

The Effect of Fast Pyrolysis Biochar Made From Poultry Litter on Soil Properties and
Plant Growth

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Abstract

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Little is known about the effect of biochar created from poultry litter on soil properties and plant growth. Five studies were conducted using biochar made by the fast pyrolysis of poultry litter. Two were greenhouse studies and three were field studies. The greenhouse studies were conducted with a sandy loam soil and a silt loam soil. First, lettuce (*Lactuca sativa* L) seeds were germinated in the greenhouse across biochar incorporation rates from 0 to 100%, and secondly a trial was conducted in which green peppers (*capsicum annum* L) were grown in soils with up to 5% biochar by weight. Elemental analysis was completed on the biochar and the soils were analyzed for bulk density (BD), water holding capacity (WHC), pH, cation exchange capacity (CEC), soluble salts (SS) and extractable nutrients. The field studies all used the rates of 0, 4.5, and 9 Mg ha⁻¹ biochar and the rates were applied in the early spring of 2009 and 2010. Biochar was surface applied on a tall fescue pasture [*Lolium arundinaceum* (Schreb.) Darbysh. (= *Festuca arundinacea* Schreb. subsp. *arundinacea*)] and tilled in on two green pepper field sites. The soils were analyzed for carbon (C) content, pH, CEC, Mehlich 1 P, and SS. No significant difference was found in yields at any of the three sites, but differences in forage quality were found. Biochar made from poultry litter showed several benefits as a soil amendment in all the studies, but application rates would be limited by soil test P and pH.

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Chapter 1 Literature Review

Introduction

Biochar is a carbon (C) rich soil amendment which can be made by the pyrolysis of biomass and has the potential to improve soil fertility and sequester C. Biomass is a broad term used to encompass materials composed of hemicellulose, cellulose, lignin, and minor amounts of other organics and it can be referred to as feedstock when it is used to produce biochar and/or renewable energy (Kim et al., 2009). Pyrolysis is the thermal decomposition of biomass in an oxygen depleted environment and the charcoal that is produced is referred to as biochar when it is intended for soil application (Lehmann et al., 2006). Pyrolysis can also be used to produce bio-oils and gas along with biochar, therefore creating multiple potential revenue streams (Demirbas and Arin, 2002).

Climate change is a major problem facing the world today and rises in global temperatures have been documented and accepted by the international scientific community (IPCC 2001). The release of greenhouse gasses from the burning of fossil fuels and the decomposition of organic matter have been cited as driving forces of the greenhouse effect (Lehmann et al., 2006). Using the soil as a C sink has been suggested as a way to offset the accumulation of greenhouse gasses in the atmosphere (Batjes, 1998; Izaurralde et al., 2001; Scholes and Noble, 2001), but organic matter additions to soil generally have limited permanency due to decomposition (Rasmussen et al., 1998). Biochar offers the potential for long term C sequestration in soils due to its resistance to microbial decay (Lehmann et al., 2006). The Amazonian rain forest is an environment with high temperatures and rain fall which contribute to the fast decay of organic matter

due to the microbial population. The presence of black Terra Preta soils in this climate points to the ability of biochar to form a soil C pool which is resistant to microbial decay (Glaser et al., 2001; Glaser et al., 2002). Also, paleoecological studies have often used buried biochar as markers for historical events as the char will remain in soil for hundreds of years after associated non-char biomass has decayed (Jones et al., 2011; Lertzman et al., 2002).

Manure Management

Poultry litter is a promising feedstock for pyrolysis because it is found in excess in regions with intensive poultry operations. The majority of poultry litter is disposed of through land application and many regions with intensive poultry production have more phosphorous (P) than local crops require (Maguire et al., 2007). Land application of manure is heavily regulated in many states to control the fate of manure nutrients (DCR, 2005). P based nutrient management is important because it prevents the over application of P and therefore protects freshwater ecosystems from surface runoff as P is a major cause of eutrophication (Schroeder et al., 2004). Due to the regulation of land application of P, much of the poultry litter has to be transported off the farm and the distance that the litter can be transported is limited by cost (Harmel et al., 2008). The greater nutrient P concentration in the biochar compared to the poultry litter feedstock could reduce the cost of exporting the P off the farm and allow for it to be transported farther (Cantrell et al., 2007).

Biochar Structure and Composition

Biochar is highly variable depending on the feedstock and the pyrolysis conditions used (Baldok and Smernik, 2002). The structure of biochar is generally amorphous in nature

and is composed of aromatic compounds (Quadeer et al., 1994), although the C skeleton does retain some of the porosity and structure of the original material (Wildman and Derbyshire, 1991). The yield of the bio-oils and biochar for a given feedstock depends on the temperature reached during pyrolysis. The amount of biochar produced typically decreases as the temperature increases but the concentration of carbon in the biochar increases (Katyal et al., 2003). These contrasting effects make it such that pyrolysis temperature has little effect on the amount of C that can potentially be sequestered (Lehmann et al., 2006). High lignin concentrations and mineral content also increase the amount of carbon recovered (Lehmann et al., 2006; Ravendran et al., 1995; Nik-Azar et al., 1997). High pyrolysis temperatures also improve exchange properties and surface area of the biochar (Glaser et al. 2002).

The ash contained in biochar is a representation of the inorganic content. Concentrations of ash in biochar range from less than 1% in softwood to sometimes greater than 60% in animal manure biochars (Kim et al., 2009). The potassium (K) content of a feedstock has been shown to catalyze biomass decomposition and char-forming reactions. The high K content of poultry litter could be responsible for the increased yields of biochar made from a poultry litter feedstock (Agblevor et al., 1996). High ash concentrations can cause ash fusion or sintering under some pyrolysis conditions and the result is a loss of structural complexity (Rodriguez-Mirasol et al., 1993).

The majority of research has been conducted on biochar made from plants and in these studies the biochar contained small amounts of inorganics (ash) and large amounts of carbon. Research has been primarily concerned with depleted, acidic soils (Steiner et

al., 2008) and systems with less than optimal fertilization regimes (Chan et al., 2008; Hossain et al., 2010). Research has shown that biochar is a good resource for improving crop yields on acid and infertile tropical soils where nutrient resources are scarce (Lehmann et al., 2006; Lehmann and Rondon, 2005) as well as increasing seed germination (Chidumayo, 1994). Negative effects on yield after additions of biochar have been found in some cases due to increases in pH for pH-sensitive plants (Tryon, 1948) or because of pH-induced micro-nutrient deficiencies (Kishimoto and Sugiura, 1985). Biochar additions have been found to increase nutrient retention and availability due to higher CEC and surface area along with increasing total nutrient amounts (Glaser et al. 2002).

Carbon to Nitrogen Ratio

The nutrient content of biochar is highly variable and the total nutrient concentrations do not necessarily correlate with the quantity of nutrients that are plant available. The C:N ratio of an organic soil amendment is used to predict whether N will be mineralized or immobilized. Below a ratio of 20:1, generic interpretations indicate that N will be mineralized and become plant available (Havlin et al., 2005, p. 119-122). Biochars cover a wide range of C:N ratios (between 7 to 400) (Lehmann and Joseph, 2009, p. 70-71). The high C:N ratio of most biochars suggests that N will be immobilized but doubt exists about whether this line of reasoning applies directly to biochar. Since a large part of the C and N in biochar is resistant to microbial decay, it has been suggested that immobilization is negligible (Lehmann et al., 2003, p. 105-124). For example, Bridle and Pritchard (2004) found that biochar made from sewage sludge had very little plant available N despite having a C:N ratio of 7 and a total N concentration of 6.4%. Bridle

and Pritchard (2004) also found that 45% of the N was lost during pyrolysis where as all the P was recovered in the biochar.

Cation Exchange Capacity

The ability of biochar to increase nutrient retention in soils is due to the increases in cation exchange capacity (CEC) that result because of application. The success of using biochar on highly weathered soils is likely due to the ability of biochar to increase the low cation retention capabilities of the soils in areas where intense rainfall causes high amounts of leaching (Lehmann et al. 2002). Large additions of biochar have been shown to increase the CEC by as much as 50% in highly weathered soils (Tryon, 1948). A study on weathered soils showed that biochar adsorbed ammonium in an iron rich oxisol and reduced leaching as compared to the unamended control (Lehmann et al., 2002). The CEC of biochar seems to increase as the pyrolysis temperature increases but freshly produced biochars have been shown to have minimal CEC compared to soil organic matter (Lehmann and Joseph, 2009, p. 75; Lehmann, 2007). As the biochar is exposed to O₂ and water it becomes oxidized and the process is likely enhanced by microbes (Cheng et al., 2006; Liang et al., 2006)

pH

Soil pH is a major factor in determining the availability of nutrients to plants and not all plants require the same pH range. The optimal pH range for green peppers is 5.5-6.5 (Havlin et al., 2005, p. 66) and 6.2-6.5 for tall fescue (Maguire and Heckendorn, 2011). P can form insoluble compounds with iron and aluminum at pHs below 6 and it can precipitate with calcium at pHs above 7; maximum P solubility occurs near a pH of 6.5 (Havlin et al., 2005, p. 173-174). Changes in soil pH due to the addition of biochar

have been cited as the cause of positive and negative plant responses. Van Zwieten et al. (2007) found 40% increases in wheat height when paper mill sludge biochar was applied to an acidic soil but no response when applied to a pH neutral soil (Lehmann and Joseph, 2009, p. 73). Soil was limed above the optimum range in a study done by Kishimoto and Sugiura (1985) and yields were reduced by up to 71%. Poultry litter has a pH of around 8 and contains CaCO_3 (Maguire et al., 2008) and Chan et al. (2008) analyzed two types of poultry litter biochar, one produced at 450°C and another at 550°C , and found that the pHs were 9.9 and 13 respectively.

Soil Physical Properties

Pore space distribution is a dominant characteristic of soil structure and influences such characteristics as water holding capacity, aeration, bulk density, and soil aggregation. The water holding capacity of a soil is an important characteristic as water is often a limiting factor in the production of crops. Soils with low water holding capacities are subject to greater amounts of leaching, especially in areas with high amounts of precipitation. Sandy soils like those found in the tropics require less water to reach the point of saturation than those with a finer texture and this causes nutrients to be leached out of the root zone, thus becoming unavailable to crops (Major et al., 2009). Organic matter can increase the water holding capacity of soils due to its positive effects on aggregation and pore space distribution and biochar has the capacity to increase water retention due to the high amount of small pores and the positive effect it has on aggregation. Karhu et al. (2011) found that 9 Mg ha^{-1} of biochar made from birch waste at a pyrolysis temperature of 400°C increased soil water holding capacity by 11% by weight. Jones et al. (2011) found that a 10% by weight application of hardwood derived

biochar decreased the bulk density of a sandy clay loam by 29% and Chan et al. (2008) found that a 10 Mg ha⁻¹ application of poultry litter biochar reduced soil strength of a hard setting Alfisol by 30%.

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Chapter 2: Influence of poultry litter biochar on soil properties and plant growth

Abstract

Biochar created from poultry litter is a way to produce a value added soil amendment that is lighter and less expensive to transport out of manure nutrient excess areas, but effects on soil properties are unknown. Two studies were conducted with a sandy loam soil and a silt loam soil. First, lettuce (*Lactuca sativa* L) seeds were germinated across biochar incorporation rates from 0 to 100% biochar, and secondly a greenhouse trial was conducted in which green peppers (*capsicum annum* L) were grown in soils with up to 5% biochar by weight. Elemental analysis was completed on the biochar and soils were analyzed for bulk density (BD), water holding capacity (WHC), pH, cation exchange capacity (CEC), and extractable nutrients. Biochar increased lettuce germination by almost 50% in the sandy loam at low rates, but became toxic at rates above 2.5% in both soils probably due to salt toxicity. Water holding capacity increased linearly with biochar additions. For example, adding 15% biochar nearly doubled the WHC of the sandy loam from 15 to 27%. The biochar had a pH of 9.3 and additions increased the pH of both soils. Total phosphorus (P) in the biochar was 43 g kg^{-1} , and although almost none of this was water soluble in the pure biochar, the Mehlich 1 P and Olsen P were greatly increased in biochar amended soils. Biochar only consistently increased CEC at high rates. Biochar made from poultry litter showed several benefits as a soil amendment, but application rates would be limited by soil test P and pH.

Introduction

Many areas in the United States with intensive poultry production operations now have more manure P applied than local crops need (Maguire et al., 2007). Due to concerns over the fate of manure nutrients, land application of manure is now heavily regulated in many states, including Virginia (DCR, 2005). The majority of poultry litter is being exported from poultry farms in Virginia because growers do not have enough land to apply the litter according to mandated P-based nutrient management plans (McGrath et al., 2010). Due to the costs of transportation and the fact that soils in areas of intensive animal production often contain available P in excess of crop needs, there is substantial interest in alternative uses for poultry litter.

Pyrolysis technology can potentially be used to convert poultry litter into value-added products such as bio-oil, gas, and biochar (Matteson and Jenkins, 2007; Kim et al., 2009). Biochar is carbonized biomass that can be used as a C sequestering soil amendment and has a range of physical and chemical characteristics depending on the feedstock and pyrolysis conditions (Baldok and Smernik, 2002). In one study, fast pyrolysis of poultry litter at 450°C using a fluidized bed reactor produced 23% bio-oil, 41% biochar and 36% gas (Kim et al., 2009). The inorganic component of poultry litter is significantly concentrated in the biochar during pyrolysis and gives it potential value as a slow release nutrient source for crops (Agblevor et al., 2010). The greater P concentrations in the biochar compared to the poultry litter feedstock could potentially reduce the cost of exporting the P off the farm and allow for it to be economically transported further (Cantrell et al., 2007).

The interest in using biochar as a soil amendment stems from its ability to improve

soil quality, maintain soil fertility, and increase soil C sequestration (Glaser et al., 2002; Lehmann et al., 2003). A majority of the research has been conducted on biochar made from wood and in these studies biochar contained small amounts of inorganics (ash) and large amounts of C with application primarily focused on depleted, acidic soils (Steiner et al., 2008) or in systems with sub-optimal fertilization regimes (Chan et al., 2008; Hossain et al., 2010). The application of biochar has produced changes in soil properties such as increased CEC (Liang et al., 2006), WHC (Laird et al., 2010), retention of nutrients (Lehmann et al., 2003), pH (Rondon et al., 2007) and decreased soil penetration resistance (Busscher et al., 2010). The formation of carboxylic functional groups during oxidation is suggested as the reason for increases in CEC and this gives biochar long-term value as an amendment (Cheng et al., 2006). There is a wide range of reported plant responses from the application of biochar to soils, for example -73.2% to +166% changes in dry matter relative to the control, which can be attributed to the variability in the studied systems (Deenik et al., 2010; van Zwieten et al., 2010; Graber et al., 2010).

