CHARACTERIZATION AND MINERALIZATION RATES OF LOW TEMPERATURE PEANUT HULL AND PINE CHIP BIOCHARS

by

KEITH R. HARRIS

(Under the Direction of Miguel Cabrera)

ABSTRACT

A defined methodology to characterize biochar is necessary to predict how specific biochars will affect C and nutrient mineralization when amended on cropland soils. We amended Tifton soil (Fine-loamy, siliceous, thermic Plinthic Kandiudults) with Peanut Hull (*Arachis hypogaea;* PH) and Pine Chip (*Pinus taeda*; PC) biochar and monitored C and N mineralization. In addition, we characterized each biochar using thermogravimetric analysis with mass spectrometer (TGA-MS), proximate analysis, Fourier transform infrared spectroscopy (FTIR), and total mineral analysis. Carbon mineralization from chars added to soils was correlated with estimated aliphatic content determined by TGA-MS but not with volatile content indicated by proximate analysis. Nitrogen was not mineralized from either biochar, indicating that biochar should not be considered a source of nitrogen for plant growth. The nitrogen in biochar may be contained in the stable aromatic structures of the biochar, as indicated by TGA-MS, and not available to soil microbes.

INDEX WORDS: Biochar, Carbon mineralization, Nitrogen mineralization, Characterization, Peanut hull, Pine chip, Aliphatic matter, Volatile matter

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CHAPTER 1

INTRODUCTION

Nature and Importance

Biochar is charcoal created by pryrolysis of biomass for energy production and is intended to sequester C from the atmosphere by storing it in the soil (Joseph et al., 2010). Several countries have requested the United Nations acknowledge biochar as a suitable tool to mitigate climate change in future climate agreements (IBI, 2011). The American Power Act, sponsored by Senator John Kerry, contains several provisions that would support biochar deployment in the United States (IBI, 2011). Given the national and international attention biochar has received in recent years, there is potential for large scale application of biochar to agricultural and silvicultural lands; therefore, production and application guidelines need to be established to insure biochar is utilized responsibly.

The International Biochar Initiative (IBI), a member-based organization, was established with two goals: one, support the generation, review, and dissemination of information on all aspects of biochar, and two, develop sustainability guidelines and monitor and evaluate biochar projects and systems against these guidelines. IBI is currently drafting *Biochar Product Definition and Standard* which attempts to establish consistent guidelines for feedstock selection and biochar production. The document also establishes a biochar classification system that will provide the end user information on the product. In this system, biochars will be separated into different classes based on whether the material meets limits of certain requirements. Class IV, the least restricted level, establishes acceptable levels of basic physical properties, e.g. ash content, and toxicity, e.g. Arsenic, while the highest class requires soil enhancement properties, e.g. cation exchange capacity, plus meeting the requirements of the lesser classes.

Methodology and limits for several of the requirements listed have yet to be determined. Three of the requirements without defined limits or methodology are Carbon sequestration value in class IV, Stable Carbon content in class II, and NPK in class I. These requirements are critical when trying to determine biochar's effect on climate change and soil fertility.

Biochar is a black, amorphous carbon similar to charcoal with a polycyclic structure and varying degrees of aromaticity (Brewer et al., 2009; Keiluweit et al., 2010) and surface oxidation (Cheng et al., 2006). Evidence from black-carbon rich Terra Preta soils in the tropics indicates black carbon resists mineralization (Liang et al., 2008) while increasing soil fertility and productivity (Glaser et al., 2002; Lehmann et al., 2003; Steiner et al., 2008); however, certain fractions of fresh biochar may be subject to mineralization when incorporated into soil (Bruun et al., 2008; Cheng et al., 2008b; Kolb et al., 2009; Kuzyakov et al., 2009; Liang et al., 2008; Smith et al., 2010; Zimmerman, 2010).

Production temperature and feedstock selection greatly affect the quantity and characteristics of biochar (Baldock and Smernik, 2002; Keiluweit et al., 2010; Meszaros et al., 2007; Pastor-Villegas et al., 2007; Yang et al., 2007). Condensation of the polycyclic aromatic structure increases with increasing production temperature (Keiluweit et al., 2010) and holding time (Brewer et al., 2009). Biochars produced at lower temperatures tend to have a larger mineralizable C fraction (Bruun et al., 2008) that mineralizes rapidly when incorporated into soil (Smith et al., 2010).

Biochar also can have an effect on N cycling in soils. The chemical stability of N in biochar increases with increasing production temperature by becoming incorporated in the aromatic structure as heteroatoms (Hilscher et al., 2009; Knicker, 2007; Schmiers et al., 1999; Stanczyk et al., 1995). Nitrogen in manure derived biochars may be available (Chan et al., 2008; Tagoe et al., 2008), but plant derived biochars may not provide N even at recommended loading rates (Gaskin et al., 2010). There is also evidence that biochar may cause N immobilization (Deenik et al., 2010; Novak et al., 2010).

Objectives

Although these studies indicate that biochar’s effect on soil fertility and mineralization rate depends on the feedstock, production conditions, and climatic conditions, there is no defined in-vitro method to estimate these effects and the quantity of carbon sequestered over decades, if not centuries. The intention of this thesis is to characterize biochars of different feedstocks and attempt to isolate a characteristic that correlates with the C and N mineralization rates of those biochars in a common agricultural soil type found in the southeastern United States. Our objective was to characterize two biochars from Gaskin et al.

(2010), prepared from peanut hull (PH) and pine chip (PC), and correlate those characteristics with C and N mineralization rates of a 136-day study under the following hypotheses.

1. Peanut hull and PC biochar will mineralize at different rates that will correlate to an aliphatic and volatile matter concentration in the biochar.
2. Aging in soil will decrease aliphatic and volatile matter as well as C and H concentrations in biochars, and will increase oxygen-containing functionalities on the surface of biochars
3. Biochar will affect the N status of the soil by either immobilizing or mineralizing N depending on the N content of the biochar.

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CHAPTER 2

LITERATURE REVIEW

Biochar Characterization

Production temperature and feedstock selection greatly affect the quantity and characteristics of biochar (Baldock and Smernik, 2002; Keiluweit et al., 2010; Meszaros et al., 2007; Pastor-Villegas et al., 2007; Yang et al., 2007). Feedstocks predominantly consist of hemicellulose, cellulose, and lignin with the ratios of these constituents depending on the feedstock selected. Understanding the effect of pryrolysis conditions on these compounds will provide insight into the fundamentals of biochar formation. Thermogravimetric analysis (TGA) has shown that hemicelluloses, cellulose, and lignin decompose at different temperatures ranges leaving various amounts of char (Yang et al., 2007). Hemicellulose and cellulose rapidly decompose from 220 -315°C and 315 - 400°C respectively with approximately 40% of the mass of hemicellulose remaining as char at 900°C while only 6.5% of the cellulose remained as char at 400°C. Lignin is the most resistant to decomposition, gradually decomposing up to 900 °C, leaving 46% char. Therefore, a majority of biochar is composed of hemicellulose and lignin residues as well as ash from the mineral content of the feedstock (Keiluweit et al., 2010).

Limited information is available on the characterization of hemicellulose and lignin chars. Hemicellulose consists of polysaccharides that decompose into chars with higher density and smaller porosity than lignin char (Lv et al., 2010). Scanning electron microscopy showed that hemicellulose char surface smoothness and porosity increased with increasing temperature. Lignin char porosity peaks at approximately 400°C and decreases at higher temperatures as the material transitions from a micro to macroporous structure (Sharma et al., 2004). Spectra from FTIR analysis showed a gradual reduction of OH and aliphatic CH bonding on the surface of lignin char with increasing temperature. Methyl oxygen bonding decreased up to approximately 375°C where CH_3 bonds were below detection while aromatic CH bonding became detectable at approximately 375°C and increased with temperature (Sharma et al., 2004). Increased aromaticity with a reduction of functional groups and aliphatic bonding with increasing temperature was validated using NMR where spectra were dominated by an aromatic peak starting at 400°C and becoming more pronounced with increasing temperature. Increased aromaticity and decreased aliphatic content of biochar with increasing production temperature is also seen in biomass derived chars (Baldock and Smernik, 2002; Brewer et al., 2009; Keiluweit et al., 2010).

Sap wood thermally altered at temperatures ranging from 70 to 350°C in a limited oxygen environment started to show a shift from O-Alkyl to Aryl C structure due to degradation of cellulose and hemicellulose above 200°C, based on NMR analysis (Baldock and Smernik, 2002). Elemental analysis showed an increase of C, N, and ash content as well as a decrease in H and O with increasing production temperature indicating dehydration, yet the increased O content of the 350°C samples indicates formation of furan compounds. No carbonaceous material remained at 400°C meaning true anoxic pryrolysis conditions did not exist and the material combusted.

Characterization of chars from ponderosa pine shavings and tall fescue straw, each pyrolyzed from 100 to 700°C in 100°C increments for 1-h, indicates that as production temperature rises, aromaticity increases followed by condensation into turbostratic crystallites (Keiluweit et al., 2010). Transition chars produced between approximately 300 and 400°C still retain the precursor structure of lignin, cellulose, and hemicellulose at 300°C, then are replaced by the formation of pyrogenic amorphous C as temp temperature rises. Transition chars are characterized by high volatile matter content, 50 to 30% by weight, and reduced H concentration and O/C ratios. Amorphous chars produced between 400 and 500°C consist primarily of pyrogenic C with increasing porosity and higher temperature and characterized by 20 to 10% volatile matter content. Composite chars produced between 500 and 700°C show increased porosity as well as condensation indicated by formation of turbostratic crystallites and are indicated by minimal volatile matter content. Biochars produced above 700°C consist of turbostratic crystallites with a nanoporus structure and are characterized by < 90% fixed C.

Similar to temperature, pryrolysis holding time also has an effect on biochar characteristics (Brewer et al., 2009). Both switchgrass and corn stover underwent slow pryrolysis, holding times 2-h and 30-min respectively at 500°C, fast pryrolysis at 500°C, and gasification at approximately 700°C. Fast pryrolysis and gasification were performed in fluidized beds. Aromaticity increased with reaction time while aromatic condensation increased with temperature. Fixed C content of chars correlated with aromaticity where slow pryrolysis and gasified chars had higher fixed C content than fast pryrolysis chars.

As with C, the chemical stability of N in biochar increases with increasing production temperature by becoming incorporated in the aromatic structure as heteroatoms (Hilscher et al., 2009; Knicker, 2007; Schmiers et al., 1999; Stanczyk et al., 1995). At low pryrolysis temperatures, < 600°C, amino groups form both pyrrolic and pyridinic structures that transition into quaternary structures at higher temperatures, 800°C (Stanczyk et al., 1995). Rye grass charred at 350°C under oxic conditions showed decrease in amide, guanidine, and amino N and increase in pyrrole and pyridine/imine N compounds compared to the uncharred feedstock (Hilscher et al., 2009).

