PHYSICAL AND CHEMICAL PROPERTIES OF A RANGE OF LABORATORY-PRODUCED FRESH AND AGED BIOCHARS

By

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To my parents and grandparents

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LIST OF ABBREVIATIONS

AEC	Anion exchange capacity
AFG	Acid functional groups
BC	Black carbon
CEC	Cation exchange capacity
DOC	Dissolve organic carbon
M1	Mehlich 1 extraction
N	Nitrogen
OM	Organic matter
P	Phosphorus
SOM	Soil organic matter
TKN	Total Kjeldahl Nitrogen
VM	Volatile matter
ZP	Zeta potential

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Biochar is the carbonaceous product obtained when plant or animal biomass is subjected to heat treatment in an oxygen-limited environment. Inspired by the anthropogenic *terra preta* (Black Earth Soils) of Amazonia, it has been suggested that biochar amendments could be used to increase soil fertility while sequestering atmospheric CO_2. Recent advancements in understanding biochar"s properties and effects have been made but progress has been hampered by the great number of individual biochars used in each of the previous studies. This work examines the physio-chemical properties of a wide range of biochars to develop a more holistic understanding of biochar"s properties and projected behavior when used as a soil amendment.

Biochars were made from pine, oak, and grass by heating for 3 h under limited oxygen (250 ^{o}C) and no oxygen (flowing N_2 at 400 and 650^{o}C) conditions. With increasing production temperature, fresh biochar surface area and pH increased, while volatile matter, acid functional groups and cation exchange capacity (CEC) decreased. Thus, higher temperature biochars would be better used to neutralize soil acidity while

lower temperature biochars could enhance soil CEC. However, one anticipates some CEC enhancement from any biochar as net surface charge was always found to be negative. Batch extraction and column nutrient leaching experiments indicated that biochars made at lower temperature and from grass released greater nutrients (organic carbon, nitrogen and phosphorus) than those made at higher temperature and from oak, respectively. Carbon and nitrogen release from biochar was related to biochar micropore surface area and acid functional group density, whereas P release was correlated to inorganic ash content. However, much of the nutrients released were in organic form and both soils tested showed some ability to sorb these components. Field aging of biochars decreased their pH and acid functional group content but increased their CEC. Combined with soils, biochar increased soil CEC up to 45%, even beyond that expected by pure additive calculation, thus indicating a positive interactive effect. These findings make progress toward the goal of designing biochars ideally suited for each soil and for each intended goal such as nutrient retention, carbon sequestration, or contaminant immobilization.

CHAPTER 1
INTRODUCTION

Black carbon (BC) is a term usually used to describe carbonaceous residuals that are produced by incomplete combustion of fossil fuels or biological materials (Hamer et al., 2004; Pignatello et al., 2006). It has only recently been realized that black carbon is ubiquitous in the environment and sometimes represents a large portion of the organic carbon found in soils, lake, river and marine sediments, and even in marine suspended particles (Goldberg, 1985; Masiello, 2004). In particular, black carbon can be a major component of soil organic matter (SOM) in regions prone to forest fires (Goldberg, 1985; Hockaday et al., 2006; Rumpel et al., 2006) or where slash and burn or slash and char agriculture is practiced (Glaser et al., 2001b; Schmidt and Noack, 2000; Skjemstad et al., 1996).

A body of research on BC has been carried out in last few decades, especially after the influential publication of the text “Black Carbon in the Environment” by Goldberg (Goldberg, 1985; Masiello, 2004). It is generally understood that BC is a highly refractory substance, which, therefore, has an extremely long environmental lifetime and could play an important role in global carbon cycling. In particular, it may strongly, enhance the long-term storage of organic carbon in soil and sediment (Goldberg, 1985; Masiello, 2004; Quenea et al., 2006). Finally, its strong sorptive ability may influence soil chemistry and the fate and transport of organic contaminant and heavy metal transport in the environment (Barring et al., 2002; Bornemann et al., 2007; Sander and Pignatello, 2005; Sander and Pignatello, 2007; Van Noort et al., 2004).

One issue hampering the advancement of BC research is the various terms for BC found in the literature. According to Rumpel et al. (2006), for example, there are two

forms of BC: (a) charcoal, composed of incomplete biomass combustion products representing the largest portion of BC on a mass basis, and (b) condensation products of hot combustion, i.e. soot. But Masiello (2004) described BC as a continuum of combustion products ranging from slightly charred biomass to highly refractory soot (condensates from the vapor phase) and, perhaps, even graphite derived from rocks (Masiello, 2004). In addition, the term biochar has become widespread and is often reserved for those carbonaceous products intentionally produced by humans, usually for use as a soil amendment. It is also this context which serves as the motivation for much of the research presented in this dissertation. Thus, the term „biochar" will be used here preferentially and will refer to all residual products of biomass combustion excluding soot.

Biochar has been gaining recent attention as a possible tool for environmental management today due to the realization that it may have a long history of use to enhance soil fertility (Glaser et al., 2004a; Glaser et al., 2004c; Glaser et al., 2001b). *Terra preta* are anthropogenic soils of Amazonia that are greatly enriched in organic carbon, much of it from biochar, and plant available nutrients relative to the surrounding depleted Oxisols. It is also quite fertile soil, prized even today for its ability to produce high crop yields year after year (Glaser, 2007; Glaser et al., 2001b; Glaser et al., 2004d). *Terra preta* soils are often associated with ceramics and charcoal fragments (Sombroek, 1966) and it is presumed by many that some method of biomass burning by the amerindians, e.g. slash and char, is responsible for the soil"s chemical properties and enhanced fertility (Glaser et al., 2001b; Lehmann et al., 2003; Rumpel et al., 2006; Solomon et al., 2007). It is the dream of many an agronomist, upon hearing of *terra*

preta, to find a way to produce a modern form of *terra preta*, thus alleviating the world‟s problems of soil degradation while sequestering large amounts of carbon into soils so that atmospheric CO_2 levels can be brought down.

Biochar can be produced by thermal decomposition of biomass species with limited or no supply of oxygen (Lehmann and Joseph, 2009). Methods to produce biochar have been studied for many centuries. For example, biochar has been used for metal smelting at least since 2000 BCE. It has been made in kilns, in earthen holes and in conical piles of biomass. More recent research has also made significant progress in understanding biochar‟s physical and chemical properties (Antal and Gronli, 2003; Antal et al., 2003; Baldock and Smernik, 2002; Bourke et al., 2007; Brown et al., 2006; Hammes et al., 2006). But these investigations have utilized a great diversity of biomass types and biochars that have been produced under a wide variety of laboratory conditions. No single study has methodically compared the physical and chemical properties of biochar made with a range of biomass types and under a range of controlled laboratory conditions. Furthermore, no studies have compared the chemical and physical properties of fresh and „aged‟ biochars and few have examined the release or sorption of nutrients from different types of biochars. These types of studies are needed to understand biochar‟s (and naturally produced black carbon‟s) role in the environment in the present and in the past. More specifically, these studies are needed to guide the design of biochars that will be ideal for each purpose for which biochar is intended such as nutrient retention, carbon sequestration or contaminant adsorption.

This study fills this need by investigating a number of environmentally relevant properties of a range of biochar types produced under controlled laboratory conditions.

Chapter 1 describes an examination of some morphological and chemical properties of laboratory-produced fresh biochars and predicts the effects that each one would have when added to soils. Chapter 2 describes various experiments examining the solubilization of nutrients such as dissolved organic carbon (DOC), nitrogen (N) and phosphorus (P) from a number of fresh and aged biochars as well as selected soil/biochar mixtures. Chapter 3 is a comparison of the properties of fresh and nine months-aged biochars and soil/biochar mixtures. The overall goals of this dissertation work are to gain insight into the various properties of laboratory-produced fresh and field-aged biochars and to develop a mechanistic theory of how various biochar properties could influence the chemistry, and ultimately the fertility, of the soils to which they are amended. Even more broadly, we may come to find a link between climate-related fire history and the biogeochemical cycling of elements through Earth history.

CHAPTER 2
SURFACE CHEMISTRY VARIATIONS AMONG A SERIES OF LABORATORY-PRODUCED BIOCHAR

Literature Review

Black carbon (BC) is one of the residuals of biomass combustion. It can be a major component of soil organic matter (SOM) 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; Glaser et al., 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; Glaser et al., 2002; Glaser et al., 2004b; Glaser et al., 2001b; 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 CO_2, 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 accidently 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). Surface area is generally found to increase with biochar production temperature (Braida et al., 2003; Nguyen et al., 2004; Pattaraprakorn et al., 2005; Rutherford, 2004; Weng et al., 2006). Other studies have examined biochar‟s ion exchange and surface charge characteristics which also vary among different chars (Cheng 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.

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; Sposito, 2008). If the soil pH is above its point of zero net change (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 SOM, 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 the CEC of the soils with high organic matter (OM) 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; Glaser et al., 2002; Glaser et al., 2001b). Thus, it is likely that biochar amendment will also increase the CEC of a soil.

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 OM 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.

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 OM 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.

Materials and Methods

Sample Preparation

Branches of *Quercus lobata* (Laurel oak: Oak) and *Pinus taeda* (Loblolly pine: Pine), and leaves of *Tripsacum floridanum* (Gamma grass: Grass) were collected from various parts of Florida, USA. Biomass species 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 ^{o}C in an oven under limited oxygen and at 400 and 650 ^{o}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 the temperature that might be present in natural forest fires (450 ^{o}C) (Turney et al., 2006) or in a backyard or industrial biochar production processes. In the presence of oxygen, temperatures higher than 250 ^{o}C were found to produce mainly ash and no biochar, whereas in the absence of oxygen, temperatures lower than 400 ^{o}C were found to yield no biochar, but only slightly charred biomass.

For the pyrolysis at 400 and 650 ^{o}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 × 50 cm length) with N_2 flowing from end to end (2.3 oven volumes exchanged min^{-1}). The temperature program was 26 °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 quickly rinsed with double distilled water to remove ash and dried at 80 ^{o}C for 5 d. The coarse biochar fraction was used to carry out all analyses. However, the ZP of the fine biochar was also examined due to the requirements of one of the instruments used (see below).

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 OM in water (Kasozi 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.

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.

Determination of Volatile Matter and Ash Content

Volatile matter (VM) 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 was kept in a drying oven for at least 2 h at 100 ^{o}C and allowed to cool in a desiccator before weighing. The percentage VM content was determined as weight loss after combustion in a ceramic crucible with a loose ceramic cap at 850 – 900 ^{o}C for 6 min.

Ash content was determined as weight loss after combustion at 750 ^{o}C for 6 h with no ceramic cap. Sample weight was taken after cooling in a desiccator for one hour.

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 mesopores (>1.5 nm diameter) were calculated using multi-point adsorption data from the 0.01 – 0.3 P/P_o linear segment of the N_2 adsorption isotherms made at 77 K using Brunauer, Emmet, and Teller (BET) theory (Brunauer, 1938). Biochar samples were degassed under vacuum (180 °C, atleast 24 h) prior to nitrogen adsorption at liquid nitrogen temperature (77 K). 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 mesopores (>1.5 nm diameter) and micropores (<1.5 nm diameter) were determined on CO_2 adsorption isotherms measured at 273 K generated in the partial pressure range 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 ^{o}C prior to analysis.

Determination of CEC, AEC and PZNC

Detailed description of traditional soil PZNC determination methods by non-specific ion adsorption has been presented elsewhere (Zelazny, 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 is 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 one hour. The solutions were then vacuum-filtered and the supernatant was discarded. The biochars left 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 μm 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).

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 ZP 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 (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 pHs of the solutions were 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.

Determination of Surface Acid Functional Group Distribution

Biochar surface acid functional group distribution was determined using the Boehm titration method (Boehm, 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).

Statistical Analyses

All of the data presented are means ± 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.

Results

Biochar Bulk Characterization

All the biochar types examined acted as buffers toward pH changes. Oak biochar are shown here as representative examples (Fig. 2-1). 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 2 h equilibration period was used for all subsequent analyses. The pH of the biochars examined ranged from 3.1 to 10 (Fig. 2-2) 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 ^{o}C, respectively. However, pH was also dependent upon the original biomass species, increasing from pine to oak to grass at all production temperatures.

The VM content ranged from 25.2 to 66.0% overall and decreased with increasing formation temperature for each biomass type (Table 2-1), 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 2-1). 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 2-1), possibly resulting from the higher K, Ca and Mg content of grass biomass and grass biochars (See Table 4-2 in Chapter 4).

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

Biochar Surface Characterization

Amongst all the biochars examined, the concentration of total surface acidic functional groups (AFG) ranged from 4.4 – 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. 2-3). 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 was less apparent (Fig. 2-3). On the other hand, no significant difference ($p < 0.05$, PROC GLM) in AFG content among the three biomass types was observed (Fig. 2-3). Acid surface functional group density was calculated as total AFG divided by the surface area, as measured by CO_2 sorptometry, of each biochar. Acid functional group density of low temperature biochars (250 and 400 ^oC) ranged from 10.2 – 21.7 nm^{-2} and that of 650 ^oC biochars were consistently lower, ranging only from 4.1 – 6.7 nm^{-2} (Table 2-1).

The CEC of all biochar samples examined ranged between 10.2 and 69.2 $cmol_c$ kg^{-1} at near neutral pH (Fig. 2-4). The average CEC of 250 ^oC biochar was much higher, 51.9 ± 15.3 $cmol_c$ kg^{-1}, compared to 400 and 650 ^oC biochars (16.2 ± 6.0 and 21.0 ± 17.2 $cmol_c$ kg^{-1}, respectively) at near neutral pH. The CEC of the 250 ^oC 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 ^oC 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.

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 formation temperature), and had an IEP of close to 1.5 (Supplemental data, Fig. S1). On the other hand, assuming oak biochar is 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. 2-5), 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.

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.

Development of Biochar Surface Characteristics with Production Conditions

Significant mesopore 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 2-1). Though the biochars produced under atmosphere at 250 ^oC had slightly greater microporous surface area than those produced at 400 ^oC, 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.

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 – 4.4 mmol g^{-1} and 250 ^oC biochar contained about twice the total, and carboxyl functional groups and about four times the phenolic functional groups as 400 ^oC 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, Diffuse Reflectance Infrared Fourier Transform (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., 2008; Rutherford, 2004). And 13C-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 (Czimczik 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 VM was progressively lost, both micropore and mesopore surface area increased, indicating that VM was likely initially present as the infilling of pores within a more refractory framework. Our data suggests that VM has surface chemical properties different from that of the non-volatile biochar component. This was most apparent in the properties of the 250 ^{o}C biochars, which, with its higher VM%, was distinct from the 400 and 650 ^{o}C biochars in its enhanced ability to exchange cations at circum-neutral pH‟s (Fig. 2-4). In addition, it appears that the VM 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. 2-6) suggests that it is acidic functional groups in the VM that is responsible for the pH-dependent CEC particularly evident in the 250 ^oC biochars.

There is also evidence that suggests that VM was not simply lost, but also changed with heating, particular in the 400 to 600 ^oC temperature interval. Not only did 650 ^oC biochars have the lowest AFG concentrations, but they also had significantly lower AFG concentration per VM content (Fig. 2-6), and significantly lower AFG concentration per surface area (i.e. AFG density, Table 2-1) compared to all other biochars. Lastly, the observation that the readily dissolved component of biochar, which may be related to VM, was 4 – 5 times more electronegative than the coarse biochar surfaces (Fig. 2-5 versus Supplementary Fig. S1) further suggests that this volatile fraction plays a dominant role in the AFG content and CEC of freshly made biochar.

Biochar Surface Charge and Ion Exchange Capacity

The biochar CEC's measured in this study (10 – 69 $cmol_c\ kg^{-1}$ 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 ^oC had a CEC of 21 $cmol_c kg^{-1}$ (Gundale and DeLuca, 2007), an oak combusted at 350 and 800 ^oC had CEC of 13.1 and 8.9 $cmol_c\ kg^{-1}$, respectively (Nguyen and Lehmann, 2009), and black locust biochar combusted at 350 to 800 ^oC ranged 14 – 25 $cmol_c\ kg^{-1}$ (Cheng et al., 2006a; Lehmann, 2007). In contrast, oak combusted in a historical charcoal blast furnace had little CEC at pH 7 (0.2 ± 1.0 $cmol_c\ kg^{-1}$) but significant AEC at pH 3.5 (8.4 ± 2.1 $cmol_c\ kg^{-1}$) (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 NH_4^+-COO^- as the exchangeable ion and K^+-Cl^- as displacing ions. Cheng et al (2008) used K^+-Cl^- as the exchangeable ions and NH_4^+-NO_3^- as the displacing ions, whereas we used K^+-Cl^- as displacing ions and Na^+-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 VM was lost, even at lower production temperatures. It is the VM 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 ^{o}C biochars possessed the greatest net negative charge and surface area, whereas the 250 ^{o}C biochars had the greatest CEC. The greater CEC of the 250 ^{o}C biochars is likely related to its greater VM 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. 2-6). 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. 2-6).

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 $cmol_c\ kg^{-1}$) is greater by at least half than the CEC of most soil orders (3 – 20 $cmol_c\ kg^{-1}$, except Histosols) (Brady and Weil, 1984). Because biochar CEC is less than that of most 2:1 layers clays, 80 – 250 $cmol_c\ kg^{-1}$ (Brady and Weil, 1984) and soil humic materials, 40 – 90 $cmol_c\ kg^{-1}$ (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, 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 N and P (DeLuca, 2009; Glaser et al., 2002). Enhanced nutrient uptake by plants has been shown to take place

from biochar-amended soils (Steiner et al., 2008b), though this may result from the nutrient content of the biochar themselves (DeLuca, 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, OM and nutrients and so it is possible that biochars may still sorb PO_4^{-3} and NO_3^- by bridge bonding using the residual charge of electrostatically attracted or ligand-bonded divalent cations such as calcium (Ca^{+2}) and magnesium (Mg^{+2}) or other metals including aluminium (Al^{+3}) and iron (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., 2008; Cheng et al., 2006b). 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 the techniques that are best used to characterize the properties of biochar and black carbon materials.

Table 2-1. Selected properties of oak, pine and grass biochar produced at three different temperatures (250, 400, and 650 ^{o}C)

Biochar type	Volatile matter (weight %)	Ash content (weight %)	N_2 Surface area (m^2g^{-1})	CO_2 Surface area (m^2g^{-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

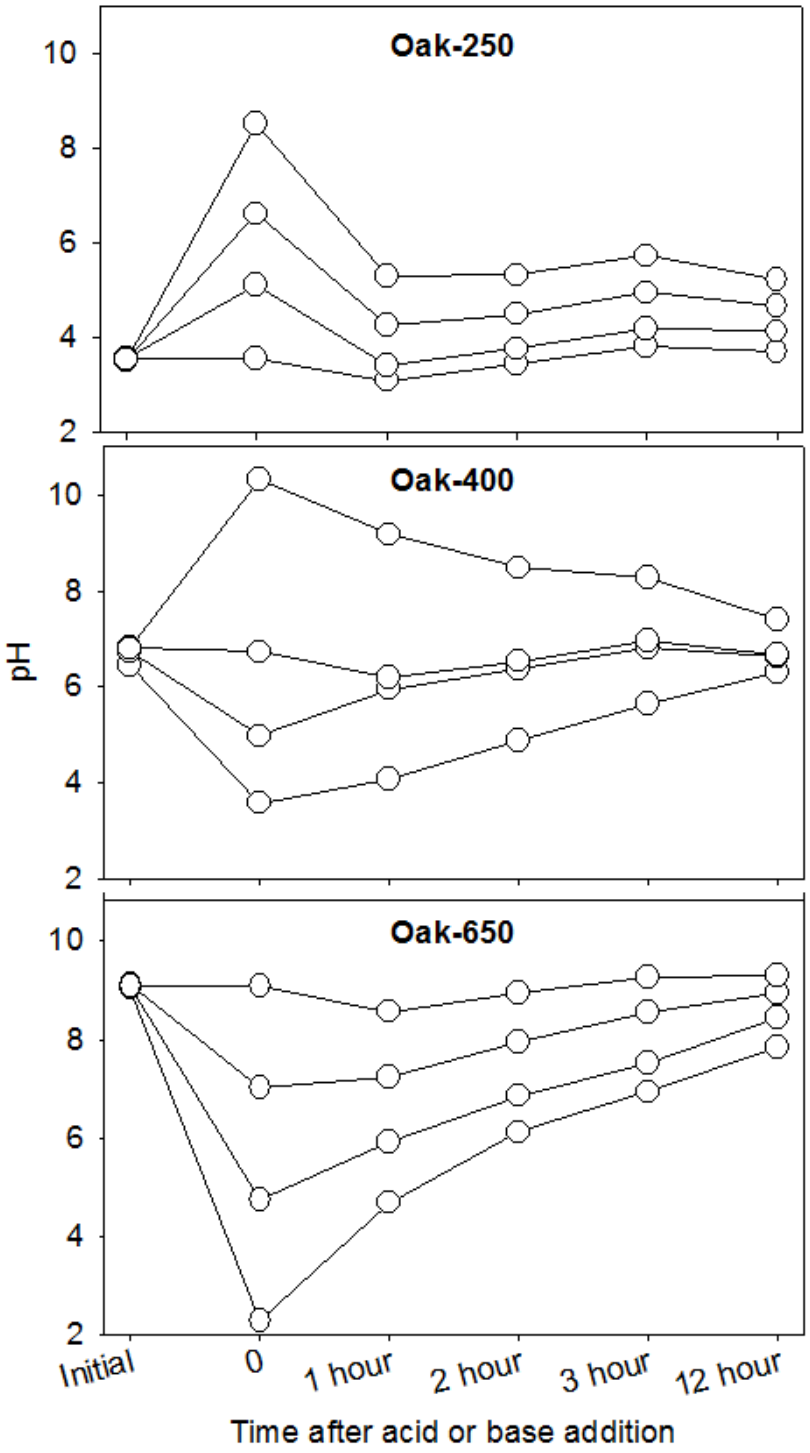


Figure 2-1. Variation in Oak-250, Oak-400 and Oak-650 biochar pH initially and after acid or base addition at time 0