Ash concentrations in biochar range from less than 1% in softwood to sometimes greater than 60% in animal manure biochars (Kim et al., 2009). Poultry litter has high amounts of potassium (K) which has been shown to catalyze biomass decomposition and char-forming reactions and could be responsible for increasing biochar yields from poultry litter (Aglevor et al., 1996). Large amounts of ash can cause ash fusion or sintering under some pyrolysis conditions and the result is a loss of structural complexity (Rodriguez-Mirasol et al., 1993). The total ash content is not an appropriate indicator of the availability of nutrients, because only a fraction of the total nutrient content is immediately available and readily taken up by plants (Pritchard, 2003). Chan et al. (2008)

conducted a greenhouse study using an Alfisol with a crust forming A horizon low in soil organic carbon and a pH of 4.5 to compare two poultry litter biochars made by slow pyrolysis at 450°C and 550°C. Both poultry litter biochars had similar effects on the dry matter yield of radishes with yield increases as compared to the unamended control of 42% at 10 Mg ha⁻¹ ranging up to 96% at 50 Mg ha⁻¹ of poultry litter biochar application. Yield increases were attributed to the biochars ability to increase N availability, even though substantial N in the feedstock is lost or converted to pyrogenic N in the pyrolysis process (Knicker, 2007). Total nutrient uptake increased with application of poultry litter biochar in relation to the control. Significant changes in soil chemical and physical properties were observed for both poultry litter biochars, including increases in C, N, K, Ca, pH, soluble salts (SS), and available P, and a reduction in soil strength (Chan et al., 2008).

If pyrolysis of poultry litter is to become more widespread, it is important to understand how biochar made from poultry litter affects soil properties and crop production. As regulations covering land application of poultry litter often limit the application based on soil test P, it is particularly important to understand how soluble the P in the biochar will become. Therefore, the objective of this research was to examine how biochar made from the fast pyrolysis of poultry litter at a temperature of 450°C affects soil properties, soil test P, lettuce seed germination, and green pepper growth.

Materials and Methods

Soil Collection and Preparation

Soils were collected that were representative of the two dominant poultry producing regions of Virginia. The Ap horizon of a Bojac sandy loam (Typic Hapludult) was collected from the Eastern Shore of VA and the Ap horizon of a Grosseclose-Poplimento silt loam (Typic Hapludult) was collected in Blacksburg, VA to represent the ridge and valley physiographic region. Soils were air dried at 25°C and sieved to 6mm so that some soil structure would be preserved.

Biochar

Biochar was made from the fast pyrolysis of broiler chicken litter mixed with a pine shaving base at a pyrolysis temperature of 450°C using a fluidized bed reactor (Mante and Agblevor, 2010). All biochar analysis was conducted in triplicate. The pH of the biochar was determined in 1M KCl at a biochar:solution ratio of 1:1 (Thomas, 1996). Total Carbon (C), total Nitrogen (N), and C:N was determined by dry combustion using a Vario Max CNS macro elemental analyzer (Elementar, Hanau, Germany). Elemental concentrations of P, K, and Ca were determined by ashing 5g of biochar in a muffle furnace at 550°C for 24 hours and then digesting 0.8g of the ash in 10ml of 1M HCl. Samples were then diluted to 100ml and elemental concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Wolf et al., 2003). Soluble salts were determined in a 1:2 biochar to water ratio (Maguire and Heckendorn, 2011a). Water soluble phosphorus (WSP) was performed in triplicate and determined by mixing 3 g of biochar with 30 mL of deionized water shaking for 1 hour

and filtering through a 0.45 µm filter (Maguire et al., 2006). The extract was immediately analyzed colorimetrically using an auto analyzer (QuickChem 8500; Lachat Instruments, Loveland, CO).

Germination Study

This experiment was carried out in a temperature-controlled glasshouse (20-26°C). The experimental design used was a factorial randomized block with 3 replications. Biochar was mixed with the two soils in the following fifteen percentages by weight: 0, 0.2, 0.5, 1, 2.5, 5, 10, 15, 20, 25, 30, 40, 60, and 80 along with three 100 % trials for a total sample size of 87. 700g of each soil and biochar mix from 0 to 30% and 350g of the 40 to 100% was placed in a 13 × 18 x 7 cm germination tray and 30 lettuce (*Lactuca sativa*) seeds were planted at a depth of 0.5 cm in each tray. The mass of the mixture was reduced from 700g to 350g due to the increase in volume caused by the addition of the less dense biochar. Soils were watered as needed by hand to maintain moisture while avoiding leaching. Germination was monitored and recorded for 14 days. The soils were collected at the end of the experiment and air dried at 25°C, mixed thoroughly, and crushed gently to pass through a 2-mm sieve. The less than 2-mm samples were analyzed for pH, which was measured at a 1:1 soil:solution ratio with deionized water and soluble salts were determined in a 1:2 soil to water ratio (Maguire and Heckendorn, 2011a). Mehlich 1 P was determined by placing five grams of soil into a 60-ml straight-walled plastic extracting beaker, and 20 ml of the Mehlich 1 extracting solution was added with an automatic pipetting machine (Maguire and Heckendorn, 2011a). The samples were then shaken on a reciprocating shaker with a stroke length of

3.8 cm for 5 minutes at 180 oscillations per minute and filtered through Whatman No. 2 11-cm filter paper soon after the shaking stopped (Maguire and Heckendorn, 2011a). Melich 1 P was then determined by analyzing with ICP-AES (Maguire and Heckendorn, 2011a). Water holding capacity was determined by the container capacity method (Bond et al., 2006). 500g of each mixture was weighted into a germination tray with the drain holes taped, the mixture was then saturated and allowed to sit for 24 hours. After 24 hours the tape on the drain holes was removed and the trays were allowed to freely drain for 24 hours. Each tray was then massed to determine the amount of water held. Cation Exchange capacity was measured using a unbuffered salt procedure with five washes of 0.2M ammonium chloride as the saturating solution, three washes with deionized water as the rinsing solution, and five washes with 0.2M potassium nitrate as the displacing solution (Sumner and Miller, 1996). Samples were centrifuged between each wash and the supernatant was analyzed colorimetrically for NH_4^+ using a QuickChem 8500 (Lachat Instruments, Loveland, CO). Olsen P was determined by shaking 1g of soil with 20ml of pH 8.5 0.5M NaHCO_3 for 30 minutes, filtering with a Whatman No. 42 filter paper and analyzing with ICP-AES (Sims, 2000).

Pot Study

This was also carried out in a temperature-controlled glasshouse (20-26°C). The experimental design used was a double factorial randomized block design with 4 replications. Five biochar rates (0, 0.5, 1, 2.5, and 5%), two N- fertilizer rates (0, 135kg ha^{-1}), and the same two soils as in the germination study (Sandy loam, Silt loam) were used, giving a sample population of 80. The biochar application rates were calculated on a percent weight basis and are equivalent to 0, 11.2, 22.4, 56 and 112 Mg biochar ha^{-1}

based on a 15 cm depth of incorporation. Soils were amended with biochar and urea using a rotating soil mixer. For each rate, 9 kg were poured into 25.4 cm pots. Four pots were filled with 9 kg of the sandy loam and another four with the silt loam, before being watered to the point of saturation and allowed to freely drain for 24 hours. Each replicate was massed after equilibrium was achieved and the dry mass of the pot and soil was subtracted to determine the water holding capacity. Then, all the 80 treatment pots for the pepper trials were slowly wetted up to 80% WHC over 48 hrs. Two hundred California Wonder bell pepper plants (*capsicum annum* L) had been grown from Burpee seed in individual 5 × 5 × 5 cm plastic pots filled with germination mix. Of these 200, 80 were selected based on uniform height and healthy appearance and were planted randomly, one plant in each pot. Over the following 166 days, pots were watered to 80% WHC as needed based on weight and their position was re-randomized every week to equalize any variability in heat and ventilation.

Plant and Soil Analysis for the Pot Study

Peppers were harvested at maturity (full red coloration) and weighed fresh. At the end of the study (194 days after the peppers germinated) all the peppers were harvested. After harvesting, BD cores were taken using a 6.35cm diameter segmented copper pipe from a depth of 2-8cm. The pipe was sunk into the soil, removed, and then the segments were separated with a knife. Cores were oven dried at 105°C and massed. The BD of the biochar was determined by allowing a known mass of biochar to settle for 24 hours in a bucket and then massing the amount of water it took to displace the biochar. The remaining soil from each pot was mixed thoroughly and then a representative sample was

air-dried at 25°C and crushed gently to pass through a 2-mm sieve. The <2-mm samples were then analyzed for pH, SS, Mehlich 1 plant available nutrients, CEC and Olsen P in the same way as the germination soils, as described above.

Statistical Analysis

Data were interpreted using the SAS 9.2 statistical software of the SAS Institute (2007). Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on graphs are standard errors.

Results and Discussion

Biochar Analysis

The biochar was composed of $56.8 \pm 0.1\%$ ash, $27 \pm 1\%$ C, and $2.26 \pm 0.01\%$ N with a C:N of 12.3 ± 0.3 . Poultry litter biochar had a lower carbon content and a higher nitrogen and ash content than biochars produced from wood or green waste, which can have C:N ratios of 65 and 400 respectively (Lehmann et al., 2003; Chan et al., 2007). Lehmann et al. (2003) found the carbon content of biochar made from wood to be 70.8%. The pH was 9.32 ± 0.01 which is typical of biochar made from poultry litter (Chan et al., 2008). The biochar contained $43.0 \pm 0.5 \text{ g kg}^{-1}$ total P, $70. \pm 3 \text{ g kg}^{-1}$ of total K, and $73 \pm 2 \text{ g kg}^{-1}$ of total Ca. These values were similar to those measured by Kim et al. (2009), who reported total P of 31.1 g kg^{-1} , total K of 47.1 g kg^{-1} and total Ca 55.0 g kg^{-1} in poultry litter biochar. The WSP was $13.0 \pm 0.3 \text{ mg kg}^{-1}$, only a tiny fraction of the total P. Biochars made from lignocellulosic biomass have much lower N and P concentrations. For example, Kim et al.

(2009) reported that biochar made from a mixture and hard and soft wood shavings had concentrations of 9.1 mg kg^{-1} P and less than 0.5% N. The high P, K, Ca, and pH values of the biochar suggests that it may have to be applied based on the nutrient demands of the cropping system and the magnitude of the soil nutrient concentrations, depending on the availability of these nutrients in the biochar.

Lettuce Germination

Biochar improved the germination of lettuce seeds in the sandy loam at the 0.2, 0.5, and 1% rates, relative to the control, before the germination dropped off at 5% and above (Fig. 1). Biochar did not significantly increase the germination of lettuce in the silt loam, but like the sandy loam, germination dropped off dramatically at 5% biochar and above. It was observed that the fine biochar particles coated the lettuce seeds, especially in the coarse textured sandy loam which obviously did not have as many fine particles as the silt loam. We suspect that this may have held water close to the lettuce seed, which led to the increase in germination at low biochar rates in the Sandy loam.

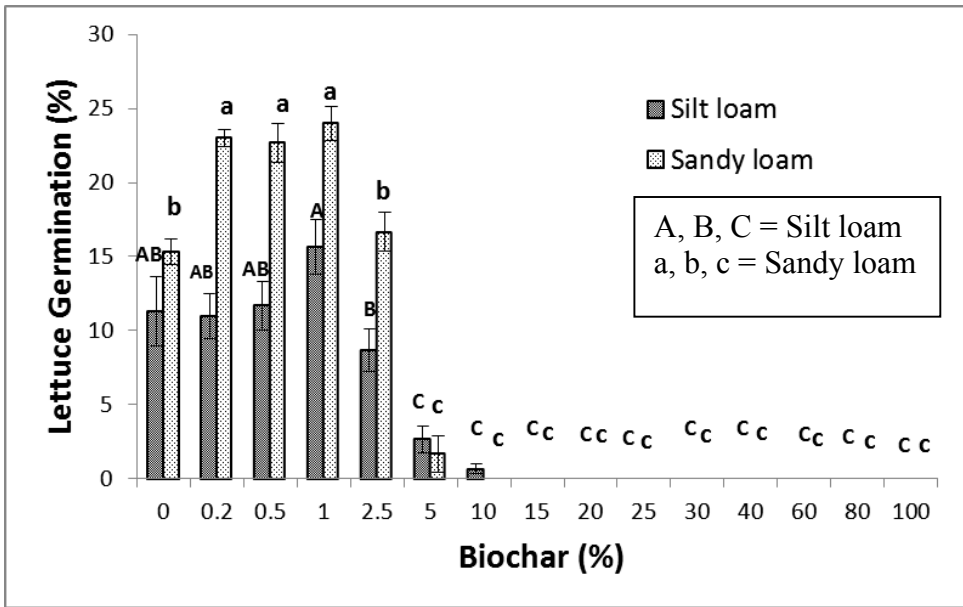


Figure 2.1. Percentage of lettuce seeds germinating in the sandy loam and the silt loam across a range of poultry litter biochar application rates. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

High levels of soluble salts were likely responsible for the reduction in germination at 5% biochar and above. Inorganic salts in poultry and swine litter have been shown to limit lettuce seed germination (Gupta and Doherty, 1990; Tam and Tiquia, 1994). Soluble salts increased linearly with biochar application in both the germination study and the pepper study as shown in Figs. 2a and 2b. Damage to lettuce occurs at 0.65 dS m⁻¹ (Havlin et al., 2005, p. 85-87) and this agrees with the observed decrease in germination above 2.5% when the SS were 0.96±0.06 dS m⁻¹ in the sandy loam and 1.26±0.13 dS m⁻¹ in the silt loam (Fig. 2a). Salts could easily be removed from the poultry litter biochar by washing with water, as shown by the 80% reduction in SS as seen in the washed biochar relative to the unwashed 100% biochar (Fig. 2a). Figure 2b

shows the SS for the pepper study and the values were similar to those in the lettuce study, showing that our zero leaching watering system for the peppers did not affect SS (Fig. 2a). If there is enough precipitation to leach the salts from soils in humid regions, repeated application of biochar could be made without inducing salt stress.

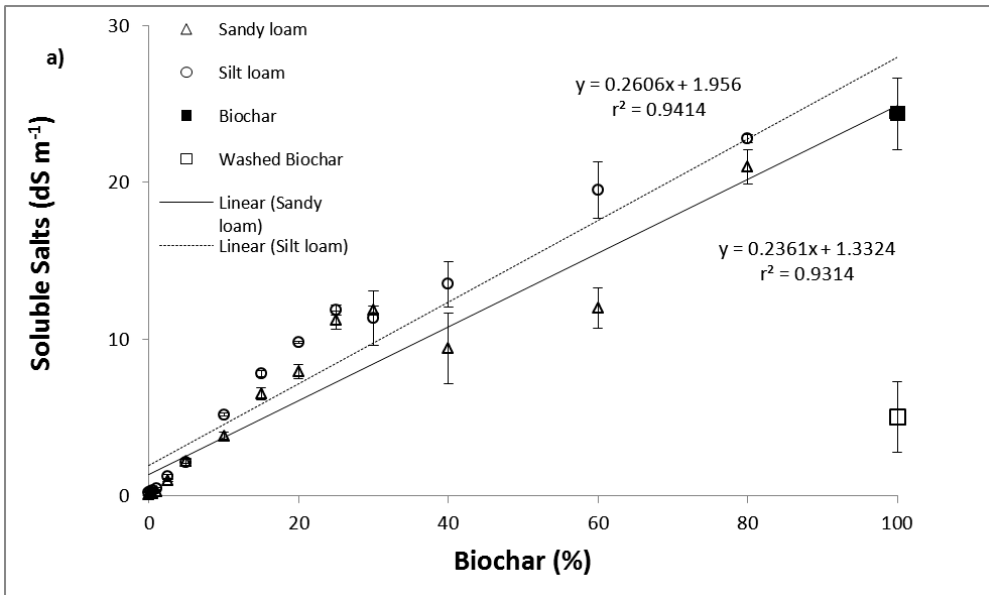


Figure 2.2a Linear regression for the soluble salts in the sandy loam and the silt loam across a range of poultry litter biochar application rates following the lettuce germination. Error bars on the graphs are standard errors.