Feedstock selection can also have an effect on biochar characteristics (Barneto et al., 2009; Brewer et al., 2009; Gaskin et al., 2008). Thermal decomposition analysis data show that feedstocks containing different amounts of hemicellulose, cellulose, and lignin decompose at different rates affecting char yields (Barneto et al., 2009; Demirbas, 2006) and characteristics (Demirbas, 2006). Feedstock selection also affects the ash content of biochar (Brewer et al., 2009; Keiluweit et al., 2010). Depending on the feedstock, ash contents can contain different concentrations of minerals (Gaskin et al., 2008), specifically K, P, Mg, and / or Na that may catalyze pryrolysis reactions that create recalcitrant oxygen containing functionalities (Meszaros et al., 2007).

Biochar Effects on Soil Processes

Mineralization

Biochar C mineralization is primarily the result of abiotic oxidation (Cheng and Lehmann, 2009; Cheng et al., 2006; Nguyen and Lehmann, 2009); however, certain fractions of biochars are microbially available (Kuzyakov et al., 2009; Smith et al., 2010; Steinbeiss et al., 2009; Zimmerman, 2010). The polycyclic aromatic component of biochar is most likely resistant to microbial mineralization (Baldock and Smernik, 2002; Hilscher et al., 2009) and decomposes slowly through abiotic oxidation (Cheng et al., 2006; Joseph et al., 2010). The proportion of aliphatic carbon to aromatic unavailable carbon depends on the temperature of the pyrolysis process with higher pyrolysis temperatures resulting in a smaller mineralizable fraction (Baldock and Smernik, 2002; Bruun et al., 2008; Zimmerman, 2010). A study using yeast and glucose biochars produced at 850°C mineralized at different rates indicating not only that high temperature biochars may have an aliphatic component but that feedstock selection may also effect aliphatic concentration (Steinbeiss et al., 2009).

Biochar typically undergoes a period of rapid mineralization the first few days to weeks after incorporation into soil (Bruun et al., 2008; Deenik et al., 2010; Hilscher et al., 2009; Kuzyakov et al., 2009; Smith et al., 2010; Zimmerman, 2010). After the initial flush of mineralization, CO_2 evolution diminishes to a rate similar to the control soil (Smith et al., 2010), though some chars with high volatile matter content may respire at a higher rate for an extended time due to the labile C in the volatile matter (Deenik et al., 2010). The amount of biochar C mineralized during initial days / weeks varies. Rye and maize biochar produced at 350°C and oak wood biochar produced at 800°C applied 1:10 (w/w) to an inoculated sand at 60% water holding capacity mineralized 0.72, 0.78, and 0.26 % of the biochar C over 60-d (Hamer et al., 2004). Rye grass and pine wood, charred at 350°C under oxic conditions, applied to a Cambisol at the same rate at the same water holding capacity mineralized 3 and 0.5 % C, respectively (Hilscher et al., 2009). Biochar from oak wood feedstock pyrolyzed at 400 and 650°C applied to an inoculated sand, wetted to water holding capacity, mineralized between 0.5 and 3 % of applied biochar C, with 600°C biochars consistently mineralizing less than 1% (Zimmerman, 2010). Mean residence times of biochar/black carbon have been estimated from < 100–y (Hamer et al., 2004; Steinbeiss et al., 2009) to 2000-y (Kuzyakov et al., 2009).

Biochar's presence may also have an effect on the residual C pool of the soil as well as additional organic amendments. The addition of biochar has been shown to promote the decomposition of soil labile carbon and humus (Wardle et al., 2008), potentially mineralizing nutrients and making them plant available. Basal respiration of a Mollisol showed the highest response to biochar amendment followed by Alfisol, Entisol, then Spodosol indicating biochar application to high fertility soils may see the greatest response (Kolb et al., 2009). The addition of biochar was shown to stimulate the mineralization of switchgrass after 67-d (Novak et al., 2010); however, black carbon rich anthrosols did not have the same effect when amended with plant residues (Liang et al., 2010). The addition of a labile C source to a biochar amended soil may stimulate the co-metabolization of both the labile C and biochar due to a sudden increase in microbial populations (Hamer et al., 2004; Kuzyakov et al., 2009).

There is limited information on N availability and mineralization from biochar and its effects on N processes. Corn grown on a Tifton soil amended with 11 Mg ha^{-1} peanut hull biochar (N application of 209 kg ha^{-1}) showed no N response in biochar only plots (Gaskin et al., 2010). In contrast, manure biochars, specifically broiler litter has been shown to provide N to plants (Chan et al., 2008; Tagoe et al., 2008) and increase overall soil fertility similar to uncarbonized broiler litter (Tagoe et al., 2008).

Biochar's effect on microbial activity also affects the nitrogen cycle. Charcoal boosts nitrification in forest ecosystems and reduces denitrification by adsorbing phenolic compounds that inhibit nitrifying bacteria (DeLuca et al., 2006); however, some biochar can contain ethylene that inhibits nitrifying bacteria (Spokas et al., 2010). Biochar may also stimulate biological nitrogen fixation, mostly by increasing B and Mo content in soil (Rondon et al., 2007) though nitrogen availability was noted as a factor but its effect was relatively small. The addition of broiler litter biochar has been shown to increase nodule formation in soybeans compared to uncarbonized broiler litter due to the greater content of available P (Tagoe et al., 2008).

Biochar has been shown to stimulate soil microbial biomass (Kolb et al., 2009; Liang et al., 2010; Steinbeiss et al., 2009) which could lead to nitrogen immobilization (Deenik et al., 2010; Novak et al., 2010). Soil microbial biomass C increased with application rate of poultry litter biochar produced a 450°C and co applied with N fertilizer yet no increase was seen with poultry litter biochar produced at 550°C (Chan et al., 2008). The study did not report biochar characterization data that would indicate a mineralizable fraction, such as volatile matter.

Based on the nutrient concentrations of the plants harvested, the system was not N limited. Biochars produced at lower temperatures tend to have higher mineralizable C fraction (Baldock and Smernik, 2002; Bruun et al., 2008; Zimmerman, 2010) potentially leading to N deficiencies in N limited systems. Nitrogen deficiencies have been noted in corn tissue grown with high volatile content matter biochars compared to low volatile content biochars (Deenik et al., 2010). In addition, extractable NH_4^+-N concentrations were lower in the high volatile matter content soil than the low volatile matter. Biochar presence may stimulate the mineralization of co-applied organic material resulting in immobilization (Novak et al., 2010). Extractable N concentrations of each an Alfisol, Entisol, and Mollisol, after a 100-d incubation, decreased with increasing biochar application rate, the greatest effect seen in the Mollisol (Kolb et al., 2009). The differences reported in C and N dynamics indicates a need for biochar characterization that will identify biochar that will have specific effects C and N cycling in soils allowing those systems to be managed properly.

Soil biology

Evidence suggests that biochar addition may benefit certain species in the soil (Steinbeiss et al., 2009; Wardle et al., 1998). Charcoal may provide habitat (Pietikainen et al., 2000) and act as an absorbent for substrates, including phenolic compounds, thus promoting certain populations (Zackrisson et al., 1996). A review by Warnock et al. (2007) presented several studies in which biochar had synergistic relationship with arbuscular, ericoid, and ectomycorrhizal symbioses, though the mechanisms are not known. Certainly charcoal's effect on increasing soil pH could be beneficial to earthworm pod production which has been shown in certain tropical soils (Topoliantz et al., 2002); however, high ash biochar such that from poultry litter can cause high earthworm mortality (Liesch et al., 2010). Yeast derived biochar was shown to promote fungal populations in arable and forest soils (Steinbeiss et al., 2009). Fire-affected soils may have soil microbial populations better suited to break down biochar than non fire effected soils (Nocentini et al., 2010) and forest soils have shown an increase in bacteria and fungi after fire (Kara and Bolat, 2009).

Nutrient availability and content

Charcoal can contain basic cations such as K, Ca, and Mg in the ash fraction that can act as fertilizer (Gaskin et al., 2008; Gaskin et al., 2010; Glaser et al., 2002). Lehmann et al. (2003) used a highly weathered Ferralsol and compared unamended and charcoal-amended treatments as well as fertilizer treatments in a pot study. The charcoal was derived from the burning of a secondary forest. The charcoal nutrient content was (g kg^{-1}): 10.9 K, 6.8 P, 0.32 Mg, 1.3 Ca, and 0.89 K and applied at 220 Mg ha^{-1} and 440 Mg ha^{-1}. The study showed an increase of available soil K, P, Ca, Zn, and Cu with the addition of charcoal. Potassium availability, though a low concentration in the charcoal, was an order of magnitude greater in the charcoal treatments than in the control soil. Nutrient losses from leaching were less than half of those of the no charcoal fertilized treatments. It should be noted that the applications rates were high in this experiment, 10 and 20% by volume, and a one-time application at this rate would not be feasible. Nevertheless, it does indicate the some minerals in biochar are available and that biochar could affect nutrient retention.

Steiner et al. (2007) tested the long-term effect of manure, charcoal, and mineral fertilizer on soil fertility and crop production of a highly weathered tropical soil. Soils were amended at 11 Mg charcoal ha^{-1}. Nutrient additions from charcoal were low compared to Lehman (2003): 59, 0.29, 2.52, 9.00, and 1.87 kg ha^{-1} of N, P, K, Ca, and Mg respectively. However, the study showed a synergistic effect of charcoal with additional nutrient input. Fertilized charcoal treatments maintained their available nutrient content over several harvests versus the fertilized plots even though significantly more nutrients were removed with the biomass. Peanut hull biochar applied at similar rates increased K concentrations in soil which resulted in higher tissue concentrations in corn grown on peanut hull biochar plots (Gaskin et al., 2010).

The ash content can also affect soil productivity by increasing pH and reducing Al toxicity of an acid soil (Glaser 2002). The addition of 25 Mg ha^{-1} poultry litter biochar, pH 9.9, raised the soil pH from 5.0 to 6.6 (Chan et al., 2008). The addition of peanut hull biochar, containing significant amounts of base cations, caused an increase in soil pH in the first year after application (Gaskin et al., 2010). Lehman (2003) had a pH of 5.14 in the control versus 5.89 in the charcoal amended treatment. Even so, Steiner (2007) did not see a significant effect on pH with the addition of charcoal which could have been the result of the low application rates, compared to other studies, and low nutrient content of the charcoal resulting in fewer metal oxides in the ash.

Exchange capacity

Charcoal's greatest effect on soil may not be the nutrients it provides but its ability to retain additional nutrients through increasing cation exchange capacity (CEC). A comparison of anthrosols, high in black carbon, to adjacent soils with similar total carbon content but low black carbon showed the high black carbon content soils had a CEC 1.9-fold higher than the adjacent soils (Liang et al., 2006). A linear regression correlating CEC and total soil carbon indicated that high black carbon anthrosols had a higher slope (8.6) than adjacent soils with low black carbon content (2.8). Higher surface area, twice the charge density, and higher oxidation on the surface of particles were presented as reasons for the higher CEC in the anthrosols.

