EFFECTS OF BIOCHAR APPLICATION ON SOIL FERTILITY AND PEARL MILLET (Pennisetum glaucum L.) YIELD.

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ABSTRACT

Biochar amendment to agricultural soils has been promoted for use in agricultural systems, both to mitigate global warming by increasing long-term soil carbon (C) sequestration and to enhance soil fertility and crop productivity. The objective of this study was to evaluate the effects of a single biochar application from peanut shell (Arachis hypogea L.) and mixed pine (Pinus spp.) wood to a Typic Hapludults in Blacksburg (VA, USA) and from peanut shell and eucalyptus (*Eucalyptus camaldulensis*) wood to a tropical, sandy, salt-affected soil in Ndoff (Fatick, Senegal) at 0, 10, and 20 Mg ha⁻¹ on soil chemical properties, inorganic nitrogen supply, and pearl millet (Pennisetum glaucum L.) production responses under field conditions for two growing seasons (2014 and 2015). Biochar application to temperate soils (Blacksburg) significantly increased total soil carbon, nitrogen, and plant available potassium in both years. In addition, pearl millet yields significant increased (53%) at the 20 Mg ha⁻¹ rate of peanut shell biochar in 2014 but did not persist in year 2. Beneficial effects largely appeared due to nutrient additions. Biochar treatment to tropical, sandy, salt-affected soils (Ndoff) had no effect on soil chemical properties. These results suggest that biochar application could improve soil fertility and crop productivity in temperate soils but had limited effects on tropical, sandy, salt-stressed soils in this study. The disparate results between these two field studies could be explained by differences in soil properties and climate, biomass feedstock, pyrolysis processes, and biochar handling, as well as experimental set-up.

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ABSTRACT FOR GENERAL AUDIENCE

Using charcoal (biochar) created from pyrolysis to improve agricultural soils has been promoted for crop production, carbon sequestration and climate change mitigation. Our objectives were to evaluate the effects biochars made from peanut shell and mixed pine wood on soil nutrients and pearl millet yields in Blacksburg (VA, USA) for two growing seasons (2014 and 2015). Biochars from peanut shell and eucalyptus wood were also applied to sandy and salt-affected soils in Ndoff (Fatick, Senegal) during a 2-year field study. In both experiments, biochars were applied once in the beginning of the experiment at three rates (0, 10, and 20 Mg ha⁻¹). In Blacksburg, addition of charcoal significantly increased total soil carbon, nitrogen, and plant available potassium in both years. In addition, peanut shell biochar applied at a rate of 20 Mg ha⁻¹ significant increased pearl millet yields up to 53% in 2014. In 2015, however, the effects of peanut shell biochar on pearl millet yields did not persist. The positive effects of charcoal addition could be explained by its ability to increase the nutrient concentrations of temperate soils. For the field study conducted in Ndoff (Senegal), application of biochar did not reduce salinity nor improve soil fertility. The results from research in Senegal were challenged by logistics factors which likely confounded the ability to see benefits fo biochar application in sandy, salt-stressed soils.

DEDICATION

I dedicate this thesis in memory of my brother,

LAMBERT DIATTA

who dedicated his career to serve his community by starting a school for students who have been dismissed from public and private institutions to give them a chance to return

to school.

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Chapter 1 – INTRODUCTION

Background

Biochar, the carbonaceous material produced during the thermochemical processing of biomass (Lehmann and Joseph, 2009; Lehmann and Joseph, 2015), has been reported as an amendment to enhance soil properties and increase productivity in agricultural systems (Asai et al., 2009; Biederman and Harpole, 2013; Jeffery et al., 2011; Jones et al., 2012; Lehmann et al., 2002; Lehmann et al., 2003a), improve soil carbon (C) sequestration potential (Sohi et al., 2009; Sohi, 2012; Spokas et al., 2009a; Spokas et al., 2012a; Stewart et al., 2013), and even alleviate the negative effects of salinization (Akhtar et al., 2015a; Thomas et al., 2013). Biochar's potential effects when applied to soils have been shown to be highly dependent on feedstock biomass (Glaser et al., 2002; Kloss et al., 2012; Thomas and Gale, 2015), pyrolysis process conditions (Amonette and Joseph, 2009; Downie et al., 2009; Laird, 2008; Lua and Yang, 2004; Trompowsky et al., 2005), and post-production processes (Azargohar and Dalai, 2008; Brewer, 2012). Several studies have demonstrated that biochar is not only more stable than the original biomass feedstock (Ameloot et al., 2013; Lehmann et al., 2006) but also the aromatic structure of much of its carbon makes the material resistant to abiotic and biotic decomposition processes (Atkinson et al., 2010; Dai et al., 2005; Wang et al., 2015a). Therefore, adding biochar to soils represents a potential means to mitigate climate change by sequestering these stable carbon compounds (Fang et al., 2014; Lehmann, 2007; Woolf et al., 2010).

