



Surface chemistry variations among a series of laboratory-produced biochars

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ABSTRACT

While the idea that adding pyrogenic carbon (referred to as 'biochar' when used as a soil amendment) will enhance soil fertility and carbon sequestration has gained widespread attention, understanding of its chemical and physical characteristics and the methods most appropriate to determine them have lagged behind. This type of information is needed to optimize the properties of biochar for specific purposes such as nutrient retention, pH amelioration or contaminant remediation. A number of surface properties of a range of biochar types were examined to better understand how these properties were related to biochar production conditions, as well as to each other. Among biochars made from oak (*Quercus lobata*), pine (*Pinus taeda*) and grass (*Tripsacum floridanum*) at 250 °C in air and 400 and 650 °C under N₂, micropore surface area (measured by CO₂ sorptometry) increased with production temperature as volatile matter (VM) decreased, indicating that VM was released from pore-fillings. The CEC, determined using K⁺ exchange, was about 10 cmol_c kg⁻¹ for 400 and 650 °C chars and did not show any pH dependency, whereas 250 °C biochar CECs were pH-dependant and rose to as much as 70 cmol_c kg⁻¹ at pH 7. Measurements of surface charge on biochar particles indicated a zeta potential of -9 to -4 mV at neutral pH and an iso-electric point of pH 2–3. However, a colloidal or dissolved biochar component was 4–5 times more electronegative. Total acid functional group concentration ranged 4.4–8.1 mmol g⁻¹ (measured by Boehm titration), decreased with production temperature, and was directly related to VM content. Together, these findings suggest that the VM component of biochar carries its acidity, negative charge, and thus, complexation ability. However, not all acid functional groups exchanged cations as the number of cation exchanging sites (CEC) was about 10 times less than the number of acid functional groups present on biochar surfaces and varied with biomass type. These findings suggest that lower temperature biochars will be better used to increase soil CEC while high temperature biochars will raise soil pH. Although no anion exchange capacity was measured in the biochars, they may sorb phosphate and nitrate by divalent cation bridging.

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1. Introduction

Black carbon (BC) is one of the residuals of biomass combustion. It can be a major component of soil organic matter (OM) in regions prone to forest fires (Goldberg, 1985; Hockaday et al., 2006; Rumpel et al., 2006) or where agricultural burning is practiced (Glaser et al., 2001a, 2001b; Schmidt and Noack, 2000; Skjemstad et al., 1996). Black carbon has received recent attention both as a soil component that may control the distribution of many organic contaminants and as a possible soil additive (Glaser et al., 2001a, 2001b, 2002, 2004; Gundale and DeLuca, 2007; Haumaier and Zech, 1995). When BC is produced by thermal decomposition of biomass under limited or absent oxygen and used as a soil amendment to increase fertility or sequester atmospheric CO₂, it is referred to as biochar. This idea was originally spawned by the observations of large amounts of BC in small plots of unusually fertile soils surrounded by the typically infertile soils of Amazonia. It has been

suggested that these 'terra preta' soils were intentionally or accidentally created by native populations through the addition of biochar (Glaser et al., 2001b).

Although it is likely the surface properties of biochar that leads to its potentially useful properties including contaminant control and nutrient retention and release, the surface structure and chemistry of biochars with variations of biomass types and production conditions has not been thoroughly studied. Many studies have examined BC or biochar-rich soils in which natural OM may complicate interpretation while others have examined a limited number of biochars. Other studies have examined only a few of biochars properties or only a limited number of biochars. For example, the surface area, porosity, and surface functional group and elemental composition have been investigated by researchers (Antal and Gronli, 2003; Antal et al., 2003; Baldock and Smernik, 2002; Bourke et al., 2007; Brown et al., 2006; Hammes et al., 2006; Zimmerman, 2010). Surface area is generally found to increase with biochar production temperature (Brida et al., 2003; Nguyen et al., 2004; Pattaraprakorn et al., 2005; Rutherford et al., 2004; Weng et al., 2006). Other studies have examined biochar's ion exchange and surface charge characteristics which also vary among different chars (Cheng

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et al., 2008; Gundale and DeLuca, 2006; Lee et al., 2010). Although both of these properties would be expected to influence ion adsorption, no study has examined the relationship between biochar's chemistry and morphology. With a better understanding of biochar's surface properties, a mechanistic theory can be constructed that will explain the adsorptive ability of different biochars for different soil components and the comparative ability of different biochars to enhance soil fertility. This sort of information could be used to guide the design and production of biochars to fulfill specific purposes such as soil amelioration, soil remediation, or carbon sequestration.

1.1. Surface ion exchange and charge in soils and carbonaceous materials

The surfaces of some common soil minerals bear electrical charges that are either permanent due to charge deficits in their structure or temporary due to specific sorption of potential-determining ions (e.g. H^+ and OH^-). The sign and magnitude of the latter usually depends on soil solution pH (Brady and Weil, 1984; Sposito, 1984, 2008). If the soil pH is above its point of zero net charge (PZNC), the soil surface will carry a net negative charge and attract exchangeable cations including some nutrients. At pH below its PZNC, a mineral will attract anions (Appel et al., 2003). In general, the PZNC of a soil will be lowered by the presence of permanent negatively-charged expansible phyllosilicate surfaces or soil OM, increasing the negative surface charge of soils. This may occur with biochar amendment but measurements of the PZNC of different biochars are needed to understand the relative ability and conditions in which biochar-amended soils will sorb nutrients of different types.

Cation exchange capacity (CEC), a measure of the negative charge of a material that can be neutralized by exchangeable cations, enhances soil's ability to hold and exchange nutrients such as ammonium, calcium and potassium (Brady and Weil, 1984). Likewise, anion exchange capacity (AEC) is a measure of a soil's ability to retain anions such as phosphate. Previously published data on the CEC of biochar are quite variable, ranging from 71 mmol kg^{-1} (Cheng et al., 2008) to 34 cmol_c kg^{-1} (Gundale and DeLuca, 2006). Soils typically range in CEC from about 3–40 cmol_c kg^{-1} , though soils with high organic matter content or expansible phyllosilicates sometimes exceed 100 cmol_c kg^{-1} (Brady and Weil, 1984). Glaser et al. (2000) reported CEC of *terra preta* soils as 10–15 cmol_c kg^{-1} , significantly higher than the adjacent oxisols (1–2 cmol_c kg^{-1}). Although the CEC of *terra preta* soils has been observed to be directly related to soil pH and clay content (Lehmann et al., 2004; Sombroek, 1966), it is also strongly correlated to BC content (Glaser et al., 2001a, 2001b, 2002). Thus, it is likely that biochar amendment will also increase the CEC of a soil, though the time period over which this may occur is unknown.