Fresh biochar does not appear to have the same surface reactivity as aged black carbon that has resided in soil for many years (Lehmann, 2007). Liang et al. (2006) found anthrosols containing black carbon and a total SOC content of 30 mg g^{-1} had CEC values of up to 211.3 $mmol_c$ kg^{-1}. Steiner et al. (2007) presented CEC values of 1.80 $mmol_c$ kg^{-1} in the fresh charcoal amended soils vs. 1.61 $mmol_c$ kg^{-1} in the control with an application rate of 11 Mg ha^{-1}. Lehmann et al. (2003) showed charcoal-amended soils had a considerably greater CEC than the control, however application rates were high and would not be feasible for a one-time application on an agronomic scale. It should be noted the CEC measurements using compulsory exchange may overestimate the exchange capacity of some fresh biochars due to interference with the ash content of the biochars because the ash fraction of the biochar may contain the displaced ion and the soluble ash would mimic exchange ions.

Abiotic oxidation of the surface of the aromatic black carbon particles appears to be the mechanism that forms surface charge (Cheng et al., 2006). The rate of this reaction may be temperature dependent with warmer climates seeing a response faster than cooler climates (Cheng et al., 2008b). The CEC of corn char produced at 600°C showed the greatest increase when incubated in unsaturated conditions while oak wood biochar showed the greatest increase under alternating saturated and unsaturated condition meaning surface charge formation may depend on the environmental water regime (Nguyen and Lehmann, 2009). Feedstock and pyrolysis conditions affect the surface chemistry of fresh biochar where woody biomass and higher temperatures tend to have lower CEC than grass and manures and lower production temperatures (Gaskin et al., 2008; Nguyen and Lehmann, 2009).

Ash concentration in biochar varies based on feedstock and production conditions (Keiluweit et al., 2010). The ash content consists of different minerals depending on the feedstock selected (Gaskin et al., 2008); therefore, some biochars may contain the same ion as the ions used to saturate exchange sites during compulsory exchange measurement of CEC. The ash derived ions may become soluble during displacement, causing interference and potentially overestimating CEC of high ash content biochars.

Water-holding capacity

There is limited information on biochar's effect on water-holding capacity. The addition of charcoal can increase the available water content of sand-textured soils (Tryon, 1948). Glaser et al. (2002) indicate that the high surface and porous structure of charcoal amendment could increase soil water-holding capacity but positive effects could only be seen at unrealistic application rates.

Erosion

Black carbon may be prone to erosion, potentially negating any soil improvement if it is not incorporated into the soil (Lehmann, 2007). Black carbon preferentially eroded under slash and burn agriculture (Rumpel et al., 2006). Data from the study showed mineral-bound SOM comprised 30% of the residual SOC, while black carbon accounted for 15%; however, black carbon represented 30% of the carbon in eroded sediments. The authors propose black carbon's low density, which allows large particles to float for long distances, and the colloidal nature of the finer fraction of black carbon as two possible reasons for its erosive properties.

Adsorption and nutrient leaching

The adsorptive properties of charcoal may reduce pesticide and nutrient leaching, therefore reducing the amount of pollutants in ground and surface waters. Biochars effects on N adsorption are not clear. Lehmann et al (2003) noted a considerable reduction in nutrient leaching from biochar-amended soils versus unamended soils. Ammonium leaching was drastically reduced with charcoal amendment. Conversely, cumulative nitrate leaching tended to be higher, 1.5 kg ha^{-1}, in the ferralsol + char + fertilizer treatment compared to the ferralsol + fertilizer treatment, 0.5 kg ha^{-1}. The increase in nitrate leaching may be due to increased nitrification seen in the presence of charcoal (DeLuca et al., 2006). Langmuir model estimated the maximum NH_4^+-N adsorption capacity of a bamboo biochar produced at 600°C to be 0.852 mg g^{-1} and the biochar was able to retard NH_4^+-N movement through a soil column and reduce leaching (Ding et al., 2010). Conversely, wood and poultry litter biochars produced at 400 and 550°C applied to each a Vertisol and Alfisol had no effect on NH_4^+-N leachate concentrations during a first leaching event nor NO_3^+-N on a second, but did have an effect on NO_3^+-N during the first leaching and NH_4^+-N during the second (Singh et al., 2010). The pH of the Vertisol, high temperature biochars, and the low temp manure biochar were all above 8; consequently, some of the NH_4^+-N adsorption could be due to volatilization losses, although the paper does not address this.

A study by Yu et al. (2006) indicates that small amounts of charcoal in soil may have major effects on adsorption and desorption of organic compounds. Redgum wood charcoal was prepared at 450 and 850°C. A sandy loam soil was amended with the charcoal at several rates, <5% for the 450 °C black carbon and <1% for the 850 °C black carbon. Adsorption isotherms were run using diuron, a pesticide, as the sorbate. The sorption capacity of the biochar-amended soils was 7 to 80-fold higher for the 450°C black carbon and 5 to 125- fold for the 850°C black carbon than the sorption capacity of unamended soils. The finer pore size of the 850 black carbon charcoal appears to be a key property, giving it a much higher surface area and adsorption capacity than the 450°C black carbon. Soils amended with high temperature biochars have been shown to have a higher polycyclic aromatic hydrocarbon sorption capacity than soils amended with lower temp biochars (Chen and Yuan, 2011) indicating those soils may need higher pesticide application rates.

Carbon sequestration and climate change

Biochar's most intriguing property and the reason behind its sudden popularity is its stability in soil and its potential ability to sequester carbon from the atmosphere. It has long been understood that black carbon was the stable form of organic carbon in the Terra Preta soil of Brazil (Glaser et al., 2000) as well as other black earth soils found around the world. That black carbon has persisted in the Brazilian soils under tropical conditions, which are conducive to high weathering and mineralization, for hundreds to thousands of years, longer than any other form of carbon in the soils (Pessenda et al., 2001), is a testament to its durability.

Black carbon's persistence in the highly weathered anthrosols of the Amazon indicate the material can persist for long periods of time, but quantifying the amount of carbon sequestered through land application of biochar may be difficult (Lehmann, 2007). Depending on feedstock and pyrolysis conditions, a some fraction of the applied carbon in the form of fresh biochar can be rapidly lost to mineralization of any aliphatic compounds present (Hamer et al., 2004) and the oxidation of the surface of the aromatic structured particulates (Cheng et al., 2006). Cheng et al. (2008) indicate there is a relationship with mean annual temperature and black carbon mineralization, indicating biochar's half-life in soil may vary with climatic conditions. While feedstock and production methods may be able to curb some of these processes, determining an accurate residence time for biochar in soil is a difficult task (Lehmann, 2007). Kuzyakov et al. (2009) reported a black carbon loss of 0.5% $yr^{-1}$and estimated a half-life of 1000 years under field conditions. Furthermore, attempting to sequester carbon in soils rich in SOM may result in a net loss of carbon due to the accelerated mineralization of native organic matter in the presence of biochar (Hamer et al., 2004; Kuzyakov et al., 2009; Wardle et al., 2008).

In addition to the potential for C sequestration, there is some evidence that biochar may reduce emission of other heat-trapping gases from soil. Biochar incorporation into soil reduced emissions of NO_x by 80% and methane completely though the mechanisms are not known (Lehmann, 2007). Over time, aged biochar may be able to mitigate N_2O emissions but soil type and biochar feedstock and production conditions need to be taken into consideration to insure short term N_2O emissions are not increased by biochar additions (Singh et al., 2010).

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CHAPTER 3

CHARACTERIZATION AND MINERALIZATION RATES OF LOW TEMPERATURE PEANUT HULL AND PINE CHIP BIOCHARS[1]

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Abstract

Biochar can potentially increase soil fertility and sequester carbon by incorporating nutrients and stable black carbon into the soil. A defined methodology to characterize biochar is necessary to predict how specific biochars will affect these soil properties.

We amended Tifton soil (Fine-loamy, siliceous, thermic Plinthic Kandiudults) with Peanut Hull (*Arachis hypogaea;* PH) and Pine Chip (*Pinus taeda*; PC) biochar at application rates of 1 and 2% (w/w) and performed a 136 day mineralization study. We also amended Tifton soil with PH and PC biochar at 2% and their respective feedstocks at equal carbon rates and performed a 24 day mineralization study. Soil carbon mineralization rates were monitored periodically throughout each study and total nitrogen mineralization rates were also observed. In addition, we characterized each biochar using thermogravimetric analysis with mass spectrometer (TGA-MS), proximate analysis, Fourier transform infrared spectroscopy (FTIR), and total mineral analysis to identify biochar characteristics that might correlate with mineralization properties.

Limited C (< 2%) mineralized from both biochars, but mineralization rates of soil amended with PH biochar were higher than PC biochar. Carbon mineralization correlated well with estimated aliphatic content determined by TGA-MS but not with volatile content indicated by proximate analysis. Nitrogen was not mineralized from either biochar despite PH biochar containing 1.9% nitrogen, indicating that plant-based biochar should not be considered a source of nitrogen for plant growth. The nitrogen in biochar may be contained in the stable aromatic structure of the biochar, as indicated by TGA-MS, and not available to soil microbes.

Introduction

Pyrolysis, an alternative energy process, converts biomass feedstock into syngas, bio-oil, and biochar through rapid heating in the absence of oxygen (Czernik and Bridgwater, 2004). It may provide carbon negative, renewable energy by land applying biochar (Gaunt and Lehmann, 2008). Biochar is a black, amorphous carbon similar to charcoal with a polycyclic structure and varying degrees aromaticity and surface oxidation (Cheng et al., 2006). Evidence from black-carbon rich Terra Preta soils in the tropics indicates black carbon resists mineralization (Liang et al., 2008) while increasing soil fertility and productivity (Glaser et al., 2002; Lehmann et al., 2003; Steiner et al., 2008). Many researchers have proposed that land application of biochar from industrial pyrolysis may create a carbon sink as well as provide similar productivity benefits (Laird et al., 2009).

Biochars characteristics vary depending on the feedstock selected and pyrolysis conditions. Feedstock affects nutrient concentration, cation exchange capacity (CEC), and soluble carbon (Gaskin et al., 2008). For example at a similar pyrolysis temperature, a manure based poultry litter biochar contains greater amounts of nutrients and CEC than a pine chip biochar. Also, higher pyrolysis temperature (500°C) compared to lower temperature (400°C) decrease the CEC and increase most macronutrient concentrations in the biochar. Production temperature (Antal and Gronli, 2003) and feedstock (Guerrero et al., 2008) result in biochars with varying concentrations of ash, volatiles, and fixed carbon content. Aromaticity of the carbon fraction in fast and slow pyrolysis biochars appears to increase with reaction time (Brewer et al., 2009). Characterization of chars from ponderosa pine shavings and tall fescue straw, each pyrolyzed from 100 to 700°C in 100°C increments for 1-h, indicates that as production temperature rises, aromaticity increases followed by condensation into turbostratic crystallites (Keiluweit et al., 2010). Temperature and oxidation during or after the pyrolysis process can increase the size and continuity of pores in biochars (Bird et al., 2008). Biochars produced from eight different species of hard and soft wood varied in porosity and pore size distribution, resulting in different adsorption capacities of phenolic compounds (Keech et al., 2005) potentially effecting soil microbial populations (Wardle et al., 2008).