Justification

These potential effects of biochar soil amendments have been mainly reported in highly weathered, nutrient-poor tropical soils. Relatively few field experiments, however, have examined the benefits of incorporating biochar into temperate soils and their potential agronomic effects in these regions (Atkinson et al., 2010; Kloss et al., 2014). As well, there are scarce data for from biochar amendment in field trials with sandy, saltaffected infertile soils in the topics suggests studies for an understanding of its potential role in mitigating salinity stress (Amini et al., 2016; Asai et al., 2009; Usman et al., 2016).

Objectives

Our hypotheses were adding biochar would:

- Ho: have no effect on soil nutrient availability and inorganic N retention, nor on crop yield;
- 2) *Ha*: increase soil nutrient availability and retention of nitrate (NO_3^--N) and ammonium (NH_4^+-N) and thus increase crop productivity in a temperate soil;
- 3) *Ha*: increase soil nutrient availability and retention of NO₃⁻-N and NH₄⁺-N and thus increase crop productivity in a tropical, sandy, salt-affected soil.

The objectives for testing these hypotheses included:

 To conduct a literature review of the published research related to biochar regarding its production processes and composition, its effects of biochar on soil physical, chemical, and biological properties, its potential in sequestering C and mitigating greenhouse gas emissions, and its impacts on plant growth and crop productivity;

- To examine the impacts of different sources and rates of biochar addition on soil nutrient status, inorganic N (NO₃⁻-N or NH₄⁺-N) availability in soil solution; and
- To investigate the effects of different biochar sources and concentrations on pearl millet growth and yields.

LITERATURE REVIEW

Biochar is a carbon-rich byproduct of biomass pyrolysis under oxygen-limited environments and is intended for soil application as a means to improve agronomic and environmental benefits (Biederman and Harpole, 2013; Enders et al., 2012; Hass and Gonzalez, 2014; Jeffery et al., 2011; Kookana et al., 2011; Lehmann and Joseph, 2009; Lehmann and Joseph, 2015; Sohi et al., 2010; Thomas and Gale, 2015; Wang et al., 2015a). Similar to charcoal in key characteristics including composition of stable, recalcitrant form of organic carbon (Zimmerman, 2010) and production by thermal decomposition of biomass under low-oxygen conditions; biochar is distinguished from similar materials by its intended use as a soil amendment (Lehmann and Rondon, 2006) and a long-term carbon (C) storage strategy (Mašek et al., 2013). Feedstocks for biochar production include a wide range of materials such agricultural crop and forestry residues, municipal wastes, animal manure, etc. (Brewer and Brown, 2012; Duku et al., 2011; Sohi et al., 2009). Biochar key properties such as high pH, porosity, specific surface area, and cation exchange capacity are mainly dependent on feedstock type and production process (Joseph and Taylor, 2014). These biochar properties affect its interactions with physical, chemical, and biological components of the soil as well as its fate within the ecosystem (Joseph et al., 2013; Liang et al., 2006). Biochar is used as a soil amendment to enhance soil fertility (Kloss et al., 2014; Lehmann et al., 2003b) and sustain crop productivity (Asai et al., 2009; Lehmann and Rondon, 2006) by improving nutrient availability while simultaneously reducing leaching losses. This can decrease fertilizer needs (Laird et al., 2010; Woolf et al., 2010; Yao et al., 2012) and may even increase nutrient supplies to plants (Glaser et al., 2002). Biochar also stimulates microbial activity and diversity

