.055	0.61	0.28	0.55	0.63
Manure*depth	2	0.96	0.19	<0.0001	0.0002	0.59	0.15	0.91	<0.0001	<0.0001	<0.0001
Biochar*depth	6	0.84	0.37	0.98	0.57	0.78	0.19	0.95	0.0024	0.80	0.94
Biochar*manure*depth	6	0.67	0.14	0.99	0.56	0.38	0.19	0.68	<0.0001	0.57	0.93

increment of the manure amended soils (Table 4). For Mehlich 3 extractable P, the biochar by manure interaction was not statistically significant ($P>F$ 0.28), however the biochar by manure by depth interaction was highly significant ($P>F<0.0001$). Furthermore, the total amount of P leached from the manure amended columns during weeks 0–45 decreased with increasing levels of biochar (33.6, 19.8, 15.2, and 10.1 mg-P per column for the C0M, C5M, C10M, and C20M treatments respectively; Laird et al., 2010). These results indicate that

Table 4
Mean values ($n=6$) for Mehlich 3 extractable nutrients measured after the 500-day incubation of soil columns with weekly leaching. Biochar treatments, C0, C5, C10, and C20 include amendment of 0, 5, 10, and 20 g-biochar kg^{-1}, respectively. The "M" in the treatment name indicates incorporation of 5 g of dried swine manure into the top 3 cm of soil on week 12 of the incubation. Minimum significant (alpha 0.05) differences between any two means are based on the Tukey Studentized Range test. Analysis of variance for these data is given in Table 3.

Element and depth	Biochar treatments without manure				Biochar treatments with manure				Tukey minimum significant difference
	C0	C5	C10	C20	C0M	C5M	C10M	C20M	
B									
0–3 cm	20	14	22	17	24	14	14	20	13
3–6 cm	16	13	19	15	18	14	14	15	
6 cm–bottom	19	13	22	14	17	18	12	19	
Ca									
0–3 cm	3513	3796	3791	4120	3373	3625	4011	4393	522
3–6 cm	3322	3610	3770	4261	3216	3550	3811	4105	
6 cm–bottom	3295	3146	3478	3967	3287	3474	3607	3954	
Cu									
0–3 cm	2.8	2.7	2.9	3	13.7	12.3	12.6	12.6	2.9
3–6 cm	2.6	2.6	2.8	3.1	6.6	5.1	5.7	5.5	
6 cm–bottom	2.7	2.8	3	2.8	3	2.8	2.8	2.8	
Fe									
0–3 cm	226	195	227	187	266	241	249	226	120
3–6 cm	224	185	202	200	238	224	230	229	
6 cm–bottom	313	300	303	198	236	225	223	221	
K									
0–3 cm	137	140	141	152	154	154	168	178	31
3–6 cm	155	149	168	182	175	190	196	204	
6 cm–bottom	180	170	192	209	193	209	223	222	
Mg									
0–3 cm	131	129	123	133	164	143	169	195	53
3–6 cm	219	195	218	211	225	242	254	259	
6 cm–bottom	304	274	283	280	301	313	307	298	
Mn									
0–3 cm	146	153	154	161	147	154	166	167	30
3–6 cm	149	146	160	166	151	158	161	165	
6 cm–bottom	153	150	159	168	160	167	163	167	
P									
0–3 cm	88	94	95	104	254	265	299	349	44
3–6 cm	100	99	111	120	187	199	215	212	
6 cm–bottom	106	94	111	127	149	147	141	139	
S									
0–3 cm	14	10	11	10	17	15	17	16	6
3–6 cm	10	11	11	9	13	10	11	11	
6 cm–bottom	12	12	12	11	11	11	11	11	
Zn									
0–3 cm	3.1	3.2	3.4	3.4	34.9	33.4	35.5	36.6	7.6
3–6 cm	2.9	2.8	3.2	3.2	14.6	10.3	12.8	11.8	
6 cm–bottom	2.8	2.6	2.8	3.2	4.2	3.2	3	3.4	

the biochar increased retention of the manure P, primarily in the 0–3 cm depth increment. By contrast, Mehlich 3 extractable B decreased with increasing levels of biochar ($P>F$ 0.026). Extractable S also decreased with increasing levels of biochar, however the effect was not significant ($P>F$ 0.11). Both B and S are present as oxyanions in soil environments, and it is plausible that these oxyanions are being tightly bound by the biochar such that they are less extractable by Mehlich 3. In soils P is present in both organic and oxyanion forms. Here we observe a small increase in total Mehlich 3 extractable P with increasing levels of biochar but the increase was less than differences in leaching losses for the manure treated columns. Thus our data suggest that some of the added P may also have been tightly bound by the biochar.

For the Clarion loam, our results demonstrate that biochar additions significantly reduced bulk density increases due to soil compaction, and increased water holding capacity, cation exchange capacity, specific surface area, pH, and the retention of P and several other plant nutrients. All of the observed changes in soil quality indicators were positive with the exception of a slight decrease in Mehlich 3 extractable B. Manure amendments by contrast had no effect on water retention at gravity drained equilibrium or ECEC, and had relatively small effects on total C, N and C:N ratios. The impact of the manure treatments on Mehlich 3 extractable nutrients was generally significant as relatively large amounts of nutrients were added with the manure. In general, the impact of the biochar amendments on soil quality was much more evident after 500 days than the impact of the manure amendments. Most previous work on the impact of biochar on soil quality has been conducted using tropical and/or degraded soils. By contrast, the Clarion loam is a highly productive temperate region agricultural soil that contains 2.0% organic C and is dominated by 2:1 phyllosilicate clay minerals. Much future research, however, is needed to determine whether crop yields respond to the observed improvement in soil quality indicators for the Clarion loam and to determine the impacts of different types of biochar and soil by biochar interactions for temperate region soils.

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