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Effect of fast pyrolysis biochar on physical and chemical properties of a sandy soil

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Effect of fast pyrolysis biochar on physical and chemical properties of a sandy soil

by

Andres Santiago Basso

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Soil Science (Soil Chemistry)

Program of Study Committee:
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Iowa State University
Ames, Iowa
2012
To:

My father, my mother and my sister, who always give me all the support and love that I need (Translation: para mi padre, mi madre y mi hermana quienes siempre me dan todo el soporte y amor que necesito)
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Abstract

Biochar is the solid product of biomass pyrolysis, which is one of the technologies available for bioenergy production. Biochar additions to soils have shown a wide range of benefits, which are strongly influenced by the nature of the feedstock and pyrolysis conditions used for the biochar production. The present study was focused on assessing the potential of a hardwood (red oak) fast pyrolysis (500°C) biochar to increase water holding capacity of a sandy loam soil and its influence on nutrient availability. We hypothesized that biochar increases the water holding capacity of the soil. Moreover, we hypothesized that the depth of biochar incorporation influences the rate of biochar surface oxidation and hence moisture retention, effective cation exchange capacity (ECEC) and nutrient availability in biochar amended soils. Biochar (0, 3 and 6% w/w) mixed with soil was placed into columns in either the bottom 11.4 cm or the top 11.4 cm of the columns to simulate deep-banding within rows (DBR) and uniform topsoil mixing (UTM) applications, respectively. Columns were incubated at 28°C and 80% relative humidity. Every 7 days 150 mL of a 0.001M calcium chloride solution was added to the columns to produce leaching. Addition of biochar increased by 23% the gravity drained water content relative to the control soils. Biochar did not affect the ECEC of the soil. Soil bulk density of the controls increased with incubation time (from 1.41 to 1.45 g/cm³), while bulk density of biochar treated soils was 9% less than the control and remained constant through the incubation period. After 91 days of incubation, soil pH increased 0.51 units (from 7.10 to 7.61) in biochar treatments relative to the controls. Soil treatments with 6% (w/w) biochar (UTM_6 and DBR_6) showed an increase of 185% in exchangeable potassium (K)
compared to the control soils (0% biochar). Exchangeable Ca and Mg decreased in biochar treated soils compared to the control. Overall, these results suggest that addition of hardwood (*red oak*) fast pyrolysis (500°C) biochar has the potential to increase water holding capacity of sandy loam soils, and that it increases availability of some nutrients. The insights of this study indicate that biochar amendments have the potential to enhance the quality of sandy soils, and therefore should be considered as a management option to enhance the sustainability of biomass harvesting for bioenergy production.
CHAPTER 1: General Introduction

In pursuit of reducing emissions of greenhouses gases, caused in part by the combustion of fossil fuels, interest is increasing in renewable sources of energy that may partially substitute for fossil fuel (Casler et al., 2009). Furthermore, new alternative sources of energy are being explored due to increasing exhaustion of fossil fuel deposits. Some estimates indicate that conventional oil reserves will be depleted in 40 years (Shafiee and Topal, 2009). When fossil fuels will be depleted, however, is a controversial issue (Muneer et al., 2005; Shafiee and Topal, 2008).

Demand for energy is expected to increase as a result of increasing global population and urbanization (Cohen, 2003). Bioenergy is renewable energy made available from material derived from biological sources. Bioenergy, along with other technologies currently available for renewable sources of energy development (Mann, 2012) have, as a whole, the potential to meet current and future global energy needs (Turner, 1999). Currently, there are several methods by which bioenergy can be produced. For example, transesterification of vegetable oils is used for biodiesel production, and fermentation of starches and sugar for elaboration of bioalcohols (e.g., ethanol). Lignocellulosic biomass, biological materials from plants, can also be used for bioenergy generation (cellulosic bioenergy). Different sources of biomass can be used for this purpose, including: corn (Zea mays L.) stover, wheat (Triticum spp.) straw, second generation biomass crops such as switchgrass (Panicum virgatum L.) and Miscanthus spp., and wood residues. Cellulose present in biomass can be chemically digested using cellulase and other enzymes which depolymerize cellulose and hemicellulose releasing simple sugars (e.g., glucose) which are then fermented to make ethanol (El-Zawawy et al., 2011; Krishnan et al., 1999).
Another possibility is thermal depolymerization of biomass at elevated temperatures without participation of oxygen in a process called pyrolysis. The products of pyrolysis are syngas (from *synthetic gas*), bio-oil, and char (Lehmann and Joseph, 2010; Antal and Grønli, 2003). One of the main advantages of generating biofuels from cellulosic biomass is that cellulosic bioenergy does not use human consumable feedstocks and helps to reduce the competition for land between food and biofuels (Rathmann et al., 2010).

Syngas, a mixture of carbon monoxide, hydrogen and carbon dioxide can be re-circulated into the pyrolyzer as a fluidizing gas or burned to provide energy for the pyrolysis process (R. Brown, 2010). Recently, production of biodiesel from bio-oil has become feasible due to technological advances, such as those related with deoxygenation for upgrading bio-oil to conventional transport fuels (Czernik and Bridgwater, 2004).

The char co-product can be used as an energy source or as a soil amendment called ‘biochar’. There are different pyrolysis technologies available which are specific to the desired end product. In fast pyrolysis, biomass is rapidly (1 to 5 s) heated to 400-550°C and the main product is bio-oil. In slow pyrolysis, the biomass is slowly heated (5 to 10°C/min) to the desired peak temperature and the main products are biochar and syngas (R. Brown, 2010).

Previous studies concerning the addition of biochar to soil have shown the potential for increasing soil water holding capacity (Novak et al., 2009a; Chan et al., 2007; Laird et al., 2010a; Brockhoff et al., 2010). This finding might be valuable in addressing another critical global issue, which is water use and availability (Hoekstra et al., 2012; Oki and Kanae, 2006). Around 20% of the world’s croplands are irrigated, however, these lands contribute 40% of total food production (FAO, 1998). The amount of irrigated land has
been increasing for the last fifty years, however, the population has also been increasing more rapidly in the same period, resulting in a decrease in the amount of irrigated area per thousand people (L. R. Brown, 2010). Although there are possibilities for increasing irrigation efficiency (Wallace, 2000), there are concerns that in the decades ahead, water withdrawals for irrigation cannot be increased and that the lack of water will impede the necessary increase in food production (Oki and Kanae, 2006). The ability of biochar to increase water holding capacity of soils might have a positive effect by either reducing the amount of water used by the agricultural sector or increasing food production for a given amount of water. However, potential benefits of biochar application are not restricted to irrigated lands. In some regions, the annual rainfall pattern is predicted to shift to higher precipitation during winter and spring and less during summer and fall (Wuebbles and Hayhoe, 2004). This will reduce water availability during the growing season in region where supplemental irrigation is not available. Moreover, frequency of extreme precipitation events are predicted to increase, leading to longer periods without rainfalls (Kyselý and Beranová, 2008) that will increase probabilities of water stress on dry-land crops. Addition of biochar to soils of these regions where supplemental irrigation is not available might increase the retention of water coming from winter and spring rainfalls and increase available water for the crop when water from precipitation is not enough to support crop evapotranspiration.

Sandy soils generally have low capacity for retaining water; hence supplemental irrigation is often needed for agricultural production on these soils. There are only a few studies testing the impact of biochar additions on water retention by sandy soils. In all the studies, the biochar used was produced by slow pyrolysis (Novak et al., 2009a). In one
study, biochar produced from hardwood did not affect soil water retention at field capacity (-1/3 bars) and wilting point (-15 bars), but increased soil water content at intermediate pressure potentials (Laird et al., 2010a). No information is yet available on the mechanisms by which biochar affects soil water retention. Studying biochar effects on parameters that characterize soil water retention curves might be beneficial to understand which soil physical properties are influenced by biochar.

Other factors that might affect soil water retention are the depth and method of biochar incorporation into soils. So far, two biochar application strategies have been studied, uniform top mixing and deep-banding. In the deep-banding method, biochar is placed between 5 and 15 cm below the soil surface. The surface layer of unamended soil might have an effect on water evaporation, drainage and the amount of water retained by the soil (water partitioning). There is a need for understanding the effect that depth and method of biochar incorporation into soil might have on water partitioning, as farmers will seek to optimize placement of biochar in agricultural soils.

This study focused on the assessment of the potential of a hardwood (red oak) fast pyrolysis biochar for increasing water holding capacity of a sandy loam soil. We used biochar made of hardwood because hardwood deciduous trees are the main component of Iowa’s forest and wood industry (Randall, 2012). Different biochar rates were mixed with soil and packed in columns using two different methods of application to simulate uniform top mixing and deep-banding. Water partitioning along with parameters describing soil water retention curves for the columns were determined. The columns were incubated for 91 days and the variables were determined at several times during incubation. The incubation was designed to determine whether changes in biochar surface properties (e.g.
oxidation) after addition to the soil affects its capacity to hold water (Liang et al., 2006; Cheng et al., 2006; Cheng et al., 2008).

Biochar additions to soil have been shown to add nutrients and influence nutrient leaching and availability (Chan et al., 2007; Chan et al., 2008; Novak et al., 2009a; Van Zwieten et al., 2009; Brockhoff et al., 2010; Novak et al., 2009b; Laird et al., 2010a). Nutrient properties and their availability once the biochar is incorporated into the soil, however, are greatly influenced by feedstocks and pyrolysis parameters used for the production of the biochar (Amonette and Joseph, 2010; Chan and Xu, 2010). Previous work has focused on biochars produced by slow pyrolysis, here we investigate the impacts of hardwood biochar produced by fast pyrolysis on nutrient availability and water retention. The study is relevant to the emerging bioenergy industry, which is anticipated to primarily use fast pyrolysis technology rather than slow pyrolysis. Moreover, no research has been conducted for assessing the effect of different biochar application methods (e.g. uniform top-mixing and deep-banding) on nutrient availability over time and within the soil profile. Oxidation of biochar surfaces and soil water retention are both potentially influenced by depth of biochar application and these factors affect nutrient availability. Therefore, in the same experiment as that used for studying soil water partitioning and soil water retention curves, we investigated the impact of the biochar on the retention and distribution of ammonium acetate extractable base cations, potassium ($K^+$), magnesium ($Mg^{2+}$), calcium ($Ca^{2+}$) and sodium ($Na^+$) within the soil profile at different times during the soil incubation.