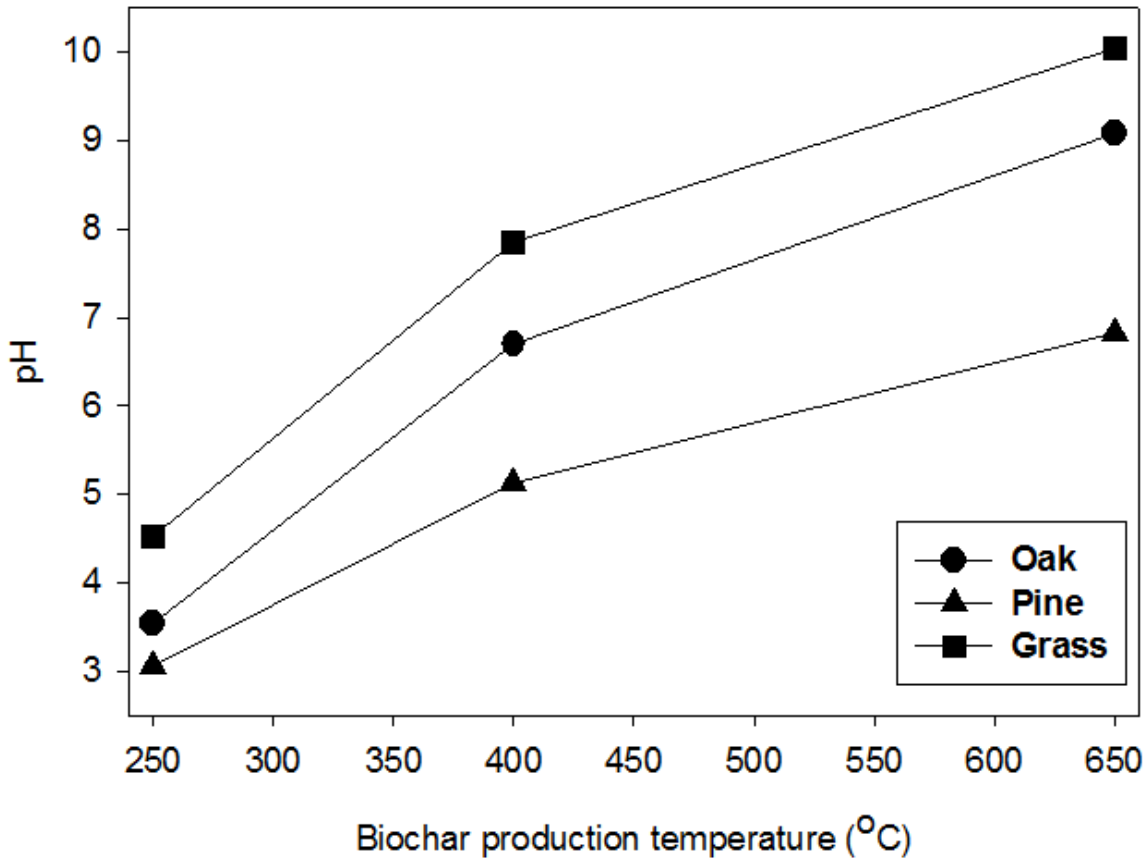


Figure 2-2. The pH of biochars made from oak, pine and grass at 250 ^{o}C under full atmosphere and at 400 and 650 ^{o}C under continuous flow N_2

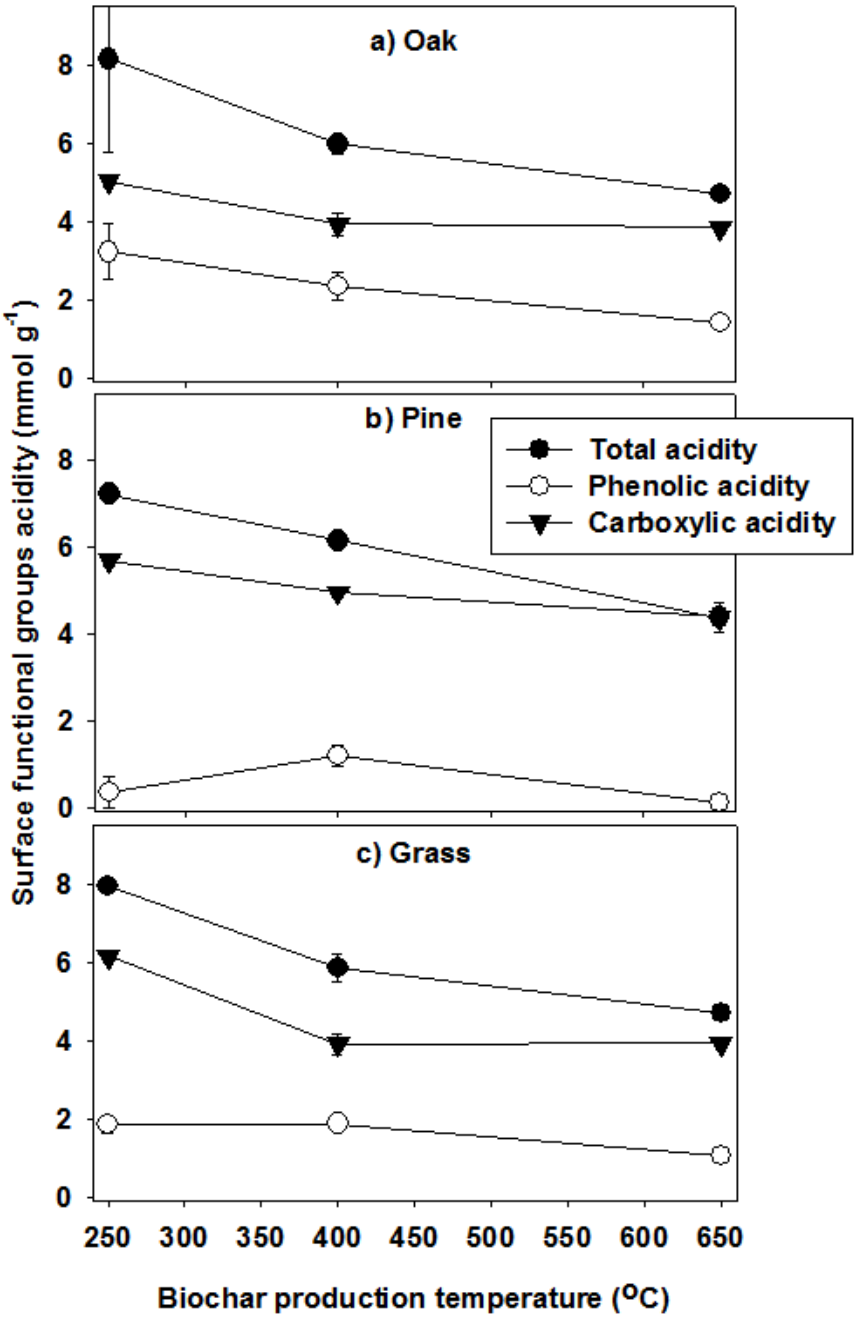


Figure 2-3. Variation in surface acidic functional group content among biochars made from a) oak, b) pine, and c) grass at 250 ^{o}C under full atmosphere and at 400 and 650 ^{o}C under continuous flow N_2

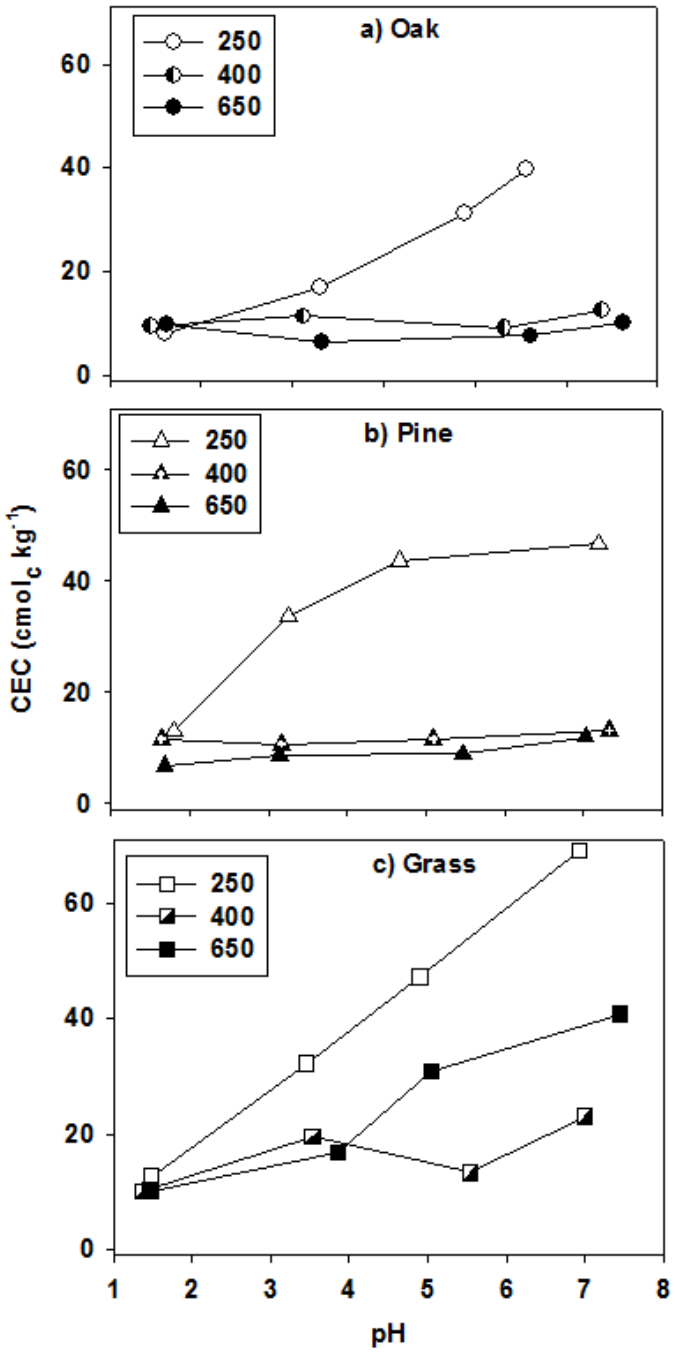


Figure 2-4. Variation in cation exchange capacity with pH for biochars made from a) oak, b) pine, and c) grass at 250 ^{o}C under full atmosphere and at 400 and 650 ^{o}C under continuous flow N_2

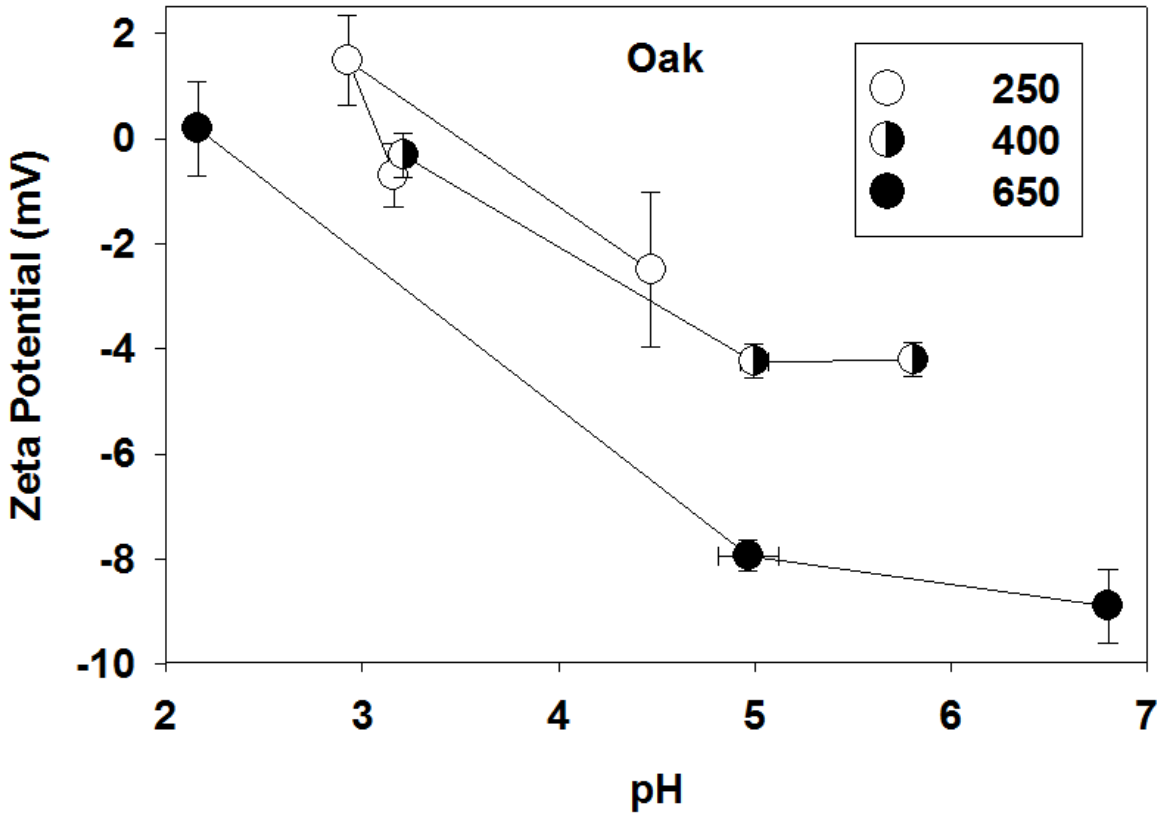


Figure 2-5. Zeta potential variation with pH for coarse particle (0.25 – 2 mm) oak biochar made at 250 ^{o}C under full atmosphere and at 400 and 650 ^{o}C under continuous flow N_2

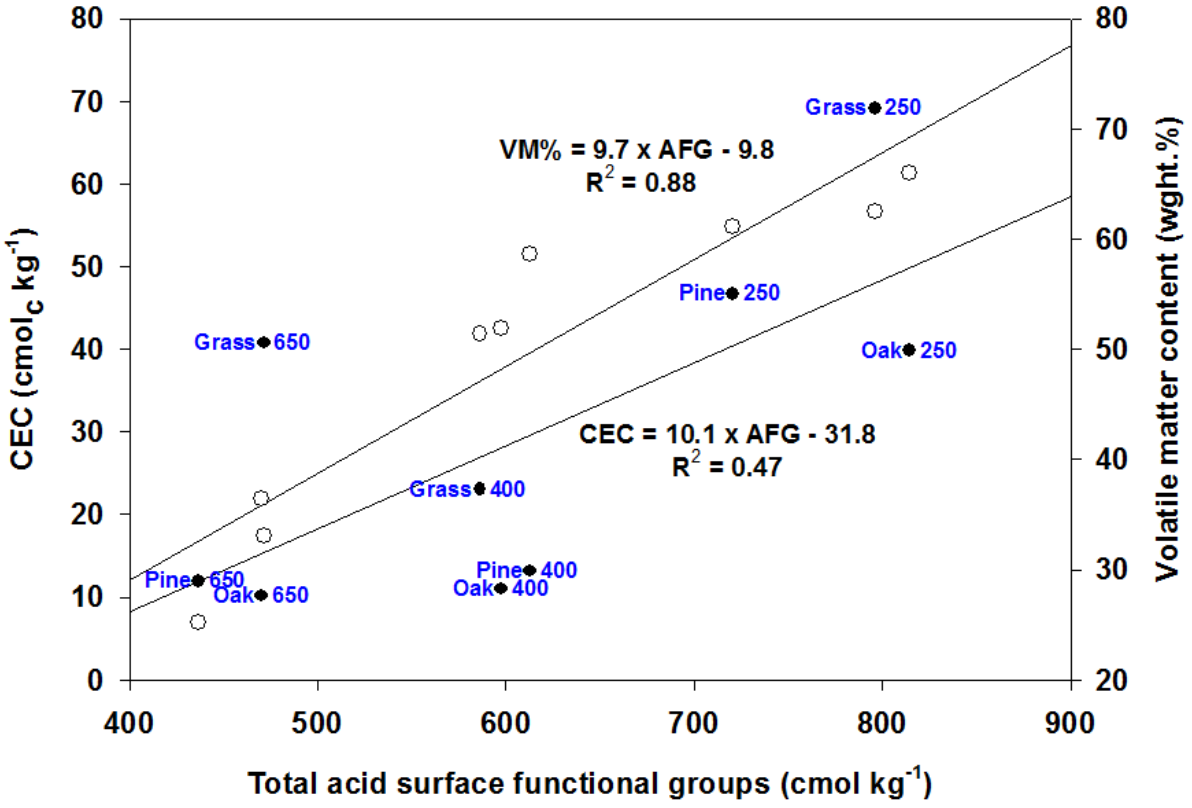


Figure 2-6. Relationship between surface total acidic functional groups (AFG) and CEC at around pH 7 (closed circles with biochar type labels), and AFG and volatile matter (VM%, open circles) for all biochars made at 250 ^{o}C under full atmosphere and at 400 and 650 ^{o}C under continuous flow N_2

CHAPTER 3
ORGANIC CARBON AND NUTRIENT SOLUBILIZATION FROM A RANGE OF LABORATORY-PRODUCED BIOCHARS AND BIOCHAR-SOIL MIXTURES

Literature Review

Biochar is the carbonaceous product obtained by removing water and other volatile components when plant or animal biomass is subjected to heat treatment. This may occur in the presence of oxygen (referred to as here simply as combustion) or without oxygen (referred to here as pyrolysis). Biochar might be used as a soil amendment able to enhance soil fertility today and possibly in the past, such as by Amazonan civilizations who made *terra preta*, anthropogenic tropical soils, that are greatly enriched in organic carbon and P relative to the surrounding depleted Oxisols (Glaser et al., 2002; Glaser et al., 2004a; Glaser et al., 2001b). More recently, biochar has gained attention for its potential to sequester carbon in soils, i.e. store CO_2 removed by plants from the atmosphere, due to its refractory nature (Zimmerman, 2010).

While there has been much recent work examining the range in biochar"s chemical characteristics (Baldock and Smernik, 2002; Mukherjee et al., 2011; Zimmerman, 2010) and effect on plant growth (Major et al., 2010b; Steiner et al., 2008b; Steiner et al., 2007), much remains to be known. For example, the optimum amount and type of biochar that should be applied to each soil or crop type is, at best, poorly known. The primary mechanism for biochar"s positive effect on fertility or biological functioning is unclear, and the possible environmental consequences that may accompany biochar amendments, such as organic contaminant or nutrient releases, have been barely examined. Nutrient leaching from soils, whether due to soil mineralogy or structure or poor soil management, has important consequences as it decreases soil fertility and crop yield while increases fertilizer cost and soil acidity (Brady and Weil, 1984). In

addition, nutrient leaching can have negative environmental consequences such as eutrophication, if these nutrients enter surface or ground waters. Here, release of DOC, N, and P (referred to here collectively as nutrients) from a range of biochars is examined in batch studies and in columns with and without soil to understand the potential for nutrient watershed contamination or soil fertilization following biochar soil amendment.

Biochar"s positive effects on the soil ecosystem, particular plants, have been proposed to derive either 1) directly from nutrients within biochar itself, or 2) indirectly from its ability to sorb and retain nutrients (Chan and Xu, 2009). Recent studies have shown the nutrient content of biochars to range widely: organic C (172-905 g kg^{-1}), N (1.7-78.2 g kg^{-1}), P (0.2-73 g kg^{-1}) and K (1-58 g kg^{-1}), and be controlled by both biomass type and combustion conditions (Chan and Xu, 2009). Some nutritive elements in biomass, such as C, N, S, and P begin to volatilize at low heating temperatures while others, such as K, P, Mg, Ca, and Mn, only volatilizes at higher temperatures, perhaps > 600 ^{o}C (Lehmann and Joseph, 2009; Neary et al., 1999). For example, Gundale and DeLuca (2006) showed that biochars made at 350 ^{o}C from ponderosa pine wood or bark had higher phosphate (PO_4^{3-}) and ammonium (NH_4^{+}) content than 800 ^{o}C biochars made from the same material. In contrast, extractable nitrate (NO_3^{-}) concentration was higher in 800 ^{o}C biochar relative to 350 ^{o}C biochars, suggesting that some NH_4^{+} may have been converted to NO_3^{-} at higher temperatures.

Given its high organic C, N and P content relative to many soil „fertilizers", biochar may be a source of nutrients, in organic or inorganic form, to soil microbes or plants if they are released from biochar upon application to the soil environment. A number of

studies have shown that some biochars stimulate soil microbial growth and activity (Ogawa, 1994; Ogawa, 1999; Ogawa et al., 1983; Saito, 1990; Steiner et al., 2008a). Additionally, release of residual organic compounds, identified as bio-oils, ash, or pyroligneous acid (PA) (Steiner et al., 2008a), or, more generally, VM (McClellan et al., 2007), may serve as substrates for microbial growth or co-metabolite with native soil OM, thus acting to increase nutrient availability indirectly. However, some of these residuals could also be toxic to plants and possibly to some microbes (McClellan et al., 2007).

The physical properties of some biochar, such as high surface area and porosity and ion exchange capacity, has led to speculation that its positive effect on plant fertility may be related to its ability to sorb, and possibly slowly released, OM or nutrients (Lehmann and Joseph, 2009). For example, Kasozi et al. (2010) showed catechol and humic acid sorption onto biochars derived from oak, pine and grass biochars and found that sorption was dependent on micropore surface area, biomass species, as well as particle sizes of the biochars. A number of studies also reported that polycyclic aromatic hydrocarbons (PAHs) and organic compounds containing benzene rings are strongly adsorbed onto biochar surfaces due to strong π- π interaction of PAHs and also to the planar nature of PAH molecules which allows access to smaller pores (Barring et al., 2002; Bornemann et al., 2007; Sander and Pignatello, 2005; Sander and Pignatello, 2007; Van Noort et al., 2004).

A number of studies have shown a promising role for biochar as a tool for enhancing nutrient retention in soil. In one study, a 45-week soil column leaching study with Midwestern agricultural (Clarion, fine-loamy) soil amended with a commercially

available slow pyrolyzed oak biochar showed a significant increase in the capacity of the soil to retain nutrients (Laird et al., 2010a). After leaching with 0.4 - 0.7 pore volume of 0.001 M $CaCl_2$ once a week for 500 days, loss of nutrients such as N, P, Mg, and Si from soil-biochar columns was reduced relative to a control soil (Laird et al., 2010a). In the columns loaded with 20 g kg^{-1} biochar and manure, the reduction in total N and P leached was 11% and 69%, respectively (Laird et al., 2010a). In another column study, a Norfolk loamy soil amended with a pecan shell biochar made at 700 ^{o}C temperature was leached twice (on days 25 and 67) with about 1.3 pore volumes of water (Novak et al., 2009). Relative to a control soil with no biochar, the second leachate contained greater K and Na concentrations, but decreased concentrations of P (by about 35%), as well as Ca, Mn and Zn. Thus, biochars were presumed to exchange multivalent cations for surficially sorbed monovalent cations (Novak et al., 2009). Another column leaching experiment using bamboo charcoal pyrolyzed at 600 ^{o}C added to a variety of sandy silt soils showed a cumulative reduction in NH_4^+-N loss of 15% over 70 d (Ding et al., 2010). Column experiments with poultry litter and garden waste biochars produced at 550 ^{o}C without soil also showed a reduction in NO_3^-, NH_4^+ and P leaching but these reduction were not maintained beyond the addition of 20 pore volumes of water (816 mm) suggesting the involvement of either weak surface interactions or water trapping (Downie et al., 2007; Major et al., 2009).