While measurement of the CEC and PZNC on soil or soil mineral components is commonly performed, application of these techniques to biochar is not common or straightforward. The two principle approaches used to determine PZNC are (i) potentiometric titration and (ii) non-specific ion adsorption (Appel et al., 2003; Tan et al., 2008). Potentiometric titration usually employs measurement of changes in surface charge across a range of pH conditions. In contrast, PZNC as determined by ion adsorption involves simultaneous measurements of CEC and AEC as a function of pH (Appel et al., 2003; Marcano-Martinez and McBride, 1989; Parker et al., 1979). The pH at which AEC equals CEC is considered the PZNC. These two methods do not always yield the same PZNC for various possible reasons including the presence of permanent negative charge on the mineral surfaces, mineral or organic matter dissolution reactions at high or low pH, and the presence of strongly adsorbed Al^{3+} ions which are included as permanent negative charge during potentiometric titration but are displaced during ion adsorption measurements (Appel et al., 2003; Marcano-Martinez and McBride, 1989; Van Raij and Peech, 1972). At present, little information is available to

determine which of these methods are best suited to biochar PZNC measurement, or even whether the concepts traditionally applied to soils can be applied to biochars.

1.2. Zeta potential and iso-electric point in soils and carbonaceous materials

Surface charge is another parameter that can be used to predict the sorption and nutrient holding characteristics of a soil or soil component. Zeta potential (ZP), which is related to a particle's surface charge, can be measured by tracking suspended particle movement in a voltage field, but is also dependent upon the concentration and speciation of electrolytes, dielectric constant of the medium. But solution pH usually has the strongest influence on the sign and magnitude of ZP (Asadi et al., 2009; Han et al., 2004; Kim et al., 2007). The pH at which the ZP becomes zero is the isoelectric point (IEP). While IEP and PZNC seem to represent similar surface characteristics, it has been argued that IEP represents the external surface charges of the materials while the PZNC includes both external and internal (pore-related) surface charges (Corapcioglu and Huang, 1987; Menéndez et al., 1995). How these concepts should be applied to soil BC is not clear. The IEP of various activated carbons has been reported to range from 1.4 to 7.1, indicating that most activated carbons carry a negative charge below circum-neutral pH (Babic et al., 1999; Menéndez et al., 1995). However, there is a lack of IEP and PZNC data on biochars or understanding of their variability among different biochars.

Although the surface properties of many soil components including minerals and organic matter have been intensively studied, there is presently very little published data detailing the surface properties of biochar or how these surface properties vary with biochar type, including production condition and parent biomass type. Biochar has a number of properties (such as its buoyant nature, high microporosity and surface area, and solubility) that make its characterization analytically unique and challenging. However, there has been little discussion of this in the literature. The goals of this study were to fill these voids and to open a discussion on this subject. First, this work tests, adapts and compares two methods traditionally used to study the surface chemical exchange properties of soil minerals to biochars: ion exchange and net charge (ZP) measurement. Second, it reports data on the pH, CEC, AEC, PZNC and IEP and surface functional group distribution of a variety of biochars prepared under a range of conditions in an effort to determine the type of biochar that may best be used as a soil amendment for various purposes such as enhancing soil fertility, reducing contaminant or nutrient leaching, or increasing C sequestration.

2. Materials and methods

2.1. Sample preparation

Quercus lobata (Laurel oak: Oak), *Pinus taeda* (Loblolly pine: Pine), and *Tripsacum floridanum* (Gamma grass: Grass) were first dried (60 °C for at least 5 days), cut into 1 cm × 1 cm × 5 cm pieces and then combusted for 3 h at 250 °C in an oven under full atmosphere (door kept slightly open) and at 400 and 650 °C in a pyrolyzer continuously flushed with 99% pure gaseous nitrogen (designated hereafter as Oak-250, Oak-400, Pine-650, etc.). These conditions were chosen to represent those that might be present in cool burn of agricultural residues, in a natural forest fires (450 °C) (Turney et al., 2006) or in a backyard or industrial biochar production processes. In the presence of oxygen, temperatures higher than 250 °C were found to produce mainly ash and no biochar, whereas in the absence of oxygen, temperatures lower than 400 °C were found to yield no biochar, but only slightly charred biomass.

For the pyrolysis at 400 and 650 °C, biomass pieces were placed in 4 cm × 4 cm × 10 cm packages of foil and placed in a steel pipe (5.5 cm

diameter \times 50 cm length) with flowing N_2 flowing from end to end (2.3 oven volumes exchanged min^{-1}). The temperature program was $26^\circ\text{C min}^{-1}$ heating rate, a 3 h peak temperature hold time, and a 3°C min^{-1} cooling rate. After cooling, biochars were gently crushed and passed through sieves to obtain fine (<0.25 mm) and coarse (0.25–2 mm) uniform size fractions. These materials were then thoroughly rinsed with double distilled water to remove ash and dried at 80°C for 5 days. The coarse biochar fraction was used to carry out all analyses. However, the zeta potential of the fine biochar was also examined due to the requirements of one of the instruments used (see below).

2.2. Analytical methods

Because of biochar's unique properties (described above), a number of 'standard' soil analytical methods had to be modified to be applied to biochar. These properties include the tendency for a portion of biochar particles to float in water, even after centrifugation. Also, many biochars leach dissolved organic matter in water (Kaszi et al., 2010). In addition, the high porosity of biochar may limit the diffusion rate of ions to its interior surfaces. Therefore, additional time often had to be allowed to reach chemical equilibrium. Adjustments made to standard methods are discussed further below.

2.2.1. Determination of pH

Because biochar does not settle from suspension, pH of the biochar samples was determined using a saturated paste approach (Kalra et al., 1995; Rhoades, 1996). About 200 mg of biochar was mixed with 1.25 mL of double distilled water. The pH was recorded with the probe submerged in the paste (Ultra basic pH meter, Denver Instruments). To examine the stability of biochar pH in solution, pH was measured initially, and then after successive 1 h equilibrium periods. Other samples were treated with either NaOH or HCl to attain a range of pHs from 3 to 9, followed by pH determinations over time.

2.2.2. Determination of volatile matter and ash content

Volatile matter and ash (inorganic) content were determined using the American Society for Testing and Materials (ASTM) method (D-1762-84) (ASTM, 1990) which we modified slightly for simplicity and replicability. About 1 mg of coarse biochar had been kept in a drying oven for at least 2 h at 100°C and allowed to cool in a desiccator before weighing. Volatile matter content (VM%) was determined as weight loss after combustion in a ceramic crucible with a loose ceramic cap at $850\text{--}900^\circ\text{C}$ for 6 min. Ash content was determined as weight loss after combustion at 750°C for 6 h with no ceramic cap. Sample weight was taken after cooling in a desiccator for 1 h.