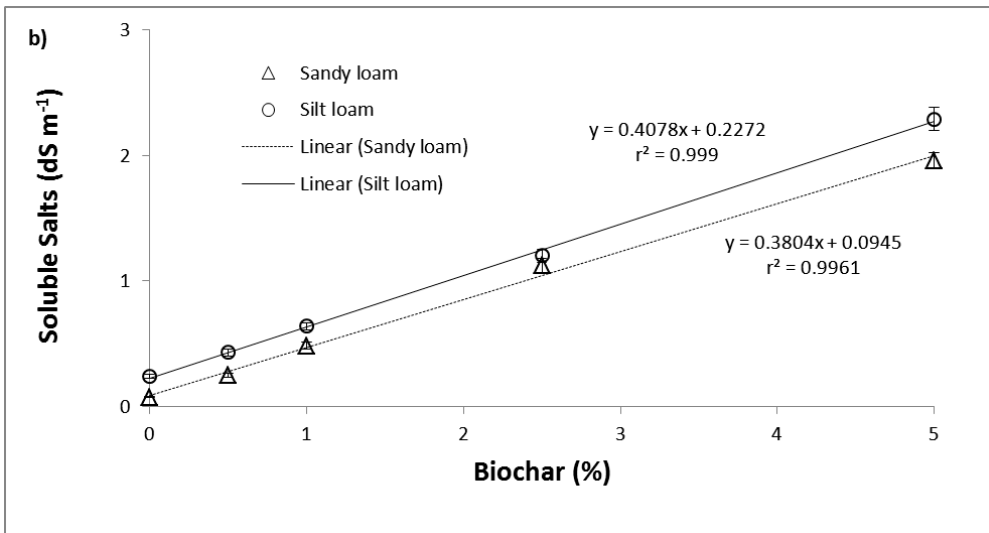


Figure 2.2b Linear regression for the soluble salts in the sandy loam and the silt loam across a range of poultry litter biochar application rates following the greenhouse pepper study. Error bars on the graphs are standard errors.

Soil Physical Properties

The BD of the poultry litter biochar was $0.63 \pm 0.02 \text{ g cm}^{-3}$ relative to a BD of $1.30 \pm 0.02 \text{ g cm}^{-3}$ for the silt loam and $1.63 \pm 0.02 \text{ g cm}^{-3}$ for the sandy loam. Lowering the BD of agricultural soils is good for crop production because it correlates to an increase in pore space (Schjønning et al., 2011). Bulk density was not affected by biochar application in the silt loam, but BD was significantly decreased in the sandy loam (Fig. 3). For example, adding 5% biochar to the Sandy loam decreased BD from 1.63 g cm^{-3} to 1.50 g cm^{-3} . This was likely due to the higher BD of the Sandy loam, and the relatively low biochar application rates. Laird et al. (2010) also found that biochar additions decreased bulk density. Most organic fertilizers, such as manures and compost, decrease BD (Herencia et al., 2011).

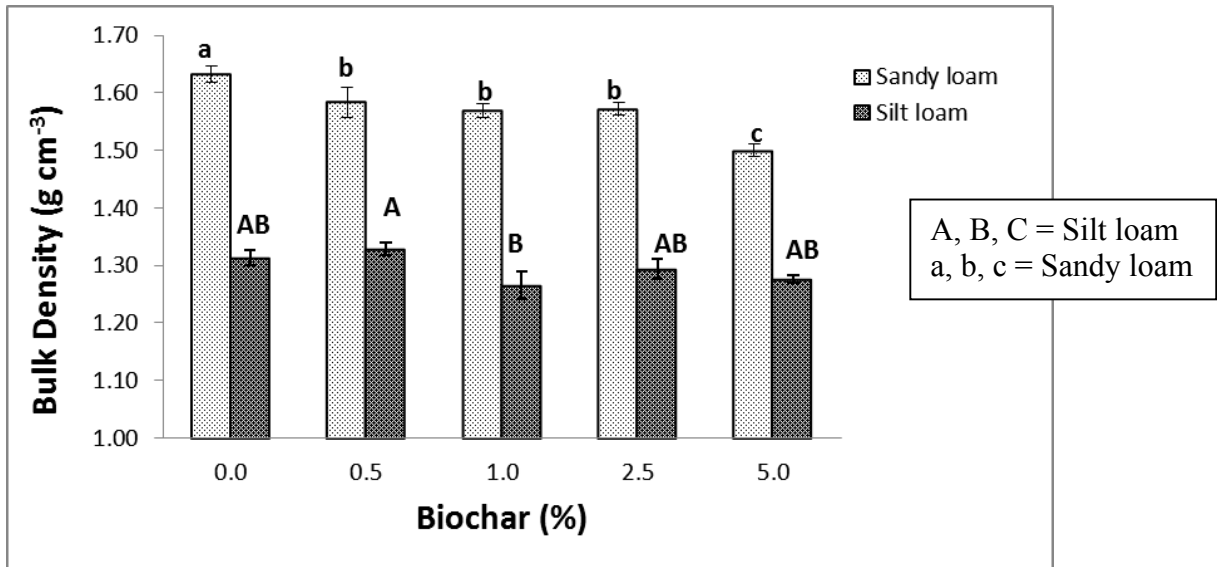


Figure 2.3. Bulk density of the sandy loam and the silt loam amended with poultry litter biochar following the greenhouse pepper study. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

Water holding capacity increased linearly with the addition of biochar to both soils used in the germination study, with the sandy loam having a lower starting value of 15% than the silt loam which had a WHC of 40%. This would be expected, as fine textured soils are known to have greater WHC than coarse textured soils (Feiziene et al., 2011). The sandy loam also had a steeper response slope than the silt loam, indicating that biochar had a greater impact of increasing the WHC in the sandy loam than in the silt loam (Fig. 4). The ability of biochar to increase the WHC of soils is one of the major benefits reported in the literature, as lack of water is a major reason for decreased crop production in many situations. Brockhoff et al. (2010) showed that 25% biochar by volume increased WHC of pure sand by as much as 370%. Kammann et al. (2011) added biochar at the rate up to 100 Mg ha⁻¹ to sandy soils and found that drought tolerance and water use efficiency improved in *Chenopodium quinoa* relative to an untreated control. Therefore, the ability of biochar to increase the WHC of soils is a great potential benefit given that most years have some times when soil moisture is limited to non-irrigated crops (Havlin et al., 2005, p. 418). The fact that biochar increased the WHC more in the sandy loam, suggests the use of biochar could be targeted to soils with a low ability to retain moisture, where the greatest response would be seen.

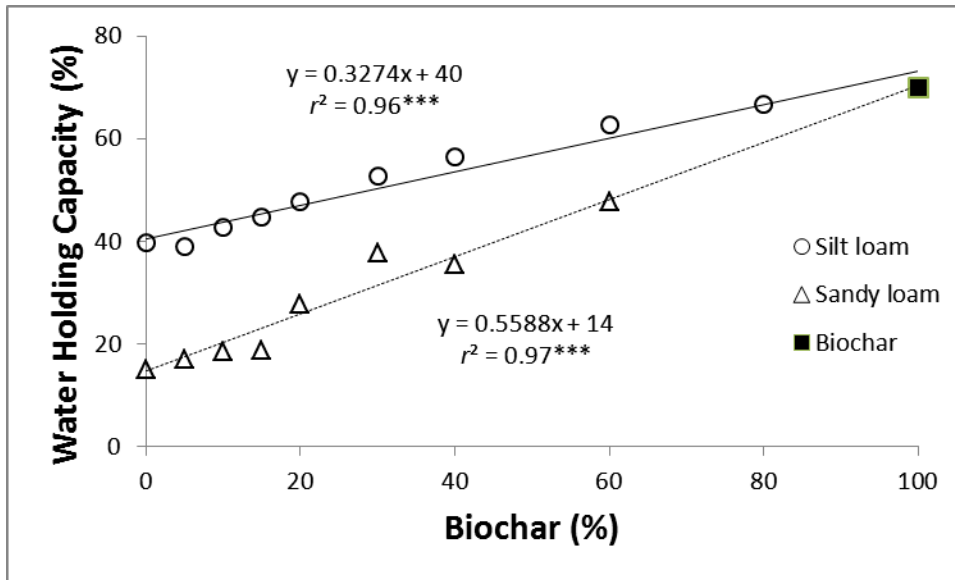


Figure 2.4. Linear regressions for the water holding capacity of the sandy loam and the silt loam across a range of poultry litter biochar application rates following lettuce germination. Error bars on the graph are standard errors.

Cation Exchange Capacity

The effect of biochar application on the CEC was soil and rate dependent in the germination soils (Fig. 5). The sandy loam exhibited a trend with a positive slope above the 5% application rate whereas the silt loam showed a negative slope with biochar application from 0 to 15% biochar application followed by a steady increases in CEC after that. Cation exchange capacity is very important to plant nutrient availability and retention in soil (Havlin et al., 2005, p. 15-24) and therefore the possibility of increased CEC due to biochar additions is an important characteristic of biochar. Both soils developed statistically similar CECs at the application rate of 20% and above. The reason for the initial negative slope in the silt loam is unclear, as pure biochar showed a higher CEC than either of the soils. The pepper study had a longer incubation period than the

germination study (166 days vs. 14 days), but the CEC was statistically similar for both studies (data not shown). There are no other studies in the literature that directly measured CEC in soils amended with poultry litter biochar. However for biochar made from wood, Cheng et al. (2008) found that freshly produced biochar had little effect on CEC, but the CEC can be increased as biochar gets oxidized and develops carboxyl functional groups. For example, over four months the CEC in biochar amended soils increased from 2.8 ± 0.14 to 8.78 ± 0.4 cmolc kg^{-1} (Cheng et al., 2008).

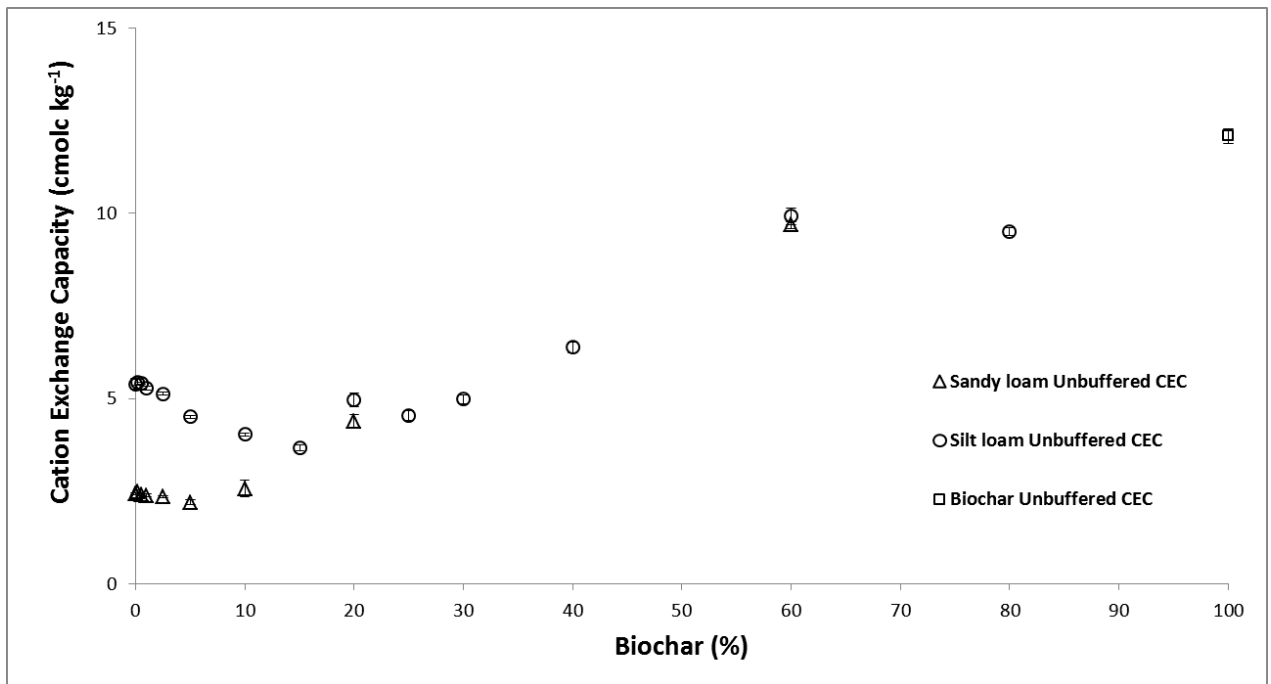


Figure 2.5. Cation exchange capacity in the sandy loam and the silt loam across a range of poultry litter biochar application rates following lettuce germination. Error bars on the graph are standard errors.

Soil pH

The sandy loam had an initial pH of 7.10 ± 0.02 and the silt loam had a pH of 7.14 ± 0.03 . Biochar increased the pH in both germination soils and biochar application had a larger effect on the sandy loam below application rates of 30%, probably due to its lower CEC and therefore pH buffering capacity (Fig. 6a; Havlin et al., 2005 p. 27-29). Both soils had identical pH at 40% biochar and above as the biochar dominated and the pH reached a maximum of 9.20 ± 0.04 at 100% biochar. The soils from the pepper study exhibited a similar trend as the germination study, with biochar increasing the pH more rapidly in the sandy loam (Fig. 6b). The silt loam in the pepper study had a starting pH of 7.28 ± 0.02 and there was no effect on the pH of the silt loam for the rates of 0.5 and 1%, but it began to rise at 2.5% to 7.59 ± 0.03 and reached a maximum at 5% of 7.75 ± 0.03 . Urea applications can be acidifying to soils, due to release of hydrogen ions during nitrification (Havlin et al., 2005; p. 124-127). However, no significant effect on the pH could be seen due to urea-N application in the silt loam. The pH in the sandy loam from the pepper study consistently climbed higher with the addition of biochar and reached a maximum at 5% of 8.23 ± 0.03 . As the sandy loam had a lower CEC, the acidifying effect of urea could be seen, with the pH dropping by 0.18 on average when urea was applied. The ability of poultry litter biochar to increase the pH of soils is an agronomic benefit to most farming systems, as crop production, leaching of cations and acidification from fertilization often lead to the need for liming to maintain soils in agronomic pH ranges.