Black carbon has long been understood to be the most stable form of carbon in soil (Glaser et al., 2002; Liang et al., 2008) because of its aromatic structure (Cheng et al., 2006; Liang et al., 2008); however, a small fraction of biochar, especially if produced at lower temperatures, may be mineralizable (Bruun et al., 2008). Low temperature biochars may have an aliphatic fraction that is microbially available (Kuzyakov et al., 2009; Smith et al., 2010; Steinbeiss et al., 2009; Zimmerman, 2010) that typically undergoes a period of rapid mineralization the first few days to weeks after incorporation into soil (Bruun et al., 2008; Deenik et al., 2010; Hilscher et al., 2009; Kuzyakov et al., 2009; Smith et al., 2010; Zimmerman, 2010). Follow this initial flush of activity, mineralization of black carbon is primarily an abiotic process over the course of months (Cheng et al., 2006); however, this loss only accounts for a few percent per year and some biochars may persist on the order of millennia (Kuzyakov et al., 2009). The soil type and use may also affect mineralization rates. Soils and loess amended with C-14 labeled biochar showed an increased rate of black carbon decomposition with addition of glucose and mechanical disturbance (Kuzyakov et al., 2009), indicating labile C sources and disturbance may accelerate biochar loss.

While biochar may be largely unavailable for microbial mineralization, the effects on native and added organic matter are still unclear. The presence of biochar may stimulate the mineralization of native soil organic matter (Wardle et al., 2008). Black carbon in anthrosols has been shown to increase incorporation of added organic matter into aggregates and organo-mineral fractions, compared to adjacent soils, without affecting the mineralization rate of the added matter (Liang et al., 2010). Charcoal may provide habitat (Pietikainen et al., 2000) and act as an absorbent for substrates, including phenolic compounds, promoting certain microbial populations (Pietikainen et al., 2000; Wardle et al., 2008; Zackrisson et al., 1996).

Biochars effects on N cycling are complex. Corn did not respond to the 209 kg ha^{-1} N in peanut hull biochar applied to a loamy sand soil (Gaskin et al., 2010); however, broiler litter biochar has been shown to provide N to plants (Chan et al., 2008; Tagoe et al., 2008). Carbonized broiler litter can have a similar effects on soil fertility as uncarbonized broiler litter (Tagoe et al., 2008). Adsorption of phenolic compounds may also boost nitrification in pine forest ecosystems (DeLuca et al., 2006), yet some biochar can contain ethylene that inhibits nitrifying bacteria (Spokas et al., 2010). Biochars with a large mineralizable fraction (Deenik et al., 2010) or the stimulated mineralization of co-applied biomass (Novak et al., 2010) may result in N immobilization.

Biochars recalcitrance coupled with improved fertility seen in charcoal-amended tropical soils may make biochar an appealing amendment to sequester C in low fertility soils; however, we need to understand how biochar characteristics will affect various soils systems and practical ways to estimate these effects. Our objective was to characterize two biochars from Gaskin et al.(2010), derived from peanut hull (PH) and pine chip (PC), and correlate those characteristics with C and N mineralization rates in a 136-day study using the following hypotheses.

1. Peanut hull and PC biochar will mineralize at different rates that will correlate to an aliphatic and volatile matter concentration in the biochar.
2. Aging in soil will decrease aliphatic and volatile matter as well as C and H concentrations in biochars, and will increase oxygen-containing functionalities on the surface of biochars.
3. Biochar will affect the N status of the soil by either immobilizing or mineralizing N depending on the N content of the biochar.

Materials and Methods

Biochar production

EPRIDA Inc. (Athens, GA) produced biochar from pelletized PH and PC feedstocks in an auger-fed pyrolysis reactor at approximately 400°C with steam as the carrier gas. The pelletized biochars were ground using a roller mill to a mean particle size of 425 µm.

Soil

The soil used for each study was a Tifton series (Fine-loamy, siliceous, thermic Plinthic Kandiudults). The top 15 cm of soil was collected from an agricultural field near Tifton, GA, air dried, and screened to 2 mm. Total soil C and N were 4.94 and 0.25 g kg^{-1}, respectively, or a C: N ratio of approximately 20:1.

Mineralization studies

Two laboratory mineralization studies were conducted. The first study tested the effect of biochar feedstock and application rate on soil respiration and N mineralization. Soil (50 g) mixed with 0, 1, and 2% (w/w) biochar, which equates to application rates of 22 or 44 Mg ha^{-1}, and was packed in 50-mL beakers to a bulk density of 1.33 g cm^{-3}. Water was added to bring the water content to 0.21 kg kg^{-1} (approximately field capacity, 33 kPa). The biochar rates used were selected because they could be realistically applied on an agronomic scale. The beakers of wetted soils were placed in one quart (0.95 L) Mason jars with a vial of DI water to maintain moisture and a vial of 1 mol L^{-1} NaOH to trap CO_2. Blanks for CO_2 contained only water and a NaOH trap. The Mason jars were placed in an incubator at 25°C. Four replications of each treatment were arranged in a completely randomized design. Respired C was determined by titrating NaOH traps to a pH 7 endpoint at day 3, 10, 25, and every two weeks up to 136 days. The study was terminated once respiration rates were static over several weeks (approximately 4.5 months).

The second study was to test the immediate nitrogen availability in the feedstock compared to their respective biochar over 24 d. Peanut hull and PC biochars were applied at the 44 Mg ha^{-1} and the feedstocks applied at equal C rates with an unamended soil as the control. Samples were prepared and measured using the same methodology and replication as the 136-d study. Respired C was measured at day 3, 10, and 24.

A 10-g subsample from d 0 and 136 from the long-term study and d 0 and 24 from the short-term study was extracted with 2 M KCl for 1 hour and filtered through Whatman 1 filter papers. Filtrate was frozen until NH_4^+-N and NO_3^+-N analysis on an autoanalyzer using cadmium reduction and phenate colorimetric methods (EnviroFlow 3000, Perstorp, Toledo, Ohio). Inorganic N (sum of NH_4^+-N and NO_3^--N) at the beginning of each study was subtracted from inorganic N at the end of each study to estimate N mineralized.

Aged biochar particles from the 44 Mg ha^{-1} treatments of the long-term respiration study were handpicked from soil. Fresh and aged biochar was ground to a consistent particle size (< 0.05 mm) using a mortar and pestle. A ball mill grinder was used to grind raw PH and PC feedstock into a fine powder.

Thermogravimetric analysis

Temperature controlled combustion and combustion gas analysis of the raw feedstock, fresh biochar, and aged biochar were analyzed on a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851 Columbus, OH) with mass spectrometer used to analyze gas composition

(Pfeiffer Vacuum Thermostar, Square Nashua, NH). Approximately 5 mg of sample was weighed into an alumina crucible and evenly distributed across the bottom of the pan. The temperature program included a 3-min isothermal stage at 30°C followed by a constant heating rate of 5°C min^{-1} to 700°C in 79% Ar and 21% O_2. The gas flow rate was 40 mL min^{-1}. The mass spectrometer was programmed to measure m/z ratio 30, the mass of nitric oxide. The percent mass remaining after temperature controlled combustion is reported as the ash content as determined by TGA (Table 4 and 5).

Isothermal decomposition was measured on fresh and aged PH and PC biochar using the same instrumentation as combustion samples and only Ar as the flow through gas. The temperature program consisted of four isothermal stages in the following order: 3-min at 25°C, 60-min at 200°C and 400°C each, followed by 7-min at 950°C. Mass loss at 200°C is an estimate of moisture content of the biochar as determined by TGA. Aliphatic content of the biochar was determined by calculating the amount of mass lost between 200 and 400 °C during thermal decomposition (Lyons et al., 2008). Volatile content was considered the mass lost from the 200 °C stage to the 950°C stage. The mass spectrometer was programmed to scan m/z ratios 1 through 200.

Moisture, volatile, fixed carbon, and ash content of the fresh PH and PC biochar were measured by proximate analysis using ASTM D5142 (2004) on a LECO TGA 701 (St. Joseph, MI). Moisture content is based on the amount of mass lost from the biochar at 110°C. After the after moisture measurement is complete, the biochar is heated to 950°C under N_2 gas for 7-m and the mass loss at this stage is considered volatile matter content. The samples are then combusted in O_2 at 750°C to measure ash content. The sum of moisture, volatile, and ash is subtracted from 100 and the remaining mass is considered fixed C.

Laboratory analysis

Peanut hull and PC biochars and their respective feedstock were analyzed for total elemental composition. Samples were digested with nitric acid, USEPA Method 3050 (USEPA, 1994), and elements were analyzed by inductively coupled plasma spectrophotometer (ICP, Thermo Jarrell-Ash model 61E,Thermo Fisher Scientific, Waltham, MA, USA). Carbon, N, and H were determined on the feedstock, fresh, and aged biochars by combustion (LECO CHNS-932, St. Joseph, MI, USA). Carbon, N, and H data were analyzed in two blocks based on the experiment: one comparing fresh biochar to the original feedstock, the second comparing fresh biochar to aged biochar.

Fourier transform infrared spectra were measured by a Varian 2000 FTIR (Palo Alto, CA). Fresh and handpicked biochars were finely ground and coated on KBr at a rate of 2% biochar. The spectra were recorded from 4400 to 400 cm^{-1} by averaging 200 scans at 2 cm^{-1} resolution.

Statistical Analysis

Proximate and thermal decomposition data comparing fresh PH and PC biochar was analyzed using a standard t-test. Carbon and N content of fresh feedstock and biochars were analyzed using PROC GLM (SAS Institute, Inc. 2008) with means separated using Waller-Duncan

K-ratio t test (K=100). Factorial analysis was performed on all other data using PROC MIXED with the SIMULATE option to compare least square means when interactions were significant.

PROC NLIN in SAS was used to fit the C respiration data (Cresp) from the 136-day mineralization to the following formula to estimate maximum respired C (rmax) and rate (k):

$$Cresp \ = rmax \ \times (1 - exp^{-k \times day})$$

Parameters rmax and k, and mineralized NH_4^+-N and NO_3^+-N were analyzed using PROC MIXED with means separated using orthogonal contrasts to test for the effect of feedstock, rate, and interaction. Analysis was performed with and without the control treatment. Statistical tests with $p < 0.05$ level were considered significant.

Dunnett-Hsu mean comparison (alpha = 0.05) was used to compare the treatment means to the control of the 136-d and 24-d mineralization studies. The control was then dropped from analysis and cumulative respiration and mineralized N were analyzed using PROC MIXED with feedstock, condition (fresh vs. aged) or state (feedstock vs. biochar), and interaction. Linear regression analysis was used to determine the relationship between the aliphatic and volatile matter added to soil and estimated maximum respired C for both PH and PC biochars.

Results

Feedstock and biochar analysis

Peanut hull feedstock had a greater concentration of major and minor nutrients than PC feedstock (Table 1). Nitrogen and K were an order of magnitude greater while other nutrients are approximately two to five times greater. The C: N ratio in the feedstock was statistically the same in the PH biochar and significantly greater in PC. With the exception of N and S, feedstock nutrient concentrations were considerably smaller than their biochars, ranging from 24 to 41 % of the biochar concentration. Nitrogen and S concentrations were similar to the biochars.

Similarly, the PH biochar contained larger concentrations of major and minor nutrients than PC biochar (Table 1). Nitrogen, P, and K concentrations were approximately an order of magnitude larger, Mg and S double, and Ca 34 % greater. Peanut hull and PC biochar C to N ratios were 35 and 214, respectively.