2.2.3. Determination of surface area

Surface morphology was measured on a Quantachrome Autosorb1 using N_2 and CO_2 sorptometry. Surface area and pore volumes including only nanopores (>1.5 nm diameter) were calculated using multi-point adsorption data from the 0.01–0.3 P/Po linear segment of the N_2 adsorption isotherms made at 77 K using Brunauer, Emmet, and Teller (BET) theory (Brunauer et al., 1938). Biochar samples were degassed under vacuum (180°C , at least 24 h) prior to nitrogen adsorption at liquid nitrogen temperature (-196°C). Because the measurement of CO_2 adsorption is carried out at higher temperatures, it is less kinetically limited compared to N_2 (Pignatello et al., 2006), and thus, is able to penetrate into biochar's micropores. Surface area and pore volume including nanopores and micropores (<1.5 nm diameter) were determined on CO_2 adsorption isotherms measured at 273 K generated in the partial pressure range of 0.001–0.15. These isotherms were interpreted using grand canonical Monte Carlo simulations of the non-local density functional theory (Jagiello and Thommes, 2004). All biochar samples were de-gassed under vacuum at least 24 h at 180°C prior to analysis.

2.2.4. Determination of CEC, AEC and PZNC

Detailed description of traditional soil PZNC determination methods by non-specific ion adsorption has been presented elsewhere (Zelazny et al., 1996). Typically, KCl solution is used to replace all surface ions with K^+ and Cl^- ions. Then the K^+ and Cl^- are replaced by mass action with ions of another salt and CEC and AEC are calculated from the K^+ and Cl^- released, respectively, accounting for entrained salt. The PZNC was determined here using a modified version of this method. One difficulty of the published method was in separation of the solid and liquid phase following the ion adsorption and ion exchange period due to the buoyant nature of biochars, even after centrifugation. A vacuum filtration method had to be substituted for centrifugation as a practical means of separating biochar from solutions.

For each biochar sample, 0.50 g was weighed into each of four 100 mL pre-weighed centrifuge tubes and 50 mL of 1 M KCl solution was added to each tube and shaken for 1 h. The solutions were then vacuum-filtered and the supernatant was discarded. The biochars in the centrifuge tubes were then washed with 0.01 M KCl solution and quantitatively transferred into pre-weighed filtration vessels fitted with $0.1\ \mu\text{m}$ filter paper and filtered under vacuum. The transferred biochars were washed four times with 50 mL of 0.01 M KCl solution using vacuum filtration. At this stage, the 1 M KCl solution entrained in the biochars should have been displaced by 0.01 M KCl solution. During a fifth and final wash with 0.01 M KCl, pH was recorded and, after 1 h equilibration, pH was adjusted by adding, drop wise, 0.5 M NaOH or 1 M HCl to reach pH values from 1 to 7. The filter holders with filter paper and wet biochars were re-weighed to obtain the mass of K^+ and Cl^- solution entrained in the biochar. The samples in the same filter holders were then washed with 20 mL of 0.5 M NaNO_3 solution to displace the adsorbed K^+ and Cl^- ions, vacuum filtered, and K^+ and Cl^- in all filtrates. All filtrates were refrigerated until K^+ and Cl^- analysis was performed using a Spectro Ciros CCD inductive couple plasma spectroscopy by EPA 200.7 and EPA 325.2 methods, respectively (Analytical Research Laboratory, University of Florida).

2.2.5. Determination of zeta potential

Zeta potential of the biochars was examined using two instruments at the Particle Engineering Research Center, University of Florida, one which examines coarse and one which requires very fine particles or colloids. The zeta potential of coarse biochar samples was determined using an Anton Paar Electro-Kinetic Analyzer (EKA). About 0.50 g of coarse (0.25–2 mm) biochar sample was placed in a cylindrical cell with perforated Ag/AgCl electrodes attached to two sides of the cell. An electrolyte solution flows through the cell carrying the sample particles and causing charge transport along the length of the cell. Depending on the flow resistance of the sample, a pressure drop is also detected along cell. The measured pressure drop and streaming potential are used served to calculate the zeta potential. Solution pH was determined during ZP measurement using an in-line pH meter.

Zeta potential of colloidal, or possibly truly dissolved biochar, was determined using the method of Asadi et al. (2009) with modification as follows. About 0.5 g of fine biochar sample was added to 50 mL double distilled water and then sonicated for 30 min. The resulting solution was filtered (Whatman 42 filter paper) and the filtrate was placed in a plastic cell between a positive and a negative palladium electrode of a PALS Zeta Potential Analyzer (Ver. 3.16). An electric field was applied across the electrophoresis cell, causing the particles to move towards the electrodes with a velocity proportional to the ZP and in a direction determined by the sign of their charge. The pH of the solutions was recorded immediately after measuring the ZP of the biochar samples. The IEP, the pH at which the ZP is zero, was determined by multiple measurements of ZP (on both instruments) as a function of pH of the solution, adjusted using 1 M HCl or NaOH.

2.2.6. Determination of surface acid functional group distribution

Biochar surface acid functional group distribution was determined using the Boehm titration method (Boehm et al., 1964; Goertzen et al., 2010). In short, about 0.50 g of coarse biochar sample was added to 50 mL of each of three 0.05 M bases: NaHCO_3 , Na_2CO_3 , and NaOH . The mixtures, along with a control solution without any biochar, were shaken for 24 h and then filtered (Whatman 42 filter paper) to remove particles. Then, a 1 mL of aliquot from each filtrate was mixed with 10 mL of excess 0.05 M acid to ensure complete neutralization of bases and then back-titrated with 0.05 M NaOH solution. The endpoint was determined using a phenolphthalein color indicator. The total surface acidity was calculated as moles neutralized by NaOH , the carboxylic acid fraction as the moles neutralized by NaHCO_3 , and the lactonic group fraction as those neutralized by Na_2CO_3 . The difference between molar NaOH and Na_2CO_3 was assumed to be the phenolic functional group content following Rutherford et al. (2008).

2.2.7. Statistical analyses

All of the data presented are means \pm standard deviation of triplicate analyses unless otherwise stated. Means, standard deviations and regression correlation coefficients were computed using Microsoft 2003 Excel software. Differences between means of various analysis results were examined using the least squares general linear model (PROC GLM) within SAS software (SAS, 2001). Statistical significance level of $p < 0.05$ was used.