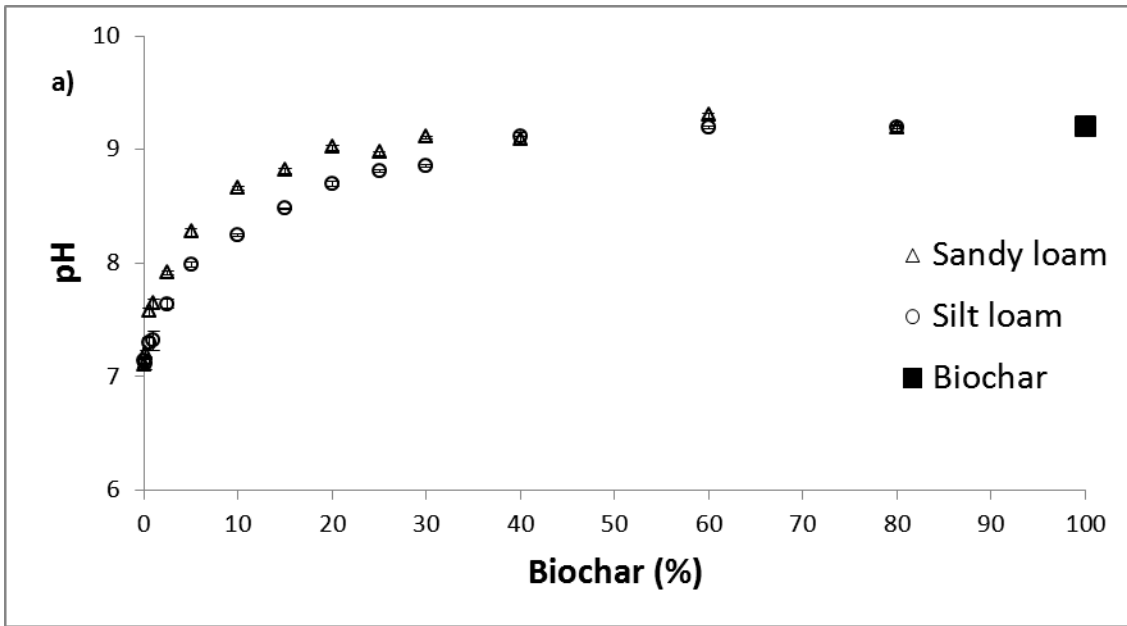


Figure 2.6a. The pH of the sandy loam and the silt loam across a range of poultry litter biochar application rates following the lettuce germination. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

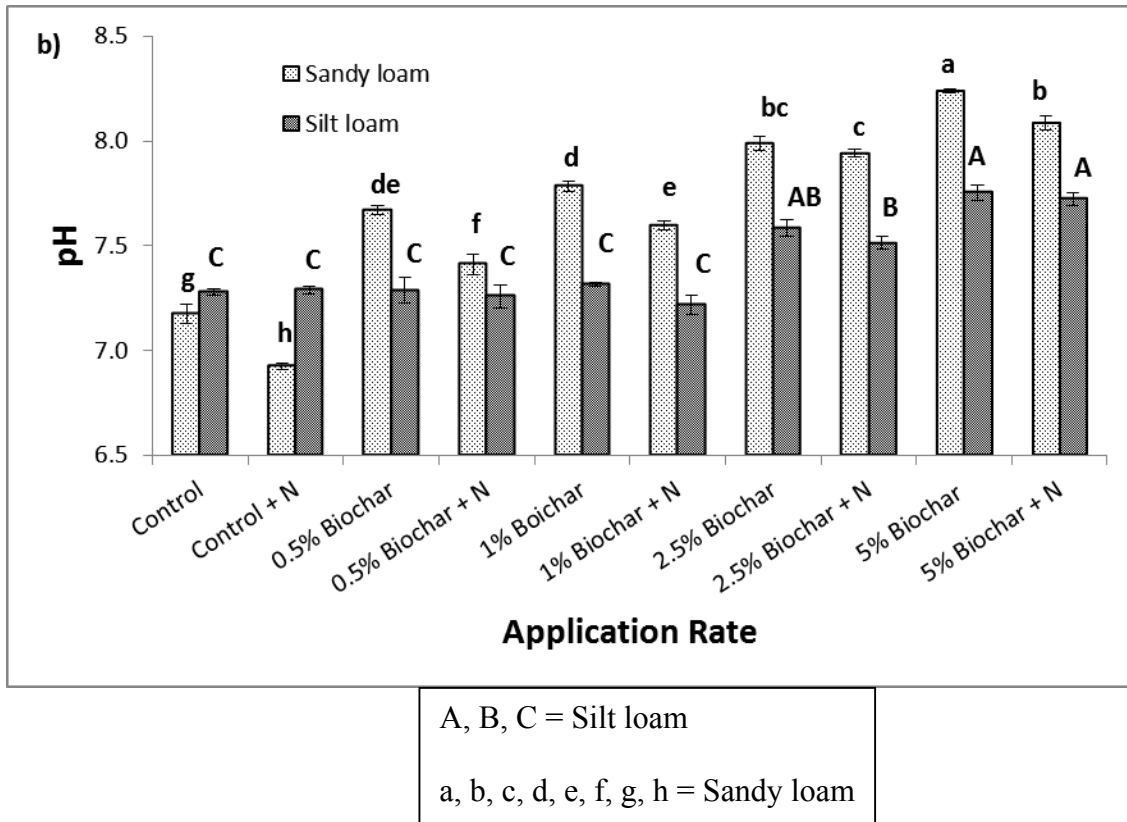


Figure 2.6b. The pH of the sandy loam and the silt loam across a range of poultry litter biochar application rates following the greenhouse pepper study. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

Plant Available Phosphorus

It is well known that P in poultry litter is largely plant available (Maguire et al., 2006), however the availability in P in poultry litter biochar has not been studied. Both Olsen and M1P increased with biochar application rate and a maximum was reached at the highest application rate of 5% in the pepper study (Fig. 7a). In the sandy loam, the M1 P increased from $24 \pm 1 \text{ mg kg}^{-1}$ in the control to $1600 \pm 70 \text{ mg kg}^{-1}$ at the 5% biochar rate and from $260 \pm 4 \text{ mg kg}^{-1}$ to $1480 \pm 17 \text{ mg kg}^{-1}$ in the silt loam. In the sandy loam, the

Olsen P increased from $19 \pm 1 \text{ mg kg}^{-1}$ in the control to $455 \pm 9 \text{ mg kg}^{-1}$ at the 5% rate and from $143 \pm 2 \text{ mg kg}^{-1}$ to $440 \pm 7 \text{ mg kg}^{-1}$ in the silt loam. These greater increases in M1P and Olsen P in the sandy loam would be expected as sandy soils generally have less Fe and Al than finer textured soils such as the silt loam. As Fe and Al hydroxides strongly retain P, the silt loam had a higher ability to retain added P which resulted in less of a change in extractable P (Maguire and Sims, 2002). Maguire et al. (2007) showed the concentration of manure production in specific counties across the US, which is of environmental concern as over-application of manures such as poultry litter in these areas has increased soil test P and associated risks of P loss to surface waters. Our results clearly show that although only a small proportion of total P in the biochar was soluble, as discussed earlier, biochar made from poultry litter will also increase soil test P.

Poultry litter also contains substantial Ca (Maguire et al., 2006), so it was suspected that P reacted with the Ca during pyrolysis to form calcium phosphate. This would explain why M1P increased more rapidly than the Olsen P, as Olsen is an alkali extract (NaHCO_3) that would not dissolve calcium phosphate in the biochar as much as the acidic Mehlich 1 extract. Supporting evidence for this is seen in Fig. 7b which shows the M1P and Olsen P for the complete application range examined in the germination soils. The M1P rises rapidly at low biochar application rates and reaches a maximum at 15% biochar before decreasing. The drop in the M1P is likely due to the influence of the high pH of the biochar neutralizing the acidic Mehlich 1 extract. The alkaline Olsen solution (pH 8.5; Havlin et al., 2005; p. 340-341) extracted more P with increasing application rate across the whole biochar application range. The agronomic optimum M1P for most row crops in Virginia is 55 mg kg^{-1} (Maguire and Heckendorn, 2011b).

Therefore poultry litter biochar has increased M1P well above crop needs, which is not surprising due to the application rate of approximately 4.82 Mg P ha⁻¹ with the addition of 5% biochar, assuming 2240 Mg soil ha⁻¹ in the furrow slice. The agronomic optimum for Olsen P is approximately 20 mg kg⁻¹ (Havlin et al., 2005, p. 341-342) and biochar should be applied based on M1P or Olsen P to avoid surpassing the agronomic optimum.

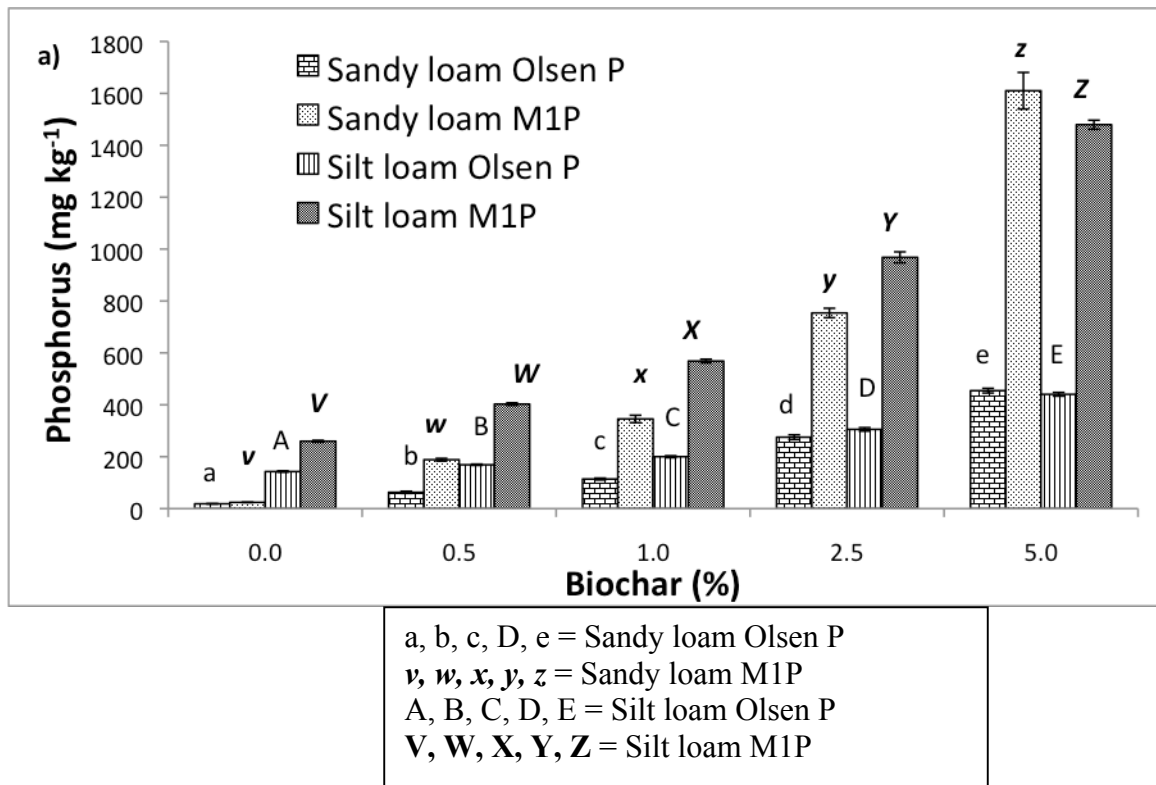


Figure 2.7a. Mehlich 1 and Olsen extractable P from the sandy loam and the silt loam following the greenhouse pepper study. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

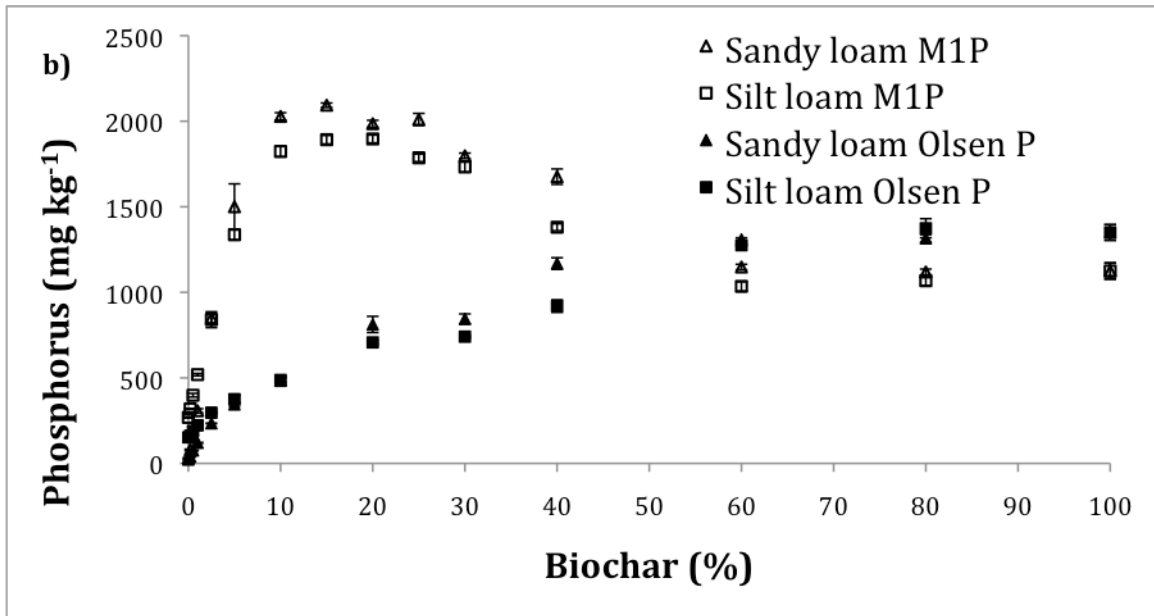


Figure 2.7b. Mehlich 1 and Olsen extractable P from the sandy loam and the silt loam following the lettuce germination. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

Effect of Biochar Applications on Pepper Yields

The silt loam produced higher fresh yields than the sandy loam for all application rates as would be expected given that it has a soil productivity rating of 2 versus the sandy loam which has a productivity rating of 3 (Fig. 8; DCR, 2005). Comparing the 0 % biochar (control) and to biochar additions up to 2.5%, the addition of biochar had no significant impact on pepper yield in either soil. However, N often increased yield in both soils at biochar application rates of 2.5% and below, especially in the sandy loam. This shows the importance of adding N with biochar, as biochar is not rich in N as much of the N in the feed material is lost during pyrolysis (Agblevor et al., 2010). In some cases the fresh yield of green peppers was reduced for both soils at the 2.5% rate of application,

relative to some lower biochar rates, and decreased further at 5% application. This is likely due a combination of high SS and pH (Mikan and Abrams, 1995). The threshold SS level for bell peppers is 0.75 dS m^{-1} and the optimal pH range is 5.5-6.5 (Havlin et al., 2005, p. 66). The SS and pH at the 2.5% application rate were $1.13 \pm 0.06 \text{ dS m}^{-1}$ and 7.99 ± 0.03 in the sandy loam and $1.20 \pm 0.05 \text{ dS m}^{-1}$ and 7.59 ± 0.04 in the silt loam so a reduction in yield is expected for the higher rates of application (Havlin et. al., 2005, p. 87).