(Gomez et al., 2014; Lehmann et al., 2011; Quilliam et al., 2013b; Steiner et al., 2008). In addition, biochar can enhance soil water holding capacity (Karhu et al., 2011; Sun and Lu, 2014; Wang et al., 2013) and reduce emissions of greenhouse gases (Singh et al., 2010; Spokas et al., 2009b; Woolf et al., 2010), as well as control the mobility, bioavailability and toxicity of contaminants (Ahmad et al., 2014; Beesley et al., 2010; Hale et al., 2011; Uchimiya et al., 2011). In addition, application of biochar to agricultural soils can increase soil carbon sequestration potential for global warming mitigation (Barrow, 2012; Lehmann and Rondon, 2006; Sohi, 2012) through withdrawal of carbon dioxide from the atmosphere. However, biochar's ability to sequester C would depend composition of stable and recalcitrant form of organic carbon from the transformation of plant organic matter into biochar. As a consequence, crop responses to BC application on temperate soils may differ from tropical soils; there may be no beneficial or even detrimental effects on soil nutrient status and plant yield, as already reported by Blackwell et al. (2009).

Biochar production and composition

Biochar, a mainly stable black carbon material, is derived from pyrolysis usually between 300 and 1000°C of biomass under oxygen-limited environments (Jeffery et al., 2011; Tan et al., 2015). Pyrolysis is the thermal decomposition of biomass material under oxygen-depleted conditions (Joseph and Lehmann, 2009). This thermochemical process, generally classified by rate of reaction into slow pyrolysis, fast pyrolysis, and flash pyrolysis, (Brewer, 2012; Laird et al., 2009), can be used to transform organic materials into bio-oil, syngas, and biochar (Bruun et al., 2012b). The two major thermal conversion processes widely used in biochar production are slow and fast pyrolysis technology

(Woolf et al., 2010). The slow pyrolysis, most widely used and carried out at lower temperatures and heating rates and longer residence times compared to fast pyrolysis (Roberts et al., 2009), optimize biochar yields over energy production (Kookana et al., 2011; Yuan et al., 2011).

The thermal conversion of biomass to biochar yields materials with greater C concentration and along with changes in the nutrient concentration and forms. Ancient Amazonian Darks Earths in Brazil also known as Terra Preta de Indio (Anthrosols) display high soil organic matter and high concentrations of exchangeable cations, and available phosphorus (Sohi et al., 2010) as a result of long term biochar application. The high concentration of nutrients and carbon in the charred materials has been suggested to be responsible for sustaining long term C stability (several hundred to several thousand years) and promoting high level of fertility of these soils (Glaser et al., 2001). The resultant materials from biomass pyrolysis are more chemical recalcitrant and resistant to biological decomposition than native organic matter, thereby maintaining or increasing stable soil organic C pools which can be used as a long-term carbon sequestration alternative (Alburquerque et al., 2014; Gaskin et al., 2008; Lehmann and Rondon, 2006).

Biochar has a biphasic character, with both labile and stable carbon pools whose ratios are determined by the proportions of hemi-cellulose, cellulose and lignin content of the feedstock (Joseph et al., 2013; Sohi et al., 2009). High pyrolysis temperature lead to an increase in aromaticity (nonvolatile, high C and low O material) of biochar. These chars are oxidized more slowly and form surficial, oxygen-containing functional groups (Jung et al., 2016). Conversely, biochars formed at lower temperature contain more

labile, volatile components of relatively low C and high oxygen content (relatively aliphatic) (Fang et al., 2014; Novak et al., 2010; Zimmerman, 2010).