Results of this study have potential implications related to the issues of water and food scarcity in the world. Increasing water holding capacity of soil in water limited areas might increase the value of the biochar and make the bioenergy production more
economically profitable. These facts will be beneficial in the attempt to partially substitute renewable sources of energies for scarce fossil fuels, contribute to the reduction of greenhouse gas emissions and ensure a steady supply of energy for the increasing global population.

**Thesis Organization**

The second chapter of this thesis, titled ‘Assessing Potential of Biochar in Increasing the Water Holding Capacity of Sandy Soils’, is intended for publication in ‘Geoderma - a global journal of soil science’. This chapter is an investigation of the physical and chemical changes in the soil after the addition of biochar and the resulting impact on the capacity of the soil to retain water. The third chapter, ‘Biochar in Sandy Soils: Effect on Soil Fertility Parameters’, addresses the impact of biochar incorporation into the soil on the distribution of base cations (K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), and Na\(^+\)) in the soil profile and on soil pH. Finally, a general conclusion and some recommendations are presented in the last chapter.
CHAPTER 2: Biochar Potential for Increasing Sandy Soils Water Holding Capacity

A paper to be submitted to Geoderma - a global journal of soil science

Authors: Andres S. Basso, Fernando E. Miguez, David Laird, Robert Horton and Mark Westgate

Abstract

Increasing the water holding capacity of sandy soils will help improve water use efficiency in dry land agricultural systems. We hypothesized that addition of biochar will increase the water holding capacity of a sandy loam soil, and that the depth of biochar incorporation will influence the rate of biochar surface oxidation in the amended soils. Hardwood biochar produced by fast pyrolysis was mixed with soil (0, 3 and 6% w/w) and placed into columns in either the bottom 11.4 cm or the top 11.4 cm of the columns to simulate deep-banding in rows (DBR) and uniform topsoil mixing (UTM) applications, respectively. Four sets of 18 columns were incubated at 28°C and 80% RH. Every seven days 150 mL of 0.001M CaCl$_2$ solution was added to the columns to produce leaching. Sets of columns were harvested after 1, 15, 29 and 91 days. Addition of biochar increased the gravity drained water content 23% on average relative to the controls. Biochar did not affect the CEC of the soil. Bulk density of the control soils increased with incubation time (from 1.41 to 1.45 g/cm$^3$), while bulk density of biochar treated soils was up to 9% less than the controls and remained constant throughout the incubation period. The results suggest that biochar added to sandy loam soil increases water holding capacity and might increase water available for crop use.
**Introduction**

Increasing population, economic growth, and climate change are putting substantial stress on the world’s water resources. Globally, 10% of the maximum available blue water (liquid water in rivers and aquifers) and 30% of green water (water that is in soils from rainfall and accessible to plant roots) is currently used for food production (Oki and Kanae, 2006). Although these numbers appear low, currently 2.4 billion people live in highly water-stressed areas (where (W-S)/Q is larger than 0.4, where W, S and Q are annual water withdrawal by all the sectors, water use from desalinated water and the annual renewable freshwater resources, respectively) because of the high variability of water resources in time and space (Hoekstra et al., 2012; Oki and Kanae, 2006). Climate change projections for the Midwest region of USA show increasing precipitation and soil moisture for winter/spring and a decrease in the same variables for summer/fall, which may adversely affect agricultural production in region where supplemental irrigation is not available (Wuebbles and Hayhoe, 2004). The agricultural sector is estimated to account for 70% of total water withdrawals, the vast majority of which is used for irrigation. From this total amount of water withdrawn, the agriculture sector consumed between 30% and 90% depending on the technology used (FAO, 1998). Only about 20% of the world’s cropland is irrigated, however, these irrigated lands contribute 40% of total food production (FAO, 1998). The amount of irrigated land has been increasing over the last fifty years. Concurrently the population has been increasing in the same period, resulting in a decrease in the irrigated area per thousand people (L. R. Brown, 2010). Some studies state that there are several possibilities for improved irrigation efficiency (Wallace, 2000), however, there are concerns that in the decades ahead, water withdrawals for irrigation cannot be
significantly increased because of water stresses and that the lack of water available for irrigation will impede growth in global food production (Oki and Kanae, 2006).

Recently, researchers have found that biochar additions have the potential to increase soil water holding capacity. This implies that soils amended with biochar could retain more water from rainfall, so less irrigation water might be needed to grow crops. Moreover, biochar addition to soil in nonirrigated regions might increase water available for crops, reducing the chances for water stress between rainfall events. Novak et al. (2009a) physically and chemically characterized biochar produced from four feedstocks (i.e. peanut (Arachis hypogaea) hull, pecan (Carya illinoinensis) shell, poultry litter and switchgrass (Panicum virgatum)) under two temperature regimes using slow pyrolysis, and examined the effects of 2% (w/w) biochar amendments on fertility and water-holding capacity of a Norfolk loamy sandy soil. They found that switchgrass biochar (made at 500°C) resulted in the largest increase in retained water, 15.9% relative to the control. Chan et al. (2007) applied biochar made from greenwaste at 450°C by slow pyrolysis to an Alfisol. They detected significant more water retained at field capacity in biochar amended soil relative to control only at application rates of 50 and 100t/ha. Laird et al. (2010a), after the addition of a mixed hardwood slow pyrolysis biochar to a Mollisol, did not detect an effect of biochar on moisture retention at -0.33 bars (field capacity) and -15 bar (wilting point) soil water potential. However, they found significant increases in moisture retention at -1 and -5 bars soil water potential for the 1 and 2% (w/w) biochar treatments compared with no-biochar controls. Moreover, they stated that the ability of biochar to increase the moisture retention capacity of soils has the potential to increase yields for crops exposed to water stress during critical periods of the growing season.
The depth and method of biochar incorporation into soils has the potential to influence soil water retention. So far, two biochar application strategies have been studied: uniform top mixing and deep-banding. Blackwell et al. (2010) evaluated banded application of biochar on dryland wheat (*Triticum* spp.) production in Western and South Australia. They used banding to reduced wind erosion and to place biochar close to crop roots. The biochars used for this study were slow pyrolysis woody greenwaste biochar and metallurgical charcoal collected from a 35-year old stockpile. They found that banding biochar can reduce fertilizer requirements without affecting yields, and suggested that increased crop nutrient and water uptake during dry seasons was due to increased arbuscular mycorrhizal fungal colonization.

Bulk density is one of the most important site characteristic affecting rainfall infiltration (Ueckert et al., 1978), and recent research has found a decrease in soil bulk density after biochar additions (Laird et al., 2010a; Oguntunde et al., 2008). Decreasing soil bulk density increases soil porosity and soil aeration, and may have a positive effect on root and microbial respiration.

Despite insights from the previous studies, there are still several gaps in understanding the impact of biochar additions on water retention and water partitioning in sandy soils. Previous studies have evaluated biochars made by slow pyrolysis. Evaluation of the impact of biochars made by fast pyrolysis on soil water relations, however needs to be assessed. In addition, an evaluation of the relative impact of uniform surface and deep banding biochar applications on water holding capacity of sandy soils may also be very valuable. We hypothesize that the addition of biochar to sandy soil will increase soil water content because evaporation and/or drainage will be reduced. Moreover, we hypothesize
that deep-banding of biochar will increase soil water retention relative to uniform mixing of biochar with topsoil because less water will evaporate from the surface. Fresh biochar tends to be hydrophobic. However, as biochar surfaces are oxidized on contact with air and water, the effective cation exchange capacity (ECEC) of biochar increases with time after being incorporated into the soil (Liang et al., 2006; Cheng et al., 2008; Cheng et al., 2006). We hypothesized that the water holding capacity of biochar amended soil will increase over time because of these chemical changes on the surface of the biochar particles. Furthermore, ECEC could be used as an indirect measure of water retention capacity of soils because cation exchange sites are polar regions where water could be retained by ion-dipole and hydrogen bonding interactions.

We carried out a soil incubation study where the objectives were:

1) Assess the capacity of biochar for increasing water holding capacity of a sandy soil

2) Test biochar placement effect on soil water partitioning (amount of water retained by the soil, evaporated and drained)

3) Estimate biochar effects on soil water retention curve parameters.