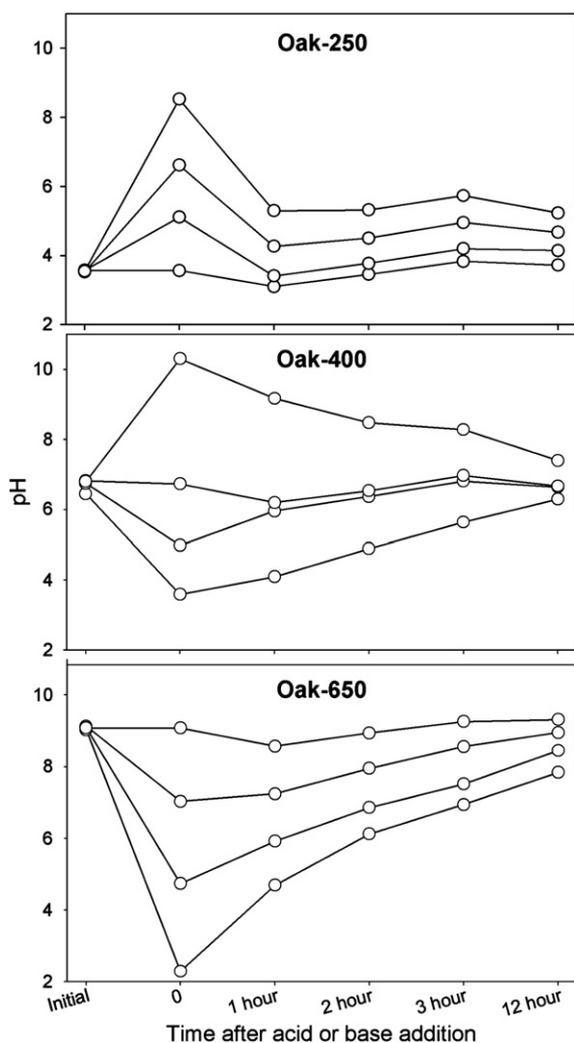


Fig. 1. Variation in Oak-250, Oak-400 and Oak-650 biochar pH initially and after acid or base addition at time 0.

3. Results

3.1. Biochar bulk characterization

All the biochar types examined acted as buffers toward pH changes. Oak biochar are shown here as representative examples (Fig. 1). After adjusting the pH to 3, 5, 7 and 9 with 1 M HCl or NaOH , the pH rebounded back toward their original values within 1 h and stabilized at its new pH values within about 2 h. Thus, a two hour equilibration period was used for all subsequent analyses. The pH of the biochars examined ranged from 3.1 to 10 (Fig. 2) and increased with increasing charring temperature. The average pH of all the biochars were 3.7 ± 0.7 , 6.6 ± 1.4 , and 8.6 ± 1.7 at 250, 400 and 650 °C, respectively. However, pH was also dependent upon the original biomass species, increasing from pine to oak to grass at all production temperatures.

The volatile content (VM%) ranged from 25.2 to 66.0% overall and decreased with increasing formation temperature for each biomass type (Table 1), indicating progressive loss of a more volatile component with charring. Ash, i.e. inorganic content, ranged from 0.3 to 15.9% and increased with increasing formation temperature (Table 1). Biomass type did not have any significant effect on VM% but ash content was 3 to 4-fold greater for grass biochars compared to oak and pine biochars (Table 1), possibly resulting from the higher K, Ca and Mg content of grass biomass and grass biochars (unpublished data).

The average nanopore surface areas (pores > 1.5 nm via N_2 sorptometry) of 250, 400 and 650 °C biochars were 2 ± 2 , 4 ± 2 , and 184 ± 126 , respectively (Table 1). The average micropore surface areas (including pores < 1.5 nm via CO_2 sorptometry) of 250, 400 and 650 °C biochars were 308 ± 79 , 259 ± 99 and 532 ± 108 , respectively. Thus, low-temperature biochars (250 and 400 °C) had little of their surface in the nanopore range, i.e. were predominantly microporous. For 650 °C biochars, 43, 44 and 10% of oak, pine and grass biochar's surface, respectively, were in the nanopore range.

3.2. Biochar surface characterization

Amongst all the biochars examined, the concentration of total surface acidic functional groups (AFG) ranged from 4.4 to 8.1 mmol g^{-1} , carboxylic acid surface functional groups ranged 3.9–6.2 mmol g^{-1} , and phenolic acid surface functional groups ranged 0.4–3.2 mmol g^{-1} (Fig. 3) No lactonic functional groups were detected. Carboxylic acids represented 76% of total AFG, on average, and was 2 to 3 times more abundant than phenolic acid functional groups. The total and carboxylic AFG decreased with increasing biochar formation temperatures, whereas the temperature trend for phenolic functional group content

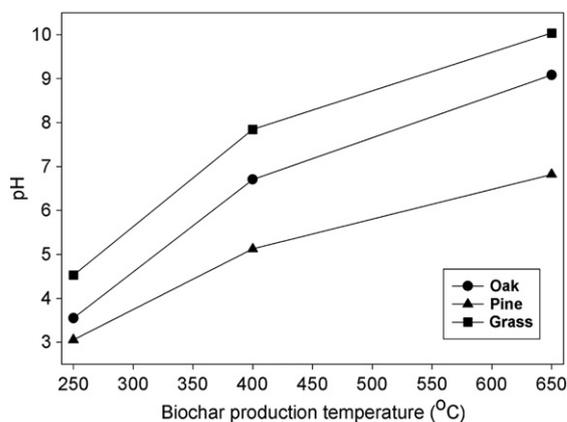


Fig. 2. The pH of biochars made from oak, pine and grass at 250 °C under full atmosphere and at 400 and 650 °C under continuous flow N_2 .

Table 1

Selected properties of oak, pine and grass biochar produced at 250 °C under full atmosphere and at 400 and 650 °C under continuous flow N₂.

Biochar type	Volatile matter (wt.%)	Ash (wt.%)	N ₂ surface area (m ² g ⁻¹)	CO ₂ surface area (m ² g ⁻¹)	AFG density (nm ⁻²)
Oak-250	66.0 ± 4.4	1.4 ± 0.1	1 ± 1	331 ± 66	14.8
Oak-400	51.9 ± 5.2	2.6 ± 0.2	2 ± 1	252 ± 90	14.3
Oak-650	36.4 ± 1.1	3.7 ± 0.2	225 ± 9	528 ± 57	5.4
Pine-250	61.1 ± 1.6	0.3 ± 0.1	1 ± 0	373 ± 112	11.6
Pine-400	58.6 ± 1.0	0.5 ± 0.2	3 ± 2	361 ± 114	10.2
Pine-650	25.2 ± 4.7	1.1 ± 0.1	285 ± 102	643 ± 80	4.1
Grass-250	62.5 ± 2.9	6.8 ± 0.2	3 ± 2	221 ± 106	21.7
Grass-400	51.4 ± 6.4	13.2 ± 0.2	6 ± 6	164 ± 49	21.6
Grass-650	33.0 ± 1.2	15.9 ± 0.5	77 ± 27	427 ± 115	6.7

was less apparent (Fig. 3). On the other hand, no significant difference ($p < 0.05$, PROC GLM) in AFG content among the three biomass types was observed (Fig. 3). Acid surface functional group density was calculated as total AFG divided by the surface area, as measured by CO₂ sorptometry, of each biochar. Acid functional group density of low temperature biochars (250 and 400 °C) ranged from 10.2 to 21.7 nm⁻² and that of 650 °C biochars were consistently lower, ranging only from 4.1 to 6.7 nm⁻² (Table 1).