The elements found in biochar are carbon with concentrations ranging between $172g \text{ kg}^{-1}$ and $905g \text{ kg}^{-1}$; for nitrogen, concentrations from $1.8g \text{ kg}^{-1}$ to $56.4g \text{ kg}^{-1}$ have been reported, total phosphorous from $2.7g \text{ kg}^{-1}$ to $480g \text{ kg}^{-1}$, and total potassium from $1.0g \text{ kg}^{-1}$ to $58g \text{ kg}^{-1}$ (Chan and Xu, 2009; Lehmann and Joseph, 2009). Biochar also contains other elements such as oxygen, hydrogen, sulfur, base cations and heavy metals to varying extents (Brewer and Brown, 2012; Preston and Schmidt, 2006). These variability in nutrient properties can be attributed to biochar feedstocks and pyrolysis conditions (Lehmann and Joseph, 2009). Biochar C/N ratios ranging from 7 to 400, with higher C/N ratios observed at high temperatures (Yuan et al., 2011), influence the slow mineralization of biochar due to the appearance of aromaticity during thermochemical conversion (Kuzyakov et al., 2009).

The pH of the resulting biochars can range from 4 to 12 (Lehmann and Joseph, 2009) with gradual increase in pH values with increasing pyrolysis temperatures (Naeem et al., 2016). The high pH values of biochar can be explained by concentration of alkaline elements at high temperatures (Chen et al., 2014; Mukherjee et al., 2011). In addition, high pyrolysis temperature has been reported to increase biochar ash content (Gunes et al., 2015) while it decreases volatile compounds (C, H, and O) (Purakayastha et al., 2016) and cation exchange capacity of biochar (Song and Guo, 2012). The latter increases with time upon incorporation to soil, exposition to O_2 and water, and occurrence of abiotic and biotic oxidation of functional group on biochar particles (Cheng et al., 2008; Liang et al., 2006). As a tool for soil remediation, high pyrolysis temperature has been suggested to

produce effective biochar for environmental contaminant sorption (Fryda and Visser, 2015; Liu et al., 2012; Xie et al., 2015) as specific surface area, microporosity and surface hydrophobicity increase with increasing pyrolysis temperature (Ahmad et al., 2014). However, the effectiveness of each type of biochar for soil amendment is greatly influenced by its physical and chemical nature, economic, logistical, and environmental factors (Gomez et al., 2014; Novak et al., 2010).

Biochar effects on soil properties

Biochar can enhance plant growth by improving soil physical characteristics (bulk density, water holding capacity, permeability (Asai et al., 2009; Sun and Lu, 2014); and soil chemical characteristics (nutrient retention and availability, CEC, surface areas and pH; (Abel et al., 2013). In addition, biochar can improve soil biological properties by increasing diversity of and providing a suitable environment for soil microbial communities (Abujabhah et al., 2016; Lehmann et al., 2011; Tong et al., 2014). The apparent high recalcitrance of biochar to chemical and biological processes supports its long term agronomic and environmental benefits environment with residence time on the magnitude of hundreds to thousands of years (Fang et al., 2014; Whitman and Lehmann, 2009; Zimmerman, 2010).

Soil physical properties

Biochar has a relatively high surface area and has been reported to influence biochar interactions with soil solution substances as well as to provoke a net increase in the total soil-specific surface of biochar-amended soils (Lehmann et al., 2009). Biochar bulk density, ranging from 0.08 g cm⁻³ (Gundale and DeLuca, 2006) to 0.43 g cm⁻³ (Pastor-Villegas et al., 2006) depending on feedstock biomass and process conditions, is

lower than that of mineral soil ranging from 1.16 to 2.00 g cm^{-3} (Chaudhari et al., 2013). Therefore, a reduction in soil bulk density (Chen et al., 2013; Laird et al., 2010; Sun et al., 2013b) is anticipated due to biochar low bulk density and its highly porous structure (Downie et al., 2009). Biochar not only improves soil water movement but also soil water retention characteristics (Lim et al., 2016; Novak et al., 2012) because of its highly porous structure (Asai et al., 2009; Karhu et al., 2011; Ogawa et al., 2006b) as production processes induce loss of volatile matter (Brewer and Brown, 2012). Notable differences in water retention has been reported by (Glaser et al., 2002) with 18% increase in terra preta compared to adjacent soils due to higher biochar concentrations and higher levels of organic matter. There is also evidence that biochar-amended soils display an increase in available moisture for coarse-grained and low organic matter content sandy soils (Liu et al., 2012), rather marginal to moderate improvement effect in medium textured soils (Laird et al., 2010), and potentially a reduction in moisture retention for clayey soils (Sohi et al., 2010). Significant improvements in aggregate stability and accompanying changes in water retention have been linked to biochar application for a clayey soil (Soinne et al., 2014; Sun and Lu, 2014).