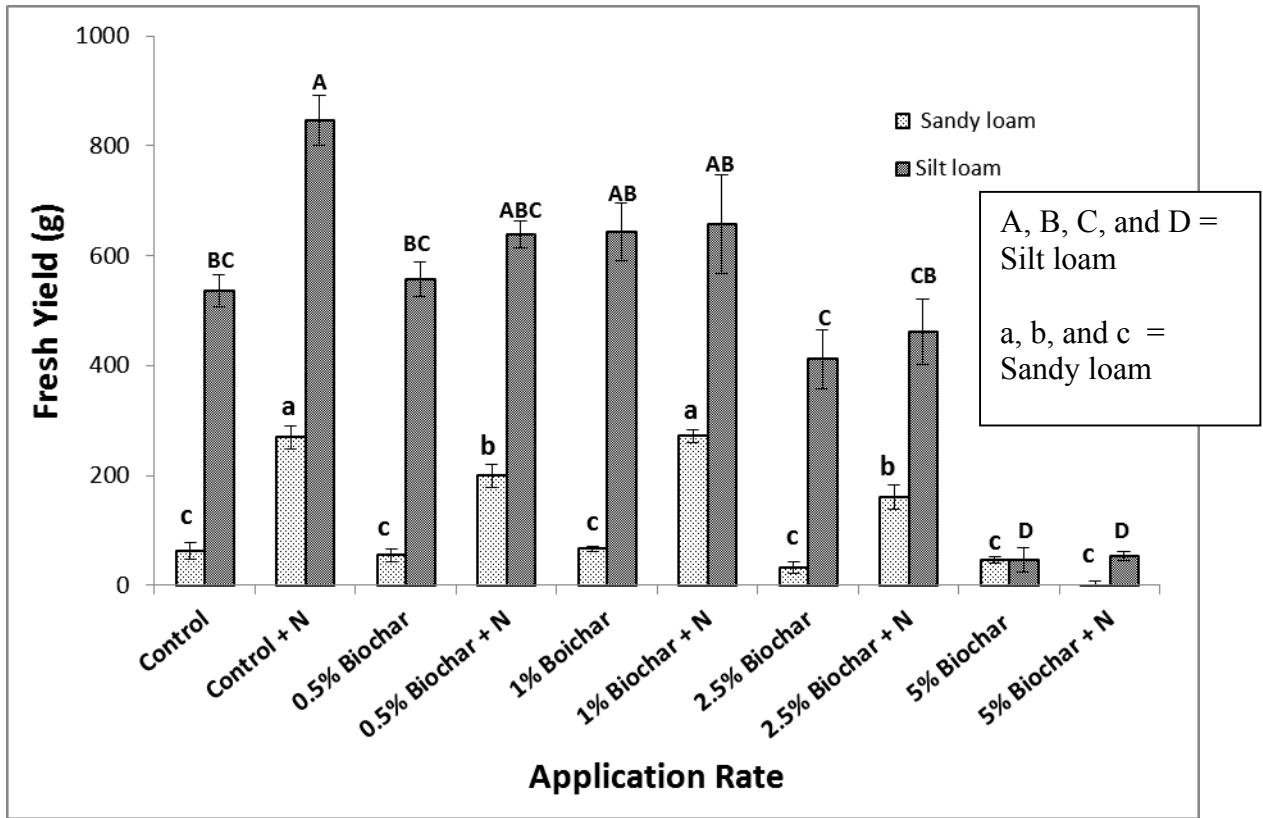


Figure 2.8. Pepper yields from soils amended with poultry litter biochar with and without supplemental nitrogen. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

Conclusions

Biochar made from poultry litter had many beneficial effects on soil properties, including increasing the WHC, CEC, bulk density and nutrient status. Biochar made from poultry litter contains most primary nutrients needed for plants and is much lighter and therefore easier to transport than the raw litter. The C in the biochar should also be much longer living in soils than the organic C in the original poultry litter. However, as biochar significantly increased SS, pH and extractable P, these factors should be taken into

account when determining an appropriate rate of application. Many poultry operations are regulated based on concerns over N and P losses to surface waters following land application of poultry litter, and although N is lost during pyrolysis, the P is maintained in the biochar and is largely plant available. Therefore, poultry litter biochar may need to be moved away from areas of intensive poultry production, but the 60% reduction in mass will facilitate cheaper transport. Since the biochar improved some properties such as the WHC of the sandy loam more than that of the silt loam, biochar applications may have more of a beneficial effect on poor quality soils.

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Chapter 3: Field trials with poultry litter biochar and its effect on forages, green peppers, and soil properties

Abstract

Pyrolysis offers a way to convert poultry litter into a value added organic soil amendment. This study was conducted to evaluate the effects of biochar made from poultry litter on soil chemical properties and plant production. The rates of 0, 4.5, and 9 Mg ha⁻¹ were used at all field sites and the rates were applied once a year in the early spring of 2009 and 2010. Biochar was surface applied on a tall fescue pasture [*Lolium arundinaceum* (Schreb.) Darbysh. (= *Festuca arundinacea* Schreb. subsp. *arundinacea*)] in the Shenandoah Valley and tilled in on two green pepper (*Capsicum annuum* L) field sites in southwestern Virginia. The biochar had a C content of 25±1% and application increased soil carbon by 0.51% after two years of application of 9 Mg ha⁻¹ at the forage site where it was surface applied and by an average of 0.38% at the two green pepper sites where it was tilled in. The biochar had a pH of 9.57±0.01 and increased the pH where it was applied each year. Changes in soil cation exchange capacity (CEC) showed no clear trends. The Mehlich 1 P was increased by 57 mg kg⁻¹ for each Mg ha⁻¹ of biochar at the forage site and by an average of 39 mg kg⁻¹ for each Mg ha⁻¹ of biochar applied at the green pepper sites. Soluble salts were numerically increased in the first year of application, but had been reduced at all sites by leaching when sampled in the early spring of 2011. No significant differences were found in yields at any of the three sites, but differences in forage quality were found at the tall fescue site, probably because biochar increased the rate at which the forage matured.

Introduction

The majority of poultry litter is disposed of through land application and many regions with intensive poultry production have more P in manure than local crops require (Maguire et al., 2007). Due to nutrient management regulations, this often means that much of the poultry litter has to be transported off the farm. Pyrolysis is the thermal decomposition of biomass in an oxygen depleted environment, and can reduce the mass of manure by 60% (Kim et al., 2009). Pyrolysis not only offers a way to reduce the cost of transport, but also may produce a value-added product as manure biochars contain higher concentrations of P and K than the original feedstocks (Ro et. al., 2010). Biochar made from poultry litter has been shown to have positive effects on soil chemical and physical properties including increased pH, soil nutrients, water holding capacity, and decreased bulk density (see Chapter 2) as well as positive effects on plant growth and yield (Chan et al., 2007). Chan et al. (2007) found that radish yield increased by 42% with the application of 10 Mg ha⁻¹ of biochar made from poultry litter, but significant reductions in yield have been found as well. Deenik et al. (2010) found that yields of both corn and lettuce were significantly reduced with the application of biochar made from macadamia nut (*Macadamia integrifolia* Maiden and Betche) shells. The reduction in yield was attributed to the high volatile matter content of the biochar and its effect on nitrogen availability.

The removal of crop residues during harvesting can lead to long term soil degradation if organic matter is not returned to the soil. Making biochar from the fast pyrolysis of poultry litter offers a way to create a nutrient rich soil amendment that also contains black carbon. Black carbon is of interest because it could offer a way to increase

the stable soil carbon pool (Lehman et al., 2003) and renewable energy can potentially be produced along with the biochar in the form of bio-oil and gas (Kim et al., 2009). There is considerable variability in the chemical and physical characteristics of biochar which both depend on the feedstock and pyrolysis conditions, making it necessary to determine the effect of biochar on a wide range of agronomic systems (Baldok and Smernik, 2002).

Biochar tends to have a high C content and small concentrations of nutrients when it is made from plant material (Lehmann et al., 2003). Wood biochar, for example, can have a C content of 70.8% (Lehmann et al., 2003) and an ash content of 0.27% (Bourke et al., 2007). These values are very different from poultry litter biochar, which can have a C content of 27% and an ash content of 56.8% (Revell et al., 2012). It is currently unknown what portion of the nutrients in biochar are available to be taken up by plants (Pritchard, 2003). Soils containing biochar have been shown in some cases to have higher CEC than adjacent soils without biochar (Lima et al., 2002). Oxidation of biochar in the soil could cause the surface charge of biochar to become more negative with time (Laing et al., 2006). Biochar made from poultry litter can also have high levels of soluble salts where as plant derived biochar has a small inorganic component. Revell et al. (2012) found that pure biochar made from poultry litter had a soluble salt concentration of 24.2 dS m⁻¹ and that the germination of lettuce was reduced at 2.5% biochar and above.

Biochar made from wood has been shown to increase the leaf area, canopy dry weight, number of nodes, and yields of buds, flowers and fruit of green pepper plants in a soilless media (Graber et al., 2010). The authors postulated two possibilities for the improved plant performance, citing increased beneficial microbial populations or chemicals in the biochar which stimulated plant growth at low doses. Elad et al. (2010)

found that the application of 1 to 5% biochar increased resistance of pepper plants to the pathogens *Botrytis cinerea* (gray mold) and *Leveillula taurica* (powdery mildew) as well as the broad mite pest (*Polyphagotarsonemus latus* Banks).

For biochar made by the fast pyrolysis of poultry litter to be adopted as a successful way to improve soil fertility, it is necessary to determine its effects on soil properties and crop production. This research was undertaken to examine the effects of biochar made by fast pyrolysis on soil chemical properties and green pepper production.

Materials and Methods

Biochar Production and Analysis

The biochar was made by the fast pyrolysis of broiler litter with a pine shaving base at a pyrolysis temperature of 450°C using a fluidized bed reactor (Mante and Agblevor, 2010). The following analysis of biochar was conducted in triplicate. The total carbon (C), total nitrogen (N), and C:N were determined by dry combustion using a Vario Max CNS macro elemental analyzer (Elementar, Hanau, Germany). The pH of the biochar was measured in 1M KCl at a soil:solution ratio of 1:1 (Thomas, 1996). Soluble salts were determined in a 1:2 soil to water ratio (Maguire and Heckendorn, 2011a). Elemental concentrations of P, K, and Ca were determined in duplicate by ashing 5g of biochar in a muffle furnace at 550°C for 24 hours and then digesting 0.8g of the ash in 10 mL of 1M HCl. Samples were then diluted to 100 mL and elemental concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Wolf et al., 2003).

Field Sites

One on-farm field trial was established in the Shenandoah Valley on a predominantly tall fescue pasture, and two were established on organic farms in southwestern Virginia with a focus on green pepper production. All three soils were Frederick silt loams (Typic Hapludults) and all three field trails were established in spring 2009. There were three treatments (0, 4.5, and 9 Mg ha⁻¹) which were each replicated four times to give a total of 12 plots per site. Biochar applications were made in the spring of 2009 and 2010. The forage study (F1) ended in the fall of 2010 and the two pepper studies (P1 and P2) ended in the early spring of 2011. “Year 1” will be used to identify the time period from spring 2009 to spring 2010 and “Year 2” will be used for spring 2010 to spring 2011. The plots for the forage study (F1) were 3.05m by 6.10 m while the pepper plots on the two organic farms (P1 and P2) had a plot size of 3.66m by 4.57m to accommodate three rows of peppers. All treatments were assigned by randomized complete block design. Biochar was surface applied by hand at field site F1 with no incorporation into the soil whereas biochar treatments were hand applied then tilled into the soil at field sites P1 and P2. The soil at P1 and P2 was then mounded into three beds with 1.22m between the center of each bed and soaker hose irrigation was installed. A staggered double row of green pepper plants was planted in each bed at field sites P1 and P2 with 30 cm between the rows and 40 cm between each plant in a row. This gave a total of 16 plants per bed or 48 plants per plot. Plastic was laid over the beds for weed control at P1, while straw mulch was applied to the beds at P2 for weed control.

Plant and Soil Sampling and Analysis

Forage yields were determined at field site F1 by using a walk behind flail harvester (Swift Machine and Welding Ltd., Saskatchewan, Canada) with a swath width was 0.76 m and a cutting height of 7.5 cm. The harvest was taken from the middle of the plot after the edges had been mowed and the harvest area was determined by measuring in field swath length and multiplying by width. Forage plots were harvested three times a year with an average of 65 day intervals. Samples were weighed and then sub-sampled to determine moisture content (McGrath et al., 2010). Subsamples were dried at 65°C until they reached a stable weight and then ground to pass a 1.0 mm sieve. An XDS near infrared rapid content analyzer (NIR) (Foss, Hoganas, Sweden) was used to determine the acid detergent fiber (ADF), neutral detergent fiber (NDF), non-structural carbohydrates (NSC), and simple sugars.

For sites P1 and P2, pepper yield was determined by harvesting the marketable peppers from a 3 m swath of the center bed of each plot. The plots were harvested three times in both year 1 and year 2.

Soil samples were taken to a depth of 10cm each fall after the last harvest of the season at site F1. Soil samples were taken to a depth of 10 cm from the center beds at sites P1 and P2 in the fall of 2009 and then again in early spring of 2011. Sampling was delayed in 2010 at sites P1 and P2 to see what the soil SS values were after a winter of leaching was allowed. The plastic at site P1 was removed in the fall of 2010 to allow the salts to be leached by precipitation over the winter. Samples were air dried and ground to pass a 2-mm sieve. The pH was measured at a 1:1 soil:solution ratio with deionized

water and SS were determined in a 1:2 soil to water ratio (Maguire and Heckendorn, 2011a). Mehlich 1 P was determined by placing five grams of soil into a 60-ml straight-walled plastic extracting beaker, and 20 ml of the Mehlich 1 extracting solution was added with an automatic pipetting machine (Maguire and Heckendorn, 2011a). The samples were then shaken on a reciprocating shaker with a stroke length of 3.8 cm for 5 minutes at 180 oscillations per minute and filtered through Whatman No. 2 11-cm filter paper soon after the shaking stopped (Maguire and Heckendorn, 2011a). Melich 1 P was then determined by analyzing with inductively coupled plasma atomic emission spectrometer (Maguire and Heckendorn, 2011a). The total soil carbon (C) was determined by dry combustion using a Vario Max CNS macro elemental analyzer (Elementar, Hanau, Germany). Cation Exchange capacity was measured using an unbuffered salt procedure with five washes of ammonium chloride as the saturating solution, three washes with deionized water as the rinsing solution, and five washes with potassium nitrate as the displacing solution (Sumner and Miller, 1996). Samples were centrifuged between each wash and the supernatant was analyzed colorimetrically for NH_4^+ using a QuickChem 8500 (Lachat Instruments, Loveland, CO).

Statistical Analysis

Data were interpreted using SAS version 9.2 statistical software from the SAS Institute (2007). Means were partitioned using the Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars are expressed as standard error.

Results and Discussion

Biochar Analysis

The biochar was composed of $64\pm 1\%$ ash, $25\pm 1\%$ carbon, and $1.98\pm 0.04\%$ nitrogen with a C to N ratio (C:N) of 12.5 ± 0.3 . The biochar contained $51\pm 2\text{g kg}^{-1}$ of total P, $77\pm 4\text{g kg}^{-1}$ of total K, and $90\pm 3\text{g kg}^{-1}$ of total Ca. It was reported in Chapter 2 that poultry litter biochar had an ash content of $56.8\pm 0.1\%$ and was composed of $27\pm 1\%$ C and $2.26\pm 0.01\%$ N with a C:N of 12.3 ± 0.3 . The increase in ash found in this study was associated with a decrease in the percent C and N along with an increase in the percent P, K, and Ca. The biochar used by Revell et al. (2012) contained $43.0\pm 0.5\text{g kg}^{-1}$ of total P, $70.\pm 3\text{g kg}^{-1}$ of total K, and $73\pm 2\text{g kg}^{-1}$ of total Ca, which are similar, but slightly lower than the values found in this study. Poultry litter has a high Ca content and an alkali pH of approximately 8 (Maguire et al., 2006). Therefore it is not surprising that the poultry litter biochar in this study was also alkali, with a pH of 9.57 ± 0.01 , similar to the pH of 9.32 ± 0.01 reported by Revell et al. (2012). The differences between litter biochar properties reported by Revell et al. (2012) and in this study illustrate the variability of feedstock and biochar.