The range in nutrient-retention properties observed for biochar are likely due to both variation in experimental conditions and duration, as well as the range in physical and chemical characteristics of biochars, such as surface area, cation exchange capacity (Lehmann and Joseph, 2009; Mukherjee et al., 2011). A number of studies

even suggested that increased nutrient leaching may result from biochar amendment. A recent study indicated that abundant dissolved organic carbon (DOC) was leached from fresh grass biochars (Kasozi et al., 2010). Soil leachates collected using lysimeteres showed 160% greater DOC concentrations over 2 y from 150 cm depth in a biochar amended Colombian savanna Oxisol (Major et al., 2010a) and significantly greater over 28 weeks in a biochar-amended northeast England soil (Bell and Worrall, 2011). And a number of studies have found greatly increased extractable (i.e. leachable) nutrient levels in biochars and biochar-amended soils (Chan et al., 2007; Chan et al., 2008). However, there are almost no reports on the forms of N and P that are to be released or retained by biochar.

Clearly, a better understanding of the nutrient retention or leaching properties of different biochars is needed so that the optimum biochar can be selected for application to a particular soil type and so that deleterious environmental effects can be avoided. Here, both batch extraction and column leaching studies were carried out using a range of biochar and soil/biochar mixtures. Specific objectives of this study were to: 1) assess the variation in DOC, N, and P leaching/retention from a range of biochar types including those freshly prepared and aged, 2) explore the interaction between biochar leachate C, N, P and two soils, 3) examine the form of N and P lost/gained by biochar, 4) use nutrient loss patterns to predict longer term nutrient loss rates, and 5) improve the prediction of biochar nutrient performance by examining relationships between nutrient release in batch and column experiments and some easily measured chemical characteristics of biochars including several common nutrient extraction methods.

Materials and Methods

Materials

Biochar was produced from *Quercus lobata* (Laurel oak), *Pinus taeda* (Loblolly pine: Pine) and *Tripsacum floridanum* (Gamma grass) by combustion for 3 h at 250 ^{o}C in an oven under limited oxygen and at 400 and 650 ^{o}C in a pyrolyzer continuously flushed with 99% pure gaseous N_2 (designated hereafter as Oak-250, Grass-650, etc.). Detailed information on biochar preparation and characteristics have been presented elsewhere (Kasozi et al., 2010; Mukherjee et al., 2011) but are summarized in Table 3-1. Only the coarse (0.25 –2 mm) size fraction, separated by sieve and quickly rinsed with double distilled water to remove ash, was used in these experiments. In addition, biochar of each type was aged by placing in containers, fine-mesh screened above and below, so that weathering by air and precipitation but not sun and could occur for a period of nine months (Dec. 2009 – Sep. 2010) in north central Florida.

Two test soils were used in these experiments: a sandy Florida Entisol collected from a forest near Gainesville, Florida (BY) and a red clayey Ultisol collected at Big Canoe, Georgia (GA). Both soils were collected from 0-10 cm depth from surface horizon and were air dried and sieved (< 2 mm) to remove plant roots and vegetation.

Batch Extraction Experiment

Batch extractions of biochar samples were carried out in water with full successive supernatant removal and water replacement. About 0.5 g of each biochar sample was added to 40 mL of distilled deionized (DI) water in 50 mL plastic centrifuge tubes and placed in the dark and horizontally on a mechanical platform shaker (150 rpm). On days 1, 2, 4, 10 and 20, tubes were weighed and centrifuged (4500 rpm) and the supernatant was removed and filtered (Whatman 40 filter paper) and stored in a refrigerator for no

longer than one week prior to chemical analysis. The remaining sample was weighed to determine the amount of entrained solution and 40 mL DI water was added for the next round of batch extraction. The amount of each component leached was calculated as the product of the solution volume (assuming a density 1 g cm^{-3}) and the concentration, less the amount of the component present at the start of the leach period (the product of the entrained volume and the previous supernatant concentration).

Column Leaching Experiment

Column leaching experiments were performed in clear polyvinyl tubes (30.5 cm × 7.5 cm) screened at the base with a fine nylon cloth and a fitted rubber stopper with a valve inserted into it attached to a tube for control of leachate collection. The columns were packed with 500 g of soil homogenized with 5 g biochar. This represented an addition of biochar C equivalent to about 20% of the native soil organic carbon. Experimental control columns consisted of 5 g biochar homogenized with 500 g cleaned combusted quartz sand (450 ^{o}C, 3 h) or 500 g soil with no biochar, making a soil column 15 cm in height. At the start of each run, soils were saturated by adding distilled water filling columns to the level of the top of the soil surface. Water was added gently using a small sprinkler system to disperse the added water across the surface of the soil. In order to initially saturate the columns 200 mL of DI water was required for sand/biochar column but 350 mL of DI water was required for BY/biochar and GA/biochar columns. After waiting for approximately 4 h to remove any air pocket in the column and gain complete saturation, the columns were drained yielding 150 mL, 175 mL and 130 mL for sand, BY and GA, respectively. Thereafter, leaching was performed three times a day using 100 mL of DI water for each column representing 0.7, 0.6 and 0.4 soil pore volumes for sand, BY and GA soil columns, respectively. A total of 1 - 1.4 L water was

added to the columns over 3-4 d. The leachates were collected in 20 mL cleaned combusted vials and refrigerated prior to chemical analyses carried out within two weeks.

Nutrient Extraction

Nutrient extractions of biochar and soil/biochar mixtures were carried out with DI water and Mehlich 1 (M1) extractant. For the water extraction, the supernatant of the 1 d batch extraction was used. The M1 extraction solution was a 1:1 ratio of 0.05 M HCl and 0.025 M H_2SO_4. As with the water extraction 40 mL of the M1 solution was mixed with 0.5 g sample, shaken for 24 h, and centrifuged, and the supernatant was filtered using Whatman 40 filter paper. All the extracted solutions were stored in refrigerator prior nutrient analyses. The M1 extraction of biochar and soil materials was also carried out using the same M1 solution but extraction time was reduced to five minutes following the traditional way of procedure. Some selected biochar and soil samples were analyzed for total P and Fe using acid digestion method following AOAC 985.01 procedure.

Analytical Methods

All the batch extraction and column leaching samples were analyzed for DOC on a total organic carbon analyzer (Shimadzu TOC-5000A) after acidification to pH 2-3 with 1 M HCl and sparging for 2 min with carbon-free air to remove inorganic C. Total Kjeldahl N (TKN: organic N plus NH_4^+-N), NH_4^+-N, and NO_3^--N were measured using a continuous autoflow analyzer using EPA methods 351.2, 350.1, and 353.2, respectively. Total P and ortho P were measured using a Spectro Ciros CCD inductively coupled plasma spectroscope using EPA methods 200.7 and 365.1, respectively. All N and P analyses were carried out at the Analytical Research Laboratory, University of Florida.

Elemental C, and N were analyzed using Carlo Erba CHNS analyzer at Geological Sciences Department at University of Florida. Using these data, organic N was calculated as TKN minus NH_4^+-N while organic P was calculated as total P minus ortho-P. The TKN was measured in all batch and column leachates whereas NH_4^+-N, and NO_3^--N were only measured in selected initial and final leachate samples. Because little NO_3^--N was found in most of the samples, TKN is referred to here as N or total N unless otherwise specified.

Statistical Methods and Modeling

Most analyte concentrations were determined in duplicate samples. Methodical and instrumental QA/QC were controlled during the instrumental analyses of each nutrients (DOC, N, P) by the requirement that duplicates of every tenth sample be within 10% error. Regression analyses, which were used to predict long term nutrient release rates and correlation between parameters, were performed using Microsoft Excel (MS, 2003) tool pack.

Results

Batch Extraction Results

Fresh biochar samples released large amounts of DOC, N and P into water that in general, decreased exponentially with time, or rather, with leachate volume (Fig. 3-1). Initial release of P was greater than N, but decreased more rapidly so that N release was greater than that of P in later leachates. Lower temperature fresh biochars leached more nutrients (by 66, 67 and 23% for DOC, N and P, on average) than higher temperature biochars, on average, and grass biochars released more nutrients (by 22, 86 and 56% for DOC, N and P, on average) than oak biochars, on average. In the batch extraction experiment, the concentrations of the nutrients released in the first 40 mL of

water addition ranged from 355 to 4429 μg DOC g^{-1}, 0.0 to 302 μg N g^{-1} and 159 to1536 μg P g^{-1}. By the third batch extraction, after 120 mL of water addition, nutrient concentrations of all fresh biochars stabilized and ranged from 187 to 1255 μg DOC g^{-1}, 0.0 to 73 μg N g^{-1} and 0.0 to 224 μg P g^{-1} (Fig. 3-1).

Aged biochars displayed trends similar to fresh biochars in regards to greater nutrient release from grass versus oak and low versus high temperature biochars (Fig. 3-2). Most nutrient concentrations in leachate from aged biochars similarly stabilized by the third batch (after 120 mL), but there was a greater degree of variability compared to fresh biochars. In all cases, aged biochars released less DOC and P than fresh biochars by 35, and 89%, on average, respectively, but more N than fresh biochars by 12%, on average.

The various forms of nutrients in the first and last batch leachate collected are tabulated in Table 3-2 and calculated as percent compositions in Table 3-3. Nitrate release from biochar was low and constant at about 0.08 mg L^{-1} in both the initial and final leachate (or 0.16 mg g^{-1} biochar), and represented only between 3 and 14% of the total N in grass biochar leachate, but between 16 and 56% of the N in oak biochar leachate. Organic N was nearly absent from oak biochar leachates, but represented about 60% of the N in the initial grass biochar leachate and closer to 80% of the final one (Table 3-3). Organic P represented between 39 and 83% of the total P in biochar leachates initially, but was absent from the final biochar leachate.

Of the different nutrient extraction procedures tested to serve as proxies for biochar nutrient leaching potential, 24 h M1 yielded similar amounts of DOC and P, but about twice the amount of N as a 24 h water extraction (Table 3-4). In addition, the

traditional 5 min M1 extraction yielded about half the amount of P (40% on average) as the 1 d M1 extraction. For the aged biochar, 24 h water extraction yielded more DOC and TKN than M1 24 h water extraction, and the opposite was true for P. Among each biochar group, or all biochar groups combined, or even when combined with soil-biochar mixture extraction data, the amount of each nutrient, especially for DOC, extracted by one method was significantly correlated to that of each of the others listed in Table 3-5.

Column Leaching Results

Column leaching of biochar displayed some trends similar to those of batch experiments, but also processed some distinct features. Similar to the batch extractions, column leaching showed greater nutrient releases from low versus high temperature biochars (shown in sand/biochar columns: Figs. 3-3a, 3-4a, and 3-5a). Release of nutrients generally decreased over time, or rather with flush volume, but not exponentially as it did for the batch leachates. In fact, DOC release from Grass-250 biochar actually increased in the second flush. Amounts of nutrient release were generally stable until after about 700 mL flush volume. Initial concentrations as well as later stable concentrations of DOC, N and P released were much less (about 99% less) than those found in batch experiments for both grass biochars.

Due to their greater nutrient release rates, grass biochars (250 and 650 ^{o}C) were chosen for column experimentation in combination with soils. In general, soil/Grass-250 mixtures exhibited greater nutrients (DOC, N, and P) release throughout the column leaching experiments compared the soil-alone control (Figs. 3-3, 3-4, and 3-5). Soil/Grass-650 mixtures, however, exhibited equal or less nutrient release compared each soil-alone control. For the BY soil, for example, DOC, N and P release was 19, 3 and 69% greater, on average, when combined with Grass-250 biochar and 14, 31, and

77% less, on average, when combined with Grass-650 biochar, respectively. Differences were much smaller between nutrient release from GA soil and GA soil/biochar mixtures. These data suggest that the ability of soils to sorb either soil nutrients or the nutrients released by biochar will depend on soil and biochar type and possibly leachate amount and type.

The composition of biochar leachate varied with biomass type and as leaching of columns progressed (Table 3-2). Much as in batch leachates, NH_4^+ was largest source of N in most of the biochar leachates; however, organic N was only significant in the initial column leachates from Grass-250 biochar. Organic P represented a much greater portion of the P in column leachates compared to that of batch experiments, with initial organic P percentages ranging from 41 to 93% (Table 3-3). The initial column leachates from the BY soil had N forms distributed 3.3, 1.1 and 0.07 mg L^{-1} for organic N, NH_4^+, and NO_3^-, respectively (Table 3-2; organic N calculated as TKN minus NH_4^+). With Grass-250 biochar added, organic N in the initial leachate was 69% greater, NH_4^+ was 43% less and NO_3^- was unchanged. While BY soil had a similar organic N and NH_4^+ composition in its final leachate, there was a large spike in NO_3^-, reaching 19 mg L^{-1}. The addition of grass biochar resulted in major decreases in organic N and unchanged NH_4^+ composition in the final leachate, but even greater concentrations of NO_3^-, especially for the Grass-250 biochar. These N trends were similar for GA soil and GA-biochar combinations except that high concentrations of NO_3^- were not measured in the final column leachates (Table 3-2). Phosphate in leachates from BY soil and BY/biochar combinations was consistently dominantly inorganic P, while that of GA soil and GA-biochar combinations was consistently dominantly organic (Table 3-3).

Discussion

The trends observed in the data must be explained by considering both the processes that may have released nutrients from the biochar or soil, as well as those that may consume it such as sorption. In addition, there may be microbial reactions which consume or transform nutrient forms prior to their release from the soil. First we examine the biochar-alone nutrient data before considering nutrient dynamics in soil-biochar systems.

Nutrient Release Controlled by Biochar Properties

Cumulative release of DOC, N and P from biochar-alone in the batch extraction studies (1.05 L total water volume) ranged from 1247 – 7073, 44 – 269, and 727 – 1500 mg kg^{-1}, respectively, and are comparable to that found in other biochars (Gaskin et al., 2008; Gundale and DeLuca, 2006). The small amount of N released from biochars has been noted by others (Gaskin et al., 2010; Joseph et al., 2010; Yao et al., 2010), except in the case of chicken litter biochar (Chan et al., 2008), and has been attributed to the formation of heterocyclic N compounds (so-called “black N”) which cannot be solubilized easily (Knicker, 2007; Knicker, 2010).

Batch extraction and column leaching results indicated similar trends in DOC, N or P release. That is, greater nutrient yields came from lower versus higher temperature biochars, from grass versus oak biochars, and from fresh versus aged biochars. Extraction concentrations of both DOC and N from biochar were most strongly correlated with biochar surface properties such as micropore surface area (CO_2-SA), acid functional group density (AFG, Table 3-6), indicating that some kind of surface exchange reaction may be the source of these nutrients. However, DOC release was also significantly correlated, although to a lower degree, to VM content, indicating that

VM does not likely contain N or P and that for DOC, dissolution may also be a release mechanism of importance. Interestingly, biochar mineralization rates have also been found to be strongly correlated with VM content (Zimmerman, 2010), suggesting that leaching of C from biochar may be a big factor in making it accessible to microbes.

In contrast to DOC and N, there were fewer significant correlations between surface properties and extractable P except ash content (Table 3-6). Instead, ash content was strongly related to both water and M1 P extraction and the latter was also correlated with biochar pH. This suggests an exchange process with the inorganic component of biochar as the dominant mechanism for P release. These results are supported by the work of others that have found biochar P to be mainly found in the ash fraction, with pH-dependent reactions and presence of chelating substances controlling its solubilization (DeLuca, 2009).

Nitrate was found to represent a very small portion of the N leached from the biochars tested (or from the soil for that matter), as found by others (Gaskin et al., 2008; Yao et al., 2010), justifying the use of TKN analyses (NH_4^+-N and organic N) as an estimator of total N in other portions of the experiments. Further research will be required to understand the reasons behind the large difference found here between the organic N/NH_4^+-N ratio in oak versus grass biochars, and in column versus batch extraction experiments.

Soil Biochar Interaction and Nutrient Leachates

These experiments clearly show that nutrients (DOC, N and P) are released from biochar into water. However, biochar soil amendment may not necessary result in nutrient leaching from soils if these nutrient forms are readily sorbed by soils. In addition, biochar may be strong sorbents of nutrient forms released naturally from soils,

resulting in the often observed net reductions in nutrient leaching from biochar-amended soils. The cumulative amount of DOC, N and P leached from soil/biochar columns, 81 – 172, 5 – 12, and 0.2 – 25 mg kg^{-1}, were not typical of nutrient leaching measurements made in a range of unamended soils (Alva, 2006; Qiang et al., 2004; Yang et al., 2008). However, the nutrient retention capacity of various soils is known to vary dramatically.

An estimate of the amount of released nutrients that may have been sorbed, one can compare the cumulative amount of nutrients predicted to have been leached from soil and biochar separately (i.e. the additive amount assuming no interaction) with that from columns containing corresponding soil-biochar mixtures (measured, including soil-biochar interactive). In Fig. 3-6, greater predicted (non-interactive) cumulative release of nutrients after 1000 mL of volume of water addition (shown in wider open bars) than that actually measured (shown in thinner striped bars) indicates loss of leachate nutrients due to soil-biochar interaction. All combinations of soil and biochar showed net losses of DOC, N and P except in the case of DOC from the GA/Grass-650 column, in which there was a net gain due to soil-biochar interaction (Fig. 3-6). Whereas one study found the presence of humic acids to increase biochar P dissolution (Yao et al., 2010), this was not borne out by the present study. The greatest losses of DOC and N were in the BY soil columns (in the 20-40% range for all). Losses of P ranged from 16-35% in BY-biochar columns and about 97% in GA-biochar columns. Mixtures of soil with higher temperature (650 ^{o}C) biochars lost DOC, N and P to greater degrees than those with lower temperature (250 ^{o}C) biochars in all cases except for DOC from GA columns.

Explanations for the generally lower amounts of nutrients leached from soil-biochar columns compared to that expected given the amount of soil and biochar

present individually, include - 1) the microbial consumption/production of nutrients which may have been stimulated in the soils by the presence of biochar or biochar leachates, 2) sorption of soil nutrients by biochar, and 3) sorption of biochar leachate nutrients by soil. The first mechanism, while possibly occurring to some degree, is not considered to predominate because the period of column flushing experiments were relatively short, 3 - 4 d, whereas microbial growth and activity response to biochar addition typically on the order of weeks to months (Bruun et al., 2008; Zimmerman et al., 2011) and typically display a lag, exponential and stationary growth phases. It is notable, however, that the large amounts of NO_3^- in the final leachates of BY soil columns were even greater in BY/biochar columns. This may be attributed to the occurrence of nitrification (oxidation of NH_4^+ or organic N) provided by biochar leachates.

There is evidence for the occurrence of both interaction mechanisms #2 and #3. First, the nutrient release curves, at least for BY soil, bear some similarity to typical breakthrough curves, providing evidence for the interaction of leached nutrients with this soil. Second, in some cases, more DOC, N or P was missing and presumed sorbed, than was released by only the biochar (for example, for DOC or N onto BY/Grass-650) or only the soils (for example, for P onto GA/Grass-250 or GA/Grass-650). Patterns of nutrient loss also provide evidence for both the effects of sorption by both soil and biochar. For example, P in leachates from GA columns was nearly all in organic form, indicating that all phosphate had been sorbed. This would be expected from a soil rich in Fe and Al oxyhydroxides (Harrison and Berkheiser, 1982; Rhoton and Bigham, 2005) as the selected Ultisol collected from Georgia state typically is high in iron content (Levi et al., 2010). Neither DOC nor N (which would have occurred as both organic N and

NH_4^+) in leachates from BY/biochar columns was sorbed to a great extent. The greater nutrients sorption (for DOC, N and P) in BY soil columns onto high versus low temperature biochar suggests the process of biochar nutrient sorption given the greater surface area and OM sorption capacity of higher temperature biochars (Kasozi et al., 2010).

Long Term Prediction of Biochar Nutrient Leaching

Nutrient release rates occurring in the later stages of column experiments (the last four data points collected) were used to predict trends in longer term nutrient leaching. This is justified since linear correlation coefficients (R^2) for plots of cumulative nutrient versus cumulative leachate volume were always greater than 0.98, that is, release rates were constant. Assuming these leaching rates do not change significantly with further water addition, the nutrients predicted to be leached from the experimental soil/biochar columns with a water addition equivalent to one year of average rainfall in Gainesville, Florida (122.8 cm, or 5.4 L added to the experimental columns) were calculated. Results for additive soil-alone and biochar-alone and that predicted from soil/biochar mixtures are shown in Fig. 3-7.

The trends in one-year predicted nutrient release were little different than those measured during the experiments (1000 mL cumulative water addition). One can generalize the findings by saying that DOC, N and P leach rates in biochar-amended soil will not be greatly different from that of the soil alone. In many cases, the enhanced nutrient release from the added biochar seems to have been countered by the sorption of soil nutrients by the same biochar. In a few cases where low temperature biochar was applied, however, nutrient release was predicted to increase, such as DOC from GA/Grass-250 and P from BY/Grass-250. Also, it should be kept in mind that the

species of each nutrient released may change, with a trend toward retention of organic forms of N and P, and a possible increase in NO_3^- release, which was not accounted for in Figs. 3-6 and 3-7.

Comparison of Nutrient Release from Batch Extraction and Column Leaching

Total cumulative nutrients released from biochar-alone in batch and column experiments, normalized to biochar weight (μg g^{-1} biochar), were compared in Fig. 3-8. Curves showing nutrient release from biochar columns, while starting lower due to the amounts of water added initially, come close to connecting with and continuing the line trend of those of biochar columns which start at higher water volume. This indicates that measurement of nutrient release from biochar was only slightly affected by contact time and energy of mixing, both of which were much greater in batch compared to column experiments, and may account for the slightly enhanced N and P release rates in the batch data. The lack of difference between batch and column suggests that there was no kinetic inhibition in the release of nutrients by biochar, but for each biochar, was mainly dependent upon water added. This implicates a solid-solution equilibrium-driven dissolution as the main biochar nutrient release mechanism. Similarly, a number of studies have found no difference between batch extraction and column leaching of polyaromatic hydrocarbon compounds from soils (eg. Comans, 2001; Kalbe et al., 2008). These finding contrasts with that of some other studies which have found greater metal leaching (Dalgren et al., 2011) and greater mobilization of colloids (Bergendahl and Grasso, 1998) from soils in batch versus column studies. In any case, column leaching is time consuming, troublesome and lengthy procedure compared to batch extraction. The above indicates that batch extraction experiments may provide sufficient information to predict nutrient leaching trends for a particular biochar under

consideration for soil amendment. But a single extraction is even simpler to carry out than a series of batch extractions.