4) Determine changes in bulk density after biochar addition to the soil

**Materials and Methods**

**Soil**

The soil used in this study was a sandy loam (Clarion loam, 68.2% sand, 25.1% silt and 6.7% clay) sampled from the surface 15 cm of a field on the Iowa State University Agronomy and Agricultural Engineering Research Farm in Boone County, Iowa, USA. The particle size analysis was carried by the Department of Agronomy’ Landscape Analysis...
Laboratory following Gee and Bauder (1986). Soil was air-dried then tumbled in a rotatory cement mixer for 10 min with six iron cylinders to crush soil aggregates and thoroughly mix the soil. After mixing, the soil was passed through a 6-mm sieve and stored in closed plastic containers until used. Characteristics determined by the Soil and Plant Analysis Laboratory (Agronomy Hall, Iowa State University, Ames) are presented in Table 1.1. Phosphorus (P) was extracted with a dilute acid fluoride solution following the procedure suggested by Bray and Kurtz (1945). P concentration was determined by measurement of the extractions in a spectrophotometer at 882 nm. Soil pH was assessed by measuring the proton (H⁺) activity of soil/water (1:1) slurry with a pH meter (Watson and Brown, 2011). Micronutrient (Z, Cu, Fe, and Mn) concentrations were determined by extraction with a DTPA solution (Lindsay and Norvell, 1978) followed by measurement in inductively coupled plasma emission spectroscopy (ICP). Concentration of potassium (K) and other base cations (Ca, Mg and Na) in the soil were determined by extraction with an 1M ammonium acetate solution following by determination of concentration of each cation in the extraction using ICP (Warncke and Brown, 2011). Effective cation exchange capacity was calculated based on the sum of concentrations for extractable K, Ca, Mg and Na (Warncke and Brown, 2011). Soil organic carbon and total nitrogen were determined by thermal combustion analysis, while the organic matter was estimated by multiplying soil organic carbon by 1.72 (Combs and Nathan, 2011). Extractable (2M KCl) inorganic nitrogen was determined using a colorimetric method (Mulvaney, 1996).

Biochar

Avello Bioenergy, Inc. (BioCentury Research Farm, 1327 U Avenue, Boone, Iowa) provided the biochar used for this experiment. The feedstock was red oak (*Quercus rubra*).
Characteristics of the biochar are provided in Tables 1.2 and 1.3. Volatile matter and fixed carbon are properties that give a relative measure of the labile and stable fraction of biochar at high temperatures, respectively. These properties along with ash content (the remaining solid after all the organic elements – carbon (C), hydrogen (H) and nitrogen (N) – have been oxidized (Joseph et al., 2010b) are determined by proximate analysis (ASTM-D3172, 2007). The ultimate analysis of biochar comprises the determination of elements C, H, N, sulfur (S) and oxygen (O) (ASTM-D3176, 2009). Ultimate, proximate analysis of the biochar used in this study along with the elemental analysis of ash of the biochar was carried out by Hazen Research Inc. (4601 Indiana Street Golden, Colorado 80403, U.S.A) using ASTM standard methods. The biochar was produced by fast pyrolysis (500°C) in a 6 inch bubbling fluidized bed reactor, using nitrogen (183 L/min) as the fluidizing gas. The average biomass feed rate was 5.0 kg/hr. After production, the biochar was stored in a sealed container for three months before it was used in the present study.

**Incubation**

The soil incubation was carried out in PVC columns of 18 cm height and 7 cm external diameter. To build the columns, individual 18 cm length PVC pipes were cut longitudinally and joined together with two clamps to avoid leaks. The purpose of cutting the pipe was to allow access to the soil for sampling with minimal disturbance. A PVC end cap on the bottom of each column had a drain hole (3 mm) with an attached tube (4.3 mm i.d.) for collecting water draining out the bottom of the columns. The concave portion of the end cap was filled with approximately 100 g of coarse sand (4-7 mm). The total mass of oven dry soil in each column was 994 g.
There were three rates of biochar application 0% (control), 3% and 6% (w/w) (3% and 6% are referenced hereafter as biochar treatments). For the 3% biochar treatment, each column contained 20 g of biochar and 974 g of soil, while columns with the 6% biochar treatment contained 40 g of biochar and 954 g of soil. Biochar was applied in two different ways, either in the bottom 11.4 cm or at the top 11.4 cm, to simulate deep-banding in rows (DBR) and uniform topsoil mixing (UTM) applications, respectively. To complete the column filling, 5 cm of soil was placed either in the top of the column above the biochar-soil mixture for DBR treatments or in the bottom of the column below the biochar-soil mixture for the UTM treatments. All columns were packed to similar bulk densities. Bulk densities values ranged from 1.31 g/cm³ to 1.41 g/cm³, depending primarily on the biochar application rate. The 4 sets of 18 columns were incubated at 30°C and 80% RH in a dark room. The first set was incubated for 1 day, the second for 15 days, the third for 29 days and the fourth for 91 days. Each set of columns had the three rates of biochar application (0, 3, and 6%), two biochar placements (DBR and UTM), and three replicates. The 72 columns were randomly distributed in two square tables, each one containing 36 holes for allocating the columns.

Every seven days 150 mL of 0.001M CaCl₂ solution was added to each column to produce a leaching event. Dilute CaCl₂ was used to reduce soil dispersion. The solution was introduced on the top of each column at approximately 3.75 mL/min, using a dropper system. Fiberglass filter paper was placed at the soil surface of each column to help disperse solution drops as they impacted the soil.
**Water Partitioning**

Water partitioning was assessed for every leaching event during the incubation by measuring the mass of water draining out the bottom of the column, water retained within the column, and water evaporated out the top of the column. The weight of each column was determined before the start of a leaching event and the mass of water retained within the column was determined by subtracting the initial dry column weight. Drainage was collected for approximately 24 h after the beginning of the leaching event in plastic bottles placed below each column and connected with the drainage tube. The collection bottles had a cap with a small hole that allowed the drain tube to be fitted into the bottle to minimize evaporation loss. The weight of each bottle was subtracted from the weight of the bottle without solution and weekly drainage was determined. Evaporation was assessed by computing the difference between water added and drainage plus any change in water content. In order to wet the entire column and produce leaching, the first leaching event was made using 350 mL of solution. The remaining leaching events were completed using 150 mL of solution. The the amount of water potentially available for evapotranspiration (ET) was the sum of water retained in the column and the amount of water lost to evaporation between watering events.

**ECEC and Gravimetric Water Content**

At the end of the incubation of each set of columns, gravimetric water content and effective cation exchange capacity (ECEC) was determined for three different depths (depth 1= 0-1.3 cm, depth 2= 5.05-6.35 cm and depth 3=13.94-15.24 cm) in each column (Figure 1.1). The second set of columns was harvested 48 h after the watering event, whereas the others three sets of columns were harvested 24 h after watering. Because of this
difference in harvest timing, values from the second set of columns were not used for interpreting water partitioning within the soil columns. Columns were dismantled by taking off the end cap and opening the columns by removing the clamps. Once the soil column was removed from the PVC pipe, samples at different depths were obtained. Immediately after the samples were taken from one column, approximately 20 g of soil from each sample was disposed into a round aluminum container (5 cm i.d., previously weighed), weighed, and placed in a tray. This procedure was done as quickly as possible to decrease loss of water by evaporation prior to weighing. The 45 samples for each set of columns were oven-dried at 105°C until no change in weight was observed (approx. 24 h). After oven-dry weight was measured, gravimetric water content was determined for each sample. The remaining soil in each sample was air dry and stored in a sealed plastic bag for later ECEC determination following Sumner and Miller (1996) with the following modification. Prior to extraction with NH₄Cl, soil was washed out with Milli-Q water. To do this, 5 g of air dry soil was placed into a 50 mL Oak Ridge centrifuge tube. Sample weight was recorded. 25 mL Milli-Q water was added, the sample was vortexed, and let sit for at least 10 min. After that, sampled were centrifuged at 13870 Relative Centrifugal Field (RCF) for 10 min. Electrical conductivity (EC) of supernatant was determined and recorded. If EC was greater than 20μS/cm, the washing procedure was repeated. If the EC was less than 20μS/cm, the sample was ready for extraction with NH₄Cl. Concentrations of Ca, Mg, Na and K were determined by inductively coupled plasma emission spectrometry (ICP).

**Soil Water Retention Curves**

At the end of the incubation of each set of columns, soil from 6.35-11.4 cm depth (Figure 1.1) for each column was used to determine soil water retention curves and examine
the effect of biochar on the different parameters of these curves. A disc of soil core 5 cm high and 7 cm diameter was sampled from each column at the same time as samples for ECEC and gravimetric water content were taken. A piece of PVC pipe (2.54 x 2.54 cm) was placed above and in the middle of each soil disc and by exerting pressure above it, the PVC pipe was filled with soil at the same bulk density as it was packed in the column and with minimum disturbance. Because the volume of the piece of PVC pipe was less than the volume of soil taken from the column, there was soil remaining in each column that was used for determination of volumetric water content at -1 and -15 bar matric potentials using pressure plates. The remaining soil from each column along with the soil/PVC pipe samples were placed into a hermetic plastic bag and stored at 6°C until used for determination of soil water retention curves.

Pressure chamber was used for determination of water held at matric potentials of -0.01, -0.025, -0.05, -0.1, -0.2, -0.33 and -0.5 bar (Klute, 1986). The soil/PVC samples were saturated from the bottom up with 0.001M CaCl$_2$ for 24h placed at 20°C. Average matric potential of saturated soil/PVC sample was -0.0013 bars, and this value was chosen as lowest matric potential in the water retention curve. Saturated samples were placed into a pressure chamber and pressure was sequentially increased to decrease water potential values. Pressure was applied until each core stopped draining water and was at equilibrium. Equilibrium water content of the individual cores was determined by recording the volume of water released at each pressure.

For determination of water held at -1 and -15 bars matric potential, the pressure plate method (Klute, 1986) was chosen using a Ceramic Plate Extractor (Soil Moisture Equipment Corp., Santa Barbara, CA). Rubber rings (1 cm thick by 3 cm diameter) were
filled with the remaining soil from each column and they were saturated from the bottom with 0.001M CaCl$_2$ at 20°C. After 7 days of pressure, the soil was weighed, oven dried at 105°C for 24 h, and reweighed to determine water content.

Available water-holding capacity of each sample was determined by calculating the difference in volumetric water content held at -0.10 and -15 bars.