Soil Carbon

All three field sites showed significant increases in soil C after the second year of 9 Mg ha^{-1} biochar application (Figs. 1a, 1b, and 1c). Soil C was increased by 0.51% at F1, 0.39% at site P1, and 0.36% at P2 after 2 applications of 9 Mg ha^{-1} of biochar. Chan et al. (2007) found that the application of 10 Mg ha^{-1} of two different biochars made from

poultry litter increased the percent C of the soil by 0.38 and 0.32%. These values are higher than those found in this study and the difference could be because the biochars used by Chan et al. (2007) had C contents of 38 and 33% while the biochar in this study had 25% C. Organic matter is a key factor of soil fertility on both organic farms and conventional farms, as it retains water and supplies N as it decomposes (Stockdale et al., 2002). Biochar can help hold water but it may not release N. Intensive agriculture can result in long term soil degradation due to reductions in soil C (Stockdale et al., 2002) and building soil C has been shown to result in increased yields of nonlegume crops (Brock et al., 2011). One interesting observation after two years at P1 and P2 was that zones were created in the soil with higher biochar. Even though the biochar was spread evenly on the soil surface and tilled in, there were obvious black spots from 1 to 5 cm in diameter in the soil where biochar had concentrated. The reason for this self attraction of biochar into concentrated spots is not clear but it could have implications in the collection of soil for analysis.

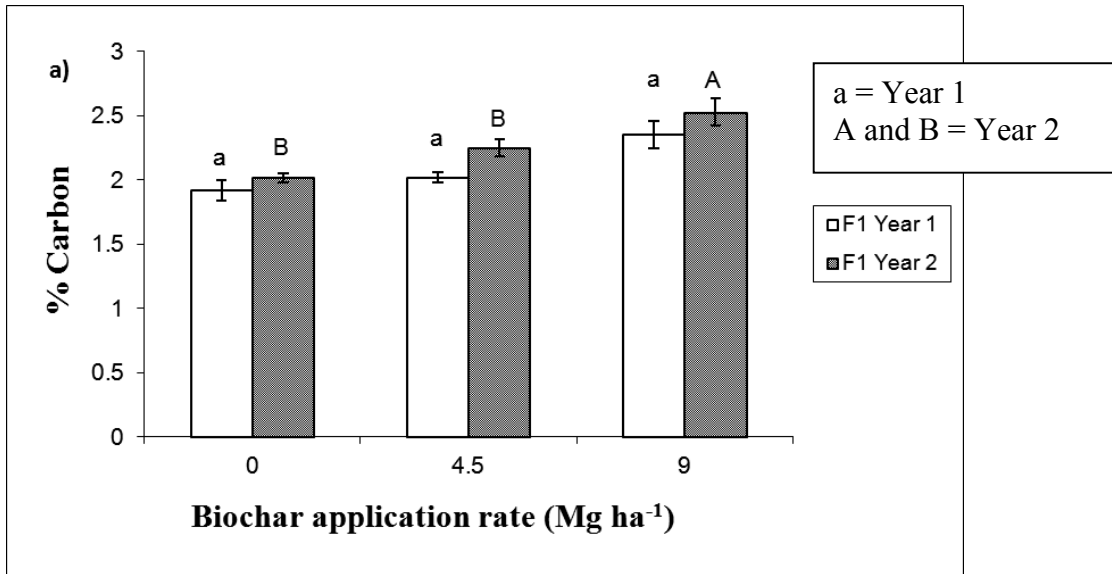


Figure 3.1a. Soil carbon at the forage site F1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors.

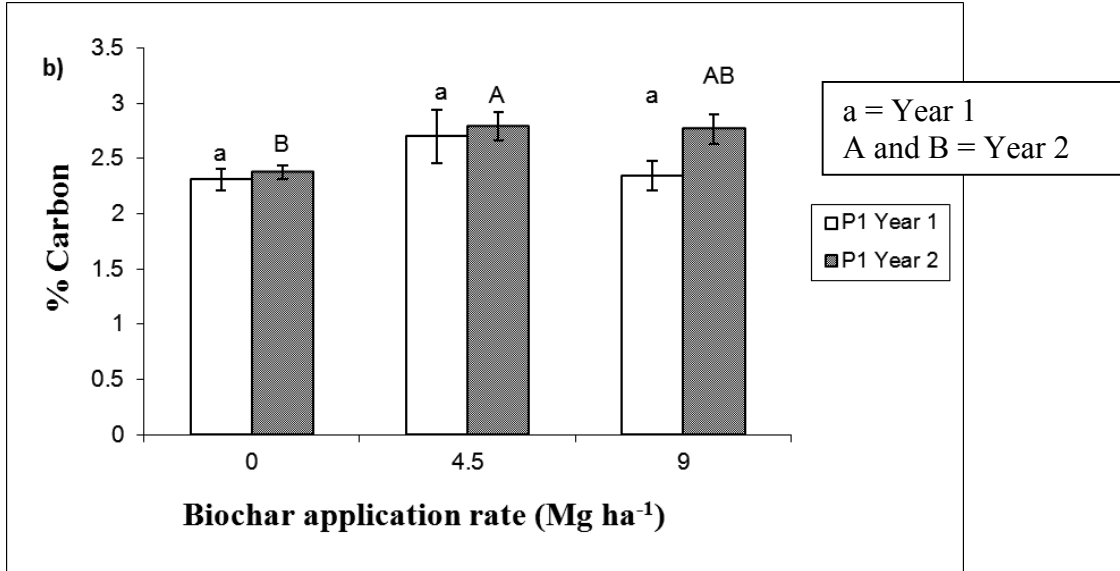


Figure 3.1b. Soil carbon at the pepper site P1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors.

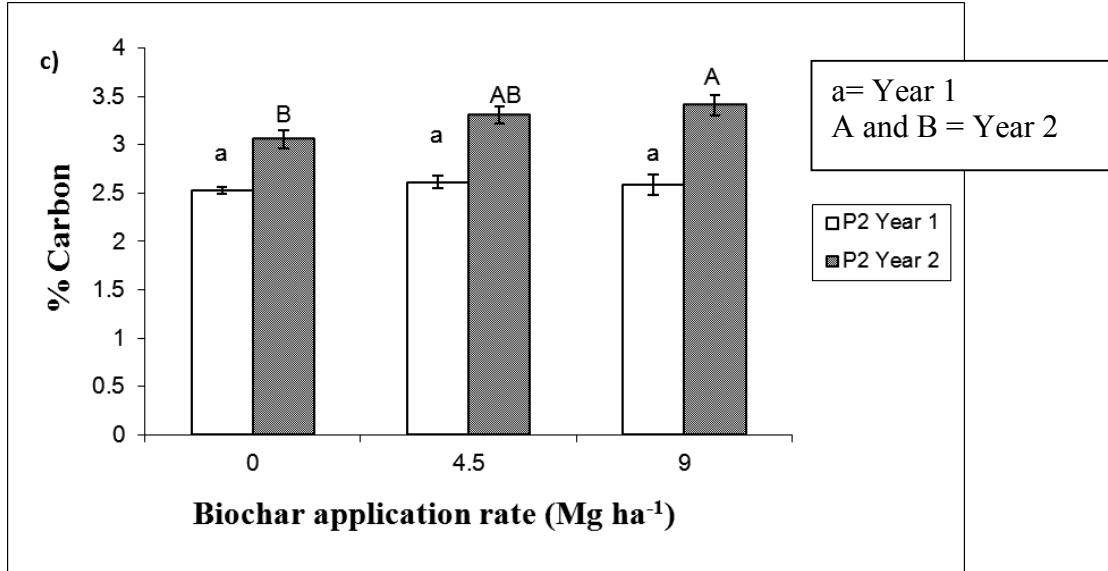


Figure 3.1c. Soil carbon at pepper site P2 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors.

Soil pH

All three field sites showed increasing pH with biochar additions (Figs. 2a, 2b, and 2c). The pH increased by 0.19 for each Mg ha⁻¹ of biochar applied at F1 and by an average of 0.15 for each Mg ha⁻¹ of biochar applied at P1 and P2. The values for the pH increase for each Mg ha⁻¹ of biochar are similar across all the field sites. The optimal pH range for tall fescue in Virginia is 6.2-6.5 (Maguire and Heckendorn, 2011b) and 5.5-6.5 for green peppers (Havlin et al., 2005, p. 66). The pH stayed in the optimal range at F1 with the applications of 4.5 Mg ha⁻¹ and 9 Mg ha⁻¹ in year 1 and 4.5 Mg ha⁻¹ in year 2, while two applications of 9 Mg ha⁻¹ raised the pH above 7. Field sites P1 and P2 both had average initial pHs of 6.33 and each application of biochar caused the pHs to exceed the

optimal range. This illustrates the need to consider both the pH status of the soil prior to application and the specific demands of the crop to be grown. The average pH increase was 0.15 per Mg of biochar for P1 and P2 shows that one Mg would have been the maximum application if determined solely by pH at these two sites. However, as these soils are acidic and require liming at regular intervals, the liming capacity of the poultry litter would be positive over the long term.

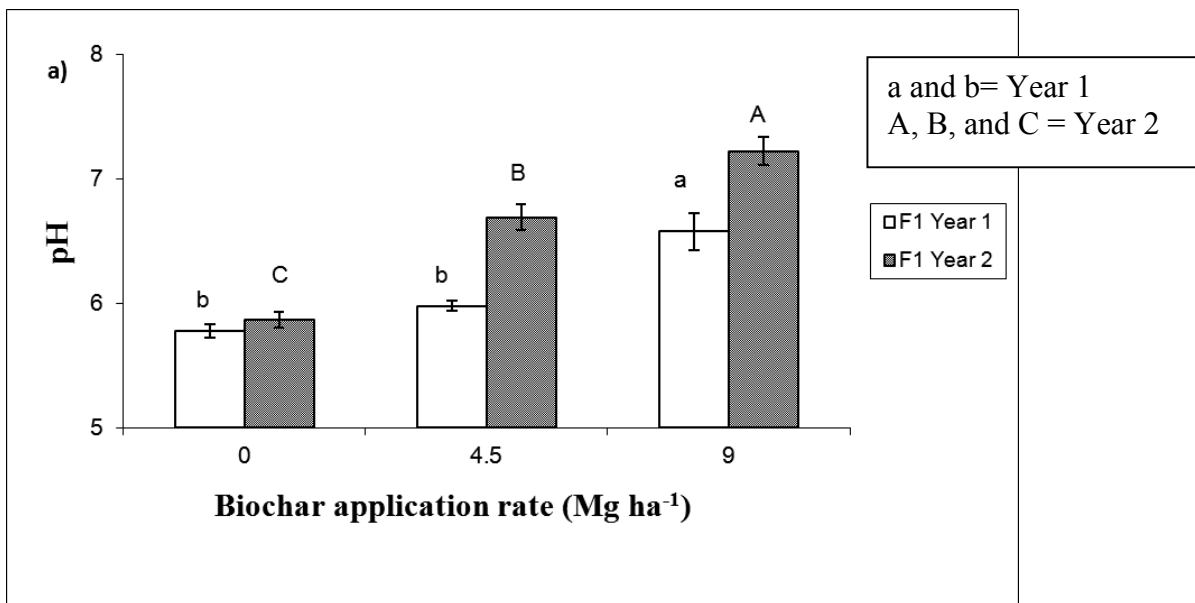


Figure 3.2a. Soil pH at the forage site F1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors

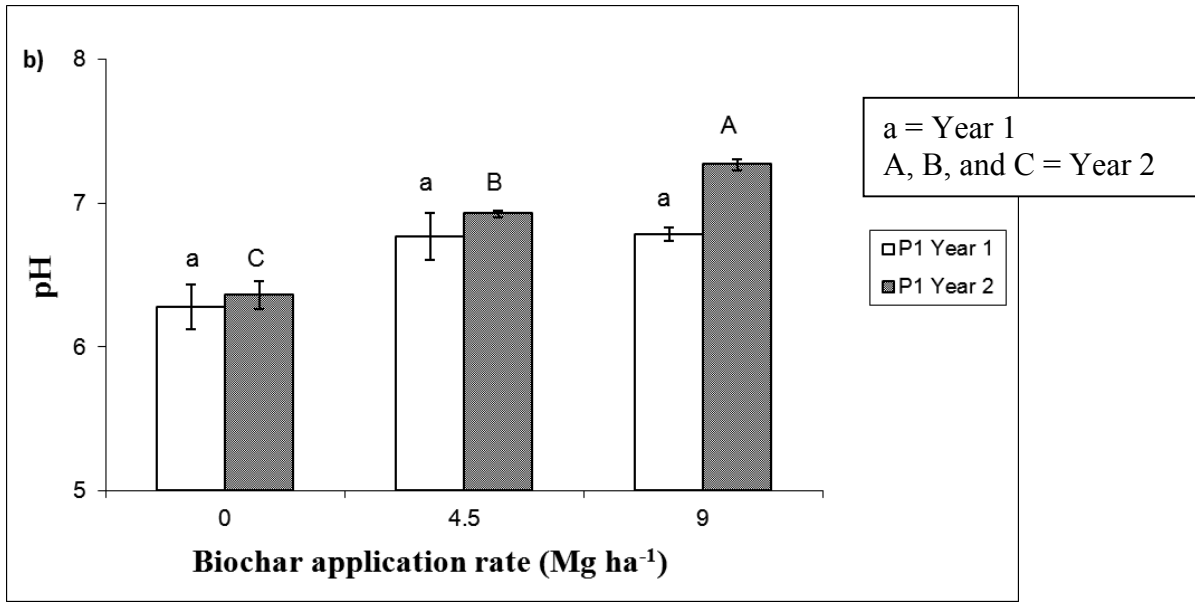


Figure 3.2b. Soil pH at the pepper site P1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