Proximate analysis of fresh biochar measured larger moisture and volatile contents and smaller ash contents than the thermogravimetric analysis; however, overall trends when comparing the PC to PH were similar (Table 2). Peanut hull biochar contains significantly more moisture, three times more ash, and approximately 12 g kg^{-1} more estimated aliphatic compounds than PC biochar. However, PC contains more volatile matter and fixed C.

Carbon and nitrogen mineralization

High variability in the control treatment resulted in the rate constant “k” being the same as other treatments and only the 44 Mg ha^{-1} treatments had a greater rmax than the control according to Dunnett-Hsu mean comparison. Univariate analysis of the long-term respiration data confirmed a large standard deviation in the control compared to other treatments for both k and rmax. Mineralized N from the control also had a large standard deviation compared to other treatments. Control means were as follows: rmax = 527 mg kg^{-1}, k = 0.001 day^{-1}, mineralized N = 28.2 mg kg^{-1}.

Maximum respired carbon was significantly larger ($p < 0.0411$) from soils amended with 44 Mg ha^{-1} biochar (Table 3). Feedstock had no significant on effect ($p < 0.0642$) on rmax. The inverse was true for rate, k, where PH mineralized at a faster rate ($p < 0.0007$) than PC biochar and feedstock had no significant effect ($p < 0.0637$). There was no interaction between feedstock and rate either for rmax or k.

Peanut hull and PC biochar had no significant effect on N mineralization rates (Table 3). Mineralization rates were no different than the control and there was no effect of biochar feedstock or application rate in the 136-d mineralization study.

Dunnett-Hsu mean comparison of treatments to the control of the 24-d respiration study showed cumulative respiration of the PC char treatment was statistically the same as the control (Table 4). The PH feedstock was the only treatment to mineralize more N than the control ($p < 0.0450$). Control means were as follows: cumulative respired C = 150 mg kg^{-1}, mineralized N = 9.55 mg kg^{-1}.

Factorial analysis of the 24-d respiration data showed a significant interaction between feedstock and state (feedstock vs. biochar) for cumulative respiration ($p < 0.0001$) and mineralized NH_4^+-N ($p < 0.0007$) (Table 4). There was no significant difference in cumulative respiration of the PH and PC biochar treatments. Each feedstock respired at a greater rate than their respective biochar; however, the PH feedstock at a much larger rate, 2277 mg C kg^{-1} soil, than PC feedstock, 692 mg C kg^{-1} soil. Pine chip feedstock, -1.43 mg N kg^{-1} soil, showed signs of immobilized N compared to the PH feedstock, 26.8 mg N kg^{-1} soil ($p < 0.0103$). There was no significant difference ($p < 0.1923$) between PH feedstock and biochar, 26.8 and 13.5 mg kg^{-1} soil respectively, due to high variability in NO_3^--N in the feedstock amended soils.

Ultimate and thermal decomposition of fresh and aged biochars

Incubating biochar in a soil matrix (aging) had a significant effect on several measured characteristics (Table 5). There was a significant interaction ($p < 0.0011$) between the feedstock, PH and PC, and condition, fresh and aged, for C: N ratio, C, and N content. The PH biochar showed a significant decrease in C, 730 to 663 g kg^{-1} char, and N, 20.9 to 17.1; however, there was no effect on the C: N ratio. PC biochar showed a significant decrease in C content, 795 to 697 g kg^{-1} char, and C: N ratio, 216 to 155 g kg^{-1} char, but no difference in N content. Aging resulted in a significant decrease in H concentration.

Surprisingly, aging resulted in a significant increase in aliphatic content ($p < 0.0001$) and volatile matter ($p < 0.0065$). As indicated in Table 1, PH contained significantly more moisture ($p < 0.0001$) and aliphatic compounds ($p < 0.0001$) while PC contained more volatile compounds

($p < 0.0473$). Ash content had a significant interaction ($p < 0.0001$) between feedstock and condition with PC accumulating 84 g ash kg^{-1} char while PH only accumulated 53 g ash kg^{-1} char. Aging increased the ash concentration of PC biochar to the same level, statistically, as the fresh PH biochar.

The mass spectrometer measured each m/z ratio between 1 and 200 approximately every 104 seconds. A majority of the masses scanned were detected; however, the response was inconsistent and did not appear to be correlated with programmed heating stages. Mass to charge ratios that were detected less than 80 % of the measurements were eliminated from data analysis in order to focus on species that were consistently detected throughout the analysis and responded to changes in temperature. Four m/z ratios were consistently measured and responded to changes in temperature, represented by peaks in intensity at consistent times between samples during measurement. The selected m/z ratios are listed with associated compounds in parentheses: 44 (CO_2), 18 (H_2O), 17 (OH, NH_3), and 16 (CH_4, NH_2). All measured peaks had the same shape between samples with the only difference being peak height all which were measured at a consistent time; therefore, the maximum intensity for each peak associated with 200, 400, and 950 °C heating stages was recorded and used for statistical analysis.

Gas evolution from the thermal decomposition of biochars did not provide detailed information on the effect of aging on biochar. We expected to see a significant increase in the amount of CO_2, OH, and CH_4 evolved from aged biochars at 400°C and H_2O at 200°C. Each prediction was true on average but none of the differences were significant. There was no significant effect of condition, fresh vs. aged, nor interaction on any of the species measured.

Thermal decomposition gas analysis did provide some corollary information relating to the decomposition data of fresh biochars. Peanut hull biochar evolved significantly more CO_2 and CH_4 / NH_2 at 400 °C which is the heating stage associated with aliphatic compounds. Peanut hull also evolved more CO_2, H_2O, OH/NH^3, and CH_4/NH_2 at 200 °C which is associated with moisture content. The only significant difference in the amount of CH_4/NH_2 occurred at 900 °C with PH evolving more CH_4/NH_2, than PC, which conflicts with the estimated volatile content.

Controlled combustion analysis

Temperature controlled combustion of PC and PH biochar and their respective feedstocks showed distinct differences in mass loss patterns and gas evolution. Mass loss curves show both PC and PH feedstock began to lose mass at approximately 200°C with both loosing approximately 40% of their mass by 300°C, the approximate temperature where biochars began to lose mass (Figure 1). Feedstocks appeared to have two distinct combustion events, indicated by a break in the slope, while biochars exhibited a single event. Peanut hull biochar began to lose mass at 280°C and lost mass at a slower rate than PC which began to lose mass at 300°C. All samples (feedstock and biochars) were completely combusted by 500°C.

Combustion gas analysis of PC data shows a shift of m/z 30 (NO^+) evolution peaks from approximately 300°C to 470°C indicating biochar N is strongly bonded compared to N in the respective feedstock (Figure 1) . Peanut hull feedstock contained two separate N pools represented by peaks at 300 and 470°C, while PH biochar only contains one peak (470°C) that was similar to the second feedstock peak. Both PC and PH appear to lose a significant amount of N during the pyrolysis process with the cumulative area under the biochar curves being less than the feedstock curves.

Fourier transform infrared spectroscopy

The broad peaks from 3000 to 2800 and 900 to 700 cm^{-1} suggests an alkyl-aromatic structure (Figure 2). Several O containing functional groups were detected in low concentrations in both fresh chars: OH (3700 – 2000 cm^{-1}), C=O (1700 cm^{-1}), and C-O-(C) (1275 cm^{-1}). Fresh PH had a slight response at 1050 cm^{-1} indicating C-O-(H) bonding. Both fresh PH and PC biochar contained C-H bonds (3000-2800 cm^{-1}) associated with aliphatic compounds.

Aged PH and PC biochars had a reduced peak intensity between 3000 and 2800 cm^{-1} compared to their respective fresh biochars indicating a reduction in aliphatic C-H bonds (Figure 2). This was more apparent in the PH biochar. Aging also increased the concentration of oxygen containing groups. Carbonyl (1700 cm^{-1}) and C-O-(H) (1050 cm^{-1}) increased in PH and PC and C-0-(C) (1275 cm^{-1}) in PH. A slight shoulder around 2600 cm^{-1} in the aged biochar spectra may indicate the formation of some carboxylic acid functional groups. The aging process did not affect the concentration of aromatic bonds (1600 cm^{-1}) and associated aromatic C-H groups (900-700 cm^{-1}).

Discussion

Carbon mineralization rates of biochar vary by feedstock; however, C mineralization rates were small considering the amount of C added to the system. Using the estimated rmax and subtracting the control rmax from the treatment rmax to correct for native organic matter mineralization, approximately 2 % of the applied C from the PH and 1 % of the PC would be mineralized over several years, with a majority of the C mineralized within the first 100 days (Figure 3). This PC mineralization rate is similar to that of oak wood pyrolyzed at 400°C which mineralized 1 % of biochar C over 100-d mineralization rate (Zimmerman, 2010). Peanut hull mineralization rates are slightly lower than rye grass produced at 350°C and applied to a Cambisol (Hilscher et al., 2009). As seen in several other studies, biochar samples underwent a brief period, approximately 2-w, of rapid mineralization (Bruun et al., 2008; Deenik et al., 2010; Hilscher et al., 2009; Kuzyakov et al., 2009; Smith et al., 2010; Zimmerman, 2010) that gradually diminished to rates similar to the control soil (Smith et al., 2010).

Volatile matter content has been proposed as an indicator of mineralizable C in biochar (Zimmerman, 2010). High volatile matter content macadamia nut biochar (225 g kg^{-1}) maintained a higher respiration rate over 14-d than the low volatile matter content biochar (63.0 g kg^{-1}; (Deenik et al., 2010). More volatile matter was added with the PC than the PH biochar (Table 2), yet there was lower estimated maximum respired C ($p < 0.0642$) from PC treatments (Table 3). Conversely, more aliphatic C was added with PH than the PC biochar, which also had higher maximum respired C. Regression analysis shows that both aliphatic and volatile matter content of PH biochar may be a good predictor ($p < 0.0012$) of estimated maximum respired C from amended soils (Figure 4). Neither aliphatic nor volatile matter would be a good predictor ($p < 0.3992$) for PC mineralization due to the variability of maximum respired C, specifically in the 22 Mg ha^{-1} treatment. The reduction in aliphatic C-H bonds indicated by FTIR (Figure 2), coupled with the reduction in biochar hydrogen content after incubation (Table 5), suggests that this fraction might have been the constituent of biochar degraded by microorganisms in soil and responsible for the initial flush of CO_2 seen in other studies (Bruun et al., 2008; Kuzyakov et al., 2009; Smith et al., 2010; Zimmerman, 2010). Peanut hull amended soils received a higher load of aliphatic C and also respired more C than PC amended soils. Aliphatic matter also was a suitable predictor of respired C; therefore, aliphatic matter content of biochar may be a better indicator of potentially mineralizable C in biochar than volatile matter content.