While, arguably, the best predictor of long term nutrient mobility was obtained from the slope of the last four points of the column leaching data, extrapolated to one year of rainfall (CL_y, shown in Fig. 3-7), this is also the most difficult parameter to measure and calculate. Thus, this parameter was compared with other simpler measures of nutrient leaching derived by batch (i.e. water and M1 extraction) and column approaches to identify a better option to assess the potential of a biochar to release nutrients (Table 3-5). Many of the parameters were significantly inter-correlated for DOC, indicating that carbon loss could be assessed by a variety of methods. However, both N and P long-term losses could only be assessed using the concentration in the final column leachate. The 24 h M1 extraction proved to be a poor predictor of long-term nutrient loss but was similar to 24 h batch water extraction in many regards. Thus, a column leaching experiment is probably the best predictor of long-term nutrient leaching in biochar-amended soils. This is most likely due to the various ways in which soil may interact with biochar. For example, further study is still warranted in some cases as we have observed changes in the N and P species extracted over the course of experiments.

Summary and Environmental Implications

Biochar application to soil has shown promise to increase crop yield in the fields or pot trials (Major et al., 2010b; Steiner et al., 2008b; Steiner et al., 2007). Specific beneficial chemical effects include increased pH, reduction of aluminum acidity and toxicity (Glaser et al., 2002; Tryon, 1948), nutrient and pesticide retention (Glaser et al., 2002; Jones et al., 2011; Lehmann and Joseph, 2009; Major et al., 2010b). But the

effects of biochar on soil fertility are not always straightforward and can vary by soil and biochar type and time period. For example, a recent study showed that maize yield did not significantly increase in the first year after wood biochar application, but increases of 140% over the control soil occurred during the fourth year of the study (Major et al., 2010b). The present study and others (eg. Zimmerman et al., 2011) show how changes in nutrient and OM dynamics in soil/biochar systems occur over time and may be expected to have time-dependant effects on associated microbial and plant productivity.

This study also highlights the importance of choosing the appropriate biochar to add to any given soil when planning a biochar amendment project. As sandy soils are less able to retain nutrients, a higher temperature or aged biochars should be used as they have a lower tendency to release nutrients. This is less of a concern in acidic or oxide-rich soils which themselves have a great deal of nutrient retention capacity. This may be the reason that biochar addition to tropical soils (Oxisols) in the Amazon, the hypothesized method for producing *terra preta*, was so effective in producing long-lasting fertile soils. Biochar amendment to organic-rich soils are less likely to affect nutrient dynamics, or fertility for that matter, as biochar neither releases nor retains quantities of nutrients significantly different from the humic matter already present in these soils.

A number of processes relating to nutrient dynamics in biochar-amended soils were not addressed in this study. One relates to the altered microbial community composition (Khodadad et al., 2011) or activity (Zimmerman et al., 2011), that may occur with biochar addition. Greater mineralization or OM solubilized from biochar might occur with greater time allowed for the development of biochar-adapted microbial

communities. Another is the possible enhancement of fungal activity due to biochar addition, leading to either competitive utilization or mutualisitc hyphae-root associations. Lastly, it is known that biochar will lend greater water retention and aeration conditions to soils (Chan et al., 2007). Its effects in this regard were not accounted for in these experiments carried out under water-saturated conditions.

Additional major conclusions of this study are that 1) DOC and N release from biochar could be related to biochar micropore surface area and acid functional group density, whereas P release was correlated to inorganic ash content, 2) batch and column studies of biochar yield similar nutrient leaching results suggesting an equilibrium partitioning of nutrients into the aqueous solvent, and 3) biochar yields of DOC, from batch extraction, column leaching, and various extraction methods are linearly correlated. However, no quick extraction method was identified to serve as an indicator for long term N and P release.

Table 3-1. Selected characteristics of biochars and soils used in the study

Biochar or soil	Bulk composition (mg g^{-1})				Surface area (m^2 g^{-1})		pH
	C[c]	N[c]	P[d]	Fe[d]	N_2	CO_2	
Fresh Oak-250	626 ± 32	1.9 ± 0.3	0.4	0.2	1 ± 1	331 ± 66	3.5
Fresh Oak-650	755 ± 14	4.6 ± 0.4	0.9	0.0	225 ± 9	528 ± 57	9.1
Fresh Grass-250	494 ± 31	12 ± 2	1.4	0.1	3 ± 2	221 ± 106	4.5
Fresh Grass-650	557 ± 5	5.7 ± 0.4	3.3	0.2	77 ± 27	427 ± 115	10.0
BY Soil[a]	28 ± 0	2.0 ± 0.4	1.1	1.7	0.5 ± 0	9 ± 1	5.8
GA Soil[b]	29	1.1 ± 0.1	0.2	2.0	18 ± 0	32 ± 3	4.2

Notes:
Abbreviations: C = total carbon, N = total nitrogen, P = total phosphorus, Fe = total iron
a: BY soil = Gainesville, Florida, U.S.A., Entisol
b: GA soil = Big Canoe, Georgia, U.S.A., Ultisol (red clayey soil)
c: The values of C and N were taken from bulk elemental analyses using CHN analyzer
d: Total P and Fe were analyzed using total digested acid extraction procedure (AOAC 985.01)

Table 3-2. Concentration of nitrogen and phosphorus forms (all in mg L^{-1}) in first and last leachate of soil and soil/biochar columns

Batch or column test material	NO_3-NO_2		NH_4-N		TKN[a]		Ortho P		Total P	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Oak-250-(Batch[b])	0.07	0.07	0.38	0.07	0.38	0.05	4.23	0.18	7.11	0.08
Oak-650-(Batch[b])	0.07	0.09	0.13	0.07	0.13	0.0	0.92	0.26	1.99	0.20
Grass-250-(Batch[b])	0.08	0.08	1.25	0.11	3.06	0.89	9.7	0.29	15.87	0.02
Grass-650-(Batch[b])	0.08	0.09	0.14	0.18	0.49	0.93	5.31	2.49	30.49	1.28
Sand/Oak-250[c]	0.11	0.05	0.68	0.21	0.48	0.13	0.11	0.79	0.72	1.20
Sand/Oak-650[c]	0.09	0.09	0.22	0.24	0.15	0.05	0.01	0.14	0.11	0.14
Sand/Grass-250[c]	0.07	0.04	1.39	0.30	3.45	0.35	10.54	1.88	17.81	5.78
Sand/Grass-650[c]	0.09	0.05	0.29	0.24	0.17	0.12	0.39	4.11	0.76	4.54
BY Soil[c]	0.07	19.46	1.10	1.47	4.40	4.46	2.72	4.46	3.53	4.80
BY/Grass-250[c]	0.09	33.86	0.63	1.54	6.22	3.16	6.40	8.40	8.71	9.44
BY/Grass-650[c]	0.46	21.23	0.93	1.65	3.55	2.64	3.62	4.88	6.48	5.51
GA Soil[c]	1.59	0.04	0.83	2.22	3.51	2.91	0.03	0.01	0.21	0.04
GA/Grass-250[c]	0.06	0.04	0.34	2.88	5.19	4.11	0.02	0.02	0.56	0.06
GA/Grass-650[c]	0.04	0.04	0.43	2.04	4.29	2.81	0.04	0.03	0.54	0.09

Notes:
a: TKN = Total Kjeldahl Nitrogen
b: Batch extraction experiments, sampled after 40 mL (first) and 200 mL (last) cumulative leach volume
c: Column leaching experiments, sampled after 100 mL (first) and 1000 mL (last) cumulative leach volume

Table 3-3. Proportion of organic nitrogen (Organic N) and phosphorus (Organic P) in first and last leachates of soil and soil/biochar columns

Batch or column test material	% Organic N		% Organic P	
	Initial	Final	Initial	Final
Oak-250-(Batch[a])	0	0	41	0
Oak-650-(Batch[a])	0	0	54	0
Grass-250-(Batch[a])	58	80	39	0
Grass-650-(Batch[a])	61	74	83	0
Sand/Oak-250[b]	0	0	85	34
Sand/Oak-650[b]	0	0	93	0
Sand/Grass-250[b]	59	13	41	67
Sand/Grass-650[b]	0	0	49	10
BY soil[b]	74	13	23	7
BY/Grass-250[b]	89	4	27	11
BY/Grass-650[b]	65	4	44	11
GA soil[b]	53	23	85	83
GA/Grass-250[b]	92	30	96	73
GA/Grass-650[b]	89	27	93	64

Notes:
a: Batch extraction experiments, sampled after 40 mL (first) and 200 mL (last) cumulative leach volume
b: Column leaching experiments, sampled after 100 mL (first) and 1000 mL (last) cumulative leach volume

Table 3-4. One-day water and Mehlich 1 extractable dissolved organic carbon (DOC), Total Kjeldahl Nitrogen (TKN) and phosphorus (P) (μg g^{-1}) and traditional Mehlich 1 extractable phosphorus (5 min) from fresh and aged biochars, soil/biochar mixtures and soils

	Water extractable			Mehlich 1 extractable			
Material	DOC	TKN (1 day)	P	DOC	TKN (1 day)	P	P (5 min)
Fresh Oak-250	3065	0	569	3517	72	530	172
Fresh Oak-400	1522	15	285	2234	30	321	105
Fresh Oak-650	355	0	159	147	32	493	129
Fresh Pine-250	0	28	76	2556	47	52	30
Fresh Pine-400	819	14	25	668	26	80	1
Fresh Pine-650	259	14	11	190	15	11	1
Fresh Grass-250	4429	302	1536	5800	245	1270	652
Fresh Grass-400	3275	174	1362	4638	186	2563	868
Fresh Grass-650	755	21	578	424	40	2439	1131
Aged Oak-250	1272	102	24	874	53	49	11
Aged Oak-400	1127	31	54	841	28	253	nm
Aged Oak-650	338	0	29	213	41	319	65
Aged Pine-250	1267	26	4	801	59	10	nm
Aged Pine-400	783	33	8	515	25	22	nm
Aged Pine-650	264	17	0	186	27	5	nm
Aged Grass-250	2692	162	42	1901	174	51	18
Aged Grass-400	1892	99	223	1395	138	1065	nm
Aged Grass-650	843	63	111	366	73	1197	281
BY/Oak-250	499	82	28	918	97	623	nm
BY/Oak-650	449	70	22	857	87	574	nm
BY/Grass-250	501	79	25	931	91	589	nm
BY/Grass-650	510	80	26	894	88	666	nm
BY Soil	438	125	24	847	192	602	379
GA Soil	187	15	0	1493	48	3	1

Notes:
nm: not measured

Table 3-5. Linear correlation coefficients (R^2) for relationships between various nutrient extraction methods and column leachate concentrations of dissolved organic carbon (DOC), Total Kjeldahl Nitrogen (TKN) and phosphorus (P) using biochar, soil, and soil/biochar mixtures. The underlined regression coefficients are significant at $p < 0.05$ level while those assigned asterisk are also significant at $p < 0.001$ level

		W_i[a]	W_f	M1	CL_i	CL_f
DOC	W_f	*0.99				
	M1	*0.97	0.97			
	CL_i	0.00	0.77	0.03		
	CL_f	0.15	0.94	0.06	0.74	
	CL_y	0.91	0.91	0.04	0.76	*0.99
TKN	Wf	0.35				
	M1	*0.86	0.23			
	CL_i	0.25	0.25	0.32		
	CL_f	0.01	0.59	0.07	0.79	
	CL_y	0.02	0.00	0.10	0.77	*0.98
Total P	Wf	0.02				
	M1	0.23	0.85			
	CL_i	0.11	0.10	0.02		
	CL_f	0.21	0.72	0.00	0.27	
	CL_y	0.24	0.33	0.13	0.26	0.76

Notes:
a: Concentration of nutrient in initial (24 h) batch water extraction (W_i), final (day 20) batch water extraction (W_f), 24 h Mehlich 1 extraction (M1), initial column leachate (CL_i), final column leachate (CL_f), and cumulative nutrient release predicted after one year of column leaching i.e. 5.4 L (CL_y)

Table 3-6. Linear correlation coefficients (R^2) for relationships between concentrations of various nutrients extracted during one day by water (W) and Mehlich 1 solution and biochar properties (n = 18, includes fresh and aged biochars). Underlined regression coefficients are significant at $p < 0.05$ level while those assigned asterisk are also significant at $p < 0.001$ level

Extraction type	pH	Volatile matter	Ash content	N_2-SA	CO_2-SA	CEC	Total acidity	AFG density
W-DOC	0.05	0.29	0.13	0.20	0.42	0.00	0.25	*0.64
W-TKN	0.03	0.15	0.19	0.09	0.25	0.05	0.07	0.44
W-P	0.03	0.03	0.30	0.03	0.14	0.08	0.24	0.56
M1-DOC	0.07	0.27	0.06	0.10	0.35	0.06	0.48	*0.81
M1-TKN	0.02	0.15	0.27	0.10	0.25	0.03	0.08	0.45
M1-P	0.38	0.03	*0.83	0.00	0.01	0.00	0.00	0.08

Notes:
Abbreviations: M1= Mehlich 1 extraction, W= water extraction, CO_2-SA= micropore surface area determined by CO_2 adsorption, N_2-SA = mesopore surface area determined by N_2 adsorption, CEC = cation exchange capacity, AFG density = acid functional group content normalized to micropore surface area, DOC = dissolved organic carbon, TKN = Total Kjeldahl Nitrogen, P = phosphorus

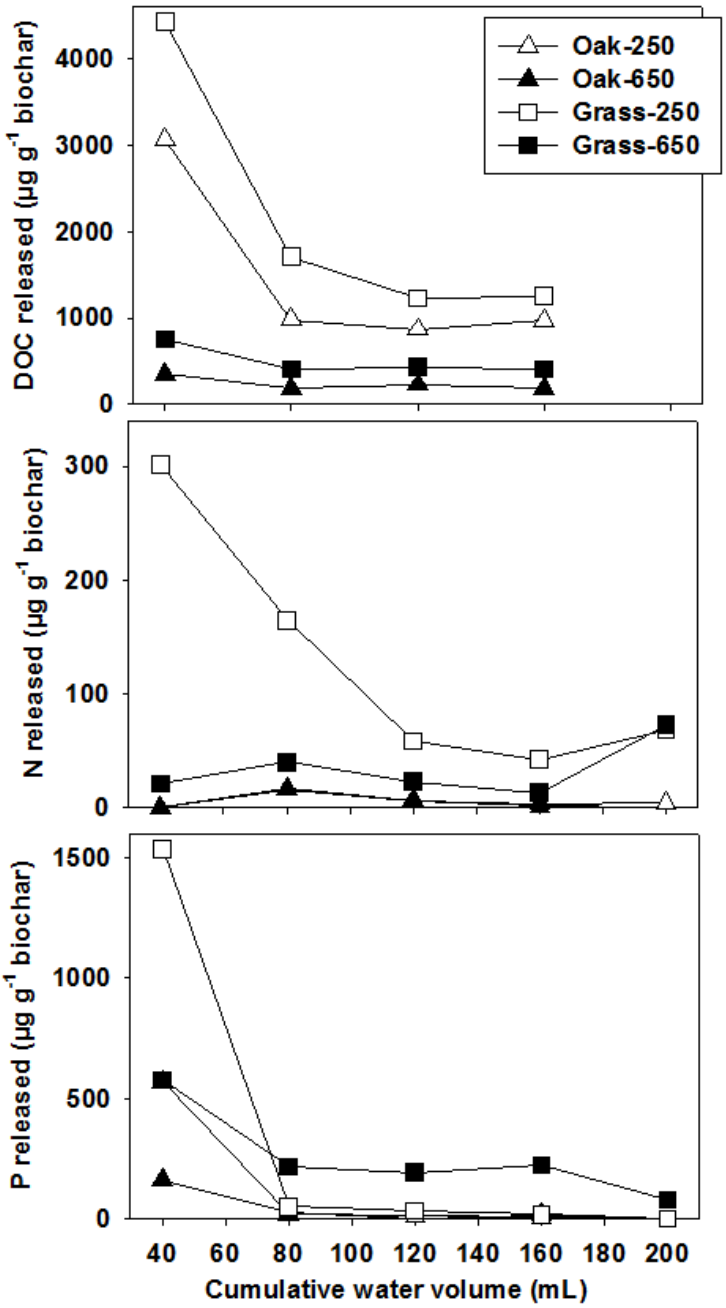


Figure 3-1. Nutrient (DOC, Total Kjeldahl Nitrogen, Total P) concentration in leachates of successive aqueous batch extractions of fresh biochars (with supernatant replacement) versus cumulative water volume

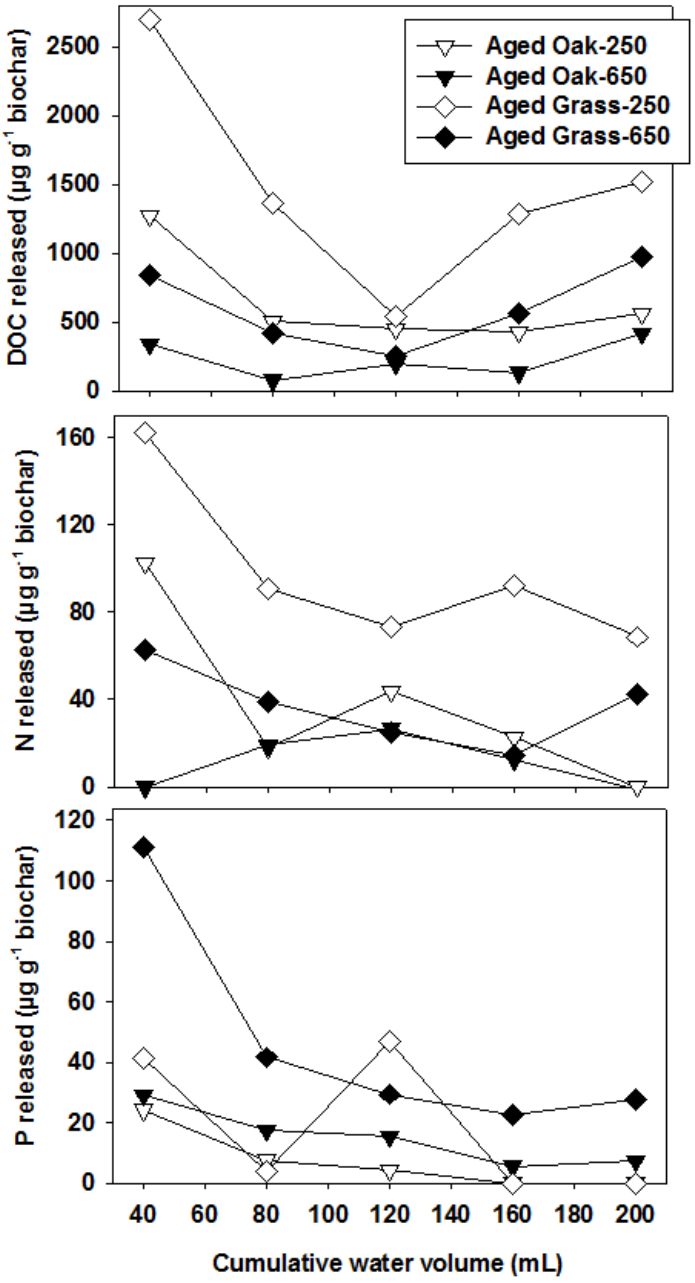


Figure 3-2. Nutrient (DOC, Total Kjeldahl Nitrogen, Total P) concentration in leachates of successive aqueous batch extractions of aged biochars (with supernatant replacement) versus cumulative water volume

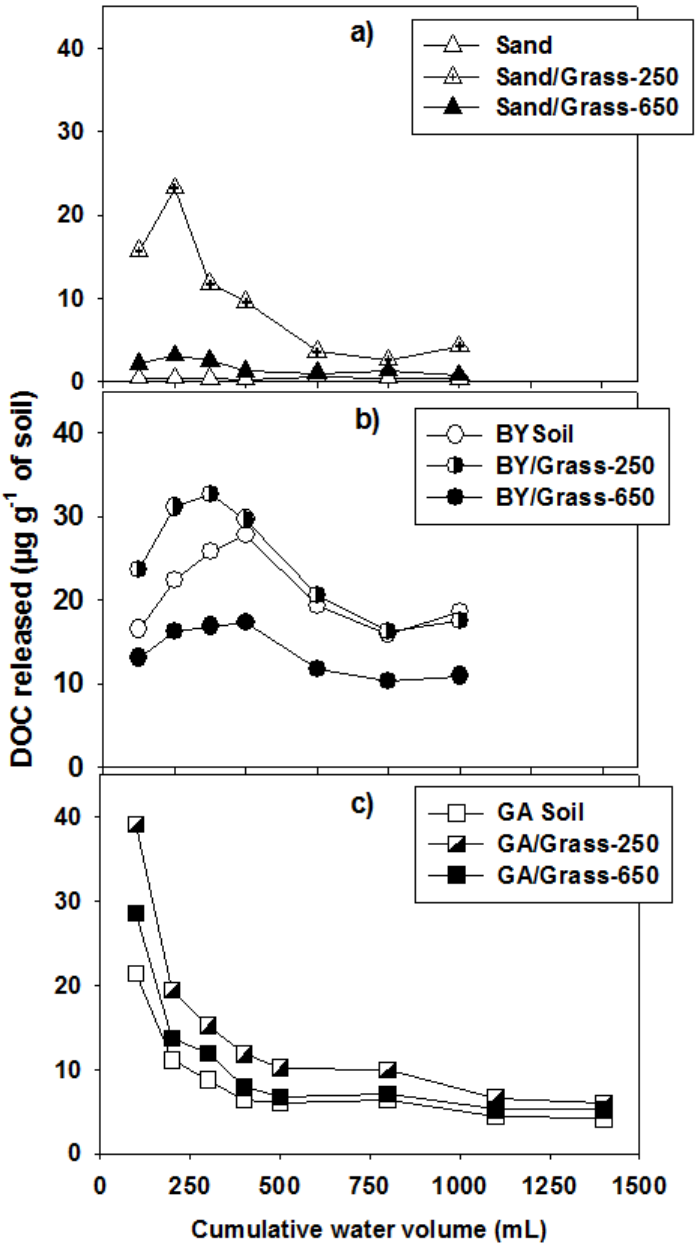


Figure 3-3. Total dissolved organic carbon (DOC) in leachates of successive biochar-quartz sand and biochar-soil column flushes versus cumulative water volume