Soil chemical properties

Biochar addition to agricultural soils has been proven as an effective and unique opportunity for soil fertility improvements and nutrient-use efficiency (Lehmann and Joseph, 2015). Expectations of increased soil fertility benefits and enhanced plant growth after biochar application arise from the sustainable fertility of the *Terra Preta* soils found in central Amazonia (Glaser et al., 2002) which has been attributed to the high contents of black carbon (Lehmann and Joseph, 2015). Biochar application induces changes in soil

chemical properties including an increase in soil pH, cation exchange capacity, and nutrient contents (Biederman and Harpole, 2013; Cheng et al., 2008; Liang et al., 2006). Biochar has the potential to increase soil pH with an accompanying decrease in the amount of exchangeable Al³⁺ (Brewer and Brown, 2012). Biochar application has been also reported to reduce the mobility of toxic elements in acid soils (Major et al., 2010; Yamato et al., 2006) as well as enhance K and P availability (Asai et al., 2009; Jeffery et al., 2011). These biochar effects have been reported to reduce lime application needs and to increase crop production in highly weathered infertile tropical soils (Liu et al., 2012). Cation exchange capacity is a measure of soil capacity to retain key exchangeable cations in the soil and has been seen to mitigate leaching losses (Brady and Weil, 1984; Sohi et al., 2009). The application of biochar in agricultural soils has been shown to increase CEC over time due to biochar surface oxidation and abundance of negatively charged surface functional groups (Cheng et al., 2008). Glaser et al. (2002) found that applied biochar can also directly provide readily available nutrients for plant growth. Biochar's porous structure, large surface area, and negative surface charge (Downie et al., 2009) increase the cation exchange capacity of the soil and allow for the retention of nutrients (Laird et al., 2010). Crop fertilizer requirements can be decreased due to an increase in nutrient use efficiency with biochar addition (Lehmann and Joseph, 2009; Lehmann and Joseph, 2015; Zheng et al., 2013a). Biochar application has also been shown to reduce the availability of heavy metals (Komkiene and Baltrenaite, 2016) and organic pollutants such as dioxins, PAHs, pesticides (Zhang et al., 2013) due to due its large surface area and high adsorption capacity (Komnitsas et al., 2015; Melo et al., 2016; Tang et al., 2013).

Soil biological properties

Biochar has the potential to stimulate the activity and diversity of soil microbial community (Lehmann et al., 2011; Steiner et al., 2004; Zheng et al., 2013a) through its porous structure, high cation exchange capacity and high sorption capacity. Biochar's intrinsic properties may enhance nutrient retention and availability to microorganisms (Lehmann et al., 2011) and also influence the interactions between soil, plant, and microorganism components (Quilliam et al., 2013a). In addition, biochar's pore space has been reported to provide a suitable habitat for microorganisms, protecting them from predation and desiccation while supplying C, energy and mineral nutrients (Warnock et al., 2007). The application of biochar at high rates has been reported to stimulate changes in soil microbial community composition towards a bacteria-dominated microbial community compared to fungi (Gomez et al., 2014; Ippolito et al., 2014; Li et al., 2015). This change in microbial community could be explained by the liming potential of biochar (Rousk et al., 2010) and addition to labile organic C in soil (Farrell et al., 2013) leading to wider C/N ratios (Thies and Rilling, 2009). Furthermore, biochar-amended soils have been found to enhance microbial abundance and growth due to sorption of toxic compounds to biochar (Kasozi et al., 2010).