The CEC of all biochar samples examined ranged between 10.2 and 69.2 cmol_c kg⁻¹ at near neutral pH (Fig. 4). The average CEC of 250 °C biochar was much higher, 51.9 ± 15.3 cmol_c kg⁻¹, compared to 400 and 650 °C biochars (16.2 ± 6.0 and 21.0 ± 17.2 cmol_c kg⁻¹, respectively) at

near neutral pH. The CEC of the 250 °C biochar of all three biomass species increased with pH by 4 to 7-fold from pH of about 1.5 to 7. However, of the 400 and 650 °C biochars, only Grass-650 showed any CEC dependency on pH, with an increase from 10.2 to 40.8 cmol_c kg⁻¹ from pH 1.5 to 7.5. On the whole, grass biochar had somewhat higher CEC than oak or pine biochar.

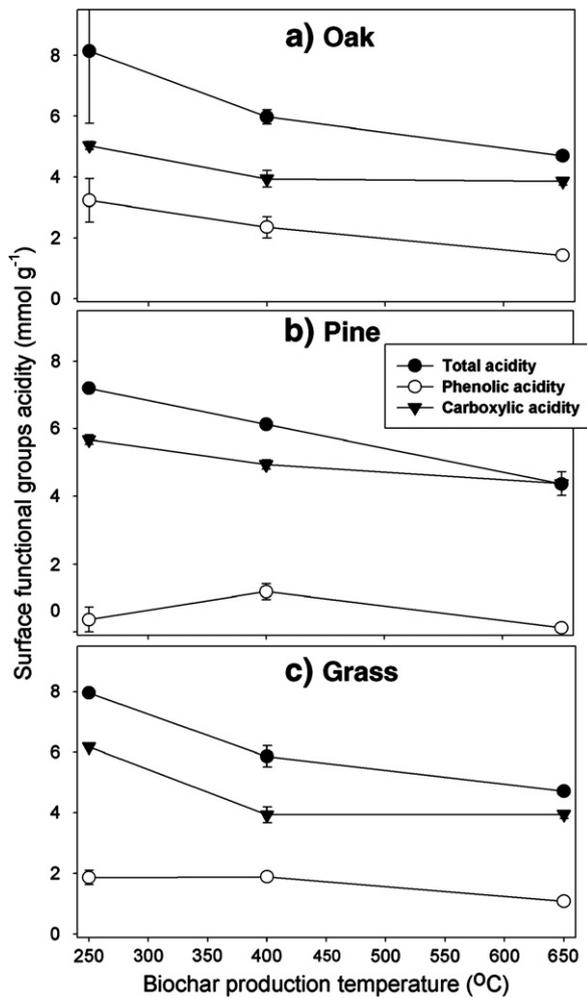


Fig. 3. Variation in surface acidic functional group content among biochars made from a) oak, b) pine, and c) grass at 250 °C under full atmosphere and at 400 and 650 °C under continuous flow N₂.

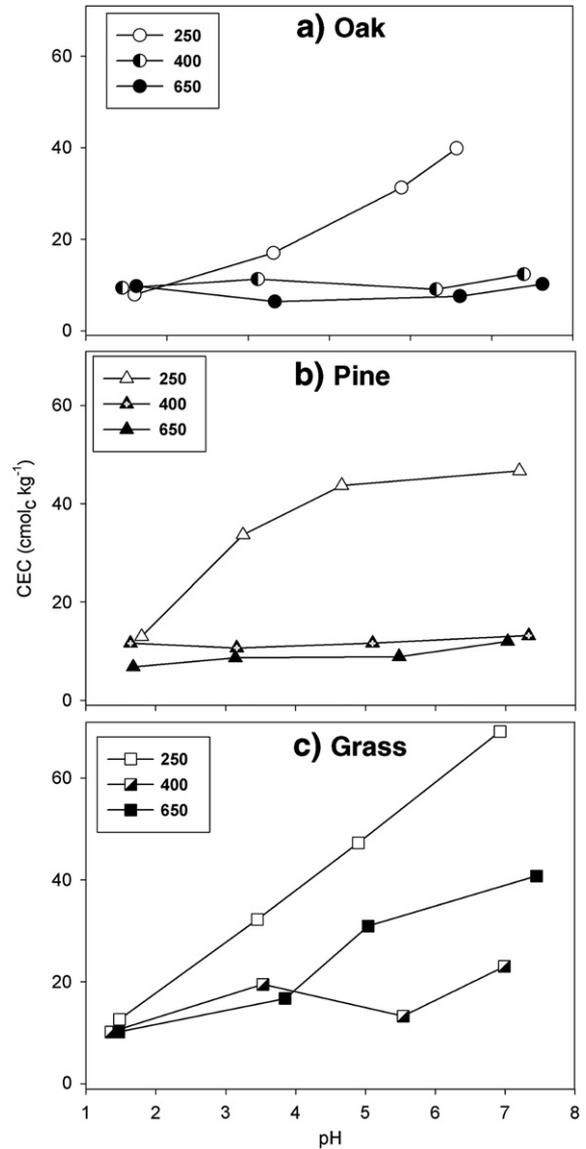


Fig. 4. Variation in cation exchange capacity with pH for biochars made from a) oak, b) pine, and c) grass at 250 °C under full atmosphere and at 400 and 650 °C under continuous flow N₂.

Nearly all measurements of biochar AEC resulted in nonsensical negative values (Supplementary data, Table S1). These values may be related to the need to add HCl during the anion exchange procedure to reach stable low pH values, which increased possible error to the calculation of entrained Cl^- . The near-zero AEC values measured in the near-neutral pH range (when HCl additions were not needed) suggest that the true AEC of all the biochars is close to zero. However, without a reliable AEC, a crossover point between AEC and CEC as a function of pH, i.e. PZNC, could not be accurately determined.