Contrary to the hypothesis, PH and PC biochar handpicked from incubated soils showed an increase in aliphatic and volatile content as estimated by TGA (Table 5). The small increase in aliphatic and volatile contents may be attributed to soil microbial biomass. Charcoal has been shown to adsorb substrate and provide habitat for soil microbes (Pietikainen et al., 2000). Substrate induced respiration and basal respiration both increased with increasing levels of biochar application across several soil types and appeared only limited by soil fertility (Kolb et al., 2009). Soils from a burned pine plantation in Turkey showed an increase in fungal and bacterial populations; however, there was no significant increase in microbial biomass C compared to the control (Kara and Bolat, 2009). Kolb et al. (2009) suggest biochar may increase microbial habitat based on seeing the largest increase in an Entisol with sandy structure and low fertility.

Biochar characteristics can have an effect on soil microbial biomass. Peanut hull biochar has dissolved organic C content of 0.20 g kg^{-1} compared to PC's 0.12 g kg^{-1} (Gaskin et al., 2008) as well as significantly more P, K, and micronutrients (Table 1). Leached C from biochar may provide a food source for soil microbes (Deenik et al., 2010) in addition to the substrate adsorbed by charcoal (Pietikainen et al., 2000). Excess major and micro nutrients from biochar may also stimulate microbial populations (Chan et al., 2008; Kolb et al., 2009). Biochars produced from different feedstocks can have a range of surface areas even when produced under the same conditions (Keiluweit et al., 2010) meaning the PH biochar may have provided more habitat than the PC biochar. Given that PH biochar contains higher dissolved organic C, major and micro nutrients, surface area, and aliphatic C we would expect to see a greater increase in aliphatic content as result of increased microbial biomass; however there was no interaction between feedstock and condition (Table 5).

As expected, C, N, and H concentrations decreased due to aging (Table 5). An unexpected increase in ash content may account for a portion of the decrease. Handpicked biochar samples had a brown tint similar to the soil matrix color which may have been the result of soil minerals attached to the biochar surface (Joseph et al., 2010). The cumulative concentration of C, N, and H was 811 g kg^{-1} in the fresh biochar and 723 g kg^{-1} in the aged. Moisture and ash accounted for 117 and 190 g kg^{-1} of the remaining mass of fresh and aged biochars, respectively, for a total of 928 and 913 g kg^{-1}. The remaining mass of the biochar is most likely attributed to oxygen (Cheng and Lehmann, 2009; Cheng et al., 2008a; Hilscher et al., 2009). Fourier transform infrared spectroscopy spectra indicate the fresh and aged PH and PC biochars have similar surface structures to other black carbon (Cheng et al., 2006; Varhegyi et al., 1998) and oxygen containing functionalities, specifically carboxylic groups, on biochars increased (Figure 2) during incubation (Cheng and Lehmann, 2009; Cheng et al., 2006).

There is no evidence that the biochar stimulated mineralization of the native organic matter as seen in other studies (Wardle et al., 2008). The control soil used in the respiration study is defined by a low organic content and fertility. As a result, the microbial populations in the soils vary greatly based on the substrate available. Control samples in the 136-d respiration had an inverse relationship between k and rmax which indicates the samples may have been substrate limited (Fisher, personal communication, August, 2008). The control soil would respire less C, on average, than biochar treatments (Figure 3) but soil organic matter would still account for a significant amount of C respired from biochar treatments if that rate remained consistent between treatments. The estimated rmax of the control soil predicts that approximately 10 % of the soil C will mineralize; however, due to variability, the estimate may not accurately represent the amount of C respired from the native organic matter in biochar amended samples.

Surprisingly, PH and PC biochar had little effect on N mineralization rates, even in PC treatments due to the high C: N ratio. High volatile matter (225 g kg^{-1}) macadamia nut shell applied to soil and incubated reduced extractable NH_4-N concentrations indicating immobilization (Deenik et al., 2010). Manure derived chars have been shown to be provide N to plants (Chan et al., 2008; Tagoe et al., 2008) so we expected to see at least some N mineralized from the PH biochar. There were no signs of N mineralization or immobilization in biochar treatments of the long term incubation study (Table 3). Peanut hull biochar has been shown to emit ethylene which can inhibit nitrification (Spokas et al., 2010); however, we saw higher nitrate, on average, in PH treatments (data not shown). Higher application rates of biochar may have stimulated nitrifying bacteria compared to the control and 22 Mg ha^{-1} but this effect wasn't significant based on the statistical analysis of NH_4^+-N and NO_3^--N data.

The short-term incubation study offered insight into why biochar had no effect on N dynamics. Peanut hull biochar and feedstock have the same C:N ratio (Table 1) which is only slightly higher than the 20:1 ratio of the soil; therefore, equal mineralization would be expected if biochar N was available as in manure chars (Chan et al., 2008; Tagoe et al., 2008). Peanut hull and PC feedstocks mineralized 16 and 5.5 % of applied C while PH and PC biochars only mineralized 1.5 and 1.1 % over the 24-d incubation (Table 4). Only PH feedstock mineralized a significant amount of N compared to the control, 9.55 mg kg^{-1}. High variability in the NO_3^--N data resulted in no differences compared to the control; however, PC feedstock appeared to immobilize N as expected. The chemical stability of N in biochar increases with increasing biochar production temperature by becoming incorporated in the aromatic structure as heteroatoms (Hilscher et al., 2009; Knicker, 2007; Schmiers et al., 1999; Stanczyk et al., 1995); therefore, N in biochar samples may have been incorporated into the biologically unavailable C complexes where N in the feedstock was still contained in mineral form or within decomposable proteins. Nitric oxide emission during controlled combustion of chars is a qualitative method that can determine the thermal stability of N compounds (Varhegyi et al., 1998). Nitric oxide analysis shows two N pools in PH feedstock but only one stable pool in PH biochar (Figure 1). Pine chip feedstock had a single N pool most likely associated with aliphatic compounds; however, the high C: N ratio caused PC feedstock systems to be N limited.

Applying a systems approach to the mineralization data provides a nice summary to PH and PC biochar's effect on C and N mineralization. Summing total C and N in soil with the total C and N added with each biochar and feedstock application and comparing that value to the rmax and mineralized N of the 136-d study and the cumulative respired C and mineralized N of the 24-d study, we see that native and applied unaltered organic matter C and N is more labile than biochar (Figure 5). The control mineralized both more system C and N than biochar treatments in each study. The PC treatment N mineralization rates were similar to the control because a majority of the N in those systems was from the native organic matter and in a labile form; however, a greater load of fixed C (Table 1) was applied with PC biochar therefore less C was mineralized in those treatments. Peanut hull treatments received a significant load of biochar N and aliphatic C and in turn less N and more C was mineralized from PH systems.

Conclusions

Aliphatic content of biochar may be a better indicator of mineralizable C than volatile matter content. Our data show that more C would be mineralized from PH biochar amended samples that received a higher load of aliphatic C than volatile matter. Both aliphatic and volatile matter content may be useful factors for modeling maximum respired C though more research is needed testing several feedstocks with a wide range of aliphatic and volatile matter concentration coupled with respiration studies to insure the models accuracy.

Aging biochar in soil did not result in lower aliphatic and volatile matter concentrations most likely because soil microbial biomass interfered with analysis of aged samples; however, aged biochar did have reduced concentrations of aliphatic C-H bonds on the surface. Carbon and N concentrations did decrease partly due to an increase in mineral / biochar complexes but also due to formation of oxygen containing functionalities.

Biochar did not have a significant effect on the N status of the soil. We did not see N mineralization from the PH biochar even though it had a favorable C: N ratio. There were also no significant signs of immobilization from either biochar. Biochar N is bound in compounds that are more thermally stable than the N in its respective feedstock and may not be available to soil microbes. Additional research investigated biochars with a range of C: N ratios, including manure derived biochars that have been shown to contain available N, is necessary to validate N characterization by TGA-MS.

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Table 1. Total concentrations of selected major and minor nutrients from peanut hull (PH) and pine chip (PC) biochars and their respective feedstock.

	C:N	C	N	P	K	S	Ca	Mg
		--mg kg^{-1}--						
Biochar								
PH	35.0 C	729,000 B	21,000 A	2,180	19,000	852	5,410	2,720
PC	214 B	785,000 A	3,710 C	577	2,820	350	4,030	1,230
Feedstock								
PH	37.5 C	504,000 C	14,000 B	893	7,510	900	1,560	790
PC	259 A	503,000 C	1,870 C	181	877	200	930	296

Different letters indicate means are statistically different (K=100) based on Waller-Duncan K-ratio t Test

Table 2. Proximate analysis (ASTM D5142) and estimated parameters from isothermal decomposition (TGA) of fresh biochar

	ASTM D5142				TGA			
	Moisture	Volatiles	Fixed C	Ash	Moisture	Aliphatic	Volatile	Ash
	--------------------------g kg^{-1}-----------------------				-------------------------------g kg^{-1}----------------------			
PH biochar	81	252	598	69	56	62.4	219	102
PC biochar	74	278	630	18	37	53.8	235	38.2

Table 3. Effect means and probabilities of estimated maximum respired carbon (rmax), rate (k), mineralized NH_4^+-N, and NO_3^--N from 136-day respiration study.

	C respiration		N mineralization
	Rmax	k	
	mg C kg^{-1} soil	day^{-1}	mg kg^{-1} soil
Effect means			
Feedstock			
PH biochar	735	0.0127	30.2
PC biochar	620	0.0086	26.5
Application Rate			
22 Mg ha^{-1}	650	0.0097	28.2
44 Mg ha^{-1}	740	0.0112	28.7
	Pr > F		Pr > F
Feedstock	0.0642	0.0007	0.1157
Application rate	0.0411	0.0637	0.7789
Interaction	0.5875	0.3551	0.3620

Table 4. Treatment and selected effect means and probabilities of cumulative C respiration, mineralized NH_4^+-N, and NO_3^--N from 24-day respiration study.

	C respiration	N mineralization
	cum. resp.	
	mg C kg^{-1} soil	mg kg^{-1} soil
Treatment means		
PH feedstock	2277	26.8#
PH biochar	222*	13.5
PC feedstock	692	-1.43#
PC biochar	171*	7.93
Effect means		
Feedstock		
PH	1250	20.2
PC	432	3.25
	Pr > F	Pr > F
Feedstock	<0.0001	0.0065
State	<0.0001	0.6941
Interaction	<0.0001	0.0431

*indicates treatment means are not significantly different based on comparison of LSM at alpha 0.05

# indicates treatment means are significantly different based on comparison of LSM at alpha 0.05

Table 5. Treatment and effect means and probabilities from ultimate and thermogravimetric analysis comparing fresh and aged peanut hull and pine chip biochars.