**Evaporative Demand**

Temperature in the room where the columns were incubated was kept constant during the incubation. Nevertheless, there were differences in temperature across the room and evaporative demand was also influenced by proximity to overhead air circulation fans. In order to take into account these differences, evaporative demand was determined. For this, PVC cups were filled with an equal amount of water and placed above each column. Several times during the period of two or three days, the PVC cups were weighed to determine average water loss per hour for each column. This measure of evaporative demand was used as a covariate in the statistical analysis.

**Bulk Density**

Bulk density was determined at 0, 21, 63 and 90 days of incubation for the fourth set of columns. The distance from the top surface soil to the top of the column was recorded and the volume of soil was determined. Bulk density was calculated by dividing the mass of soil by the soil volume. This approach assumes no changes in soil mass during the incubation and the value obtained was the average bulk density of the column.

**Statistical Analysis**

A linear model was used to analyze water partitioning, water available for ET, bulk density, gravimetric water content and ECEC (Proc Mixed, SAS 9.2, SAS Institute Inc.,
The terms in the linear model used for water partitioning, water available for ET, and bulk density analysis were incubation day (1, 15, 29 and 91 days), biochar (control, DRR_3, DBR_6, UTM_3 and UTM_6), and the interaction terms between incubation day and biochar. In addition to these terms, for the gravimetric water content and ECEC analysis, the term depth (depth 1= 0-1.3 cm, depth 2= 5.05-6.35 cm and depth 3= 13.94-15.24 cm) and the terms for the interaction between biochar incubation days and depth was added to the linear model. To account for the correlation of residuals in variables that were measured repeatedly over the duration of the experiment the covariance structure of the residuals was modeled. The structures chosen (based on AIC criteria) were “First order ante-dependence covariance structure” for ECEC and gravimetric water content and “Variance components” for bulk density, water partitioning and water available for ET. Evaporative demand was used as a covariate in each model. Mean separation was conducted based on linear contrasts at an alpha of 0.05. The function chosen for the parameter estimation of the water retention curves was Gardner’s function:

\[
\theta_h = \theta_r + (\theta_s - \theta_r)[1 + (\alpha h)^n]^{-1}
\]

Where:

- \( \theta_r \) = Residual water content
- \( \theta_s \) = Saturation water content
- \( \alpha \sim 1/P \) (Pressure at which slope is the steepest)
- ‘n’ is related to slope at P (greater slope, greater ‘n’)

(Parameter explanation was extracted from van Genuchten (1980))
The analysis of the water retention curves was carried out using a non-linear mixed model (HydroMe R package (Omuto and Gumbe, 2009)). Available water-holding capacity was analyzed using a linear model (Proc Mixed, SAS 9.2, SAS Institute Inc., Cary, NC, USA), where the terms in the model were incubation day (1, 15, 29 and 91 days), biochar (control, DRR_3, DBR_6, UTM_3 and UTM_6), and the interaction between incubation day and biochar. Mean separation was conducted based on linear contrast at an alpha of 0.05.

**Results and Discussion**

**Water Partitioning**

Figure 1.2 shows that biochar amended columns had a significant average increase of 23% in gravity drained water content, relative to the controls. Biochar increased gravimetric water content in experiments by other researchers (Laird et al., 2010a; Novak et al., 2009a; Tryon, 1948). Differences in water content between biochar treatments were not significant except for the UTM_6 treatment, which showed slightly higher water content ($p<0.05$) than the other biochar treatments. From the total amount of water added during the 91 days of incubation, an average of 15.5% was retained by columns receiving the biochar treatments, and the remaining 84.5% was either drained or evaporated. Columns receiving the 6% biochar treatment lost significantly ($p<0.05$) less water to drainage and more water to evaporation compared to columns receiving the 3% biochar treatment. There were no significantly differences in evaporation and drainage between DBR_3 and UTM_3 treatments. On the other hand, values of drainage observed in the UTM_6 treatment were significantly ($p<0.05$) less than the values of drainage for the DBR_6 treatment. This
difference might be due to the fact that UTM_6 columns had slower water infiltration rates during most of the incubation time compared to the others treatments, resulting not only in the least drainage, but also in greater evaporation due to ponding of water. Moreover, the water was concentrated close to the soil surface in the UTM_6 columns (see Figure 1.6), so more water was readily available for evaporation between watering events than in the DBR_6 columns, where most of the water was in the bottom of the column. Tryon (1948) observed that addition of charcoal to soil reduced slightly the loss of moisture by evaporation, and that the effect was more pronounced when a sandy soil was used instead of a clayey soil. In the present study, we observed a reduction in evaporation relative to the controls only for the 3% wt/wt biochar treatments. However, in the experiment setup that Tryon (1948) used to determine evaporation there was no possibility for drainage and the quantities of biochar used were much greater than in the present experiment, so his results are not directly comparable with those obtained here.

During most of the incubation time, water infiltration was very slow in the columns of the UTM_6 treatment, requiring approximately 40 min for all of the added water to infiltrate. In all the other treatments, around 10min was sufficient for all of the water to infiltrate. The infiltration rate of the UTM_6 columns, however, increased with time and became similar to the infiltration rate of the other treatments by the end of the incubation period. Infiltration rate was not measured in this experiment; these values are estimates from observation made during the incubation. However, this observation suggests that the biochar used might be hydrophobic when it is fresh and that it become more hydrophilic after prolonged contact with soil, air and watering solution, as observed in other studies (Cheng et al., 2008; Joseph et al., 2010a).
Some studies have shown that water flowing over the land surface is one of the most important driving forces for soil erosion (Moore and Singer, 1990; Renard and Foster, 1983). Water films covering the soil surface, however, might moderate the impact of water drops (rainfall drops, for example), reducing soil erosion (Moore and Singer, 1990). Moreover, factors like crop residue and landscape slope influence not only soil erosion but also runoff and rate of intake of water by soils (Duley, 1939). We observed that uniform top mixing 6% (w/w) of biochar within the soil (UTM_6 treatment) might reduce water infiltration in the soil, creating a water layer on the soil surface, which depending on factors described before might increase soil erosion and runoff in the period initially after biochar application while it remains hydrophobic. Effects of biochar on soil water infiltration need further research.

A comparison between water content of the different methods of biochar application is shown in Figure 1.3. Significantly less water evaporated from soil amended with 6% (w/w) biochar applied as a deep-band (DBR_6) than when it was uniformly mixed with the top soil (UTM_6). Significantly more water was held in UTM_6, however, because it had significantly less water loss to drainage than did the DBR_6 treatment.

Soil water content of columns treated with biochar were relatively constant during the incubation period while the water content of the control slowly decreased during the incubation from day 7 to 91 (Fig. 1.4), probably due to the increase in soil bulk density observed for the control columns (Fig. 1.5). In comparing day 14 and 91, there were no significant decreases in water content for columns that received biochar, while water content of control columns decreased significantly ($p<0.05$) during the same period.
Average values of available water for ET for each treatment at incubation day 91 were 0.24, 0.27, 0.28, 0.28 and 0.30 g of water per g of oven-dry soil for the Control, DBR_3, UTM_3, DBR_6 and UTM_6 treatment, respectively. These values represent a significant increase in available water for ET for the biochar treatments relative to the controls of 13, 18, 17 and 25% for DBR_3, UTM_3, DBR_6 and UTM_6 treatments, respectively.

**Bulk Density**

Bulk density of the control columns increased significantly during the incubation from 1.41 to 1.45 g/cm$^3$ for incubation day 0 and 90, respectively (Fig. 1.5). On the other hand, changes in bulk density for the biochar treatments were not significant along the incubation period (Fig. 1.5). At the end of the incubation, the average values of bulk density were 1.43 (control), 1.42 (DBR_3), 1.36 (DBR_6), 1.37 (UTM_3) and 1.32 (UTM_6) g/cm$^3$. Other researchers have also found a decrease in soil bulk density after biochar additions (Laird et al., 2010a; Oguntunde et al., 2008), probably due to the low bulk density of the biochar itself (Downie et al., 2009). The DBR_3 treatment did not have significant effect on bulk density, compared to the control on incubation day 0. On incubation day 90, however, we observed a significant ($p<0.05$) lower bulk densities of 1.6, 5.1, 6.2 and 9.0% for DBR_3, UTM_3, DBR_6 and UTM_6 treatments, respectively, relative to controls. Decrease in bulk densities may promote plant root elongation (Siemer and Grable, 1968) and root density (Thompson et al., 1987). In addition, reduction of bulk density by 12% has been shown to improve water infiltration by 27% (Franzluebbers, 2002).
**Water Retention Curves**

The UTM_6 treatment significantly \( (p<0.05) \) increased, compared with the control, the amount of water held at tensions of saturation point \( (\Theta_s) \) after 29 and 91 days of incubation (second and fourth set of column, respectively) and significantly \( (p<0.05) \) increased \( \Theta_r \) after 91 days of incubation (Fig. 1.6). Moreover, DBR_3 significantly \( (p<0.05) \) increased \( \Theta_s \) compared to the control in the fourth set of columns.

The greatest differences in water content between the biochar treated columns and the controls occurred mainly at low pressures and these differences increased as the incubation advanced (Fig. 1.6). The amount of water retained at matric potentials between 0 and 1 bar, which describe the shape of the water retention curve, depends on the capillary effect and the pore-size distribution (Hillel, 1998; Jury and Horton, 2004). Parameters ‘\( \alpha \)’ and ‘\( n \)’ within the Gardner function determine the shape of the water retention curve. In the present study, no significant changes in ‘\( \alpha \)’ or ‘\( n \)’ were found for different harvesting times when comparisons between control and biochar treatments were made. So, incorporation of 3% or 6% (w/w) of this particular type of biochar does not appear to affect capillarity and pore-size distribution of the soil. The differences observed in water content between biochar treatments and the control in this study appear to be mostly due to higher total porosity of the biochar treated soil, which allows more water to be physically retained (Downie et al., 2009).