The ZP measured on the colloidal or dissolved biochar components varied from 2.6 to -53.4 mV in the 1–7 pH range, did not vary with biochar type (biomass or formations temperature), and had an IEP of close to 1.5 (Supplementary data, Table S2). On the other hand, assuming oak biochar is a representative, the ZP of the coarse biochar, ranged from 1.5 to -8.9 mV within the pH range of 2.2–6.8 (Fig. 5), which was 5 to 7-fold less electronegative than the colloidal or dissolved component of biochar. For any given pH, the ZP of Oak-650 was significantly more electronegative than the lower temperature oak biochars, and the ZP of all the biochar became more electronegative with increasing pH. The pH at which ZP approached zero (IEP) was between 2 and 3.5 for all coarse biochars examined.

4. Discussion

While some chemical characteristics of the biochars varied with parent biomass type, the most significant and consistent changes in bulk and surface chemistry occurred with production conditions. To interpret the cause of these changes, the associations between each of the parameters measured and how they each vary among the biochar types are examined.

4.1. Development of biochar surface characteristics with production conditions

Significant nanopore surface area, as measured by N_2 sorptometry, was only found in higher temperature biochars, while all biochar samples has significant microporous surface area, as measured by CO_2 sorptometry (Table 1). Though the biochars produced under atmosphere at 250°C had slightly greater microporous surface area than those produced at 400°C , for the same biomass type, VM% and microporous surface area were significantly negatively correlated ($R^2 = 0.53$, $p < 0.05$). Thus, it seems clear that volatile components fill micropores dominating the surface of biochars and are released from pores at higher production temperatures, making them accessible to ions. As many other surface characteristics of biochar were found to be related to VM% (discussed further below), it is here recommended that CO_2 sorptometry (micropore surface area measurement) be used to access the quality of biochars for soil amelioration. Further, recent work

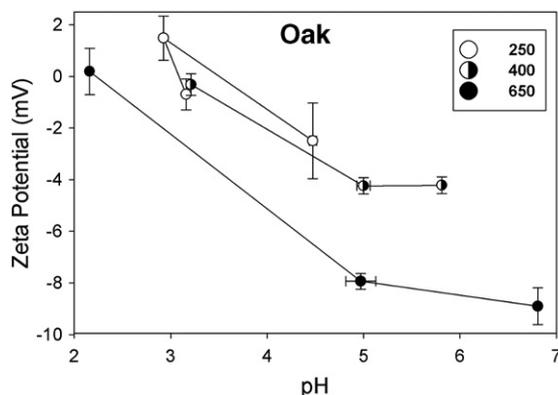


Fig. 5. Zeta potential variation with pH for coarse particle (0.25–2 mm) oak biochar made at 250°C under full atmosphere and at 400 and 650°C under continuous flow N_2 .

has found such characteristics as organic compound sorption affinity to be correlated to micropore (CO_2) surface area (Kasozi et al., 2010).

To generalize across all biochar biomass types, with increasing production temperature, biochar surface area and pH increased, while VM%, AFG content and CEC decreased. The most obvious interpretation is that pH increases were due to a progressive loss of acidic surface functional groups, mainly aliphatic carboxylic acids as suggested by the Boehm titration data. Similar to this study, some works (Reeves et al., 2007; Rutherford et al., 2008) found that biochars made from ponderosa pine wood combusted for 8 h ranged in total AFG from 1.4 to 4.4 mmol g^{-1} and 250°C biochar contained about twice the total, and carboxyl functional groups and about four times the phenolic functional groups as 400°C biochar. However, they also found that AFG increased with production time up to a maximum of 7.8 mmol g^{-1} .

These trends in surface functional groups are echoed by previous findings that have used other methods. For example, DRIFT spectroscopy studies have reported conversion of aliphatic alcohol and acid surface functional groups to neutral or basic fused aromatic groups with increasing biomass production temperatures (Baldock and Smernik, 2002; Cheng et al., 2008; Rutherford et al., 2004, 2008). And ^{13}C -NMR spectroscopy, which detects changes in bulk chemistry, has shown increasing aromatic C and decreasing alkyl C content with higher production temperatures of wood biochars (Czimeczik et al., 2002). All of these studies indicated peaks in the alkyl and O-alkyl carbon region for wood prior to pyrolysis that progressively diminished with charring, while progressively increasing dominance of conjugation among aryl carbon groups indicated increases in aromatic compounds with increasing production temperatures.

This study suggests, however, that beside the conversion of aliphatic to aromatic moieties, an additional process may be important for the development of biochar's surface properties with increasing production temperature, which will also affect how it may interact with soil components. As the biomass was heated and volatile OM was progressively lost, both micropore and nanopore surface area increased, indicating that volatile matter was likely initially present as the infilling of pores within a more refractory framework. Our data suggests that volatile OM has surface chemical properties different from that of the non-volatile biochar component. This was most apparent in the properties of the 250°C biochars, which, with its higher VM%, was distinct from the 400 and 650°C biochars in its enhanced ability to exchange cations at circum-neutral pHs (Fig. 4). In addition, it appears that the volatile OM imparted a pH dependency on the CEC of low temperature biochars (and other grass chars to some extent), which was lacking in the other biochars. The strong direct linear correlation between VM% and total AFG ($R^2 = 0.88$, $p < 0.05$, Fig. 6) suggests that it is

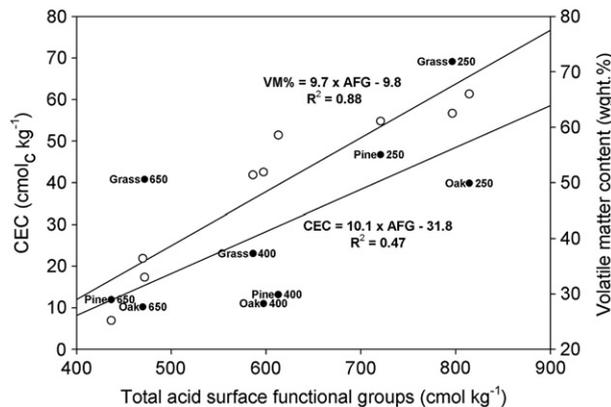


Fig. 6. Relationship between surface total acidic functional groups (AFG) and CEC at around pH 7 (closed circles with biochar type labels), and AFG and volatile matter (VM%, open circles) for all biochars made at 250°C under full atmosphere and at 400 and 650°C under continuous flow N_2 .

acidic functional groups in the volatile OM that is responsible for the pH-dependent CEC particularly evident in the 250 °C biochars.