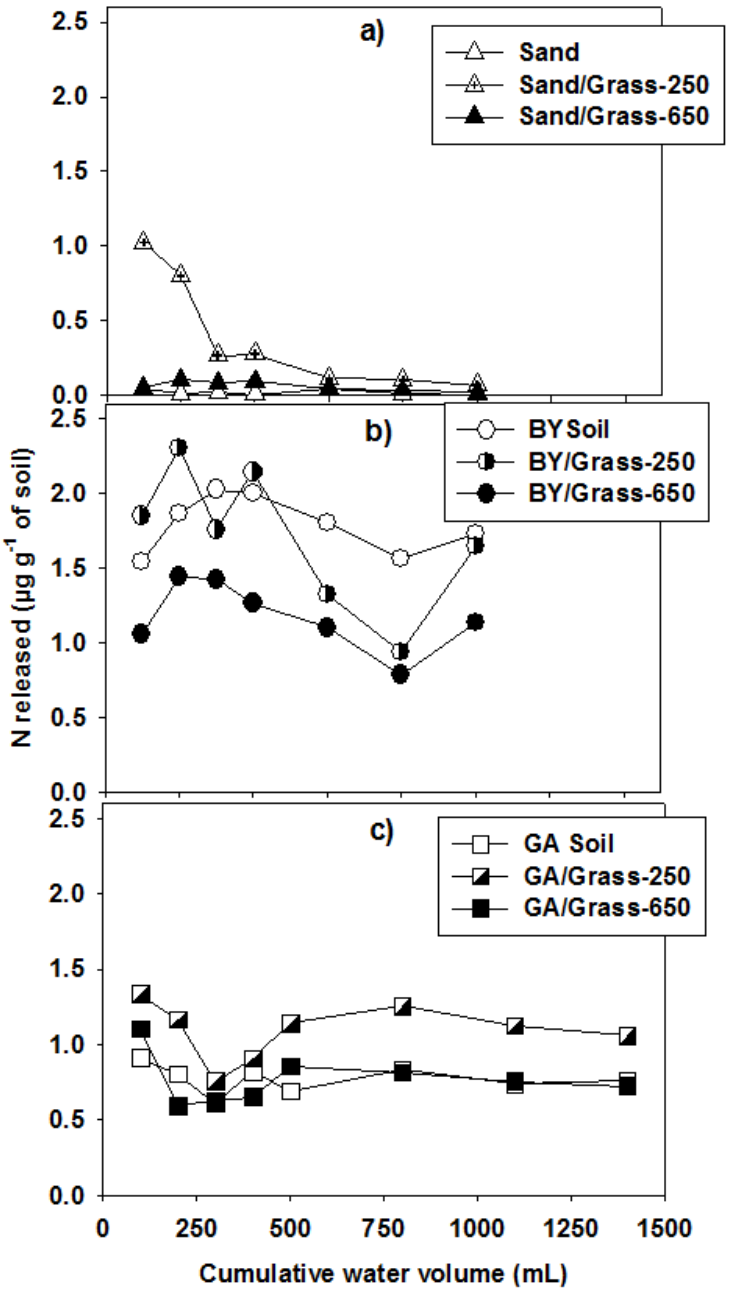


Figure 3-4. Total Kjeldahl Nitrogen (N) in leachates of successive biochar-quartz sand and biochar-soil column flushes versus cumulative water volume

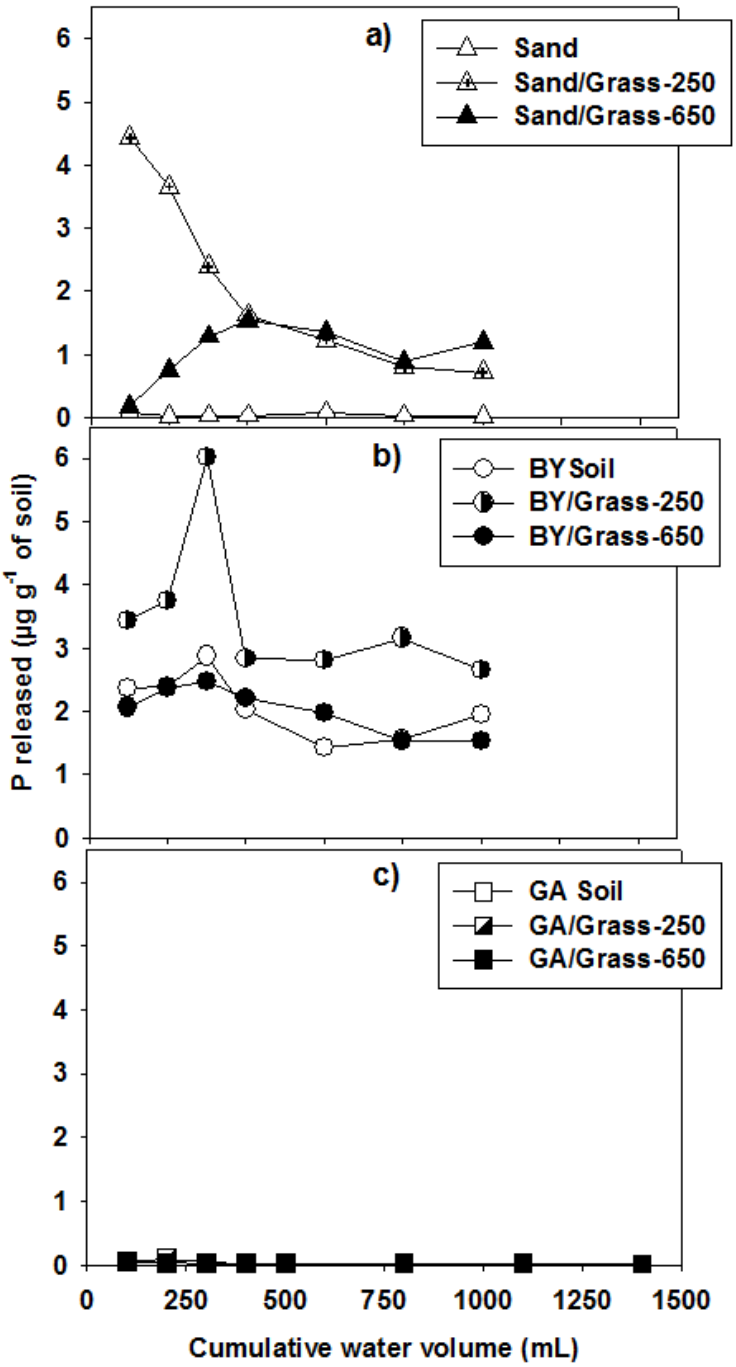


Figure 3-5. Total phosphorus (P) in leachates of successive biochar-soil column flushes (and biochar-quartz controls) versus cumulative water volume

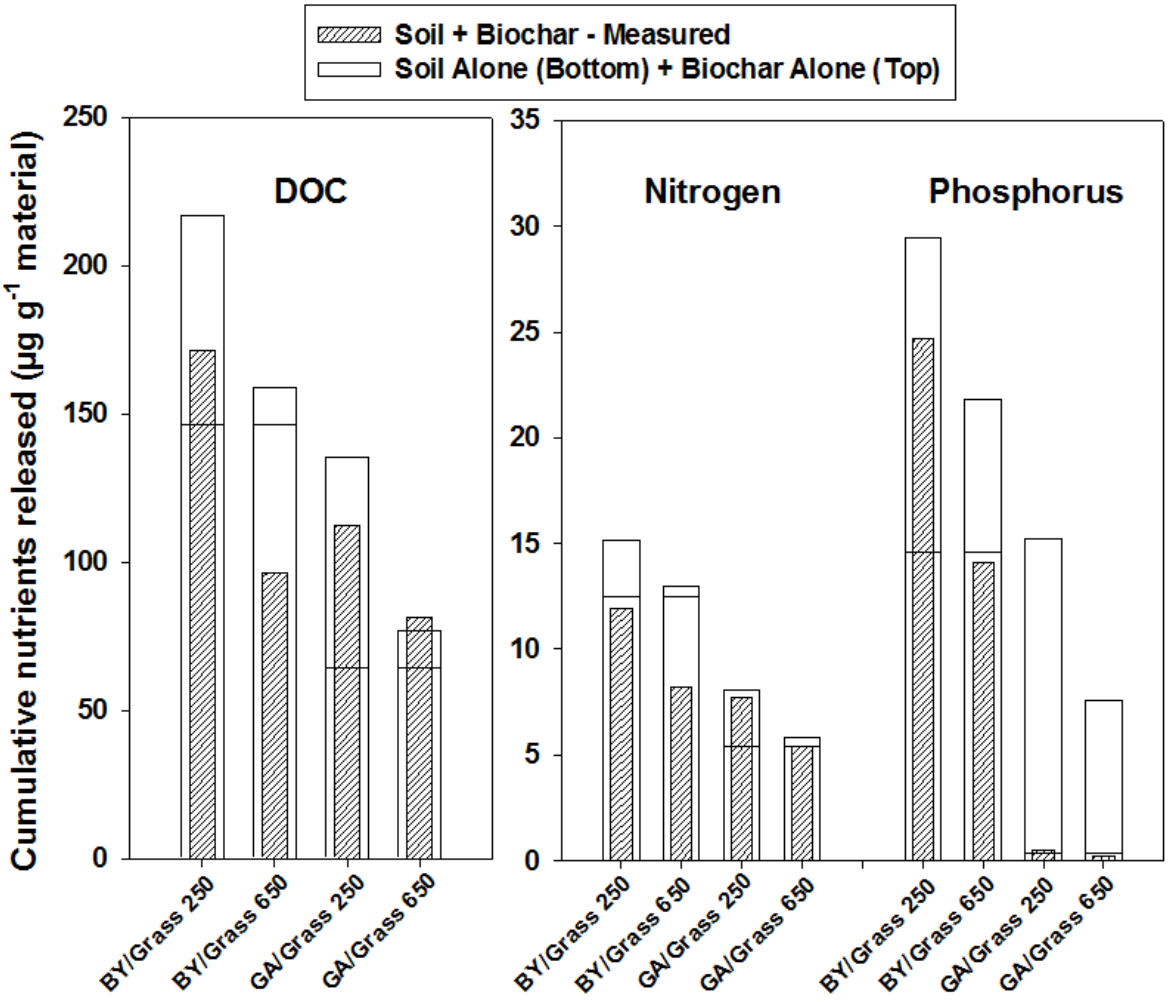


Figure 3-6. Cumulative amount of nutrients released after 10th flush (1000 mL) from BY and GA soil/biochar columns (Note the different y-axis scales)

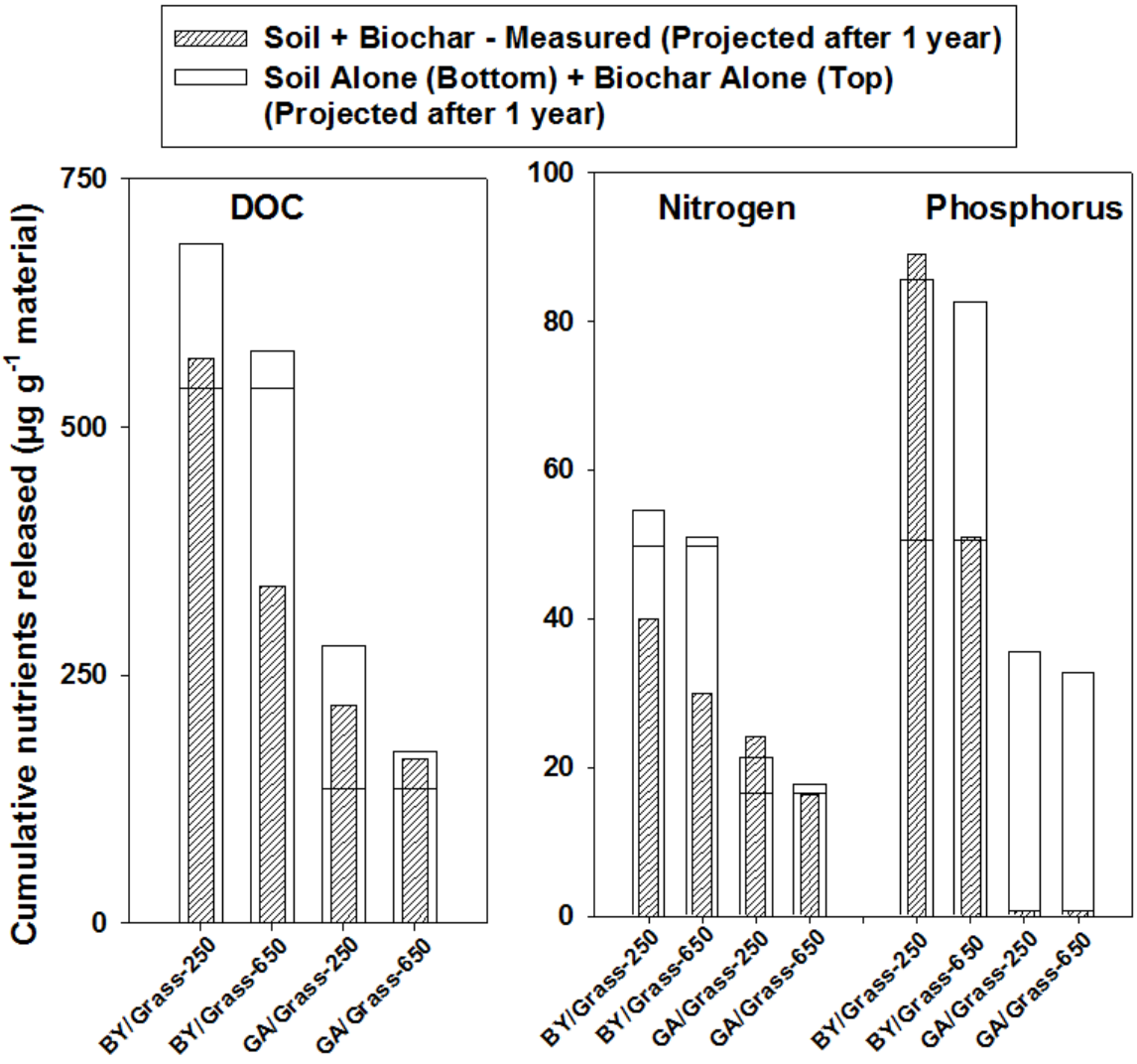


Figure 3-7. Projected cumulative nutrients released after one year of average North Florida rainfall (122.8 cm) based on column leaching rate data (Note the different y-axis scales)

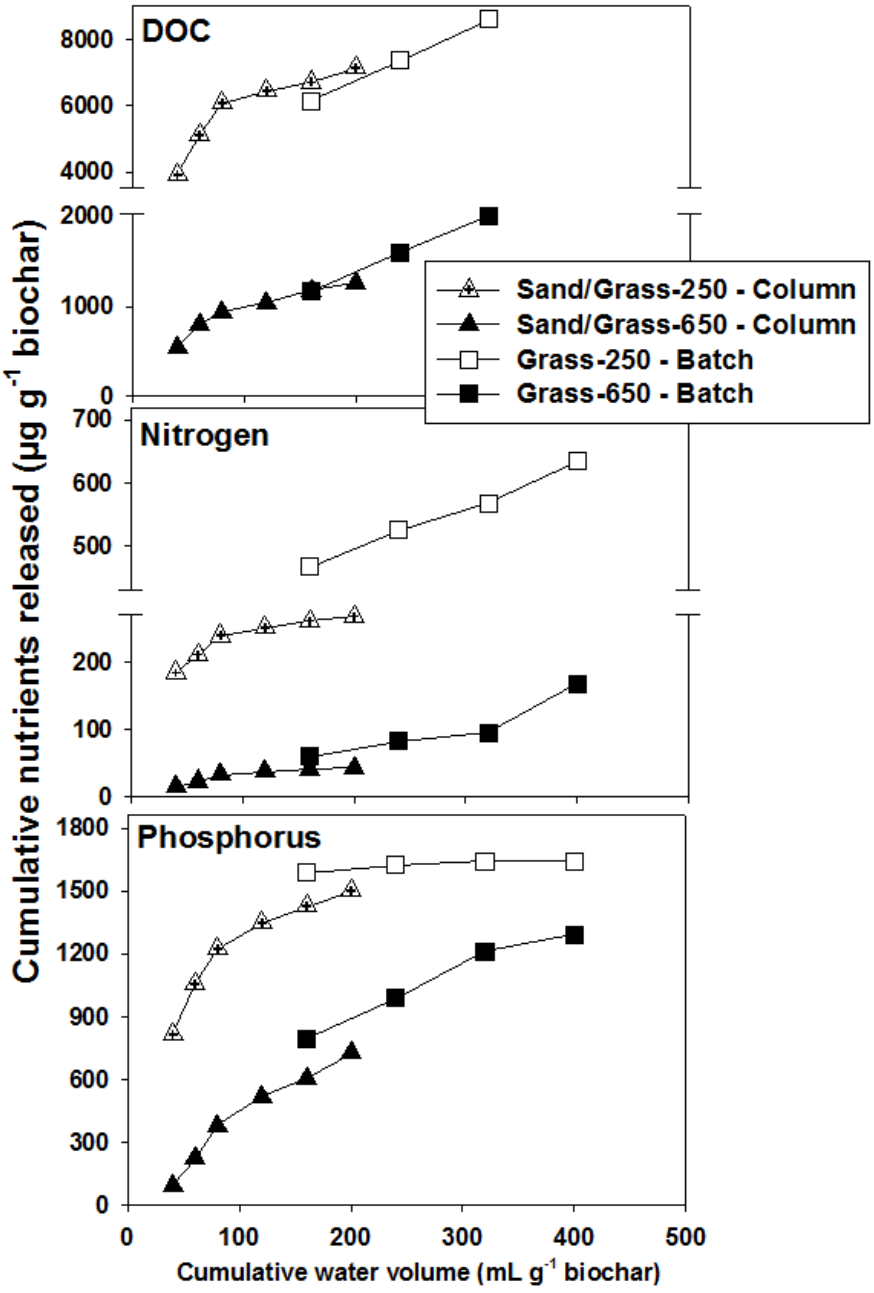


Figure 3-8. Cumulative nutrients released from successive batch extraction and column biochar leaching experiments versus cumulative water volume added

CHAPTER 4
COMPARISON OF SELECTED CHARACTERISTICS OF FRESHLY LABORATORY-PRODUCED AND FIELD-AGED BIOCHARS

Literature Review

Biochar is the carbonaceous product of biomass obtained by removing water and other volatile components when plant or animal biomass is subjected to heat treatment. This may occur in the presence of oxygen (referred to as here simply as combustion) or without oxygen (referred to here as pyrolysis). Biochar has been used for many centuries such as metal smelting, beginning in 2000 BCE. More recently, research on biochar has focused on its possible use for soil C sequestration, soil amelioration or soil remediation. The general characteristics of biochar which may make it well-suited to these purpose are its abundant and refractory organic carbon (Glaser et al., 2001a; Glaser et al., 2002; Glaser et al., 2004a; Glaser et al., 2001b), high CEC (Mukherjee et al., 2011), and high OM and organic compounds sorptive ability (Kasozi et al., 2010; Smernik, 2009). However, it has become quite clear that these characteristics can vary a great deal, thus some biochars are better suited to certain applications than others.

Properties of Fresh Biochars

Freshly-produced biochars have been shown to have a range of characteristics, depending upon their parent biomass type and temperature, including surface charge (Mukherjee et al., 2011), low to medium CEC (Lehmann, 2007; Lehmann and Joseph, 2009; Mukherjee et al., 2011) and high AFG (Mukherjee et al., 2011; Rutherford et al., 2008; Rutherford, 2004). The VM, ash content, pH, and surface area of the fresh biochars were also reportedly correlated to biochar production temperatures (Mukherjee et al., 2011). Elemental composition has been also found to vary markedly among biochars produced at different temperatures and from various feedstocks such as peas,

pitch pine wood, chestnut wood, and sawgrass (Braadbaart et al., 2004; Brown et al., 2006; Hammes et al., 2006). For example, Baldock and Smernik (2002) found that the elemental molar ratios of H/C, O/C, H/O all decreased, while the N/C ratio increased, when *pinus resinosa* sapwood was heated from 150 to 300 ^{o}C. Relative to C, progressive loss of elemental H and O may indicate the formation of structures with aromatic rings and the increase in N/C ratio suggests inclusion of heteroatom in the fused aromatic ring structure. With further heating to 350 ^{o}C, the H/C ratio continued to decrease, but O/C and H/O ratios increased and N/C ratio decreased. These changes indicate that the nature of material heated above 350 ^{o}C differed from the material heated at lower temperatures as the resulting char chemistry changes.

Properties of Aged Biochars

While it is clear from the above that biochar chemical and physical characteristics vary with production conditions, there are also some studies which suggest that its characteristics also vary with time, referred to here as „aging". For example, some studies showed that aged biochars produced higher CEC than fresh biochars due to greater oxidation on biochar surfaces leading to higher amounts of carboxylic functional groups compared to fresh biochars over time (Cheng et al., 2008; Cheng et al., 2006a; Liang et al., 2006). Oxidation of fresh biochar particles may begin on the surface (Lehmann et al., 2005), creating negatively charged surface functional groups (Cheng et al., 2006a; Liang et al., 2006) consequently leading to high CEC and oxygen content due to formation of carboxylic functional groups as suggested by Boehm titration and FTIR spectroscopic analyses (Cheng et al., 2008; Cheng et al., 2006a; Liang et al., 2006). It was also reported that one year laboratory incubated saturated, unsaturated and alternating saturated-unsaturated conditions increased carboxylic and OH

functional groups of corn stover and oak biochars compared to initial stage parameters (Nguyen and Lehmann, 2009). Cheng et al. (2008) compared fresh, that is, newly produced biochars, to 130 years naturally oxidized historical or aged and one year incubated biochars and showed increase in oxygen concentration, formation of carboxylic and phenolic surface functional groups, disappearance of surface positive charge and formation of surface negative charge from fresh to aged biochar materials. Liang et al. (2006) showed higher aromaticity and surface oxidation of aged biochars based on O/C ratio obtained by microprobe elemental analysis. But a comparison of these ratios in fresh and aged biochars produced from a range of biomass types and over a range of temperatures is lacking. Here we compare the bulk and surface chemical characteristics of a range of fresh biochars to their aged counterparts. Biochars were and soil/biochar mixtures were field-aged for nine months under north Florida climatic conditions.