The water content of the control decreased proportionally at each matric potential value compared to the biochar treatments (Fig. 1.6). This observation is consistent with the observation that water retention by biochar treated columns was relatively constant during the incubation period (Fig. 1.4). The reason for the differences in water content between
treatments at the saturation point was probably due to the differences in bulk density between treatments. The bulk density of the control columns increased during the incubation (reducing the space where water could be retained) while bulk density of the biochar treated columns remained relatively constant during the incubation (Fig. 1.5).

Available water-holding capacity (AWHC) on incubation day 15 was not significantly different between the control and biochar treatments. By incubation day 29, however, all of the biochar treatments showed greater AWHC than the controls, and for UTM treatments this difference was statistically significant. By incubation day 91, all of the biochar treatments had significantly ($p<0.05$) larger AWHC relative to the controls. Values of AWHC for each treatment at incubation day 91 were 0.14, 0.25, 0.19, 0.17 and 0.19 cm$^3$ of water per cm$^3$ of soil for the Control, DBR_3, UTM_3, DBR_6 and UTM_6 treatment, respectively. These values represent an increase in AWHC for the biochar treatments relative to the controls of 84, 44, 29 and 38% for DBR_3, UTM_3, DBR_6 and UTM_6 treatments, respectively. Considering a soil with an average AWHC of 0.14 cm$^3$ cm$^{-3}$, amending a 10 cm layer of soil with biochar (average AWHC of 0.20 cm$^3$ cm$^{-3}$), would represent an increase of 3% in equivalent depth of water in the 150 cm soil profile. This 3% is the extra amount of water that would be available in the root zone for crops during a mid season drought.

Biochar treatments did not show significant differences in AWHC between them, except for DBR_3 that show significant greater AWHC than the others. We did not observe a significant increase in AWHC for the UTM_3, DBR_6 and UTM_6 biochar treatments from incubation days 15 to 91. This might be due to the fact that the volumetric water content retained at -15bars matric potential (permanent wilting point, WP) increased in a
greater proportion than the volumetric water content retained at -0.1 bars (field capacity, FC) from incubation day 15 to 91. On the other hand, AWHC for the DBR_3 significantly increased between incubation days 15 to 91. For this treatment, we observed a decrease in water content at WP from incubation day 15 to 91 while water content at FC increased during the same period. These differences in water content at FC and WP between the biochar treatments are the reason for the greater AWHC of treatment DBR_3.

The increase in volumetric water content retained at -15 bar matric potential (WP) observed for the UTM_3, DBR_6 and UTM_6 treatments might be due to the opening of obstructed capillary pores by dissolution of oxides that were blocking them. Another reason could be a change in the nature of biochar surfaces from hydrophobic to hydrophilic as was evidenced by an increase in infiltration rate for the UTM_6 columns as noted earlier in the Water Partitioning discussion. These processes did not affect the DBR_3 columns in the same way as columns receiving the other biochar treatments.

**Gravimetric Water Content and ECEC**

The distribution of biochar within the columns influenced the gravimetric water content distribution within the columns (Fig. 1.7). For the UTM treatments, depths 1 and 2 had greater water content than depth 3, coincident with the fact that samples taken at depths 1 and 2 had biochar while those taken at depth 3 did not. Similarly, for DBR treatments, water content for depths 2 and 3 were greater than water content at depth 1. In DBR treatments samples taken at depths 2 and 3 had biochar but those taken at depth 1 did not. Moreover, treatments that received 6% wt/wt of biochar had greater gravimetric water content than those receiving 3% wt/wt biochar. Unlike samples having biochar, water
content of controls significantly decreased from harvesting time 1 toward harvesting time 4. This result is consistent with what was observed in Figure 1.4, where water content of columns with biochar showed little variation during the incubation period, while the water content of the controls significantly decreased during the 91 day incubation.

The incorporation of biochar did not increase the ECEC of the soil (Fig. 1.8). Figure 1.8 depicts that ECEC was not related to biochar placement. Moreover, there was not a clear trend in ECEC along the different columns’ harvesting time and the different depths (figure 1.8).

Biochar addition to soil has been shown to increase the ECEC of soils (Cheng et al., 2006; Van Zwieten et al., 2009; Laird et al., 2010a; Chan et al., 2007), although in other studies biochar did not have a measurable effect on the capacity of the soil to retain positively charged ions (Novak et al. 2009a; Novak et al. 2009b). Researcher have found an increase in ECEC values of biochar with time which has been attributed to surface oxidation and creation of carboxylic and phenolic surface functional groups (Liang et al., 2006; Cheng et al., 2008; Cheng et al., 2006). In this study, the relationship between biochar placement and ECEC was expected to be similar to what was observed for water content, with higher ECEC values where biochar was located, in addition to increasing ECEC during incubation due to oxidation of biochar surfaces. Moreover, it was also expected to observe greater surface oxidation on biochar of UTM treatments compared to biochar of DBR treatments. We observed that the ECEC of biochar amended soils, however, was not significant different from that of the controls, and this parameter did not explain the increase in water holding capacity of the sandy soil after biochar addition during 91 days of incubation.
Conclusion

The major impact of adding biochar to the sandy loam soil was an increase in water holding capacity. Our results suggest that addition of this type of biochar (red oak, fast pyrolysis, 500°C) has the potential to increase total water retained against gravity by the soil, as well as to maintain this water in the soil for an extended period of time. There were no significant differences in water partitioning (water retention, evaporation and drainage) between biochar application techniques at 3% wt/wt biochar addition rate. Uniform top mixing of 6% wt/wt biochar (UTM_6), however, significantly increased water retention relative to deep banding 6% wt/wt biochar (DBR_6). Biochar application did not increase ECEC of the soil during the 91 day incubation, thus demonstrating that the transformation from hydrophobic to hydrophilic biochar surfaces observed in this study was not accompanied by a measureable increase in ECEC. Another interesting finding from this study is that biochar addition helped in keeping the average bulk density relatively constant during the incubation while bulk density for the controls significantly decreased during the same period of time. The analysis of the water retention curves suggested that differences observed in water content between biochar treatments and the controls were mostly due to the high porosity of the biochar that might allow more water to be physically retained which is consistent with the lack of a change in ECEC. Addition of biochar significantly increased available water-holding capacity of the soil after 91 days of incubation. Overall, biochar could be added to sandy soils to increase water holding capacity and thereby to retain greater amounts of plant available water for crops for longer periods of times. However, field research is still needed to assess the crop response to biochar along with
experiments to determine specific mechanisms by which water is retained in biochar amended soils.
Table 1-1. Analysis of the sandy loam soil (particle size analysis carried by the Department of Agronomy’ Soil and Plant Analysis Laboratory following Gee and Bauder (1986)). Values are in ppm units unless otherwise noted. Mean (n=2) ± standard deviation

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>27 ± 1</td>
<td>117.5 ± 0.5</td>
<td>1871.5 ± 11.5</td>
<td>261 ± 1</td>
<td>3.5 ± 0.5</td>
<td>0.4 ± 0.0</td>
<td>0.7 ± 0.0</td>
<td>30 ± 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>NH4-N</th>
<th>NO3-N</th>
<th>Total C (%)</th>
<th>Total N (%)</th>
<th>OM (%)</th>
<th>pH</th>
<th>ECEC * (meq/100g oven-dry soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.5 ± 0.5</td>
<td>2.5 ± 0.5</td>
<td>13.5 ± 0.5</td>
<td>1.372 ± 0.011</td>
<td>0.1148 ± 0.0007</td>
<td>2.5 ± 0.0</td>
<td>7.3 ± 0.0</td>
<td>11.85 ± 0.05</td>
</tr>
</tbody>
</table>

* Extraction with NH₄OAc
Table 1.2. Ultimate and Proximate analysis of the hardwood (red oak) fast pyrolysis (500°C) biochar carried out by Hazen Research Inc. following ASTM standard methods (ASTM-D3172, 2007; ASTM-D3176, 2009)

<table>
<thead>
<tr>
<th>Ultimate</th>
<th>As received, %</th>
<th>Dry, %</th>
<th>Air Dry, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>1.45</td>
<td>0.00</td>
<td>1.45</td>
</tr>
<tr>
<td>Ash</td>
<td>21.58</td>
<td>21.90</td>
<td>21.58</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Carbon</td>
<td>84.97</td>
<td>86.22</td>
<td>84.97</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.45</td>
<td>3.50</td>
<td>3.45</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Oxygen</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate</th>
<th>As received, %</th>
<th>Dry, %</th>
<th>Air Dry, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>1.45</td>
<td>0.00</td>
<td>1.45</td>
</tr>
<tr>
<td>Ash</td>
<td>21.58</td>
<td>21.90</td>
<td>21.58</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>15.75</td>
<td>16.01</td>
<td>15.78</td>
</tr>
<tr>
<td>Fixed Carbon *</td>
<td>61.19</td>
<td>62.09</td>
<td>61.19</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

* By difference
Table 1-3. Elemental analysis of the Ash of the hardwood (red oak) fast pyrolysis (500°C) biochar carried out by Hazen Research Inc. following ASTM standard methods (ASTM-D3172, 2007)