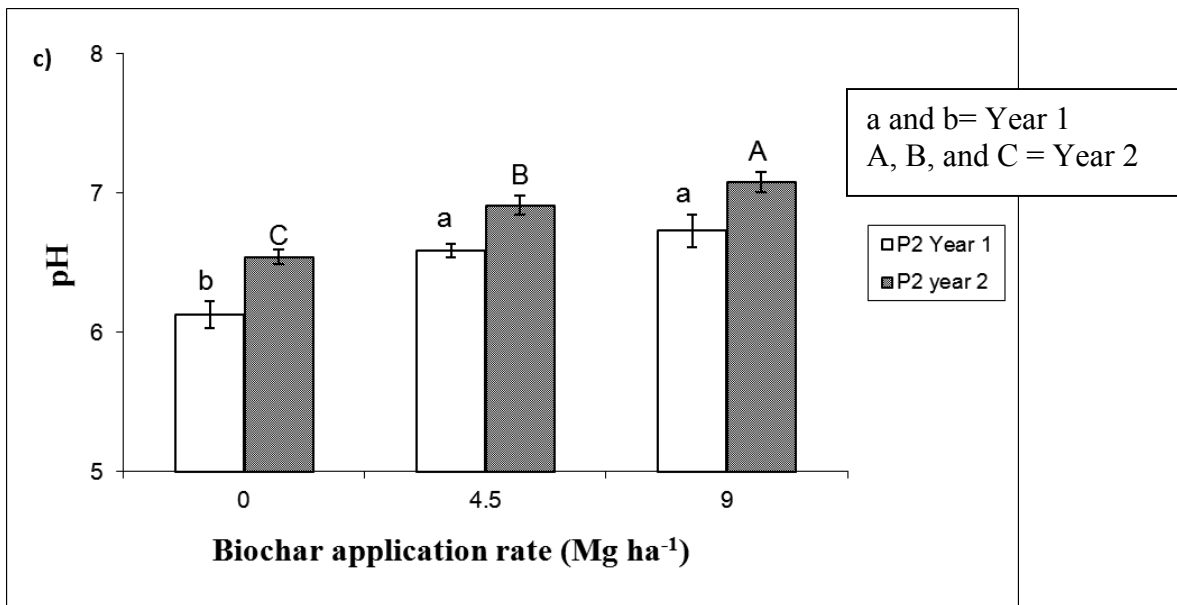


Figure 3.2c. Soil pH at the pepper site P2 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

Soil Cation Exchange Capacity

There was no clear trend for biochar affecting soil CEC across the three sites (Figs. 3a, 3b, and 3c). Biochar increased the CEC at site F1 by 0.66 and 0.82 cmolc kg^{-1} for the 4.5 Mg ha^{-1} application rate in year 1 and year 2. However, the CEC decreased at F1 from the 4.5 Mg ha^{-1} to the 9 Mg ha^{-1} application rate. The CEC also increased at site P1 in year 1 by 1.4 cmolc kg^{-1} with the 4.5 Mg ha^{-1} application rate, but no significant difference was found in CEC at either biochar application rate at P1 in year 2. No significant effect was found for any treatments at site P2. Soils containing biochar have been shown to have CEC values that are 1.9 times higher than similar soils containing no biochar (Liang, 2006). Cation exchange capacity represents the total quantity of negative surface charge available to attract cations in solution and it is one of the most important soil chemical properties influencing nutrient availability and retention in soil (Havlin et al., 2005, p. 19). The surface charge of biochar can become more negative over time through oxidation and this can lead to an increase in CEC, but oxidation and mineralization rates have not been established (Glaser et al., 2002; Baldock and Smernik, 2002). Therefore, it is unclear if the CEC would have increased if the field trials were continued for more years.

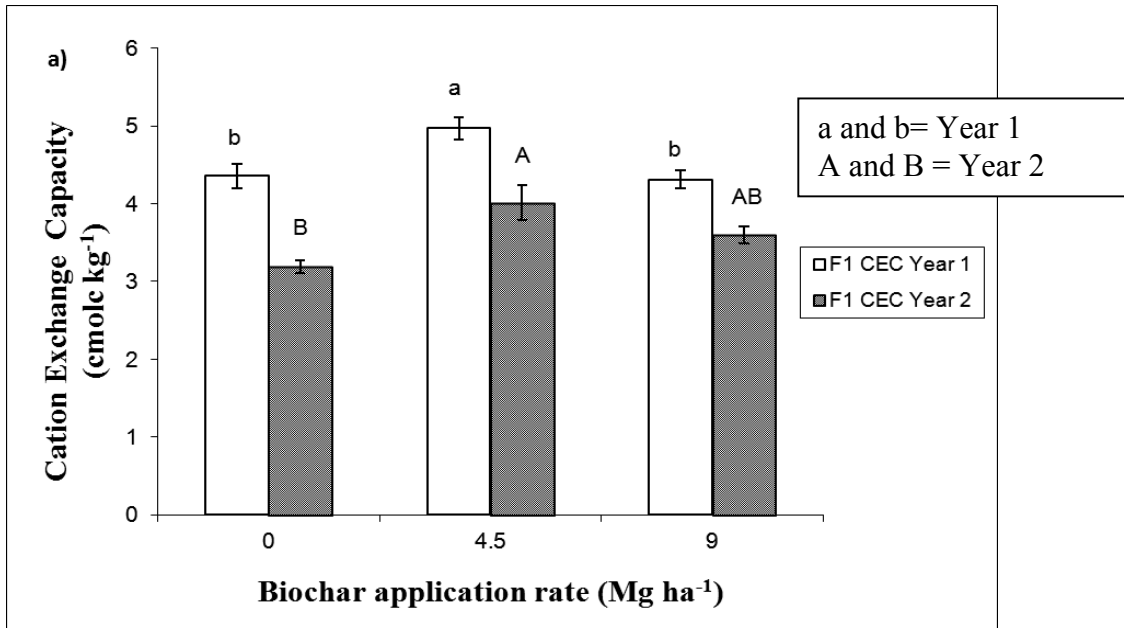


Figure 3.3a. Soil cation exchange capacity at the forage site F1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

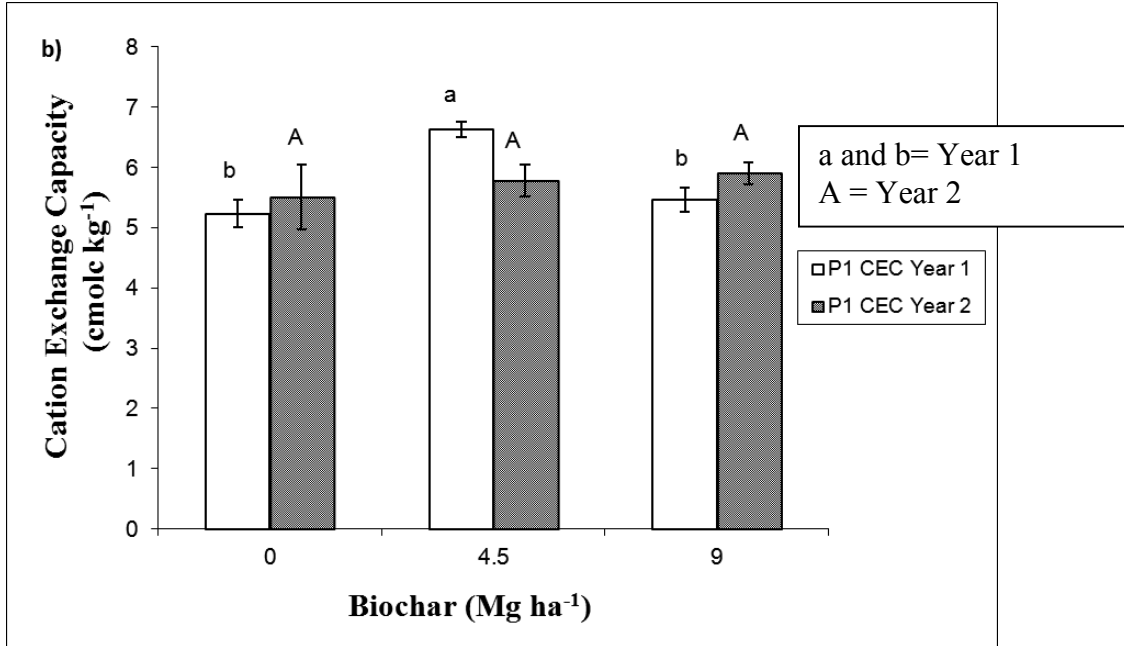


Figure 3.3b. Soil cation exchange capacity at the pepper site P1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

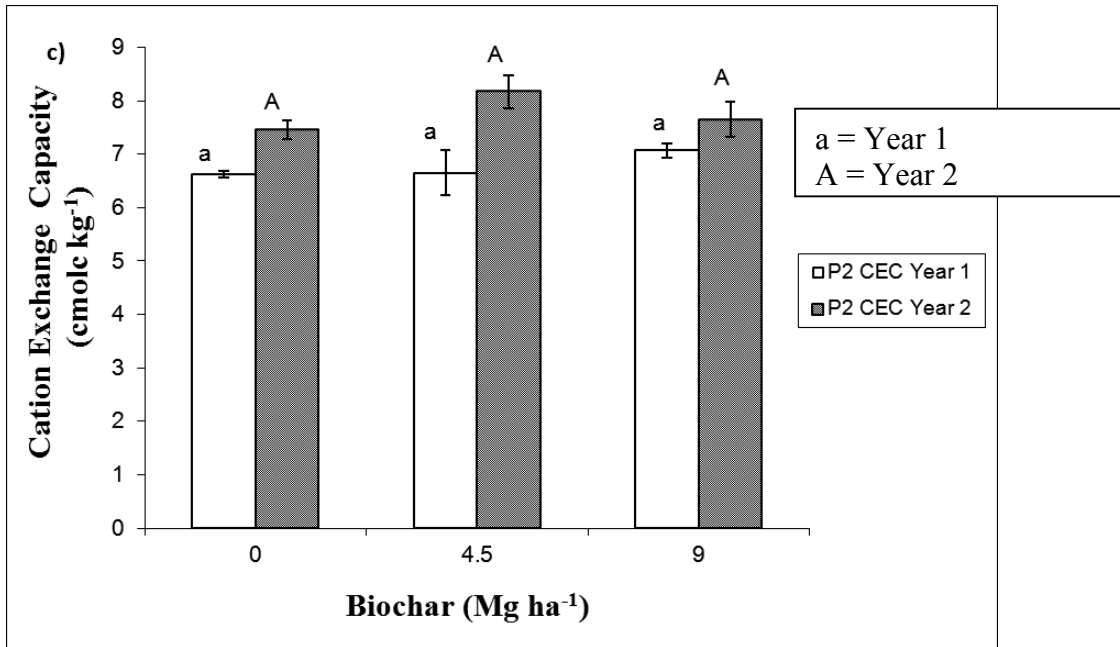


Figure 3.3c. Soil cation exchange capacity at the pepper site P2 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors

Soil Mehlich 1 Phosphorus

All three field sites had initial M1P values in the High range (28 to 43 mg kg⁻¹) and all application rates raised the M1P values above the agronomic optimum of 55 mg kg⁻¹ (Maguire and Heckendorn, 2011b; Figs. 4a, 4b, and 4c). Therefore, the application of poultry litter biochar may be limited based on its P concentration, as there are regulations in many areas to prevent buildup of soil P above agronomic optimum and protect surface water resources (DCR, 2005). This means that on farms that currently need to export poultry litter to meet nutrient management regulations, they will still have to export poultry litter biochar to avoid raising soil test P. However, as the biochar is only about

40% of the weight of the feedstock poultry litter (Kim et al., 2009), transport cost would be greatly reduced. Each Mg ha⁻¹ of biochar added 51 kg P ha⁻¹ and increased the soil M1P at site F1 by 57 mg kg⁻¹ and by an average of 39 mg kg⁻¹ at sites P1 and P2. The method of application and mounding of planting rows could be responsible for some of this difference. Biochar was surface applied at F1, which resulted in a distinct layer of biochar on the top of the soil after two years. At P1 and P2 the biochar was tilled into the soil, which probably encouraged more interaction of the biochar with the soil than at the F1 site.

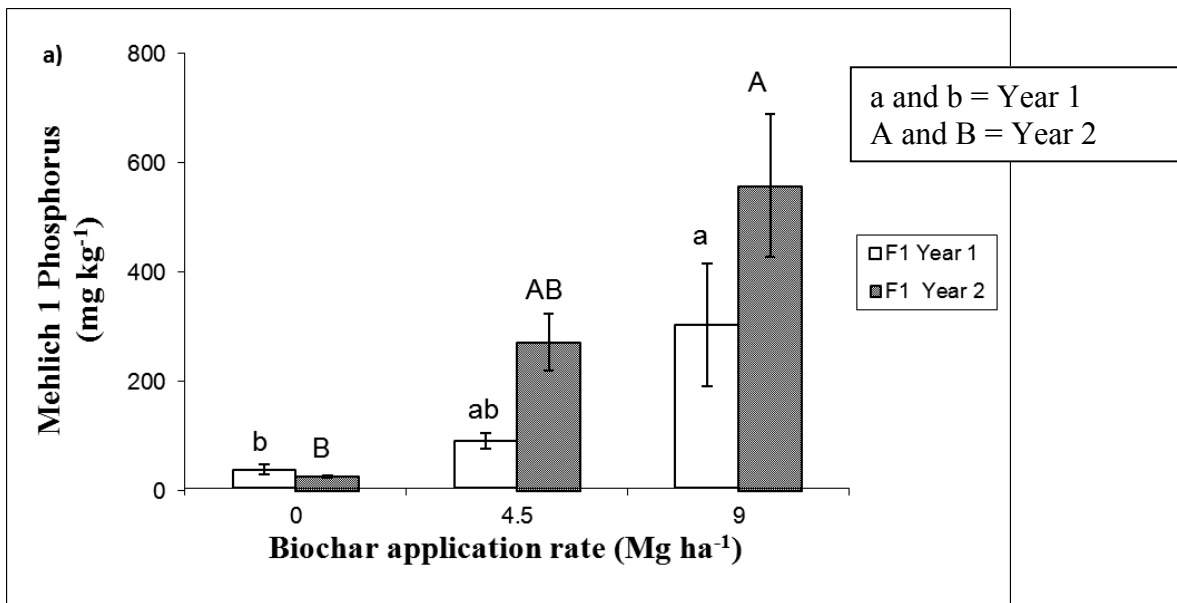


Figure 3.4a. Soil Mehlich 1 Phosphorus at the forage site F1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors

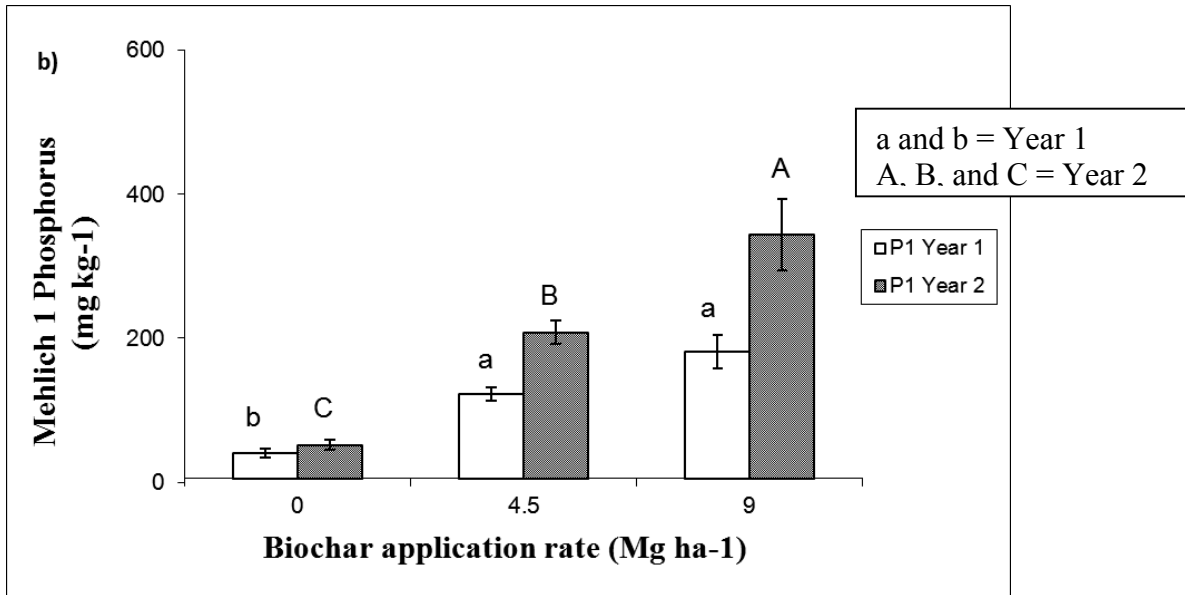


Figure 3.4b. Soil Mehlich 1 Phosphorous at the pepper site P1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