Thus, the goals of this study were: 1) determination of a range of characteristics such as, pH, surface functional groups acidity, VM, exchange capacities of the aged biochars and compare these properties with freshly produced biochars, 2) documentation of changes in biochar chemical and physiological properties over time, 3) assessment of changes in exchange capacities of soil/biochar mixture after nine months aging, and 4) get insight of prospects of biochar amendment for long term fertility of various soils. These results could be used to identify the types of biochar which may be more suited to any specific purpose.

Materials and Methods

Materials

Biochar was produced from *Quercus lobata* (Laurel oak: Oak), *Pinus taeda* (Loblolly pine: Pine), and *Tripsacum floridanum* (Gamma grass: Grass) by combustion for 3 h at 250 ^{o}C in an oven under limited oxygen and at 400 and 650 ^{o}C in a pyrolyzer continuously flushed with 99% pure gaseous N_2 (designated hereafter as Oak-250, Grass-650, etc.). Detailed information on biochar preparation and chemical and physical characteristics of the freshly prepared biochars were presented elsewhere (Kasozi et al., 2010; Mukherjee et al., 2011). Only the coarse (0.25 –2 mm) size fraction, separated by sieve and quickly rinsed with double distilled water to remove ash, was used in these experiments. In addition, biochar of each type was „aged" by placing in plastic 2.5 quart containers, screened above and below with 0.5 mm fine-mesh metal screening as well as landscaping cloth above for shade, so that weathering by air and precipitation but not sunlight and macro-organisms could occur for a period of nine months (Dec. 2009 – Sep. 2010). During this period, in north central Florida, the average temperature was 69 ^{o}F, and 92.1 cm of total precipitation fell, all as rain, with 60% occurring during the period from May to September. Among all the aged biochars, only a subset of four samples (oak and grass, 250 and 650 ^{o}C biochars) were analyzed for selected characteristics such as acid surface functional groups, CEC and AEC.

To study the effect of soil interaction on biochar chemistry over time, and vise versa, the four biochars were mixed and incubated with a sandy Florida Entisol (assigned name as: BY) and a Spodosol (assigned named as: PR). The soils were collected from 0-10 cm depth of surface horizon in a forest located in southwest Gainesville, Alachua County, Florida (BY), and at the border of Alachua and Marion

County, Florida (PR), respectively. The soils were sieved (2 mm) to remove plant roots, vegetation, and air dried for four days before mixing with biochars. For each biochar, 6 g biochar was mixed with 2.6 kg air-dried soil, making a biochar weight percentage of 0.23. This mixture of biochar and soil was sub-sampled and put into 2.5 quart size plastic pails screened as described above, but in this case, the pails were buried in the forest soil to a depth even with the soil in the pail (about 20 cm from pail bottom). Samples were buried from Dec. 10, 2009 until Sep. 5, 2010 and were kept free from debris by periodic removal of forest litter. The average temperature during these nine months at the site was 69 ^{o}F and the total rainfall was 92.1 cm.

Analytical Methods

The analytical methods used here were specifically chosen for or adapted to the examining of the chemical and physical characteristic of biochar and are described under Materials and Methods section in Chapter 2 of this dissertation. The detailed descriptions of determination of pH, VM, ash content, surface area, elemental analyses, CEC, AEC, and surface AFG were also listed elsewhere (Mukherjee et al., 2011). Briefly, the 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 and pH was recorded Ultra basic pH meter (Denver Instruments) after waiting 2 h equilibration time. The VM content was determined as weight loss after combustion in a ceramic crucible with a loose ceramic cap at 850 – 900 ^{o}C for 6 min and ash content was determined as weight loss after combustion at 750 ^{o}C for 6 h with no ceramic cap. The mesoporous (>1.5 nm diameter) surface area was measured using N_2 sorptometry at 77 K using Brunauer, Emmet, and Teller (BET) theory (Brunauer, 1938) and microporous surface area (<1.5 nm diameter) was

measured using CO_2 sorptometry at 273 K using grand canonical Monte Carlo simulations of the non-local density functional theory (Jagiello and Thommes, 2004). Elemental C, H and N were analyzed using Carlo Erba CHNS analyzer and the O concentration was calculated by subtracting the sum of C, H and N weight from the total weight of the sample (Baldock and Smernik, 2002) assuming biochars were consisted of only C, H, N, and O. In order to determine CEC and AEC of biochars, KCl solution was used to replace all surface ions with K^+ and Cl^- ions. Then the K^+ and Cl^- were replaced by mass action with ions of another salt and CEC and AEC was calculated from the K^+ and Cl^- released, respectively, accounting for entrained salt (Mukherjee et al., 2011). Biochar surface AFG distribution was determined using the Boehm titration method (Boehm, 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, 1 mL of aliquot from each filtrate was mixed with 10 mL of excess 0.05 M HCl 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).

Some selected biochar and soil samples were analyzed for total P, K, Ca, Mg, and Al using acid digestion method following AOAC 985.01 procedure. All of the data

presented are means ± standard deviation of duplicate analyses unless otherwise stated. Means, standard deviations and regression correlation coefficients were computed using Microsoft 2003 Excel software. The one tail t-test was performed using Microsoft Excel data analysis tool pack in order to determine the significant differences between the O/C ratios and phenol content of fresh and aged biochars.

Results

The pHs of the aged oak and grass biochars increased with increasing biochar production temperatures and ranged from 3.7 to 7 (Fig. 4-1). The average pHs of all the biochars made from all parent materials were 4.1 ± 0.1, 5.8 ± 0.3, and 6.8 ± 0.2 for 250, 400 and 650 ^{o}C, respectively. Compared to the fresh biochars, the aged biochars showed less pH variation with biochar parent biomass types (Fig. 4-1).

The average mesopore surface areas (via N_2 sorptometry) of 250 and 650 ^{o}C aged biochars were 2.6 ± 2.6, and 36 ± 16, respectively, while the average micropore surface areas (via CO_2 sorptometry) of 250 and 650 ^{o}C biochars were 223 ± 17, and 534 ± 5, respectively (Table 4-1). Thus, low-temperature aged biochars had little of their surface in the mesopore range, i.e. were predominantly microporous, similar to fresh biochars (Mukherjee et al., 2011).

Similar to fresh biochars (Mukherjee et al., 2011), the phenolic and carboxylic acid functional groups (AFG) of aged biochars decreased with increasing biochar production temperatures (Fig. 4-2) and no lactonic acid was detected. The concentrations of total AFG ranged from 1.9 to 5.6 $mmol_c\ g^{-1}$, phenolic AFG ranged from 0.8 to 3.8 $mmol_c\ g^{-1}$ and carboxylic AFG ranged from 0.8 to 2.2 $mmol_c\ g^{-1}$ for all the aged biochars examined in this study. The increase in phenolic functional groups during aging was not statistically significant ($p > 0.05$, one tail t-test, n = 4). However, the average phenolic

functional group content represented 56% of total AFG for aged biochars (Fig. 4-2) which was about two fold higher than that of fresh biochars (Mukherjee et al., 2011).

The VM and ash content of aged biochars were similar to that of fresh biochars , i.e. within the statistical error, for both oak and grass biomass types except for the lower ash content of aged Grass-650 biochar compared to its fresh counterpart (Table 4-1).

The CECs of aged biochars were not pH-dependent and ranged from 93 to 222 $cmol_c\ kg^{-1}$ at near neutral pH for all aged biochars examined (Fig. 4-3). At near neutral pH, the he average CEC of aged 250 ^oC was not significantly higher than 650 ^oC aged biochar (161.2 ± 53.6 $cmol_c\ kg^{-1}$ versus 149.8 ± 65.7 $cmol_c\ kg^{-1}$). On average, aged grass biochar (193 ± 60.7 $cmol_c\ kg^{-1}$) had higher CEC than aged oak biochar (118.1 ± 19.5 $cmol_c\ kg^{-1}$). The CEC of aged biochars was up to 10 times greater than that of fresh biochars for both 250 and 650 ^oC biochars (Fig. 4-3). The CEC trends of aged biochars showed no pH dependency as higher temperature fresh biochars (Mukherjee et al., 2011).

While the AECs of fresh biochars were negligible (Mukherjee et al., 2011), the AEC of aged biochars were significant (shown as a negative number in Fig. 4-3) and showed no pH dependency. The AEC of all aged biochars ranged from 38.1 to 87.1 $cmol_c\ kg^{-1}$ at near neutral pH. The average AEC of lower temperature aged biochar (58 ± 18.1 $cmol_c\ kg^{-1}$) was similar to higher temperature aged biochars (60.8 ± 28.5 $cmol_c\ kg^{-1}$) at near neutral pH. However, aged grass biochars (72.3 ± 26.8 $cmol_c\ kg^{-1}$) had significatnly greater AEC than aged oak biochars (46.5 ± 7 $cmol_c\ kg^{-1}$).

The CEC and AEC of soil-biochar mixtures was not pH-dependent and ranged from 10 to 25 $cmol_c\ kg^{-1}$ and 3 to 10 $cmol_c\ kg^{-1}$, respectively, and was much less than

aged biochars alone (Figs. 4-3, 4-4). However, they displayed similar trends as the biochar alone. For example, the CEC of BY/grass biochars were an average of two-fold greater than BY/oak biochars. The CEC and AEC of PR soil and PR/biochar mixtures were measured only at around pH 7 and ranged from 15.3 to 22.2 $cmol_c\ kg^{-1}$, and 6.5 to 9.3 $cmol_c\ kg^{-1}$, for CEC and AEC, respectively (Table 4-3).

Discussion

The aged biochars had surface characteristics quite different than their fresh biochar counterparts (such as pH, surface functional group acidity, CEC, AEC, surface area), but similar bulk properties (such as elemental, VM, and ash content). An examination of the trends and inter-realtionships between these parameters can provide clues as to the chemical processes which occur during the aging of biochar.

Aging Processes of Biochars

About half of the biochar total AFGs were was lost during nine months of aging in the Florida climate. These losses were mainly carboxylic surface AFGs with little change in phenolic or lactone functional groups. Paradoxically, the pHs of aged biochars were similar for 250 ^{o}C biochars, and even less for 650 ^{o}C biochars, than that of fresh biochars (Fig. 4-1). This fact might be explained by the high VM content of both fresh and aged biochars. VM of aged biochars was significantly correlated with pH, total AFG and micropore surface area (Table 4-4) and was similar to that of fresh biochars (Mukherjee et al., 2011). On the other hand, the difference in O/C ratios of fresh and aged biochars (Table 4-2) was not statistically significant (as $p > 0.5$). The similar oxygen content in the aged biochars compared to fresh ones strongly indicates conversion of carboxylic to other types of oxygen containing acid functional groups on aged biochar surfaces. Although Cheng and Lehman (2009) also found decreases in

pH, they recorded increases in surface AFG during aging and ascribed it to increased formation of carboxylic functional groups. A possible explanation is that acidic functional groups may have developed that were not measured by Boehm titration such as hydroxyl groups, as suggested by a recent study (Nguyen and Lehmann, 2009).

The VM content was proposed to be responsible for the observed pH dependent CEC of the fresh low temperature biochars (Mukherjee et al., 2011). However, in this study, the CEC increased compared to the fresh biochars after one year aging (Fig. 4-3) even though there was no significant VM change over time (Table 4-1). The higher amount of CEC of aged biochars compared to fresh biochars suggests that not only the VM or AFG of the biochar surface control the exchange capacity as described for the fresh biochars (Mukherjee et al., 2011), but there might be some other factors such as soil-microbe interaction that could control CEC of aged biochars. The higher CEC of aged biochars compared to fresh ones due to generation of oxygenated surface functional groups by surface oxidation process was reported in recent studies (Cheng and Lehmann, 2009; Cheng et al., 2008; Cheng et al., 2006b). However, in this study the decrease in carboxylic acid surface functional groups during aging could not support the hypothesis of surface oxidation and generation of oxygenated surface. In addition, various studies reported that, due to loss of surface positive charge, AEC of biochars decreased over time (Cheng and Lehmann, 2009; Cheng et al., 2008; Cheng et al., 2006b). In contrast, this study found an increase in AEC during the nine months of biochar aging time.

While some have recorded only an increase in CEC during aging (Cheng and Lehmann, 2009; Cheng et al., 2008; Cheng et al., 2006b), we observed increases in

both the CEC and AEC during the aging period.This suggests that both cations and anions will be attracted to the biochar surfaces in the soil. Liang et al. (2006) found the presence of both anions (Cl^-) and cations (K^+) on the aged biochar surface, also suggesting the possible development of positive surface charges during aging.

There was no significant correlations ($p < 0.05$) found between the CEC of and other surface variable properties of aged biochars (Table 4-4). So the source of the increase in cation and anion exchange capacities which occurs during biochar aging is far from clear. At present, our data point to three likely processes - 1) conversion of carboxylic to other types of AFG, 2) addition of hydroxyl or other types of oxygen containing functional groups as suggested by other studies (Nguyen and Lehmann, 2009), and 3) adsorption of microbially-derived OM onto the biochar surface (Laird et al., 2010b; Liang et al., 2006). All of these processes would occur, most likely to an even greater extent, in the presence of soil with native OM and microbial populations.

Aging Processes in Biochar/Soil Mixtures

As one might expect, the addition of a material with a higher CEC and AEC (aged biochar) to soil with a lower CEC and AEC will result in a soil with a somewhat higher CEC or AEC (i.e. a weighted additive value). But the critical question is whether the aged soil/biochar mixture will have a CEC or AEC (or any other parameter of interest) different from the additive value, a difference which would indicate an interactive effect between soil and biochar. Compared to its additive value, the CEC and AEC of aged soil/biochar mixtures observed in this study were up to 45% and 42% greater, respectively (Table 4-3). The percent difference between measured and additive CEC and AEC was greatest for biochar mixed with the sandier, lower organic C soil (PR), but was much less or negative in all cases of aged BY soil mixed with biochar. This

suggests that, at least for the sandy, low organic C soil, biochar amendment positively interacted with the little organic C present, or stimulated the microbial community present, to create a soil with even more exchange capacity than would be expected from the quality of the biochar alone. Such a positive interaction may be the key to the development of fertile *terra preta,* over time, from typically infertile tropical soils. The nature of the positive interaction in the studied sandier soils may be related to release of pyrogenic dissolved OM such as organic acids or nutrients from the biochar which coat the exposed mineral surfaces in the soil and encourage microbial colonization, but this mechanism is very speculative at present. The less substantial positive interaction between soil and biochar in the forest soil may have been caused by OM sorption to the biochar surface, clogging pores and preventing OM and nutrient release or surface oxidation.

Laird et al. (2010a) estimated that a fine loamy Clarion soil mixed with biochar made from mixed hardwoods (oak and hickory) for 500 days significantly increased CEC by up to 20% relative to the control and they attributed this increase to surface oxidation of biochar and adsorption of organic acids by the biochar during aging. However, without separate examination of biochar-alone aged characteristics, it cannot be said if there was positive interaction in this case. However, the Boehm titration data of the current study suggested that the higher CEC and AEC of aged biochars in compared to fresh may be due to a change in surface functional group distribution rather than just the simple creation of more carboxylic acids via oxidation.

Environmental Implications

The findings of this study have important implications as to the effects of biochars amendments on soil chemistry and fertility. It may be that aging time and soil-microbe

interaction are both required to enhance beneficial qualities of soil such as exchange capacities when amended with biochars. The data of this study suggests that the surface and bulk chemistry of fresh biochars change over time including conversion of some AFG such as carboxylic acids and introduction of different types of AFG such as hydroxyl groups, and creation of surface exchange sites, both of which may enhance the ability of soils to retain nutrients and OM and encourage stable microbial populations. . In particular, the appearance of AEC during aging would decrease losses of phosphorous by leaching, and may explain the high phosphorous concentrations found in *terra preta*. The difference between the calculated additive properties of aged soil and biochar compared to its measured aged properties show a positive interaction, likely involving soil-biochar-microbes and OM. However, this positive interaction was greater for sandier soil than the re OM-rich soil, indicating that soil properties could also control the effects of biochar amendment. These finding suggest that pre-testing and careful strategies are needed in the matching of biochar type to soil type when carrying out amendment projects. However, more studies are required in order to (i) identify the new functional groups which were hypothesized to have been formed during aging, and (ii) investigate the mechanism(s) of exchange capacity increase during aging which are not fully explainable by the present data.

Table 4-1. Selected physical characteristics of fresh and aged biochars used in the study

Fresh and Aged Biochars	VM (%)	AC	SA ($m^2 g^{-1}$)	
			CO_2	N_2
Fresh Oak-250	66.0 ± 4.4	1.4 ± 0.1	331 ± 66	1.0 ± 1.0
Fresh Oak-400	51.9 ± 5.2	2.6 ± 0.2	252 ± 90	2.0 ± 1.0
Fresh Oak-650	36.4 ± 1.1	3.7 ± 0.2	528 ± 57	225 ± 9.0
Fresh Pine-250	61.1 ± 1.6	0.3 ± 0.1	373 ± 112	1.0 ± 0
Fresh Pine-400	58.6 ± 1.0	0.5 ± 0.2	361 ± 114	3.0 ± 2.0
Fresh Pine-650	25.2 ± 4.7	1.1 ± 0.1	643 ± 80	285 ± 102
Fresh Grass-250	62.5 ± 2.9	6.8 ± 0.2	221 ± 106	3.0 ± 2.0
Fresh Grass-400	51.4 ± 6.4	13.2 ± 0.2	164 ± 49	6.0 ± 6.0
Fresh Grass-650	33.0 ± 1.2	15.9 ± 0.5	427 ± 115	77 ± 27
Aged Oak-250	66.1 ± 0.9	2.0 ± 0.3	208 ± 17	0.6 ± 0.0
Aged Oak-400	50.2 ± 1.5	2.2 ± 0.2	283 ± 20	0.7 ± 0.0
Aged Oak-650	29.4 ± 4.3	2.9 (0.8	556 ± 10	35 ± 19
Aged Pine-250	63.7 ± 2.3	1.1 ± 0.5	249 ± 2	0.5 ± 0.1
Aged Pine-400	63.2 ± 2.5	1.1 ± 0.0	222 ± 14	1.7 ± 0.9
Aged Pine-650	24.7 ± 1.4	0.3 ± 0.2	577 ± 10	0.5 ± 0.1
Aged Grass-250	65.2 ± 1.4	7.7 ± 0.1	238 ± 17	4.6 ± 2.2
Aged Grass-400	53.1 ± 2.4	8.2 ± 0.5	237 ± 2	1.8 ± 0.1
Aged Grass-650	41.5 ± 3.1	10.0 ± 0.3	517 ± 9	39 ± 8

Notes:
Abbreviations: VM = volatile matter, AC = ash content, SA = surface area

Table 4-2. Total nutrient amounts in fresh and aged biochars and soil/biochar mixtures (from field) used in the study

Biochar or Soil/Biochar Mix	C[c]	N[c]	H[c]	P[d]	K[d]	Mg[d]	Ca[d]	S[d]	B[d]	Zn[d]	Mn[d]	Fe[d]	Cu[d]	O/C
						(mg g^{-1})								
Fresh Oak-250	626 ± 32	1.9 ± 0.3	31 ± 0.4	0.4	3.4	0.6	7.1	0.2	0.00	0.0	0.1	0.2	0.00	0.8
Fresh Oak-400	679 ± 57	3.7 ± 0.7	42 ± 0.7	1.3	6.4	1.1	11.8	0.2	0.01	0.0	0.2	0.0	0.00	0.4
Fresh Oak-650	754 ± 14	4.6 ± 0.4	28 ± 1.2	0.9	6.3	0.5	10.3	0.1	0.00	0.0	0.1	0.0	0.00	0.2
Fresh Pine-250	624 ± 4	0.0 ± 0.0	26 ± 0.7	0.1	0.6	0.5	2.4	0.1	0.00	0.0	0.1	0.0	0.01	0.7
Fresh Pine-400	758 ± 7	0.7 ± 0.9	37 ± 0.4	0.1	1.0	0.7	4.7	0.2	0.00	0.0	0.1	0.0	0.00	0.4
Fresh Pine-650	552 ± 0	0.0 ± 0.0	33 ± 0.4	0.1	0.5	0.2	2.7	0.1	0.00	0.0	0.1	0.0	0.00	0.2
Fresh Grass-250	494 ± 31	12 ± 2	36 ± 1.0	1.4	5.0	3.0	8.2	0.6	0.00	0.1	0.1	0.1	0.01	0.8
Fresh Grass-400	523 ± 4	14 ± 0.2	46 ± 0.1	4.2	15.3	3.7	9.9	0.6	0.01	0.2	0.2	0.1	0.01	0.6
Fresh Grass-650	557 ± 5	5.7 ± 0.4	30 ± 1.0	3.3	7.9	5.8	16.9	0.6	0.01	0.2	0.3	0.2	0.01	0.5
Aged Oak-250	594 ± 22	2.5 ± 0.3	47 ± 6.2	0.1	1.8	0.7	8.2	0.2	0.00	0.0	0.1	0.0	0.01	0.6
Aged Oak-400	710 ± 19	3.0 ± 0.7	50 ± 0.6	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.3
Aged Oak-650	813 ± 2	2.8 ± 1.2	76 ± 7.8	0.8	0.9	0.5	11.6	0.1	0.00	0.0	0.1	0.0	0.01	0.4
Aged Pine-250	560 ± 53	1.2 ± 0.6	56 ± 4.2	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.8
Aged Pine-400	634 ± 72	1.4 ± 0.4	46 ± 38	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.6
Aged Pine-650	780 ± 101	0.8 ± 0.8	90 ± 21	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.7
Aged Grass-250	575 ± 20	9.8 ± 1.2	43 ± 0.8	0.2	1.4	2.9	12.5	0.3	0.00	0.2	0.2	0.2	0.02	0.7
Aged Grass-400	635 ± 8	15 ± 2.1	27 ± 34	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.5
Aged Grass-650	704 ± 24	15 ± 1.8	35 ± 1.6	1.9	1.3	3.0	15.9	0.5	0.00	0.3	0.3	0.5	0.02	0.3