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>91.82</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.38</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.32</td>
</tr>
<tr>
<td>CaO</td>
<td>4.17</td>
</tr>
<tr>
<td>MgO</td>
<td>0.33</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.26</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.44</td>
</tr>
<tr>
<td>Cl</td>
<td>0.03</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>101.46</strong></td>
</tr>
</tbody>
</table>
Figure 1.1. Graphical representation of the sampling strategy for the different measurements. Dark brown represent biochar plus soil and light brown represents soil only. At the end of the incubation period, the columns were dismantled and samples at different depths were obtained.
Figure 1.2. Water partitioning for each treatment averaged across 91 days of incubation. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively. Treatment means within each component of water partitioning with different letters indicate statistically significant differences ($p < 0.05$).
Figure 1.3. Differences in water content between biochar treatments after 91 days of incubation. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively. Each column represents the difference between treatments for each component of water partitioning. Stars denote statistically significant differences ($p < 0.05$) from 0. Error bars show standard error of the difference.
Figure 1.4. Temporal dynamic of gravimetric water content for each treatment during the 91 days of incubation. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively. Error bars show standard error of the mean.
Figure 1.5. Temporal dynamics of bulk density for each treatment during the 91 days of incubation. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively. Error bars show standard error of the mean.
Figure 1.6. Water retention curves for biochar treatments at different times during the incubation. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively.
Figure 1.7. Distribution of water content by depth and incubation day for soil columns containing biochar treatments. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively.
Figure 1.8. Distribution of effective cation exchange capacity (ECEC) by depths and incubation day for soil columns containing biochar treatments. Biochar rates (3 and 6% wt/wt) were applied in the bottom 11.4 cm or in the top 11.4 cm, to simulate deep-banding in rows (DBR_3 and DBR_6) and uniform topsoil mixing (UTM_3 and UTM_6) applications, respectively.
CHAPTER 3: Biochar in Sandy Soils: Effect on Soil Fertility Parameters

Abstract

The effects of biochar on nutrient availability and soil pH are strongly influenced by properties of the feedstock, the pyrolysis process (fast or slow pyrolysis), and soil type. Moreover, the depth of biochar application might affect nutrient distribution in the soil. The objective of this study was to assess the impact of a fast pyrolysis hardwood (red oak) biochar on pH and the availability of base cations (K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and Na\(^+\)) in a sandy loam soil over time and at different soil depths. Biochar (0, 3, and 6% w/w) mixed with soil was placed into columns in either the bottom 11.4 cm or at the top 11.4 cm of the columns, to simulate deep-banding within rows (DBR) and uniform topsoil mixing (UTM) applications, respectively. Four sets of 18 columns were incubated at 28°C and 80% RH for 91 days. Every seven days during the incubation, 150 mL of 0.001M calcium chloride solution was added to the columns to produce leaching. Sets of columns were harvested after 1 day, 15 days, 29 days and 91 days. After 91 days of incubation, we found an increase in soil pH of 0.41 units for the biochar treatment relative to the control. Soils treated with 6% (w/w) biochar showed an increase of 185% in exchangeable potassium (K\(^+\)), compared to control soils (0% biochar). Soil receiving the UTM treatment had higher levels of extractable K\(^+\) in the surface soil than did soil in columns receiving the DBR treatment. Exchangeable Ca\(^{2+}\) and Mg\(^{2+}\) decreased in biochar treatments compared to the control. These results suggest that biochar might be effective in improving the fertility of sandy soils.
Introduction

Biochar additions to soil have shown various benefits, including improvements in soil quality (Chan et al., 2007; Chan et al., 2008; Novak et al., 2009a; Van Zwieten et al., 2009; Brockhoff et al., 2010; Novak et al., 2009b; Laird et al., 2010a). Adding biochar may increase exchangeable potassium (K) levels in soil through both the addition of K which is in the ash fraction of the biochar and by reducing losses of K through leaching (Laird et al., 2010a; Novak et al., 2009b; Chan et al., 2007).

Biochar applications have various effects on availability of other cations like magnesium (Mg) and Calcium (Ca) in soils. Biochar incorporation into soils has been shown to increase exchangeable Ca in some experiments (Laird et al., 2010a; Novak et al., 2009b; Van Zwieten et al., 2009), but in other experiments biochar did not have a measurable effect on exchangeable Ca (Brewer et al., 2011; Chan et al., 2007). Similar results have been reported for exchangeable Mg (Laird et al., 2010a; Novak et al., 2009b; Van Zwieten et al., 2009). Soil pH has increased in most studies reporting effects of biochar additions on soil pH (Laird et al., 2010a; Brockhoff et al., 2010). Few studies have reported changes in levels of exchangeable cations and pH over time and at different depths in the soil profile (Laird et al., 2010a; Novak et al., 2009b).

The depth and method of biochar incorporation into the soil has the potential to influence soil water retention and nutrient availability. Two biochar application strategies have been investigated: uniform top mixing and deep-banding within rows. Blackwell et al. (2010) used band applications of biochar in dryland wheat production study in order to reduced wind erosion and to place biochar close to crop roots. They found that banding biochar reduced fertilizer requirements without affecting yields.
Nutrient properties, including bioavailability once biochar is incorporated into the soil, are highly influenced by properties of the pyrolysis feedstock and the thermochemical conditions used for the production of the biochar (Amonette and Joseph, 2010; Chan and Xu, 2010). Despite insights from previous studies, there is still a gap in understanding the impact of biochar applications on soil fertility relative to the specific type of biochar used, especially when biochar is added to sandy soils. The impact of different methods of biochar application on soil fertility also has not been evaluated. Moreover, changes in soil pH and exchangeable cations over time and at different soil depths after biochar additions needs to be assessed. Here we tested the hypothesis that the use of a fast pyrolysis biochar as a soil amendment will enhance the quality of a sandy soil by increasing soil pH. We further hypothesize that concentrations of exchangeable base cations in the soil will increase over time after biochar additions, and that the distribution of these cations will be influenced by the placement of biochar within the soil profile. Specifically, we hypothesize that deep banding of biochar will shift the distribution of exchangeable base cations deeper in the soil profile compared to uniform top mixing of biochar.

Material and Methods

Soil

The soil used in this study was a sandy loam (Clarion loam; 68.2% sand, 25.1% silt and 6.7% clay) sampled from the surface 15cm of a field on the Iowa State University Agronomy and Agricultural Engineering Research Farm in Boone County, Iowa, USA. The particle size analysis was carried by the Department of Agronomy’ Soil and Plant Analysis Laboratory following the Gee and Bauder method (1986).
Bulk soil collected from the farm was air-dry then tumbled in a rotatory cement mixer for 10 min with six iron cylinders to crush soil aggregates and thoroughly mix the soil. After mixing, the soil was passed through a 6-mm sieve and stored in closed plastic containers until it was used. Characteristics determined by the Soil and Plant Analysis Laboratory (Agronomy Hall, Iowa State University, Ames) are presented in Table 1.1. Available phosphorus (P) was extracted with a dilute acid fluoride solution following the procedure suggested by Bray and Kurtz (1945). P concentrations in the extracts were determined by using a spectrophotometer at 882 nm. Soil pH was assessed by measuring the proton (H⁺) activity of a soil/water (1:1) slurry with a pH meter (Watson and Brown, 2011). Available micronutrient (Z, Cu, Fe, and Mn) concentrations were determined using a DTPA extraction (Lindsay and Norvell, 1978) and analysis of the metals using an inductively coupled plasma emission spectroscopy (ICP). Concentrations of available potassium (K) and other base cations (Ca, Mg and Na) in the soils were determined by extraction with a 1M ammonium acetate solution following by ICP analysis (Warncke and Brown, 2011). Effective cation exchange capacity was calculated based on the sum of concentrations for extractable K, Ca, Mg and Na (Warncke and Brown, 2011). Soil organic carbon and total nitrogen were determined by thermal combustion analysis, while the organic matter was estimated by multiplying soil organic carbon by 1.72 (Combs and Nathan, 2011). Extractable (2M KCl) inorganic nitrogen was determined using a colorimetric method (Mulvaney, 1996).

**Biochar**

Avello Bioenergy, Inc. (BioCentury Research Farm, 1327 U Avenue, Boone, Iowa) provided the biochar used for this experiment. The feedstock was *red oak*. The biochar was
produced by fast pyrolysis (500°C) in a 6 inch bubbling fluidized bed reactor, using nitrogen (183 L/min) as the fluidizing gas. The average biomass feed rate was 5.0 kg/hr. After production the biochar was stored in a sealed container for three months before it was used in the present study.

Characteristics of the biochar are provided in tables 1.2 and 1.3. Volatile matter and fixed carbon are properties that give relative measures of the labile and stable carbon fractions of the biochar, respectively. These properties along with ash content (the remaining solid after all the organic elements – carbon (C), hydrogen (H) and nitrogen (N) – have been oxidized (Joseph et al., 2010b)) are determined by proximate analysis (ASTM-D3172, 2007). Ultimate analysis is the determination of total concentrations of C, H, N, sulfur (S) and oxygen (O) in the biochar (ASTM-D3176, 2009). Ultimate and proximate analysis of the biochar used in this study along with elemental analysis of the biochar ash was carried out by Hazen Research Inc. (4601 Indiana Street Golden, Colorado 80403, U.S.A) using ASTM standard methods.

Incubation

The soil incubation was carried out in PVC columns of 18cm height and 7 cm external diameter. To build the columns, individual 18cm length PVC pipes were cut longitudinally and joined together with two clamps to avoid leaks. The purpose of cutting the pipe was to allow access to the soil for sampling with minimal disturbance at the end of the incubation. Each column had a PVC end cap on the bottom with a drain hole (3 mm) and an attached tube (4.3mm i.d.) for collecting water draining out the bottom of the columns. The concave portion of the end cap was filled with approximately 100 g of coarse sand (4-7 mm). The total mass of oven dry soil in each column was 994 g. There were three
rates of biochar application; 0% (control), 3% and 6% (w/w) (3 and 6% are referenced hereafter as *biochar treatments*). For the 3% biochar treatment, each column contained 20 g of biochar and 974 g of soil, while columns with the 6% biochar treatment contained 40 g of biochar and 954 g of soil. Biochar was applied in two different ways, either in the bottom 11.4 cm or in the top 11.4 cm of the column, to simulate deep-banding in rows (DBR) and uniform topsoil mixing (UTM) applications, respectively. To complete the column filling, 5 cm of soil was placed either in the top of the column above the biochar-soil mixture for DBR treatments or in the bottom of the column below the biochar-soil mixture for the UTM treatments. All columns were packed to similar bulk densities. Bulk densities values used in this experiment ranged from 1.31 g/cm³ to 1.41 g/cm³, depending primarily on the biochar treatment. The 4 sets of 18 columns were incubated at 30 °C and 80% RH in a dark room. The first set was incubated for 1 day, the second for 15 days, the third for 29 days, and the fourth for 91 days. Each set of columns had the three rates of biochar application (0, 3, and 6%), two biochar placements (DBR and UTM), and three replicates. The 72 columns were randomly distributed on two square tables, each one containing 36 holes for allocating the columns.