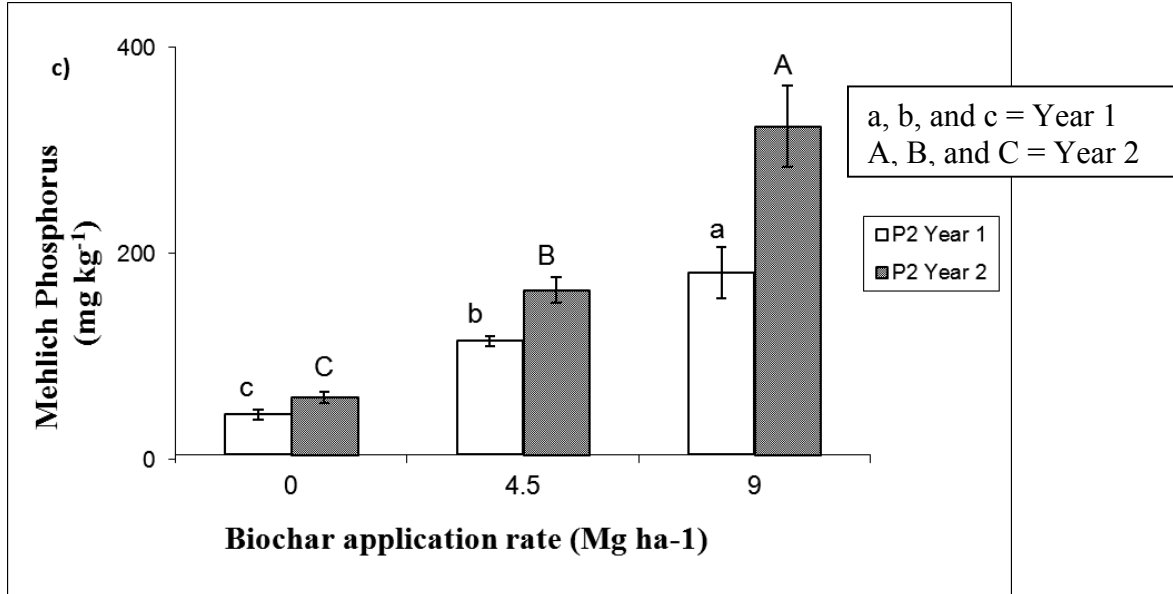


Figure 3.4c. Soil Mehlich 1 Phosphorous at the pepper site P2 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

Soil Soluble Salts

Soil SS concentrations were numerically higher following the application of biochar at all the field sites, although this was not always significant (Figs. 5a, 5b, and 5c). Site F1 showed similar increases in SS for both year 1 and year 2 with an average increase of 0.017dS m⁻¹ for each Mg ha⁻¹ of biochar applied. The largest numerical difference in SS concentrations was for P1 in year 1 with an average numerical difference of 0.046 dS m⁻¹ for each Mg ha⁻¹ of biochar applied. This is likely because plastic was used for weed control at P1 and thus rain was prevented from leaching salts out of the system. The plastic was removed at P1 in the fall of year 2 to allow leaching to occur

over the winter. This drastically reduced the scale of the increase of SS concentrations to 0.007 dS m^{-1} for each Mg ha^{-1} of biochar applied. Site P2 showed an increase of 0.015 dS m^{-1} for each Mg ha^{-1} of biochar applied in year 1, with samples taken in the fall. Samples taken in year 2 from site P2 also showed a decrease in SS concentrations following winter leaching, with the average increase per Mg ha^{-1} being 0.0016 dS m^{-1} . Poultry litter contains high concentrations of SS and there is a potential risk of secondary soil salinization when high rates are applied (Li-Xian, 2007). High concentrations of soluble salts in contact with roots can injure plants through plasmolysis or actual toxicity (Havlin et al., 2005, p. 380). The results show that the SS concentrations are reduced by leaching and therefore multiple applications of biochar are possible without raising SS to damaging concentrations over a several year time period. However, the results for pH and MIP discussed above show that poultry litter biochar applications would be limited by P and pH long before SS would become an issue.

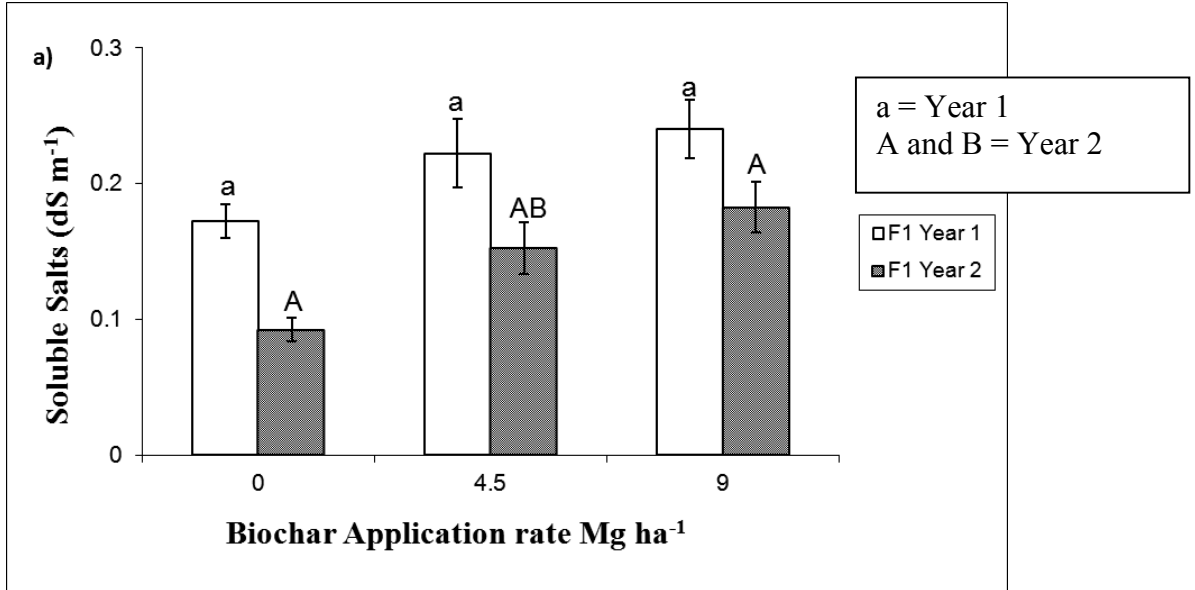


Figure 3.5a. Soil soluble salts at the forage site F1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

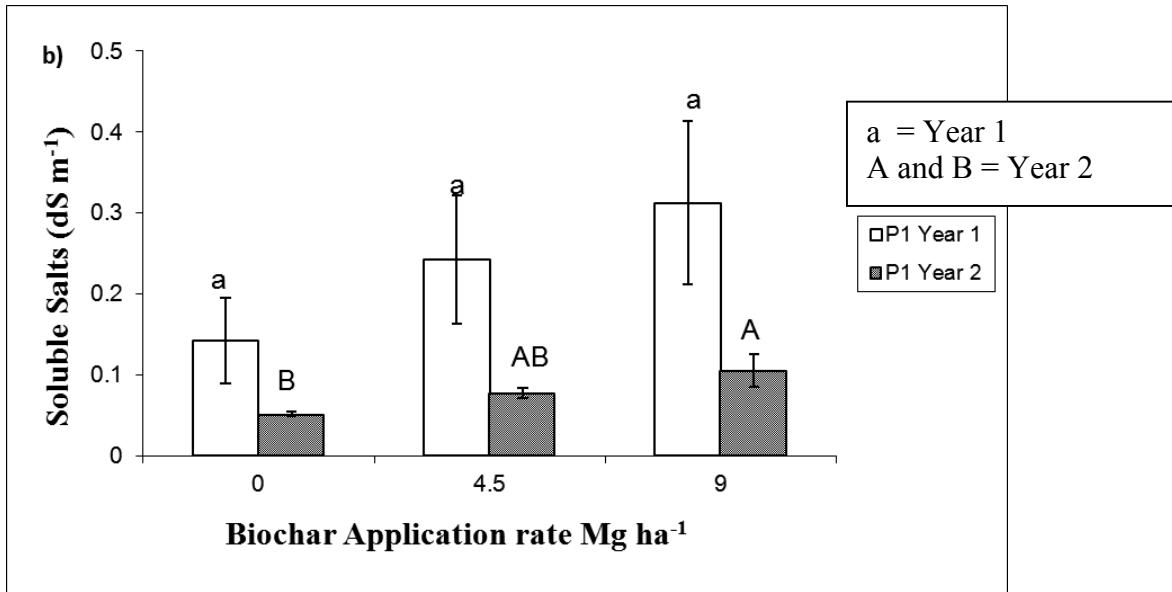


Figure 3.5b. Soil soluble salts at the pepper site P1 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graphs are standard errors

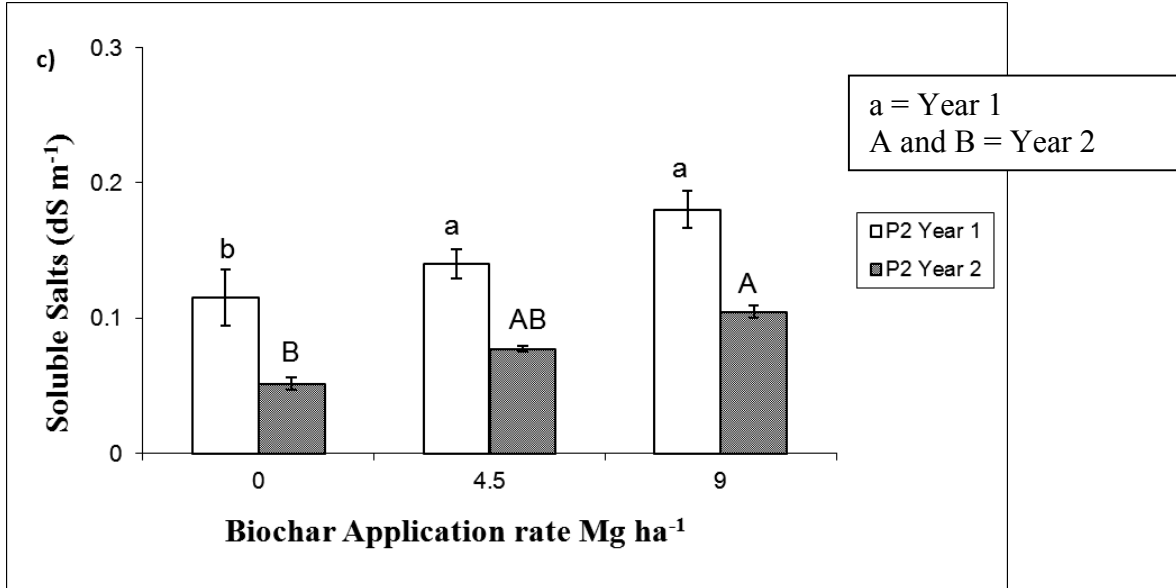


Figure 3.5c. Soil soluble salts at the pepper site P2 for the three biochar application rates over 2 years. Means were partitioned using a Tukey test and statements of statistical significance were based on the significance level of 0.05. Error bars on the graph are standard errors

Green Pepper Yield

No statistical difference was found in the pepper yields for sites P1 and P2 in either year 1 or 2. The total yield of peppers at P1 was 12 ± 1 Mg ha⁻¹ in year 1 and 19 ± 1 Mg ha⁻¹ in year 2 and at P2 they were 11 ± 1 Mg ha⁻¹ in year 1 and 19 ± 2 Mg ha⁻¹ in year 2. These yield results are smaller than those found by Sezen et al. (2011), who report yields from 21.4 to 35.9 Mg ha⁻¹. The difference in yields can be attributed to the two month longer growing season in the Mediterranean. The lack of differences between yields was probably due to the high variability of fruit set between replicates.

Forage Yield and Quality

No significant difference between treatments at F1 was found in the yields for either year 1 or year 2. In year 1, the average total yield for all treatments was 6.4 ± 0.3 Mg ha⁻¹ and in year 2 it was 6.0 ± 0.3 Mg ha⁻¹, which were similar to other reported yields obtained in the area (McGrath et al., 2010). Table 1 shows the NIR results for ADF, NDF, NFC, and simple sugars. The first cuttings from each year were the only ones that showed significant differences so the second and third cuttings are not reported. The ADF and NDF were both increased while NSC and simple sugars decreased with increasing biochar application. Increases in ADF and NDF represent a decrease in forage quality due to lower digestibility and voluntary intake (Ball et al., 2007, pg. 143). The constituents of forage can be divided into the two main categories of non-structural (NSC and simple sugars) and structural components (ADF and NDF) (Ball et al., 2007, pg. 139). The ADF of a forage is an estimate of the cellulose and lignin content. The NDF includes ADF as well as the hemicellulose content (Ball et al., 2007, pg. 143). The NSC in forages includes simple sugars and it is readily digested by animals of all types (Ball et al., 2007, pg. 139). A decrease in NSC and simple sugars therefore indicates a decrease in forage quality. Forage quality is affected by the interaction of many factors, but the stage of plant maturity is the primary determinant and forage quality generally decreases as maturity increases (Ball et al., 2007, pg. 9). It is possible that the increase in soil P due to biochar application was responsible for the increase in maturity at harvest as P can reduce the time required to reach maturity (Havlin et al., 2005, p. 163). Sanderson (1993)

showed that alfalfa maturity at harvest and NDF concentration increased with increasing P fertilizer rate.

Table 3.1. NIR results for the forage trials.

Harvest	Biochar	ADF	NDF	NSC	Simple Sugars
	Mg ha ⁻¹	-----%			
1 st cutting	0	41.6 a	68.0 b	18.5 a	5.1 a
2009	4.5	42.4 a	69.2 ab	18.0 a	5.0 a
	9	42.8 a	70.0 a	17.0 b	4.2 a
1 st cutting	0	35.4 c	62.0 c	19.9 a	4.5 a
2010	4.5	39.5 b	65.5 b	17.1 b	3.2 b
	9	45.7 a	69.6 a	16.6 b	2.4 b

† Means were partitioned using a Tukey test and statements of statistical significance

were based on the significance level of 0.05.

Conclusions

Converting poultry litter into biochar provides a way to generate a value added product that can be transported out of areas of excess manure production. This biochar has the potential to be used as a soil amendment due to its ability to increase soil C, which other studies have shown to be long lasting in soils. As acidic soils need frequent applications of lime and fertilizer, the increased pH, and M1P following biochar application are also potential benefits. Pyrolysis offers a way to produce an organic product that can be applied repeatedly as it is possible for SS to be leached from the system. However, attention should be given to the soil M1P, and pH before application to

ensure that these values are not raised above the agronomic optimum. It is possible that excessive application can decrease the time to maturity in a forage system therefore changing the optimum harvest date.

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