Table 4-2 Continued

Biochar or Soil/Biochar Mix	C[c]	N[c]	H[c]	P[d]	K[d]	Mg[d]	Ca[d]	S[d]	B[d]	Zn[d]	Mn[d]	Fe[d]	Cu[d]	O/C
						(mg g^{-1})								
BY[a]	27 ± 4	2.2 ± 0.3	4.7 ± 0.7	1.1	0.2	0.4	5.7	0.2	0.0	0.0	0.2	1.7	0.0	---
BY/Aged Oak-250[a]	49 ± 6	3.1 ± 0.3	7.1 ± 0.1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	---
BY/Aged Oak-650[a]	54 ± 4	3.4 ± 0.1	7.9 ± 0.3	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	---
PR[b]	3.3 ± 3.8	0.2 ± 0.2	0.7 ± 0.1	0.4	0.2	0.2	2.2	0.1	0.0	0.0	0.0	0.6	0.0	---
PR/Aged Oak-250[b]	10 ± 2	0.4 ± 0.1	0.8 ± 0.1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	---
PR/Aged Oak-650[b]	11 ± 0.0	0.5 ± 0.0	1.1 ± 0.1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	---

Notes:
a: BY: Gainesville, Florida, USA, Entisol
b: PR: Marion county, Florida, USA, Spodosol
c: The values of C, N, and H were taken from bulk elemental analyses using CHN analyzer
d: Total P, K, Mg, Ca, S, B, Zn, Mn, Fe, and Cu were analyzed using total digested acid extraction procedure (AOAC 985.01)
---: not applicable
nm: not measured

Table 4-3. Observed cation exchange capacity (CEC) and anion exchange capacity (AEC) of aged biochars and soil/biochar mixtures (from field) and that predicted from the arithmetic combination of aged biochar and soil; the change percentage is the difference between the observed and predicted CEC or AEC

Soil/Biochar	CEC at pH 7 ($cmol_c\ kg^{-1}$)					AEC at pH 7 ($cmol_c\ kg^{-1}$)				
	Soil	Biochar	Add	Obs	Change%	Soil	Biochar	Add	Obs	Change%
BY/Oak-250[a]	21.3	132.1	21.5	21.6	0.5	6.5	51.1	6.6	5.9	-11.4
BY/Oak-650[a]	21.3	92.7	21.4	12.9	-39.7	6.5	38.1	6.6	4.0	-39.2
BY/Grass-250[a]	21.3	146.2	21.5	22.3	3.6	6.5	46.8	6.6	7.0	6.2
BY/Grass-650[a]	21.3	222.1	21.7	25.3	16.6	6.5	87.1	6.7	7.4	10.8
PR/Oak-250[b]	15.3	132.1	15.6	20.5	33.5	6.5	51.1	6.6	8.7	32.6
PR/Oak-650[b]	15.3	92.7	15.5	22.2	44.8	6.5	38.1	6.5	9.3	41.7
PR/Grass-250[b]	15.3	146.2	15.6	21.5	40.2	6.5	46.8	6.6	9.2	40.5
PR/Grass-650[b]	15.3	222.1	15.8	19.9	29.9	6.5	87.1	6.7	8.1	21.2

Notes:
a: BY: Gainesville, Florida, USA, Entisol
b: PR: Marion county, Florida, USA, Spodosol
Abbreviation: Add = additive, Obs = observed

Table 4-4. Correlation coefficients (R^2) between various biochar properties. The underlined values are significant at $p < 0.05$ and those with an asterisk are significant at $p < 0.001$ level

Biochar properties	N_2 SA[a]	CO_2 SA[a]	VM[a]	AC[a]	pH[a]	CEC[b]	AEC[b]	TA[b]
CO_2 SA[a]	0.40							
VM[a]	0.26	*0.90						
AC[a]	0.30	0.00	0.00					
pH[a]	0.64	0.45	0.52	0.18				
CEC[b]	0.07	0.01	0.01	0.72	0.07			
AEC[b]	0.18	0.07	0.01	0.55	0.18	0.94		
TA[b]	0.97	0.97	0.91	0.11	0.96	0.03	0.10	
O/C[a]	0.48	0.14	0.19	0.12	0.71	0.03	0.14	0.84

Notes:
Abbreviations: SA = surface area, VM = volatile matter, AC = ash content, TA = total acid functional groups content
a: Total number of samples = n = 9
b: Total number of samples = n = 4

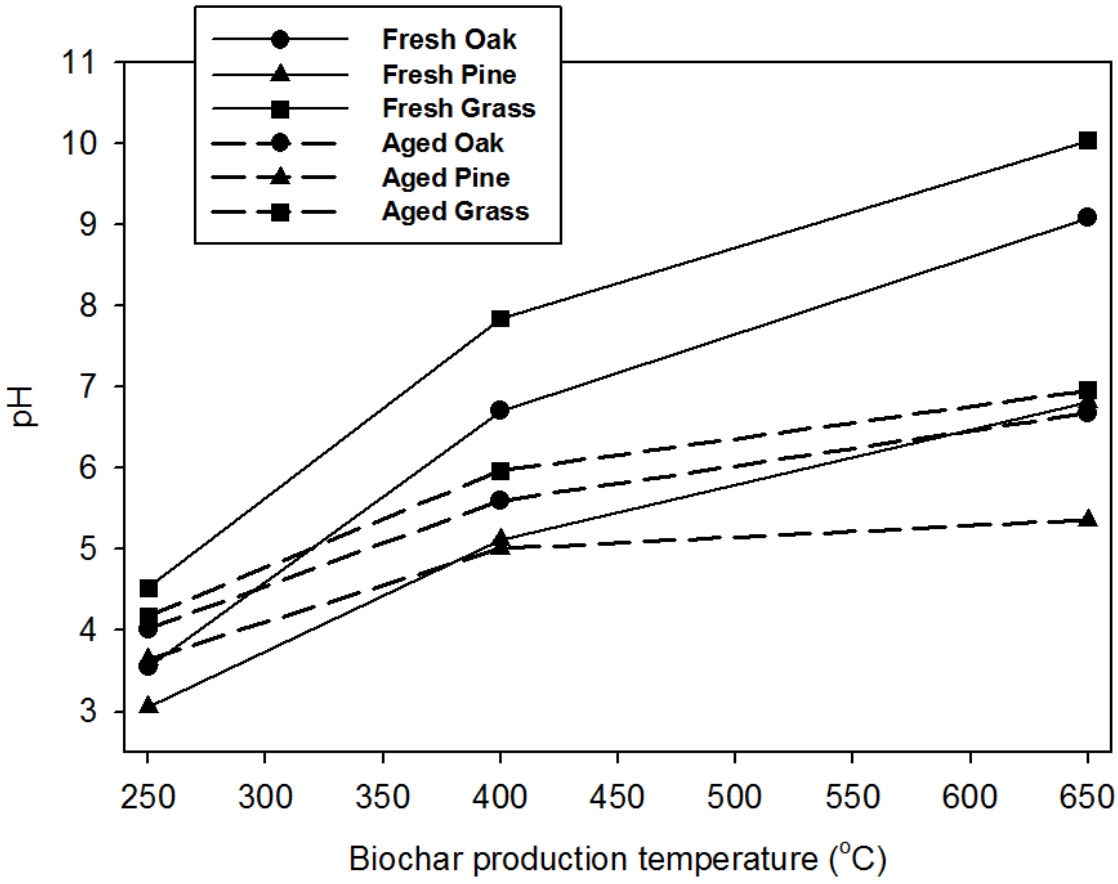


Figure 4-1. Comparison between the pH of fresh and aged biochars produced at different temperatures

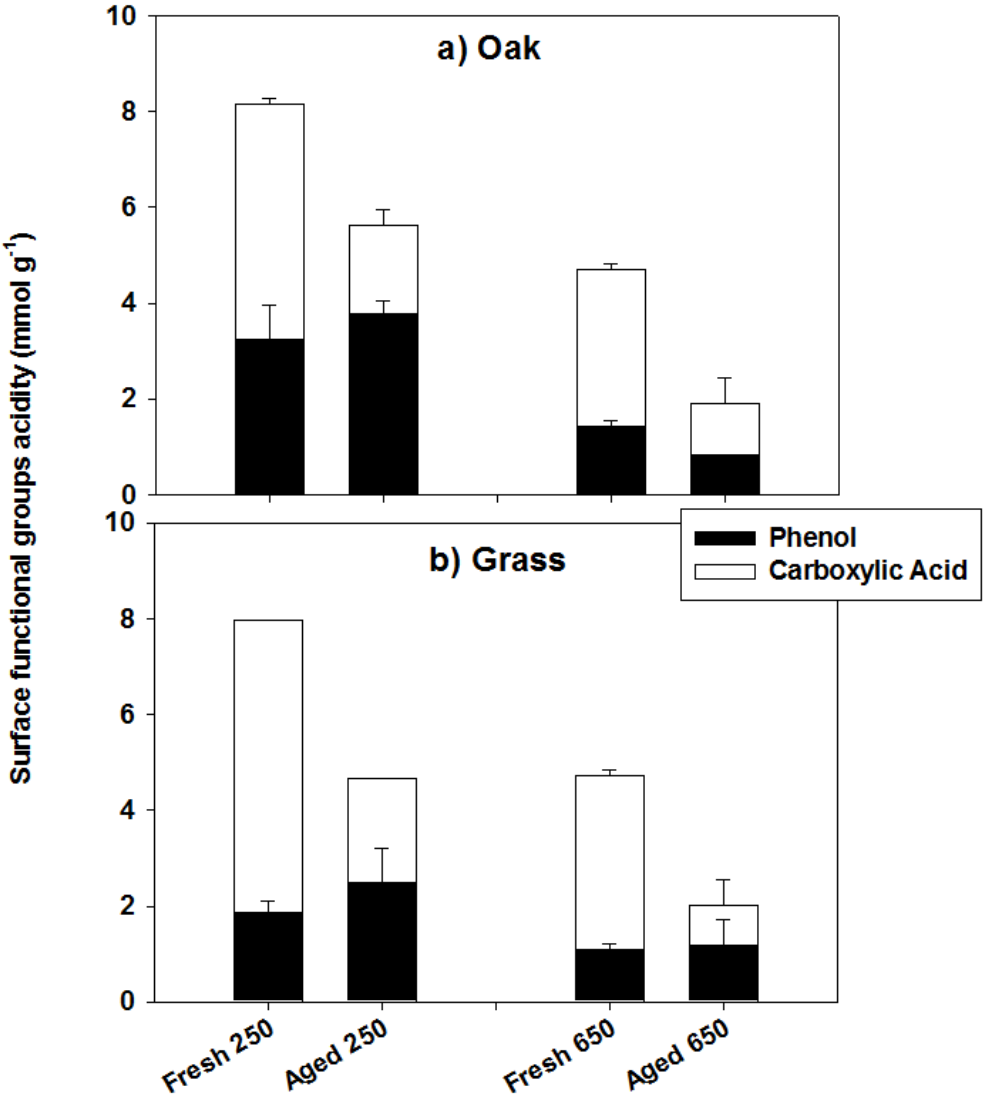


Figure 4-2. Comparison between the acidic surface functional group content of fresh and aged a) oak and b) grass biochars produced at two temperatures. All the stacked data are average of three analytical measurements

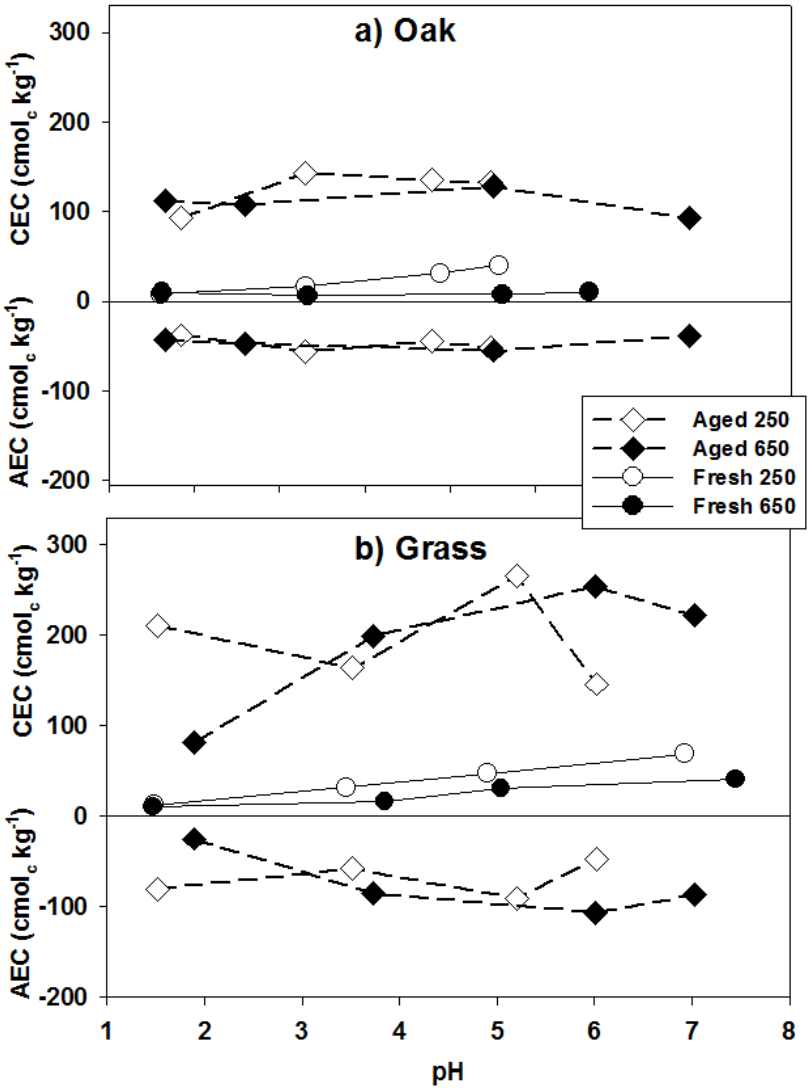


Figure 4-3. Cation and anion exchange capacities (CEC and AEC, respectively) of (a) oak and (b) grass fresh and aged biochars produced at 250 and 650 ^{o}C measured at a range background pHs

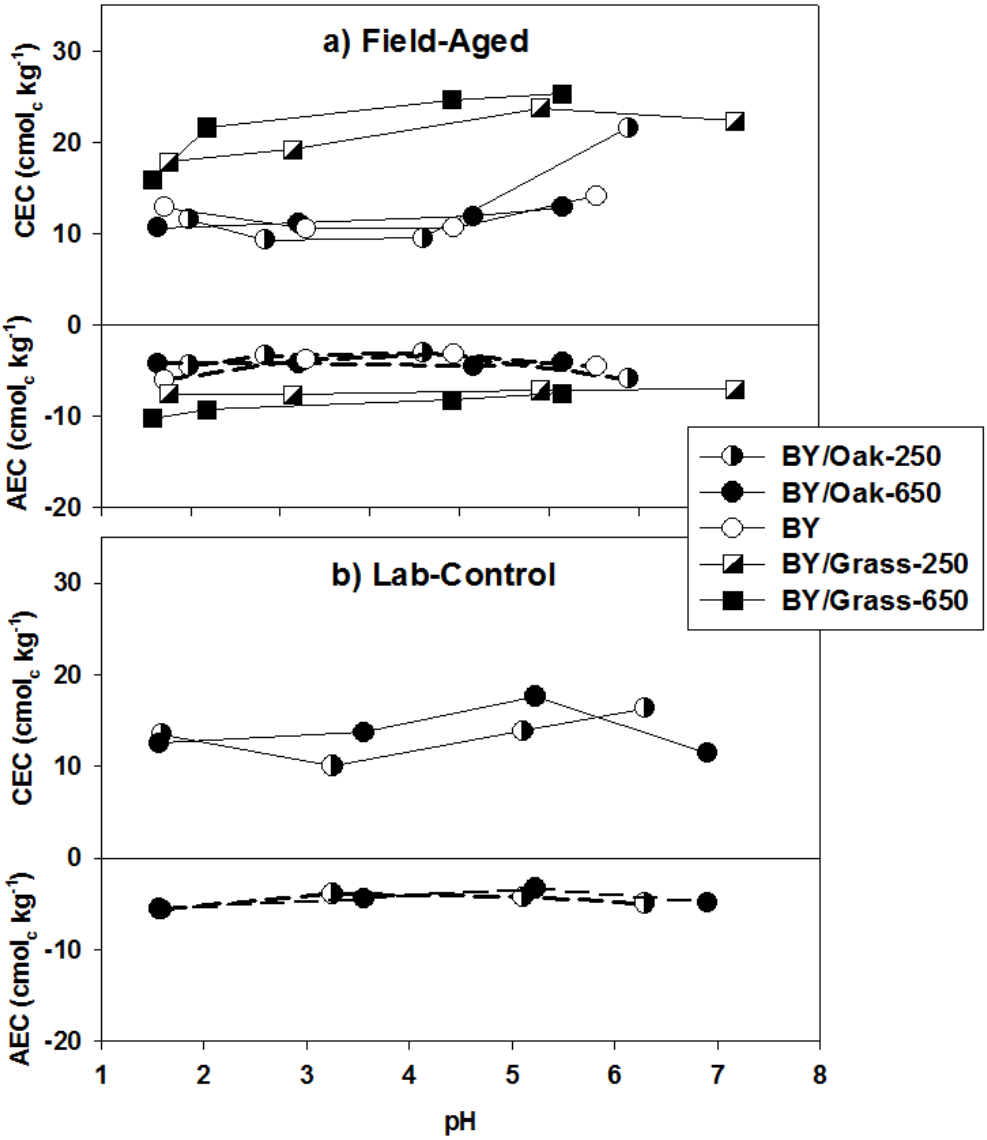


Figure 4-4. Cation and anion exchange capacities (CEC and AEC, respectively) of (a) nine months field-aged and (b) lab-control BY soil and BY soil/biochar (oak and grass) mixtures measured at a range of background pHs

CHAPTER 5
CONCLUSIONS

It is clear from this research that biochar is a substance with morphological and chemical properties which range widely based upon its production conditions. Various analytical methods were employed to understand the range in properties and the overall conclusions are outlined below.

The laboratory-produced fresh biochars demonstrated most variation in properties based on their production temperatures, and only secondarily on the biomass species. To generalize across all biochar biomass types, with increasing production temperature, biochar surface area and pH increased, while %VM, AFG content and CEC decreased. Our data also indicates that all fresh biochars had significant micrporous surface area while only higher temperature biochars had mesoporous (>1.5 nm diameter) surface area. This finding indicates that it is important to measure CO_2 sorptometry in addition to N_2 sorptometry during surface area analyses; otherwise there is a chance of underestimating the overall surface area of biochars.

It seems that volatile components fill micropores dominating the surface of fresh 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. Our data suggests that VM has surface chemical properties different from that of the non-volatile biochar component as evident from the properties of the 250 ^{o}C fresh biochars, which, with its higher VM%, was distinct from it‟s higher temperature counterparts in its enhanced ability to exchange cations at circum-neutral pH‟s. The strong direct linear correlation between VM% and total AFG suggests that it is acidic functional groups in the volatile OM that is responsible for the pH-dependent CEC

particularly evident in the 250 ^{o}C biochars. The volatile fraction also plays a dominant role in the AFG content and CEC of freshly made biochar.

The fresh biochar CEC measured in this study (10 – 69 $cmol_c$ 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. We found no consistent differences in CEC resulting from the determination method used in this study. 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 VM was lost, even at lower production temperatures.

Fresh biochars were also found to 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.

The batch extraction study showed that lower temperature biochars (250 ^{o}C) released more nutrients than higher temperature (650 ^{o}C) biochars and grass species released greater amount of nutrients compared to oak species. In addition, fresh biochars released greater nutrients than aged biochars. The column leaching studies also reflected similar trends as well as significant sorption of OC, N and P by both soil and biochar. These findings indicate that careful choice of biochar is required before based upon the soil to be amended and the nutrient requirements of the crop to be planted.

The aged biochars showed different characteristics than the freshly made biochars of this study. While the 250 ^{o}C biochars had similar pH for fresh and aged biochars, the 650 ^{o}C aged biochars showed much lower pH than fresh biochars. Paradoxically, the AFG content data of aged biochars showed lower concentrations of total, phenolic and carboxylic acid content compared to fresh biochars. The CEC of aged biochars were up to 10 times greater than the fresh biochars for both 250 and 650 ^{o}C biochars and the CEC trend showed no pH dependency. These changes may be due to the loss or transformation of surface functional groups or VM. While the AECs of fresh biochars were negligible, the AEC of aged biochars were quite high showing no pH dependency. Both CEC and AEC of selected soils amended with biochars increased up to 45% and 42%, respectively, beyond the arithmetic prediction due to soil-biochar interaction during the field trial of nine months.

The findings provide insight into, not just the range, but also the causes of the range in biochar properties. These findings indicate that, while fresh 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. These data also will help guide the production of biochar that will be ideal for each intended purpose and each

soil type. For example, as aged biochars release higher amounts of nutrients and have higher CEC than fresh biochars, they could be amended with soils with low exchangeable capacity so that plants could benefit through the interaction of biochar and soils over time.

It is hoped that these findings and interpretations will be helpful in designing biochars ideally suited for each soil and for each intended goal such as nutrient retention, carbon sequestration, or contaminant immobilization.