Every seven days 150 mL of 0.001M CaCl₂ solution was added to each column to produce a leaching event. Dilute CaCl₂ was used in order to reduce soil dispersion. The solution was introduced on the top of each column at approximately 150 mL/40 min, using a dropper system. Fiberglass filter paper was placed on the soil surface of each column to help disperse solution drops as they impacted the soil.
**Soil pH and Cations Distribution**

At the end of the incubation of each set of columns, pH and the distribution of extractable cations (K$^+$, Ca$^{2+}$, Mg$^{2+}$, and Na$^+$) was determined in each column for 3 different depths (0-1.3 cm, 5.05-6.35 cm and 13.94-15.24 cm) (Fig. 2.1). The harvesting of the second set of columns was made 48h after a watering event a difference from the others three sets where harvesting was made 24h after watering. Because of this difference in harvest timing, results from the second set of column were not used for interpreting soil pH and distribution of cation within the soil columns. For the soil sampling procedure, columns were dismantled by removing the end cap and losing the clamps that held the two halves of the PVC pipe together. Once the in-tact soil column was removed from the PVC pipe, soil samples at different depths were obtained by sectioning the column (figure 2.1), air dried and stored in sealed plastic bags until analyzed. Soil pH was determined using the standard method suggested by Thomas (1996). The method of Sumner and Miller (1996) was used to determine NH$_4$Cl extractable base cations and ECEC with quantified by Inductively Coupled Plasma (ICP).

**Evaporative Demand**

Temperature in the room where the columns were incubated was kept constant during the incubation. Nevertheless, there were differences in temperature across the room and evaporative demand was also influenced by proximity to overhead air circulation fans. In order to take into account these differences, evaporative demand was determined. For this, PVC cups were filled with an equal amount of water and placed above each column. Several times during the period of two or three days, the PVC cups were weighed to
determine average water loss per hour for each column. This measure of evaporative demand was used as a covariate in the statistical analysis.

**Statistical Analysis**

A linear model was used to analyze pH and exchangeable cations (Proc Mixed, SAS 9.2, SAS Institute Inc., Cary, NC, USA), where the terms in the linear model were incubation day (1, 15, 29 and 91 days), biochar (control, DRR_3, DBR_6, UTM_3 and UTM_6), depth (depth 1= 0-1.3 cm, depth 2= 5.05-6.35 cm and depth 3=13.94-15.24 cm), and the interaction terms between incubation day, biochar and depth. To account for the correlation of residuals in variables that were measured repeatedly over the duration of the experiment the covariance structure of the residuals was modeled. The structures chosen (based on AIC criteria) were “First order autoregressive covariance structure” for pH and Na, “Heterogeneous First order autoregressive covariance structure” for Mg and “Heterogeneous Compound symmetry covariance structure” for K. Evaporative demand was used as a covariate in each model. Mean separation was conducted based on linear contrasts at an alpha of 0.05.

**Results and Discussion**

**Soil pH**

Twenty four hours after the incubation began, the pH values for the biochar treatments were lower or equal to the controls, except for the DBR-3 depth 1 treatment (Fig. 2.2). Later as the incubation progressed (incubation day 29 and 91), the pH values for all biochar treatments in all depths increased compared to the controls (Fig. 2.2). The pHs for the biochar treatments on incubation day 91 were all significant (p<0.01) greater than
the controls except for DBR_3. Averaged across the three depths for day 91, the increase in pH for biochar treatments relative to the controls was: 0.21 (DBR_3), 0.44 (DBR_6), 0.47 (UTM_3) and 0.51 (UTM_6) units of pH.

The observed increase in soil pH in the biochar treatments compared to the controls is likely due to the dissolution of alkaline carbonates, oxides, and hydroxides minerals present mainly in the ash fraction of the biochar (Lehmann et al., 2011; Joseph et al. 2010a). The increase in soil pH with incubation time observed in the present study is in contrast with results of Novak et al. (2009b) who did not find an increase in soil pH after incubating a loamy sand soil for 67 days with pecan shell-based biochar. Differences in results of these studies might be due to differences in the type of biochar used. The pecan shell biochar used by Novak et al. (2009b) was 3.8% (wt/wt) ash compared to the 21.6% (wt/wt) ash content of the biochar used here.

Soil pH did not show a depth pattern consistent with the biochar distribution (Fig. 2.2). Soil pH values are characteristic of the soil solution and tend equalize across soil layers.

**Cation Distribution**

Exchangeable potassium (K⁺) concentrations followed the depth distribution of biochar in the soil profile (Fig. 2.3). UTM treatment soils at depths 1 and 2, where the biochar was placed, had higher K⁺ concentrations than at depth 3, with no biochar (Fig. 2.3). These results are contrast with those of Laird et al. (2010a) who observed an overall increase in K⁺ concentrations with depth in both biochar and control treatments. In their study, biochar was uniformly mixed through the soil profile and then columns were leached for 500 days. The K⁺ distribution indicated that K⁺ mobility was retarded by the presence
of biochar. In the present study, the DBR treatment soils at depths 2 and 3, where the biochar was placed, had higher exchangeable K values than at depth 1, with no biochar (Figure 2.3). Moreover, exchangeable K was proportional to biochar application rate; treatments that received 6% wt/wt biochar had higher exchangeable K⁺ than those that receiving 3% wt/wt biochar (Fig. 2.3).

In general, exchangeable K⁺ concentrations increased with incubation time in the biochar treated soils. The exchangeable K⁺ at depth 2 for the UTM_3 treatment samples significantly \((p<0.01)\) increased from 0.15 on incubation day 1 to 0.20 \([\text{mg g}^{-1} \text{ oven dry soil}]\) on day 91. For the UTM_6 treatment, exchangeable K significantly \((p<0.001)\) increased from 0.19 to 0.28 \([\text{mg g}^{-1}]\), for the same depth and during the same period. Relative to the control, treatments UTM_3 and UTM_6 showed significant \((p<0.01)\) increases of 100% and 180%, respectively, in exchangeable K for incubation day 91 (depth 2) relative to day 1. The exchangeable K⁺ at depth 3 for the DBR_3 treatment significantly \((p<0.01)\) increased from 0.14 on incubation day 1 to 0.19 \([\text{mg g}^{-1} \text{ oven dry soil}]\) on day 91. While for the same depth and period, the exchangeable K for DBR_6 significantly \((p<0.001)\) increase from 0.17 to 0.29 \([\text{mg g}^{-1}]\). On incubation day 91 (depth 3), DBR_3 and DBR_6 had 90% and 190%, respectively, significantly higher levels of exchangeable K⁺ relative to the control. By contrast, the extractable K⁺ concentrations for the controls at depths 2 and 3 did not significantly increase during the incubation period. Depths 2 and 3 in the UTM and DBR treatments, respectively, were chosen for comparison based on the downward movement of the K⁺ due to leaching and because depths 2 and 3 are the deepest samples having biochar in each of the biochar treatments. The increase in exchangeable K⁺ observed in the present study with incubation period in the biochar amended soils contrasts
with the results obtained by Novak et al. (2009b), who found a decrease in K\(^+\) concentration after incubating a loamy sand soil with a pecan shell-based biochar for 67 days. The likely difference is due to lower levels of K\(^+\) in the pecan shell-biochar.

The observed increase in extractable K\(^+\) with incubation time for the biochar amended soils could be explained by the presence of occluded K\(^+\) within the biochar structure, which only slowly diffused out of the biochar particles to the soil solution or by the presence of weakly soluble K compounds that only slowly dissolved during the incubation. For either of these mechanisms, leaching of K\(^+\) once released to the soil solution would be retarded by retention of the K on soil and biochar CEC sites.

Biochar treatments decreased the exchangeable calcium (Ca\(^{2+}\)) concentration [mg g\(^{-1}\) oven dry soil] for depths 2 and 3 relative to the controls (Figure 2.4, and incubation day 91). This decrease in exchangeable Ca\(^{2+}\) was significant (p<0.05) for all biochar treatments and depths except for depth 2 in the UTM_3 treatment (incubation day 91). Across treatments, higher values of exchangeable Ca\(^{2+}\) were observed at depth 1 than at depths 2 and 3 (Fig. 2.4) suggesting an accumulation of Ca\(^{2+}\) added with the leaching water (0.001 M CaCl\(_2\)) and an overall low mobility of Ca\(^{2+}\) in the soil. The total amount of exchangeable Ca\(^{2+}\) present in the soil was 1.87 mg per gram oven dry soil (Table 1.1). A total of 0.085 mg of Ca\(^{2+}\) per gram of oven dry soil was added with the leaching solution; hence the amount of Ca\(^{2+}\) added with the leaching solution was a small percentage of the total exchangeable Ca\(^{2+}\) present in the soil. Treatments having 3% biochar (DBR_3 and UTM_3) received 0.13 mg of Ca\(^{2+}\) per gram oven dry soil with the biochar addition, and those amended with 6% biochar (DBR_6 and UTM_6) received 0.26 mg of Ca\(^{2+}\) per gram oven dry soil through the biochar additions. It is likely, that most of the Ca\(^{2+}\) present in the biochar was not
solubilized during the time of the incubation because the average amount of exchangeable Ca\(^{2+}\) obtained for the biochar treatments was approximately equal to the amount of exchangeable Ca\(^{2+}\) present in the controls (Fig. 2.4 and Table 1.1). For incubation days 29 and 91 (Fig. 2.4), the amount of exchangeable Ca\(^{2+}\) across the three depths in the biochar treatments was lower than in the controls, suggesting that either Ca\(^{2+}\) had a higher mobility in the biochar treated soils than in the control or more likely that Ca\(^{2+}\) precipitated as insoluble carbonate due to the higher pH of biochar treated soils. Laird et al. (2010b) by contrast observed significantly higher Ca concentrations in leachate from biochar treated soils than from the controls, suggesting that at least part of the Ca\(^{2+}\) in the biochar ash was solubilized during the 500 day leaching-incubation study.