Biochar C sequestration and greenhouse gas emission reduction

Application of biochar has been proposed as a means to increase the long-term C sequestration potential and reduce emission of greenhouse gases (Lehmann and Joseph, 2015; Lehmann and Rondon, 2006; Spokas et al., 2012b) representing therefore beneficial strategy in mitigating global warming (Woolf et al., 2010; Zhang et al., 2013). Biochar potential in sequestering C may be explained by the production of a highly

stabilized C by pyrolysis of biomass (Forbes et al., 2006) which is very slowly decomposed in soil (Sohi et al., 2009). Lehmann and Rondon (2006) reported a 50% loss of biomass C in biochar production, however compared to biomass inputs in agricultural fields, a considerably greater fraction of the stable C remains in soil for longer time periods. Additional potentially benefits of biochar included avoided emission of CO₂ through reduction of fertilizer demands to achieve crop yields by improving soil waterand nutrient-retention capacities (Woolf et al., 2010). In addition of reduction in emissions of CO₂ (Lehmann, 2007; Stewart et al., 2013), biochar soil amendment may mitigate the emissions of nitrous oxide (N₂O) (Shanthi et al., 2013; Spokas et al., 2009a) and methane (CH₄) (Leng et al., 2012; Rondon et al., 2006) from agricultural soils by improving soil aeration and reducing of changes in land use due to optimization of crop yields.

Biochar effects on plant growth and crop productivity

Enhancement of plant growth and crop yields with biochar application has been reported and could be attributed to modification of soil physical properties (Glaser et al., 2002). These changes in soil physical properties are due to improvements on soil structure and water holding capacity (Zhang et al., 2012b) and improved crop nutrient availability (Atkinson et al., 2010) via its indirect nutrient value (Lehmann and Joseph, 2015), liming effect (Rondon et al., 2007), increased surface area (Sohi et al., 2009). Jeffery et al. (2011) reported –28% to 39% changes in plant productivity (crop yield and above-ground biomass) following biochar amendment to soils which are partly explained by biochar's liming effect and enhanced soil moisture retention, associated with increased nutrient availability to plants.

Significant crop yield benefits from biochar application to soils have been reported for various crops and plants in different environments (Lehmann and Joseph, 2015). In Amazonia, biochar application in combination with fertilizers sustained crop yields (Steiner et al., 2008) due to soil property improvements (Lehmann et al., 2003b). (Crane-Droesch et al., 2013) reported positive crop yield response as a result of biochar application over much of Sub-Saharan Africa, parts of South America, Southeast Asia, and southeastern North America.. The observed increase in crop yields in these highly weathered and nutrient-poor soils could be explained by biochar soil amendments improving soil aggregation, increasing nutrients retention, and enhancing soil water holding capacity.

Biochar application has been reported to increase by ~10% plant productivity (Liu et al., 2013) and ~25% for aboveground biomass (Biederman and Harpole, 2013). Yamato et al. (2006) explored biochar effect on crop yield and reported increase in maize, cowpea and peanut yield under fertilized conditions due to increased soil pH, cation exchange capacity, nutrient availability and decreased exchangeable Al³⁺ content. Uzoma et al. (2011) attributed a 150% and 98% increase in maize grain yield at 15 and 20 t/ha biochar application respectively to enhancement of soil physical and chemical properties.

Despite biochar's agronomic benefits, negative effects under biochar amendment on plant productivity have also been reported in peat soils whereas moderate to negative yield response could be observed in most of the leading countries in grain production (Crane-Droesch et al., 2013). Significant crop yield decrease in biochar-amended soils has been also attributed to significant increase in soil C: N ratios which in turn could

result in nitrogen immobilization (Bridle and Pritchard, 2004; Chan et al., 2008). Zhang et al. (2012a) investigated the effect of biochar on soil quality, plant yield and the emission of greenhouse gas in a rice paddy study in China and found increase in rice yield due increased soil pH, soil organic carbon, total nitrogen and decreased soil bulk density. Kloss et al. (2014) reported a 68 % yield reduction of mustard and barley after biochar application due to significant decrease (Cu, Fe, Mn, Zn) and increases (Mo) in micronutrient concentrations of plant tissues.