APPENDIX: SUPPLEMENTARY FIGURES AND TABLES

Table A1. Anion exchange capacity (AEC) at ranges of pH in 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

Table A2. Bulk elemental composition of biochars produced

Biomass Species	C[a]	N[a]	H[a]	O[a]	P[b]	K[b]	Ca[b]	Mg[b]	Mn[b]	Na[b]	Fe[b]	Al[b]
	(mg g^{-1})											
QL Oak-250	626 ± 32	1.9 ± 0.3	31 ± 0	342	0.4	3.4	7.1	0.6	0.1	nm	0.2	nm
QL Oak-400	679 ± 57	3.7 ± 0.7	42 ± 1	276	1.3	6.4	11.8	1.1	0.2	nm	0.0	nm
QL Oak-525	799 ± 9	2.8 ± 0.4	29 ± 0	170	3.4	4.9	5.8	0.7	0.0	0.2	0.2	0.0
QL Oak-650	754 ± 14	4.6 ± 0.4	28 ± 1	213	0.9	6.3	10.3	0.5	0.1	nm	0.0	nm
Loblolly Pine-250	624 ± 4	0 ± 0	26 ± 1	350	0.1	0.6	2.4	0.5	0.1	nm	0.0	nm
Loblolly Pine-400	758 ± 7	0.7 ± 0	37 ± 0	204	0.1	1.0	4.7	0.7	0.1	nm	0.0	nm
Loblolly Pine-525	532 ± 23	0 ± 0	40 ± 0	428	0.2	0.7	0.9	0.3	0.0	0.2	0.1	0.0
Loblolly Pine-650	552 ± 0	0 ± 0	33 ± 0	415	0.1	0.5	2.7	0.2	0.1	nm	0.0	nm
Gamma Grass-250	494 ± 31	12 ± 2	36 ± 1	458	1.4	5.0	8.2	3.0	0.1	nm	0.1	nm
Gamma Grass-400	523 ± 4	14 ± 0	46 ± 0	417	4.2	15.3	9.9	3.7	0.2	nm	0.1	nm
Gamma Grass-525	485 ± 2	12 ± 0	29 ± 0	474	3.8	22.3	3.6	1.5	0.0	0.3	0.1	0.0
Gamma Grass-650	557 ± 5	5.7 ± 0.4	30 ± 1	408	3.3	7.9	16.9	5.8	0.3	nm	0.2	nm
Palmetto Palm-400	648 ± 5	8.1 ± 0	43 ± 1	301	2.9	1.5	6.8	1.9	0.0	2.4	0.1	0.0
Palmetto Palm-525	652 ± 5	9.3 ± 0.5	35 ± 1	304	nm	nm	nm	nm	nm	nm	nm	nm
Palmetto Palm-650	743 ± 47	7.3 ± 0.9	27 ± 2	223	nm	nm	nm	nm	nm	nm	nm	nm
Melaleuca-400	790 ± 5	2.1 ± 0.1	37 ± 0	171	0.2	1.0	1.4	0.3	0.0	1.9	0.8	0.0
Melaleuca-525	806 ± 13	1.6 ± 0.3	39 ± 0	153	nm	nm	nm	nm	nm	nm	nm	nm
Melaleuca-650	888 ± 6	1.7 ± 0.1	29 ± 0	81	nm	nm	nm	nm	nm	nm	nm	nm
Eastern Red Cedar-250	656 ± 26	2.4 ± 0.3	27 ± 2	315	nm	nm	nm	nm	nm	nm	nm	nm
Eastern Red Cedar-400	778 ± 3	0 ± 0	40 ± 2	182	0.1	0.4	1.3	0.2	0.0	0.2	0.3	0.0
Eastern Red Cedar-525	854 ± 9	0 ± 0	31 ± 1	115	nm	nm	nm	nm	nm	nm	nm	nm
Eastern Red Cedar-650	842 ± 26	0 ± 0	28 ± 3	131	nm	nm	nm	nm	nm	nm	nm	nm
Sugar Cane Bagasse-250	562 ± 2	8.3 ± 0.6	26 ± 0	403	nm	nm	nm	nm	nm	nm	nm	nm
Sugar Cane Bagasse-400	644 ± 17	5.9 ± 0.8	47 ± 2	303	0.2	0.9	1.1	0.3	0.0	0.1	0.3	0.1
Sugar Cane Bagasse-525	658 ± 64	5.3 ± 0.4	32 ± 0	304	nm	nm	nm	nm	nm	nm	nm	nm
Sugar Cane Bagasse-650	765 ± 12	8.5 ± 0.3	31 ± 0	195	nm	nm	nm	nm	nm	nm	nm	nm
Bubinga-250	615 ± 6	0 ± 0	35 ± 0	350	nm	nm	nm	nm	nm	nm	nm	nm

Table A2 Continued

Biomass Species	C[a]	N[a]	H[a]	O[a]	P[b]	K[b]	Ca[b]	Mg[b]	Mn[b]	Na[b]	Fe[b]	Al[b]
	(mg g^{-1})											
Bubinga-400	786 ± 5	1.3 ± 0.1	37 ± 0	176	0.0	0.0	1.5	0.4	0.0	0.1	0.1	0.0
Bubinga-525	854 ± 18	0.8 ± 0	30 ± 0	115	nm	nm	nm	nm	nm	nm	nm	nm
Bubinga-650	830 ± 1	0 ± 0	31 ± 1	139	nm	nm	nm	nm	nm	nm	nm	nm
Lignum Vitae-400	763 ± 7	5.1 ± 1.1	36 ± 0	196	nm	nm	nm	nm	nm	nm	nm	nm
Lignum Vitae-525	831 ± 3	5.7 ± 0.1	28 ± 0	135	0.0	0.0	8.4	0.0	0.0	0.0	1.3	0.0
Lignum Vitae-650	774 ± 1	7.4 ± 0.2	26 ± 2	192	nm	nm	nm	nm	nm	nm	nm	nm
Redwood-400	741 ± 2	0 ± 0	38 ± 0	222	0.0	0.0	0.4	0.1	0.1	0.1	2.8	0.0
Redwood-525	809 ± 14	0 ± 0	29 ± 1	162	nm	nm	nm	nm	nm	nm	nm	nm
Redwood-650	819 ± 2	0 ± 0	28 ± 0	153	nm	nm	nm	nm	nm	nm	nm	nm
White Pine-400	773 ± 3	0 ± 0	33 ± 1	193	nm	nm	nm	nm	nm	nm	nm	nm
White Pine-525	797 ± 16	0 ± 0	23 ± 2	180	0.0	0.0	0.5	0.2	0.0	0.1	1.2	0.0
White Pine-650	829 ± 2	0 ± 0	28 ± 2	144	nm	nm	nm	nm	nm	nm	nm	nm
Red Oak-400	736 ± 1	0 ± 0	35 ± 2	229	0.0	0.2	0.6	0.1	0.1	0.3	0.1	0.0
Red Oak-525	824 ± 8	0 ± 0	28 ± 0	148	nm	nm	nm	nm	nm	nm	nm	nm
Red Oak-650	787 ± 33	0 ± 0	29 ± 0	184	nm	nm	nm	nm	nm	nm	nm	nm
Walnut-400	730 ± 0	0 ± 0	33 ± 1	236	0.1	1.2	2.3	0.7	0.1	0.5	1.9	0.0
Walnut-525	819 ± 2	0 ± 0	27 ± 0	154	nm	nm	nm	nm	nm	nm	nm	nm
Walnut-650	810 ± 2	0 ± 0	29 ± 0	161	nm	nm	nm	nm	nm	nm	nm	nm
Silver Maple-400	750 ± 1	0 ± 0	36 ± 0	214	nm	nm	nm	nm	nm	nm	nm	nm
Silver Maple-525	801 ± 7	0 ± 0	29 ± 2	170	0.1	3.2	2.3	0.4	0.0	0.6	0.4	0.0
Silver Maple-650	817 ± 3	0 ± 0	29 ± 0	155	nm	nm	nm	nm	nm	nm	nm	nm
Bigleaf Maple-400	750 ± 2	0 ± 0	36 ± 0	214	0.2	0.3	1.1	0.2	0.0	0.4	0.8	0.0
Bigleaf Maple-525	829 ± 2	0 ± 0	27 ± 0	144	nm	nm	nm	nm	nm	nm	nm	nm
Bigleaf Maple-650	803 ± 13	0 ± 0	27 ± 3	170	nm	nm	nm	nm	nm	nm	nm	nm
Corncob-400	691 ± 7	13 ± 1	46 ± 0	250	1.7	4.3	0.5	0.6	0.0	0.9	0.1	0.0
Corncob-525	743 ± 1	14 ± 1	38 ± 1	205	nm	nm	nm	nm	nm	nm	nm	nm
Corncob-650	691 ± 103	9.5 ± 2.4	27 ± 1	273	nm	nm	nm	nm	nm	nm	nm	nm

Table A2 Continued

Biomass Species	C[a]	N[a]	H[a]	O[a]	P[b]	K[b]	Ca[b]	Mg[b]	Mn[b]	Na[b]	Fe[b]	Al[b]
	(mg g^{-1})											
Cornstalks-400	668 ± 3	13 ± 0	48 ± 0	271	1.4	5.2	0.9	0.9	0.1	0.4	1.7	0.0
Cornstalks-525	691 ± 7	14 ± 0	38 ± 0	257	nm	nm	nm	nm	nm	nm	nm	nm
Cornstalks-650	763 ± 6	13 ± 1	33 ± 1	192	nm	nm	nm	nm	nm	nm	nm	nm
Cattail-400	623 ± 4	8.3 ± 0	48 ± 1	321	nm	nm	nm	nm	nm	nm	nm	nm
Cattail-525	658 ± 2	12 ± 0	40 ± 0	290	1.5	12.3	8.9	1.5	0.1	2.5	0.1	nm
Cattail-650	647 ± 1	13 ± 0	30 ± 0	310	nm	nm	nm	nm	nm	nm	nm	nm
Coconut Shell-400	773 ± 0	2.1 ± 0.3	41 ± 0	185	nm	nm	nm	nm	nm	nm	nm	nm
Coconut Shell-525	781 ± 16	1.5 ± 0.1	36 ± 1	181	nm	nm	nm	nm	nm	nm	nm	nm
Coconut Shell-650	779 ± 29	1.9 ± 0.1	34 ± 0	185	0.1	1.3	0.2	0.1	0.1	0.6	2.9	nm
Elephant Grass-400	565 ± 0	23 ± 1	46 ± 0	366	nm	nm	nm	nm	nm	nm	nm	nm
Elephant Grass-525	510 ± 18	17 ± 1	39 ± 3	435	nm	nm	nm	nm	nm	nm	nm	nm
Elephant Grass-650	563 ± 40	15 ± 5	26 ± 0	395	nm	nm	nm	nm	nm	nm	nm	nm
Pearl Millet-400	557 ± 2	26 ± 1	47 ± 0	370	nm	nm	nm	nm	nm	nm	nm	nm
Pearl Millet-525	575 ± 6	21 ± 1	43 ± 0	361	nm	nm	nm	nm	nm	nm	nm	nm
Pearl Millet-650	555 ± 13	17 ± 1	35 ± 2	393	nm	nm	nm	nm	nm	nm	nm	nm

Notes:
Values represent mean ± standard deviation where indicated
a: The values of C, N, and H were derived from a CHN analyzer, and O was calculated by difference (100% - C% - N% - H%)
b: Total P, K, Ca, Mg, Mn, Na, Fe, and Al were derived from a total digested acid extraction procedure (AOAC 985.01)
nm: not measured

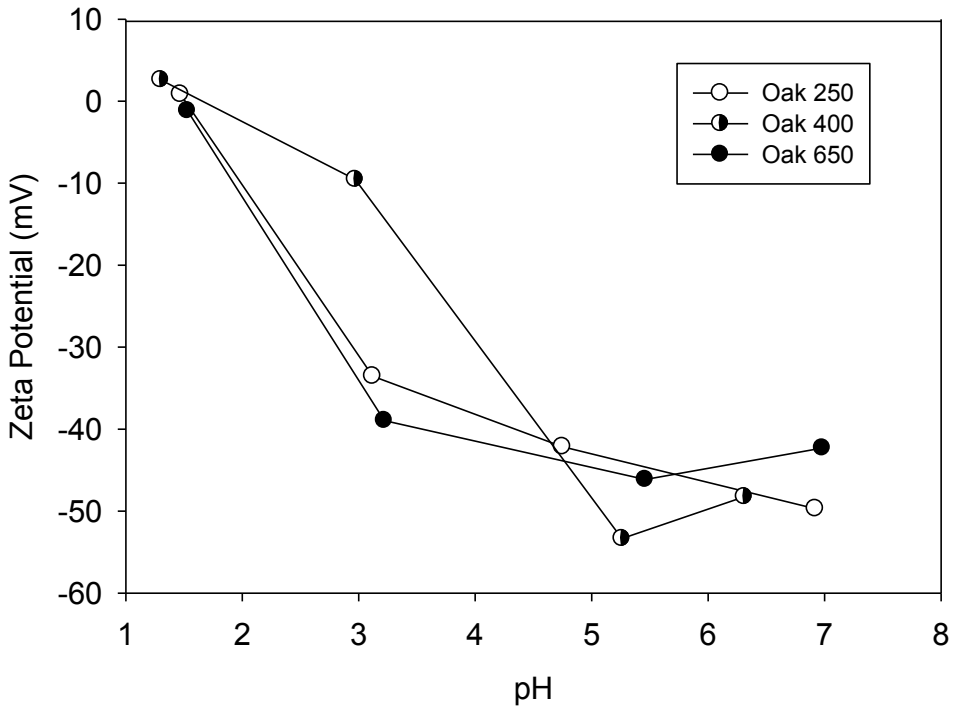
Table A3. Surface area (using N_2 and CO_2 sorptometry) and % yield of biochars produced

Biomass Species	Scientific Name	Surface Area (m^2 g^{-1}) N_2	Surface Area (m^2 g^{-1}) CO_2	% Yield[a]
QL Oak-250	*Quercus lobata*	1 ± 1	331 ± 66	28 ± 23
QL Oak-400	*Quercus lobata*	2 ± 1	252 ± 90	36 ± 7
QL Oak-525	*Quercus lobata*	nm	525	26 ± 4
QL Oak-650	*Quercus lobata*	225 ± 9	528 ± 57	30 ± 3
Loblolly Pine-250	*Pinus taeda*	1 ± 0	373 ± 112	21 ± 10
Loblolly Pine-400	*Pinus taeda*	3 ± 2	361 ± 114	33 ± 5
Loblolly Pine-525	*Pinus taeda*	166 ± 45	396	26 ± 1
Loblolly Pine-650	*Pinus taeda*	285 ± 102	643 ± 80	27 ± 0
Gamma Grass-250	*Tripsacum floridanum*	3 ± 2	221 ± 106	51 ± 2
Gamma Grass-400	*Tripsacum floridanum*	6 ± 6	164 ± 49	37 ± 20
Gamma Grass-525	*Tripsacum floridanum*	18 ± 11	335	26 ± 11
Gamma Grass-650	*Tripsacum floridanum*	77 ± 27	427 ± 115	35 ± 1
Bubinga-250	*Guibourtia demeusei*	5.4	244 ± 27	52
Bubinga-400	*Guibourtia demeusei*	6.4 ± 0.4	427 ± 3	33
Bubinga-525	*Guibourtia demeusei*	501	622 ± 12	29
Bubinga-650	*Guibourtia demeusei*	549	625 ± 3	33 ± 5
Cattail-400	*Typha spp. L.*	6.1	187	57
Cattail-525	*Typha spp. L.*	6	257	41
Cattail-650	*Typha spp. L.*	44	434	35
Eastern Red Cedar-250	*Juniperus virginiana*	nm	522	25
Eastern Red Cedar-400	*Juniperus virginiana*	8.2 ± 1.4	354	33 ± 4
Eastern Red Cedar-525	*Juniperus virginiana*	389 ± 3	598	30
Eastern Red Cedar-650	*Juniperus virginiana*	516 ± 37	607	29
Coconut Shell-400	*Cocos nucifera*	1.2	297	41 ± 2
Coconut Shell-525	*Cocos nucifera*	1.4	407	35 ± 1
Coconut Shell-650	*Cocos nucifera*	5.8 ± 3.9	445	36
Corncob-400	*Euphorbia mammillaris L.*	1.4	262	42
Corncob-525	*Euphorbia mammillaris L.*	4	366	32 ± 1
Corncob-650	*Euphorbia mammillaris L.*	85	563	30
Cornstalks-400	*Zea mays*	4.2 ± 1.3	256	61
Cornstalks-525	*Zea mays*	8.4	386	34
Cornstalks-650	*Zea mays*	26.3	494	30
Elephant Grass-400	*Pennisetum purpureum*	2.3	185	43
Elephant Grass-525	*Pennisetum purpureum*	6.1	186	31
Elephant Grass-650	*Pennisetum purpureum*	7.6	409	28
Bigleaf Maple-400	*Acer macrophyllum*	5.5	428	30

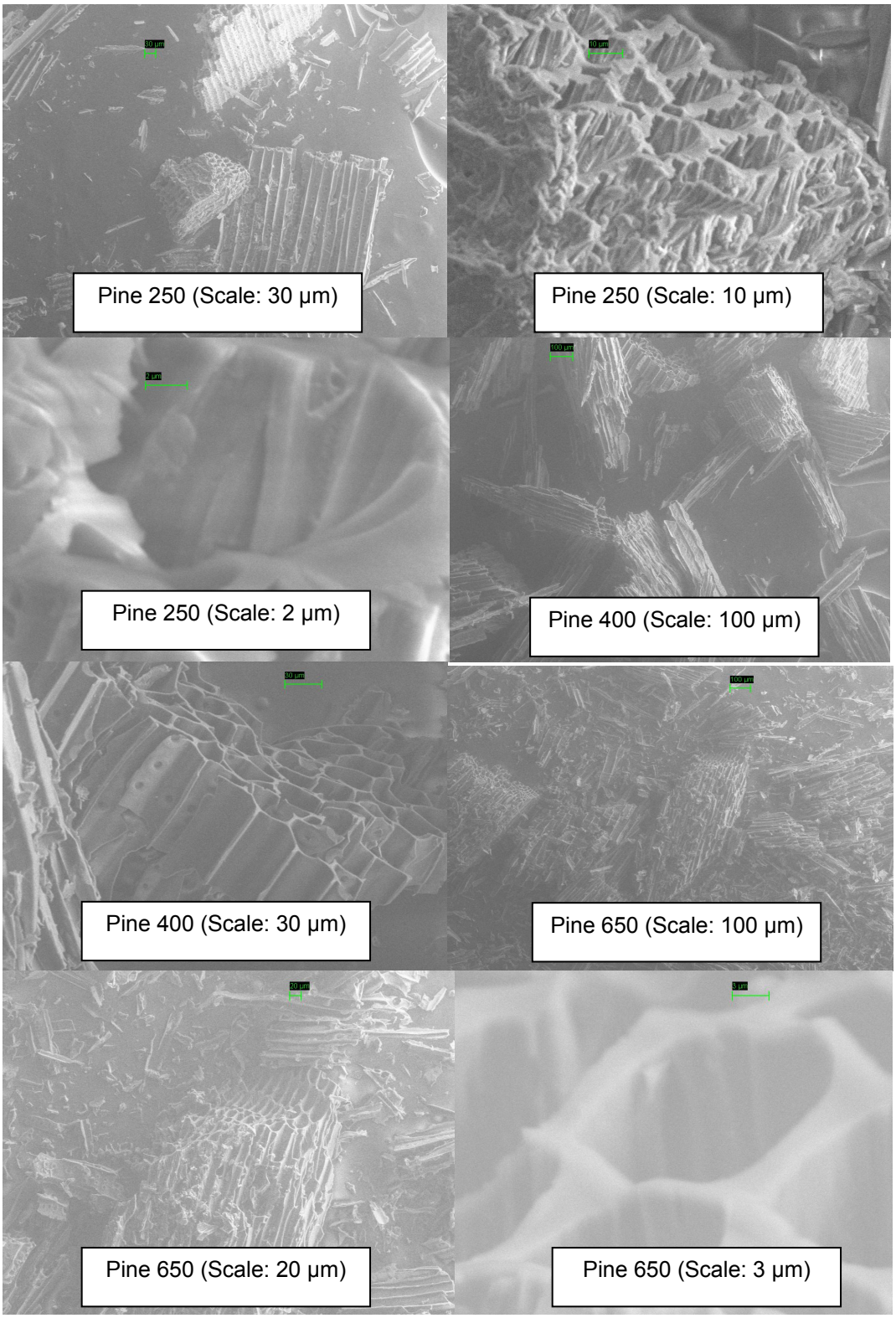
Table A3 Continued

Biomass Species	Scientific Name	Surface Area (m^2 g^{-1}) N_2	Surface Area (m^2 g^{-1}) CO_2	% Yield[a]
Bigleaf Maple-525	*Acer macrophyllum*	545	607	24
Bigleaf Maple-650	*Acer macrophyllum*	547	606	25
Lignum Vitae-400	*Guaiacum officinale*	69 ± 117	428	31 ± 7
Lignum Vitae-525	*Guaiacum officinale*	458	624	22
Lignum Vitae-650	*Guaiacum officinale*	426	542	22
Melaleuca-400	*Melaleuca quinquenervia*	6.0 ± 0.6	402	29 ± 0
Melaleuca-525	*Melaleuca quinquenervia*	481	400	28 ± 5
Melaleuca-650	*Melaleuca quinquenervia*	430	611	26
Palmetto Palm-400	*Sabal minor*	7.5 ± 2.1	223	34 ± 14
Palmetto Palm-525	*Sabal minor*	327 ± 23	369	25 ± 12
Palmetto Palm-650	*Sabal minor*	15 ± 5	518	34
Pearl Millet-400	*Pennisetum glaucum*	2.9	146	52
Pearl Millet-525	*Pennisetum glaucum*	2.7	256	36
Pearl Millet-650	*Pennisetum glaucum*	7.4	287	34
Red Oak-400	*Quercus rubra*	nm	418	29
Red Oak-525	*Quercus rubra*	395	579	24
Red Oak-650	*Quercus rubra*	548	608	26
Redwood-400	*Sequoia sempervirens*	3.8 ± 0.8	381	36
Redwood-525	*Sequoia sempervirens*	377	603	29
Redwood-650	*Sequoia sempervirens*	509	656	30
Silver Maple-400	*Acer saccharinum*	6.1	403	28
Silver Maple-525	*Acer saccharinum*	170	590	25
Silver Maple-650	*Acer saccharinum*	360	583	25
Sugar Cane Bagasse-250	*Saccharum officinarum L.*	nm	335	33
Sugar Cane Bagasse-400	*Saccharum officinarum L.*	7.9 ± 3.5	208 ± 5	24
Sugar Cane Bagasse-525	*Saccharum officinarum L.*	276 ± 123	523	12 ± 6
Sugar Cane Bagasse-650	*Saccharum officinarum L.*	153 ± 36	588 ± 17	37
Walnut-400	*Juglans regia*	3.9 ± 0.4	374	37
Walnut-525	*Juglans regia*	238	557	36
Walnut-650	*Juglans regia*	181	532	30
White Pine-400	*Pinus strobus*	17	490	27
White Pine-525	*Pinus strobus*	573	694	26 ± 3
White Pine-650	*Pinus strobus*	599	845	18

Notes:
a: % Yield was calculated as final weight of biochar after combustion divided by initial weight of the biomass
Values represent mean ± standard deviation where indicated
nm: not measured



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



Supplemental Figure S2. Scanning Electron Microscopy (SEM) images of loblolly pine biochar samples

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BIOGRAPHICAL SKETCH

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