	Combustion				TGA			
	C:N	C	N	H	Moisture	Aliphatic	Volatile	Ash
			g kg^{-1} char			g kg^{-1} char		
Treatment means								
PH fresh	35.4*	730	20.9	34.6	55.8	62.4	219	102*
PH aged	38.8*	663	17.1	31.9	57.8	77.2	241	155
PC fresh	216	795	3.75*	35.7	37.2	53.8	235	38.2
PC aged	155	697	4.58*	31.9	45.1	68.3	252	122*
Effect means								
Feedstock								
PH	37.1	697	19.0	33.2	56.8	69.8	230	128
PC	185	746	4.16	33.8	41.1	61.0	243	80.2
Condition								
Fresh	126	763	12.3	35.2	46.5	58.1	227	70.0
Aged	96.7	680	10.8	31.8	51.4	72.7	247	139
		Pr > F				Pr > F		
Feedstock	<0.0001	<0.0001	<0.0001	0.2165	<0.0001	<0.0001	0.0473	<0.0001
Condition	<0.0001	<0.0001	0.0002	<0.0001	0.0715	<0.0001	0.0065	<0.0001
Interaction	<0.0001	0.0011	<0.0001	0.4039	0.2670	0.9380	0.7248	0.0235

*indicates treatment means are not significantly different based on comparison of LSM at alpha 0.05

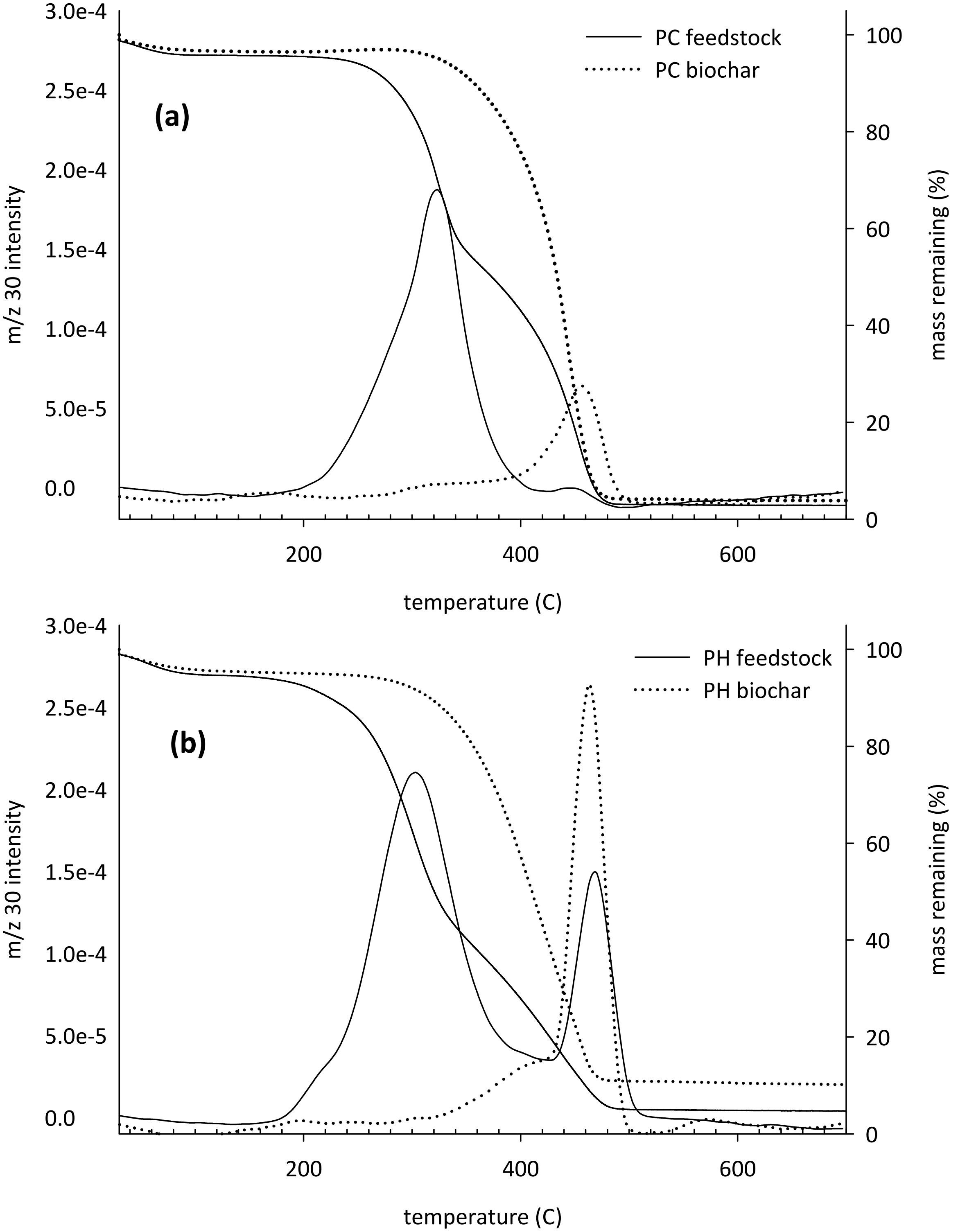

Figure 1. Combustion mass loss curve and intensity of m/z 30 (NO^+) of pine chip (a) and peanut hull (b) biochars and feedstock

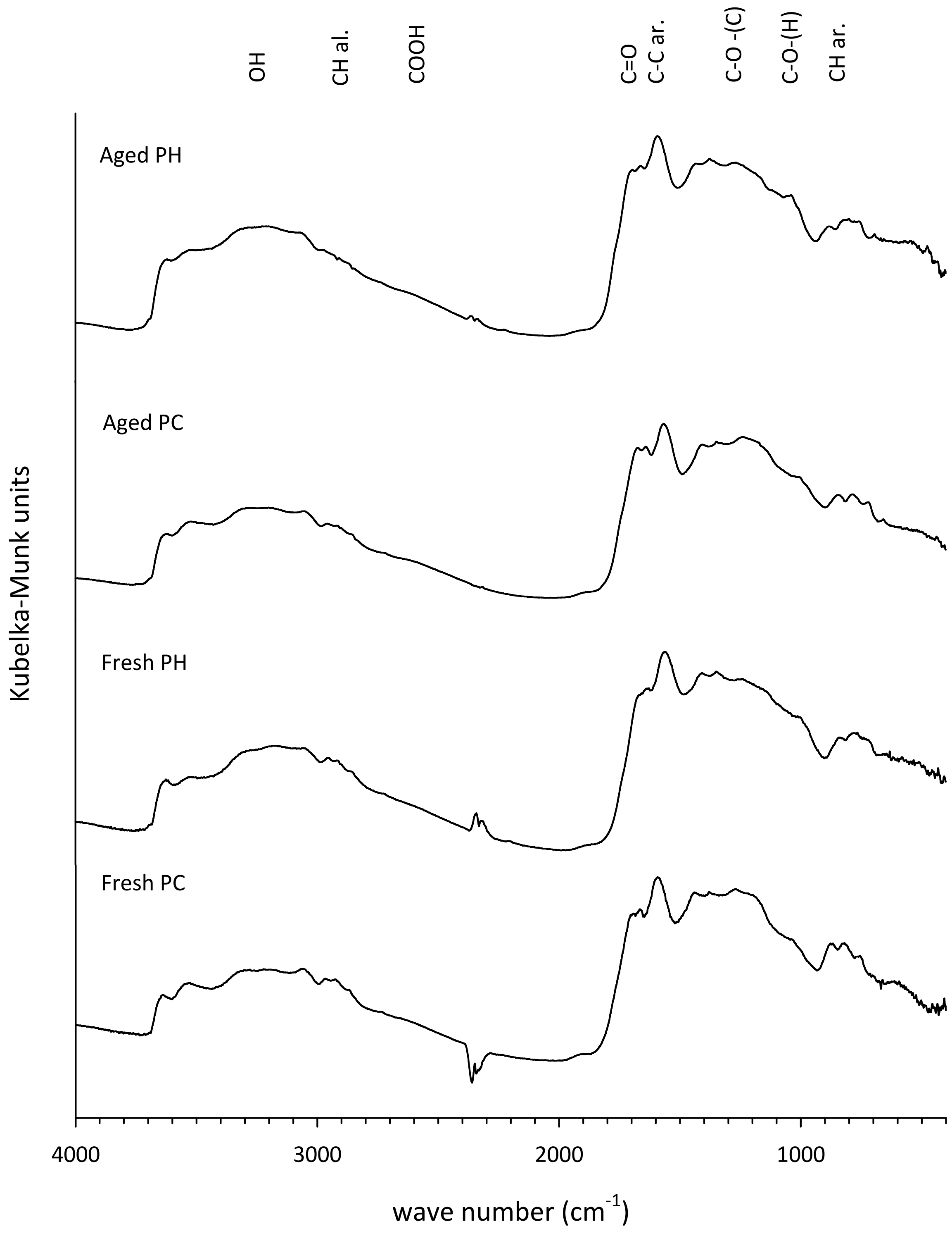

Figure 2. FTIR spectra of fresh and aged PH and PC biochars by incubating in soil for 136 -d

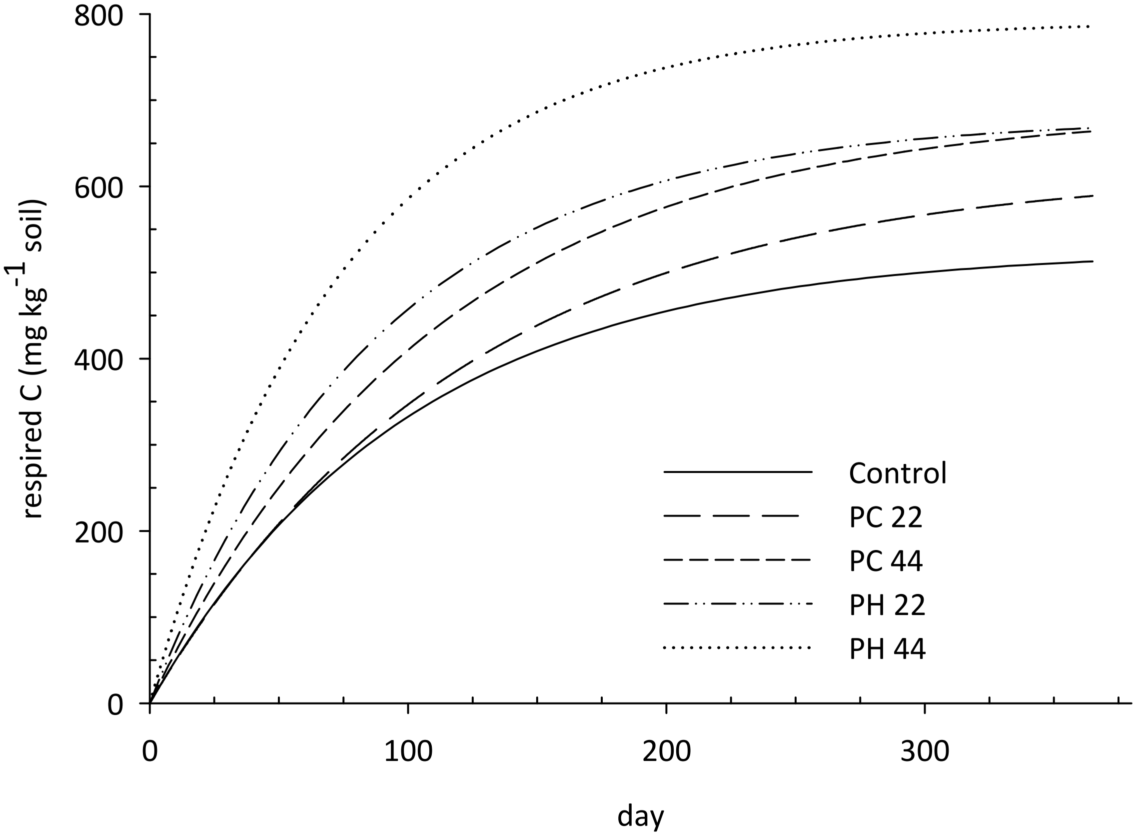

Figure 3. Estimated C respired over 365 days at 25°C based on average k and rmax for each treatment