Biochar addition did not have a significant effect on sodium (Na\(^{+}\)) concentrations in the soils (Fig. 2.5). After 24hs of incubation, the exchangeable Na\(^{+}\) present was on average 0.004 mg of Na per gram of oven dry soil, approximately equal to the amount of exchangeable Na presented in the soil before starting the incubation (figure 5 and Table 1.1). As the incubation progressed (incubation days 29 and 91, Fig. 2.5), the concentration of exchangeable Na\(^{+}\) for all the treatments increased.

Exchangeable magnesium (Mg\(^{2+}\)) at depth 2 in the biochar treated soils significantly \((p<0.05)\) decreased after 91 days of incubation relative to the controls (Fig. 2.6). At depth 3, the exchangeable Mg\(^{2+}\) for all of the biochar treated soils also decreased relative to the controls, but only for the DBR was the reduction significant \((p<0.05)\). The amount of exchangeable Mg\(^{2+}\) present in the control soil was approximately 0.26 mg per gram of oven dry soil. Treatments amended with 3% biochar (DBR_3 and UTM_3) received 0.009 mg of Mg\(^{2+}\) per gram oven dry soil in the biochar, and those with 6% biochar treatments (DBR_6
and UTM_6) received 0.017 mg of Mg$^{2+}$ per gram oven dry soil with the biochar amendments. Similar with what was observed for Ca$^{2+}$, it is likely that little of the Mg$^{2+}$ present in the biochar was solubilized during the incubation because the average amount of exchangeable Mg$^{2+}$ obtained from biochar treated soils was approximately equal to that extracted from the control soils (Fig. 2.6).

From incubation day 15 onwards, the average exchangeable Mg$^{2+}$ was higher in the control soils than in the biochar amended soils (Fig. 2.6). The exchangeable Mg$^{2+}$ at depth 1 (Fig. 2.6) was always lower for UTM than for DBR treatments, but at depth 3 exchangeable Mg was always lower in DBR than in UTM treatments. UTM samples taken at depth 1 had biochar while those taken at depth 3 did not; and DBR samples taken at depth 3 had biochar while those taken at depth 1 did not. This suggests, as with Ca$^{2+}$, either higher mobility of Mg$^{2+}$ in the biochar treatments than in the controls or precipitation of Mg$^{2+}$ as insoluble carbonates due to the higher soil pH of biochar treated soils. Laird et al. (2010b) found a significant increase in leached Mg$^{2+}$ after adding 2% (wt/wt) biochar to a loamy soil, suggesting that some of the Mg added with the biochar was soluble in their study.

**Conclusion**

After 91 days of incubating a sandy loam soil with hardwood fast pyrolysis biochar, we observed an average increase in soil pH of 0.41 units relative to the control soils. Soil samples having biochar showed significantly greater exchangeable potassium (K$^+$) than control soils without biochar. Results also showed that calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$) were either more mobile in biochar treated soil than in the control or that these elements precipitated as insoluble carbonates due to higher pH in the biochar treated soils.
There were not significant differences in soil pH, exchangeable sodium (Na\(^+\)), Mg\(^{2+}\) and Ca\(^{2+}\) between treatments where biochar was deep banded (DBR) and treatments where biochar was uniform top mixed (UTM). However, there were significant differences in exchangeable K\(^+\) between DBR and UTM treatments at the same depth in the soil columns. Exchangeable K\(^+\) followed the distribution of biochar in the soil profile, such that UTM treated soils had the highest K\(^+\) concentrations at the top of the column while DBR treatments had the highest K\(^+\) concentrations at the bottom of the soil column. Deep banding biochar might be more suitable than uniform top mixed biochar when plants are under K\(^+\) deficiencies because DBR will keep exchangeable K closer to the roots than UTM. Measurements of plant productivity in field environments under nutrient deficient situations are needed to advance understanding of the impact of biochar on crop production.
Figure 2.1. Graphical representation of the sampling strategy for the different measurements. Dark brown represent biochar plus soil and light brown represents soil only. At the end of the incubation period, the columns were dismantled and samples at different depths were obtained.
Figure 2.2. Distribution of soil pH values by depths and incubation day for soil columns containing biochar treatments. Biochar (3 and 6% wt/wt) was applied in the bottom 11.4 cm (DBR) or in the top 11.4 cm (UTM), resulting in four treatment combinations: DBR_3, DBR_6, UTM_3 and UTM_6.
Figure 2.3. Distribution of exchangeable Potassium (K) by depths and incubation day for soil columns containing biochar treatments. Biochar (3 and 6% wt/wt) was applied in the bottom 11.4 cm (DBR) or in the top 11.4 cm (UTM), resulting in four treatment combinations: DBR_3, DBR_6, UTM_3 and UTM_6.
Figure 2.4. Distribution of exchangeable Calcium (Ca) by depths and incubation day for soil columns containing biochar treatments. Biochar (3 and 6% wt/wt) was applied in the bottom 11.4 cm (DBR) or in the top 11.4 cm (UTM), resulting in four treatment combinations: DBR_3, DBR_6, UTM_3 and UTM_6.
Figure 2.5. Distribution of exchangeable Sodium (Na) by depths and incubation day for soil columns containing biochar treatments. Biochar (3 and 6% wt/wt) was applied in the bottom 11.4 cm (DBR) or in the top 11.4 cm (UTM), resulting in four treatment combinations: DBR_3, DBR_6, UTM_3 and UTM_6.
Figure 2.6. Distribution of exchangeable Magnesium (Mg) by depths and incubation day for soil columns containing biochar treatments. Biochar (3 and 6% wt/wt) was applied in the bottom 11.4 cm (DBR) or in the top 11.4 cm (UTM), resulting in four treatment combinations: DBR_3, DBR_6, UTM_3 and UTM_6.
CHAPTER 4: General Conclusion

The results presented in this thesis indicate that biochar, the solid co-product of biomass pyrolysis, has the potential to be used as a soil amendment in sandy soils. In this study, the addition of red oak, fast pyrolysis (500°C) biochar was shown to increase total water retained against gravity by the soil and the available water-holding capacity of the soil. After 91 days of incubating a sandy loam soil with biochar, we did not find significant differences in water partitioning (water retention, evaporation and drainage) between two methods of biochar application (uniform top mixing (UTM) and deep banded (DBR)) at 3% wt/wt biochar addition rate. At 6% wt/wt biochar addition, however, UTM_6 significantly increased water retention relative to DBR_6. Biochar applications did not increase ECEC of the soil during the incubation. Average bulk density of soils receiving biochar remained relatively constant during the incubation while the bulk density for control soils significantly increased from 1.41 to 1.45 g/cm³ during the same period of time.

This study also showed that after 91 days of incubation, there was an average increase in soil pH of 0.41 units in the biochar treated soils relative to the control soils. Soil samples having biochar showed significantly higher levels of exchangeable potassium (K⁺) than samples without biochar. Calcium (Ca²⁺) and magnesium (Mg²⁺) were either more mobile in biochar treated soils than in the control soils or these elements precipitated as insoluble carbonates in the biochar treated soils due to higher pH resulting in lower exchangeable Ca²⁺ and Mg²⁺ in biochar treatments than in the controls.

Biochar applications are effective for increasing water holding capacity and nutrients availability when applied to sandy soils due to the naturally low values of these properties for sandy soils in comparison to loamy and clayey soils. Soils of farms located in
arid regions are often sandy, and most of the time supplemental irrigation is needed for growing crops in these fields. The DBR application method may be more appropriate for use in arid regions because the soil disturbance required for biochar incorporation is less than for UTM, and less disturbance of the soil surface should reduce soil erosion and water lost by evaporation. A reduction in the amount of water used to produce irrigated crops may be expected after biochar applications because biochar increases available water-holding capacity of sandy soils and should reduce the loss of water to deep percolation. Moreover, addition of biochar to soil on non-irrigated farms may be beneficial because more water coming from rainfall can be stored in the biochar amended soil, reducing the chances of crop water stress during dry periods between rainfall events. The results suggest that biochar applications could help to enhance food scarcity in arid and semi-arid regions with sandy soils by reducing the amount of water needed for production of irrigated and non-irrigated crops. In addition to these potential benefits of biochar, the findings of this study may also help increase the value of biochar thereby making bioenergy production industry more economically viable. Biofuels offer one option for partially substituting renewable sources of energies for scarce fossil fuels to reduce greenhouse gas emissions and enhance energy security. However, field research is still needed to assess crop response to biochar added using different methods of application. Because biochar helps keep water and nutrients in the upper 20cm of the soil profile, this could have a negative effect on root development, for example. Moreover, experiments to determine specific mechanisms by which water is retained in biochar amended soils are still needed.
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References