There is also evidence that suggests that volatile OM was not simply lost, but also changed with heating, particular in the 400 to 600 °C temperature interval. Not only did 650 °C biochars have the lowest AFG concentrations, but they also had significantly lower AFG concentration per VM content (Fig. 6), and significantly lower AFG concentration per surface area (i.e. AFG density, Table 1) compared to all other biochars. Lastly, the observation that the readily dissolved component of biochar, which may be related to volatile OM, was 4–5 times more electronegative than the coarse biochar surfaces (Fig. 5 versus Supplementary data Fig. S1) further suggests that this volatile fraction plays a dominant role in the AFG content and CEC of freshly made biochar.

4.2. Biochar surface charge and ion exchange capacity

The biochar CECs measured in this study (10–69 $\text{cmol}_c \text{kg}^{-1}$ at near neutral pH) were in the range of those reported by others despite the fact that the methods of CEC measurement differed in some cases. For example, a Douglas fir wood combusted at 350 °C had a CEC of 21 $\text{cmol}_c \text{kg}^{-1}$ (Gundale and DeLuca, 2007), an oak combusted at 350 and 800 °C had CEC of 13.1 and 8.9 $\text{cmol}_c \text{kg}^{-1}$, respectively (Nguyen and Lehmann, 2009), and black locust biochar combusted at 350 to 800 °C ranged 14–25 $\text{cmol}_c \text{kg}^{-1}$ (Cheng et al., 2006; Lehmann, 2007). In contrast, oak combusted in a historical charcoal blast furnace had little CEC at pH 7 ($0.2 \pm 1.0 \text{ cmol}_c \text{kg}^{-1}$) but significant AEC at pH 3.5 ($8.4 \pm 2.1 \text{ cmol}_c \text{kg}^{-1}$) (Cheng et al., 2008). Possible reasons for these variations could include differences in the both the biomass types and production conditions used, as well as the methods by which ion exchange capacity was determined. For example, Gundale and DeLuca (2007) and Lehmann (2007) used $\text{NH}_4^+ - \text{COO}^-$ as the exchangeable ion and $\text{K}^+ - \text{Cl}^-$ as displacing ions. Cheng et al. (2008) used $\text{K}^+ - \text{Cl}^-$ as the exchangeable ions and $\text{NH}_4^+ - \text{NO}_3^-$ as the displacing ions, whereas we used $\text{K}^+ - \text{Cl}^-$ as displacing ions and $\text{Na}^+ - \text{NO}_3^-$ as the displacing ions. We found no consistent differences in CEC resulting from the determination method used. Another major difference is that, whereas Lehmann (2007) showed CEC (pH 7) to increase with production temperature, our study showed the opposite. An explanation for this may be that, with the >16 h charring time used in the Lehmann study, the majority of volatile OM was lost, even at lower production temperatures. This may be indicated in the much greater N_2 -surface areas measured by Lehmann (2007). It is the volatile OM that we found to carry the majority of cation exchange capacity on biochar surfaces, particularly at circum-neutral pH.

The CEC data collected in this study suggesting a PZNC of below pH 1, and the ZP data indicating an IEP of pH 2–3. This may correspond to an internal charge which includes pore surfaces and an external charge, much as been previously suggested for soil minerals (Corapcioglu and Huang, 1987; Menéndez et al., 1995). In any case, biochars certainly have negatively charged surfaces at all but the lowest pH conditions. The negative charge is likely derived from biochar's abundant acid surface functional groups that are expected to be predominantly negatively charged at likely soil solution pH conditions.

While one would expect both AFG and negative surface charge to favor cation exchange, these are not equivalent concepts. A number of observations suggest that biochar AFG and surficial charge do not completely explain its CEC variations. First, whereas CEC at neutral pH varied strongly with production temperature, AFG variation with temperature was much less dramatic. Second, the 650 °C biochars possessed the greatest net negative charge and surface area, whereas the 250 °C biochars had the greatest CEC. The greater CEC of the 250 °C biochars is likely related to its greater volatile OM content, but while AFG was significantly linearly related to VM%, CEC (at pH 7) was not. Further, neither CEC nor AFG was significantly related to surface area (neither in the whole data set nor within biomass types), indicating

that these characteristics are not purely surface specific but are dependent upon changes in biochar surface chemistry variations.

Although AFG and CEC were weakly linearly correlated ($R^2 = 0.47$, $p < 0.05$), AFG concentrations were about ten times greater than the concentration of cation exchangeable sites on biochar surfaces, on average (Fig. 6). A number of reasons may explain why most biochar surface acid functional groups did not contribute toward CEC. First, cation exchange phenomena is mainly electrostatic in nature, whereas Boehm titration measures the number of acidic chemical sites, which may be more closely associated with other bonding phenomena such as covalent bonding or ligand exchange. Second, the acidic functional groups measured by Boehm titration were not necessarily all speciated in a de-protonated form that would be attractive sites for cation exchange. Lastly, the microporous structure of the biochars may have inhibited penetration by the K^+ cation used to measure CEC, whereas the diffusion of the much smaller H^+ ion exchanged during titration was less likely kinetically limited. In addition, the poor correlation between AFG and CEC may be due, in part, to parent biomass-type variation. For example, the grass biochars had consistently greater CEC per unit AFG than biochars of other biomass types (Fig. 6).

4.3. Environmental implications and conclusions

These findings indicate that, while biochars have a range of characteristics that may improve soil quality, not all biochars are the same and some biochars may be better suited for particular purposes than others. For example, higher temperature biochars would be better used to neutralize soil acidity. But the pH buffering capacity of all biochars may help a soil to control nutrient retention and movement over a wide range of soil solution pH conditions. While amendments of biochar made at lower temperatures (or perhaps in the presence of some oxygen) will likely enhance soil CEC most, especially for near-neutral pH soils, some CEC enhancement is likely from any biochar at all pH conditions. The average CEC of biochars tested in this study (about 30 $\text{cmol}_c \text{kg}^{-1}$) is greater by at least half than the CEC of most soil orders (3–20 $\text{cmol}_c \text{kg}^{-1}$, except Histosols) (Brady and Weil, 1984). Because biochar CEC is less than that of most 2:1 layers clays, 80–250 $\text{cmol}_c \text{kg}^{-1}$ (Brady and Weil, 1984) and soil humic materials, 40–90 $\text{cmol}_c \text{kg}^{-1}$ (Sposito, 2008), its positive effects in this regard will be most strongly felt in soils lacking an abundance of these components. Biochar does, however, have acidity on par with that of soil humic materials (Sposito, 2008) and so may have similar ability to complex nutrients and metals in soils. Further, the low IEP of biochar (pH 1–3) are similar to that found in some pure metal oxides or hydroxides (Mohamed and Anita, 1998) and organic soils (Asadi et al., 2009).