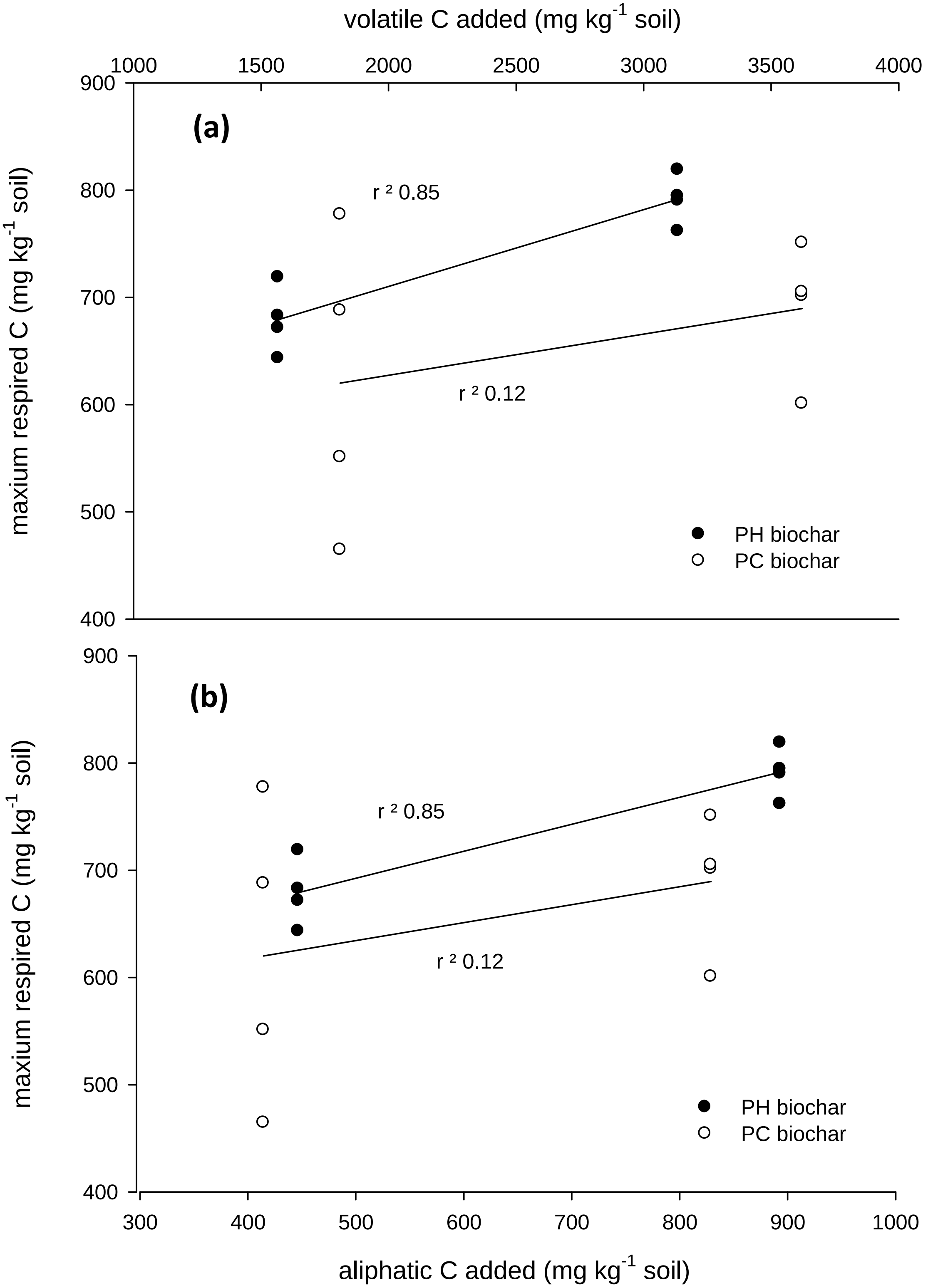

Figure 4. Correlation between model estimated maximum respired C from 136-d resp. study and volatile (a) and aliphatic (b) matter added to soil from peanut hull and pine chip biochars.

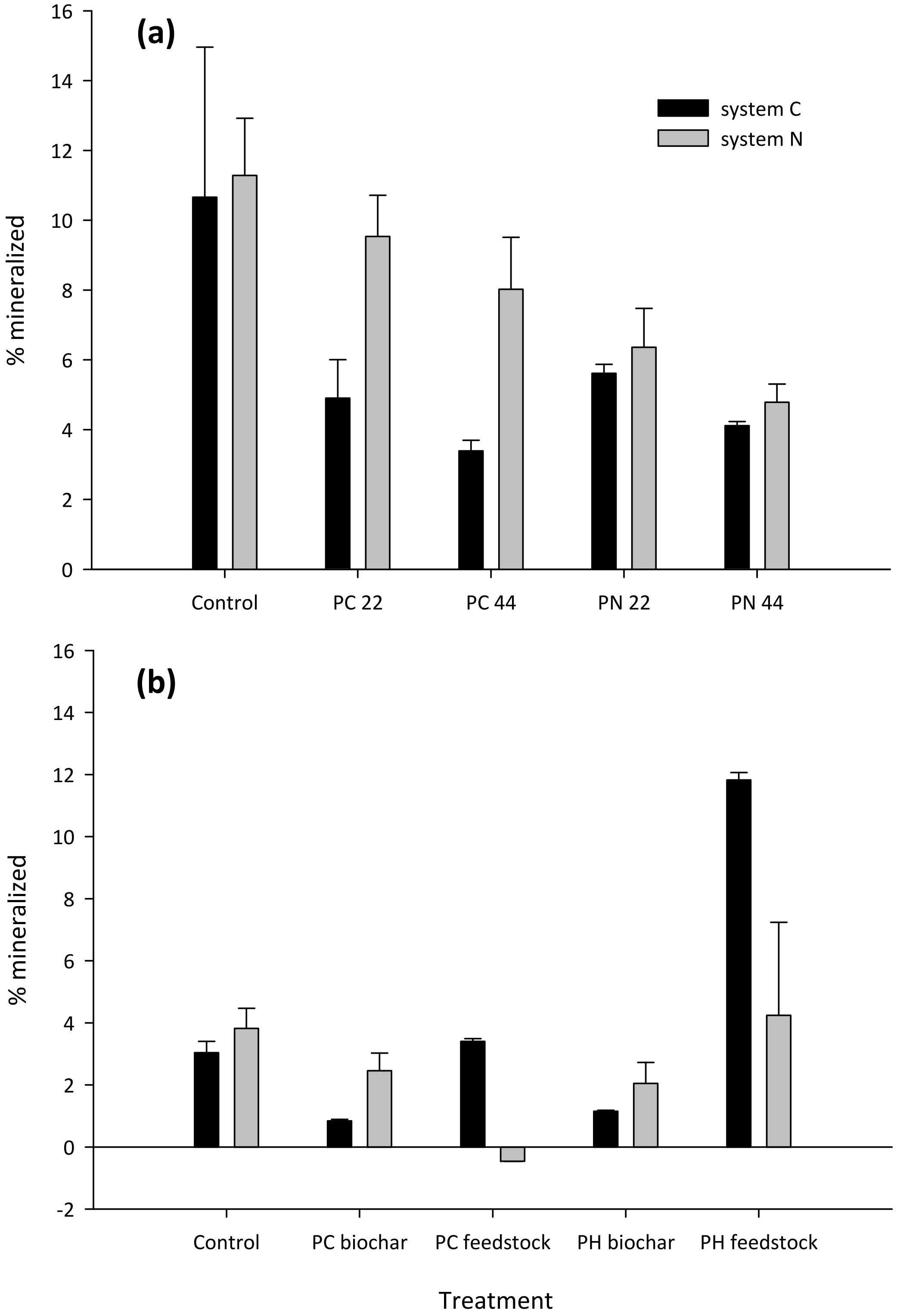

Figure 5. Percent of total C and N mineralized, with standard deviation, from treatment systems of the (a) 136-d and (b) 24-d mineralization studies

CHAPTER 4

CONCLUSIONS

Aliphatic content of biochar may be a better indicator of mineralizable C than volatile matter content. Our data show that more C would be mineralized from PH biochar amended samples that received a higher load of aliphatic C than volatile matter. Both aliphatic and volatile matter content may be useful factors for modeling maximum respired C though more research is needed testing several feedstocks with a wide range of aliphatic and volatile matter concentration coupled with respiration studies to insure the models accuracy.

Aging biochar in soil did not result in lower aliphatic and volatile matter concentrations most likely because soil microbial biomass interfered with analysis of aged samples; however, aged biochar did have reduced concentrations of aliphatic C-H bonds on the surface. Carbon and N concentrations did decrease partly due to an increase in mineral / biochar complexes but also due to formation of oxygen containing functionalities.

Biochar did not have a significant effect on the N status of the soil. We did not see N mineralization from the PH biochar even though it had a favorable C: N ratio. There were also no significant signs of immobilization from either biochar. Biochar N is bound in compounds that are more thermally stable than the N in its respective feedstock and may not be available to soil microbes. Additional research investigated biochars with a range of C: N ratios, including manure derived biochars that have been shown to contain available N, is necessary to validate N characterization by TGA-MS.

Biochar's popularity arose out of the Amazon where high black carbon containing Terra Preta soils have increased fertility compared to adjacent soils with low carbon content. Research has shown increased fertility in plots with fresh biochar applied compared to unammended soils. It was assumed that since the black carbon resisted mineralization and increased fertility in Oxisols, similar effects would be seen in other soil types and climates; however, there is no significant evidence that fresh biochar can significantly influence fertility when applied at realistic rates to low fertility soils of the Southeastern United States. Long term studies are necessary to determine if biochars influence on soil properties may change over years or decades. The Terra Preta soils found in the Amazon have been in place for centuries allowing ample time for oxidation and biological adaptation. This type of long-term research should focus on pyrolyzing residues found on-site or in the immediate vicinity with an onsite mobile-pyrolyzer to reduce transportation cost and fossil fuel consumption.

This thesis research indicates that biochar is a potential C sink and possibly a useful tool for sequestering C from the atmosphere into soil for centuries, if not millennia; however, significant hurdles in biological and engineering research remain. Without the added effect of increased soil fertility, biochar holds little value to farmers and foresters aside from its C credit value. Biochar production costs are estimated in the hundreds of dollars per ton. Couple production cost with biomass harvesting, biomass and biochar transportation, and biochar incorporation, the cost of incorporating biochar into production lands far exceeds current carbon credit prices. Carbon emissions resulting from production and transportation also have to be deducted from awarded carbon credits in effect reducing the value of biochar as a carbon sink. Engineering research and development must bring cost and emissions down to make biochar a viable option in carbon markets.