It is generally thought that biochar can be used as a soil amendment to enhance soil fertility due to its ability to hold soil macronutrients such as nitrogen and phosphorus (DeLuca et al., 2009; Glaser et al., 2002). Enhanced nutrient uptake by plants has been shown to take place from biochar-amended soils (Steiner et al., 2008), though this may result from the nutrient content of the biochar themselves (DeLuca et al., 2009). But this study showed that recently produced biochar surfaces were mainly characterized by negative surface functional groups and would, therefore, directly attract only cations such as ammonium (NH_4^+), but not nitrate (NO_3^-), or phosphate (PO_4^{3-}) if amended with soils. However, as soil is a typical mixtures of clays, organic matter and nutrients and so it is possible that biochars may still sorb phosphate and nitrate by bridge bonding using the residual charge of electrostatically attracted or ligand-bonded divalent cations such as Ca^{+2} and Mg^{+2} or other metals including Al^{+3} and Fe^{+3} . It is also possible that the beneficial effects of biochar may derive from the release of N and P nutrients by decomposing OM sorbed onto biochar's surface or even within the biochar pore structure. Lastly, it is likely that biochar's surface changes with age, developing more oxidized surface functional groups with time. For example, studies have found that, natural oxidation of biochars increased oxygen content, carboxylic and phenolic functional

groups, and negative charges and decreased carbon content and surface positive charge (Cheng et al., 2006, 2008). These changes over time would progressively enhance the sorption and exchange capacity of soils containing the biochars. On the other hand, sorption of natural OM onto biochar may either block biochar surfaces, reducing its nutrient-holding capacity, or increase it by increasing the total OM of the soil.

At present, our understanding of biochar surface chemistry and its interaction with nutrients and other soil components is immature. In particular, N and P-binding and exchange mechanisms need to be better understood to facilitate the use of biochar as a soil amendment, as well as to understand the effect of fire on soil nutrient and carbon cycling. This will require focused N and P adsorption/desorption and leaching experiments using a range of well-characterized biochars and soils. In addition, further efforts must be made to identify and standardize and the techniques that are best used to characterize the properties of biochar and black carbon materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.geoderma.2011.04.021.

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Surface chemistry variations among a series of laboratory-produced biochars

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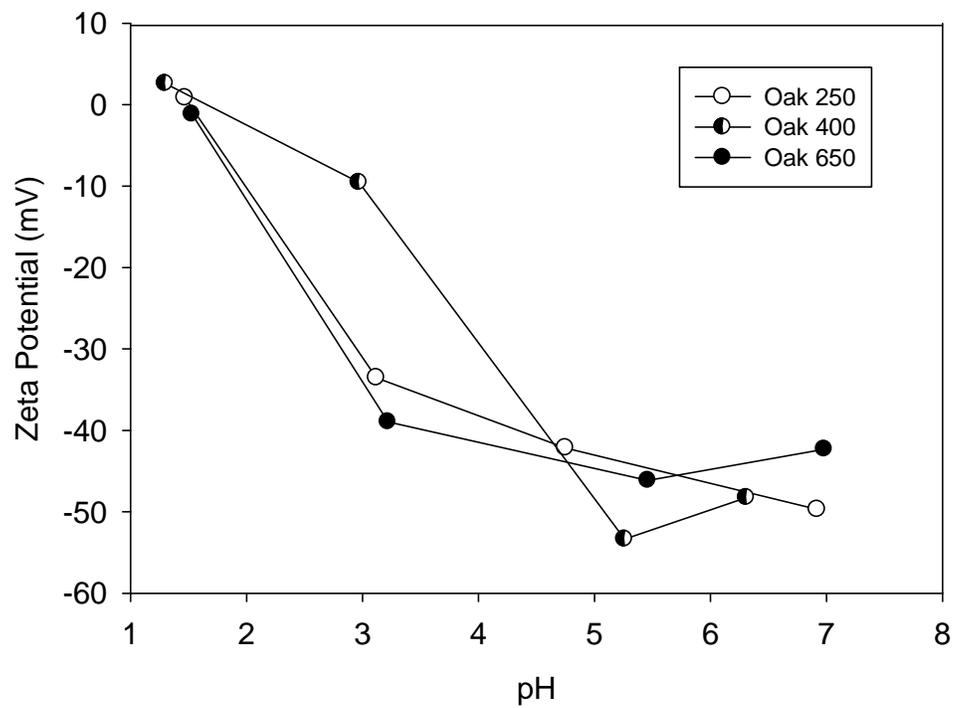
* Corresponding author

Supplemental Table S1. Anion exchange capacity (AEC) and pH of pine, oak and grass biochars.

Pine												
Formation Temperature	250 °C				400 °C				650 °C			
pH	1.8	3.3	4.7	7.2	1.6	3.2	5.1	7.3	1.7	3.1	5.5	7.0
AEC (cmol _c kg ⁻¹)	-6.3	-4.1	-1.9	-1.1	10.3	-5.0	-1.7	-1.4	-2.2	-7.3	-3.4	-1.8
Oak												
Formation Temperature	250 °C				400 °C				650 °C			
pH	1.6	3.3	4.9	5.6	1.5	3.1	5.3	6.4	1.6	3.3	5.6	6.6
AEC (cmol _c kg ⁻¹)	-39.2	-22.7	-4.5	-4.9	15.9	12.4	-5.4	-1.0	-24.9	-9.8	-13.0	4.5
Grass												
Formation Temperature	250 °C				400 °C				650 °C			
pH	1.5	3.5	4.9	6.9	1.4	3.5	5.5	7.0	1.5	3.9	5.0	7.5
AEC (cmol _c kg ⁻¹)	-12.9	-3.3	-1.2	-1.8	-4.5	-1.4	-23.9	-1.8	4.5	-5.1	-3.1	-1.4

Supplemental Table S2. Additional selected properties of oak, pine and grass biochar produced at three different temperatures

Biochar type	C	N	H	O	Wgt. Loss	C Recovery
	Wgt. %				(%)	
Oak 250	55.2	0.2	3.1	41.5	55.9	62.0
Oak 400	69.6	0.4	4.2	25.9	53.1	71.6
Oak 650	78.8	0.5	2.8	18.0	67.9	54.4
Pine 250	58.0	0.0	2.6	39.4	71.6	39.0
Pine 400	68.6	0.1	3.7	27.6	68.5	52.5
Pine 650	83.0	0.0	3.3	13.8	73.4	32.4
Grass 250	52.7	1.2	3.6	42.5	50.6	59.5
Grass 400	58.6	1.3	4.6	35.4	63.6	46.4
Grass 650	63.8	0.6	3.0	32.7	65.4	46.9



Supplemental Figure S1: Variation in zeta potential of leachate from oak fine biochar with pH.