Effectiveness of biochar in improving plant productivity is variable (Liu et al., 2013) considering variations in climate, soil properties, investigated crops, and experimental conditions (Wang et al., 2012). These differences could also be explained by biochar feedstock and pyrolysis processes along with the interactions between soil biotic and abiotic components and biochar occurring when biochar is applied to soil (Sohi et al., 2009). In biochar experiments, positive crop productivity occurred in pot experiments more than in field, in acidic than in neutral soils, in sandy than in loam and silt soils (Crane-Droesch et al., 2013; Jeffery et al., 2011). In addition, crops grown with biochar resulted with a 10.6% increase on average on dryland soils whereas a 5.6 % increase has been reported for paddy rice (Liu et al., 2013). For biochar source's effects on yield response, poultry litter showed the strongest (significant) positive effect (28%), in contrast to biosolids, which were the only feedstock showing a statistically significant negative effect (-28%) (Jeffery et al., 2011).

Senegal

Senegal, located in the western most part of continental Africa, is in the Sudano-Sahelian zone between latitudes 12° and 16° North and longitudes 11°30' and 17°32' West

and covers an area of 196,722 km². The climate, Sahelian in the North, Soudano-Sahelian in the Center and Sudanese in the South, is characterized by unimodal rainfall with a long-term dry season and a short-term rainy season, with only 2 months of rain in in the North, and 4 to 5 months in the South. Senegal's population has increased from 3 million in 1960 to 15 million in 2015 (FAOSTAT, 2016d) with an estimated annual population growth rate of 3.1 per cent in 2014 (The World Bank, 2016). Senegal has an economy based on agriculture which employs about 70% of the active population (FAOSTAT, 2016c) but which contributes only 15.8% of GDP in 2014 (The World Bank, 2016). Arable land was estimated at 3.3 million hectares in 2013 (FAOSTAT, 2016a). Senegalese soils are diverse and are sandy and dry in the north, iron-rich in central, and lateritic in the south (Tappan et al., 2004) (Figure 3.1). Their distribution is based on two main soil forming factors: parent material and topography, which allow the differentiation of hydromorphic character of salinity or acidity, associated with a water excess or deficit (Fall, 2008).

Senegalese agriculture is mainly rainfed, although rice and maize are also grown in irrigated systems along the Senegal River. The main crops include peanut (*Arachis hypogaea* L.), millet (*Pennisetum glaucum* L.), rice (*Oryza sativa* L.), sorghum (*Sorghum bicolor* (L.) Moench), maize (*Zea mays* L.), cowpea (*Vigna unguiculata* L. Walp.), and cassava (*Manihot esculenta* Crantz) (Dieye and Gueye, 2002; Sokona et al., 2003; World Food Programme, 2013). Millet is the dominant staple crop among cereals with a production of 408,993 tons (FAOSTAT, 2016b). Agricultural production is primarily devoted to meeting local needs (food crops and animal production) and then directed to

the external market (cotton, peanuts, and some animal production including hides and skins).

Senegalese agricultural systems are facing various constraints which are mainly due to climate variability and increased frequency of extreme climatic events (Brown, 2008; Diouf et al., 2014; Sene et al., 2014), deforestation and expansion of cultivated areas (Mbow et al., 2008), salt-water intrusion (Mikhailov and Isupova, 2008), and inadequate agricultural policies and inappropriate farming practices (MEDD, 2014; Sall et al., 2015; Sonneveld et al., 2010). In addition, degradation of soils by salinization is estimated to affect more than 1.7 million hectares of land in Senegal (CSE, 2003), significantly affecting the potential of agricultural production. Strategies that have been undertaken to reclaim salt-affected soils in Senegal include the introduction of structures to change hydrology and minimize salt intrusion and the use of salt-tolerant crop varieties or introduction of exotic species (Boivin et al., 1991; Diouf et al., 2014; Faye et al., 2015; Planchon and Dieye, 2002).

Salt-affected soils

Salt-affected soils occur in the areas where excess dissolved mineral salts (such sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chloride (Cl⁻), sulfate (SO₄²⁻) and carbonate (CO₃²⁻; including bicarbonate) (Qadir et al., 2000; Rengasamy, 2010)) accumulate in the root zone. This results in imbalances of nutrients in soils (Abrol et al., 1988; Rengasamy, 2006) which constrains crop production (Allakhverdiev et al., 2000; Amini et al., 2016; Chaiyasit et al., 2016; Rengasamy, 2010; Tanji, 2002). High concentrations of water-soluble salts (salinity) or exchangeable sodium (sodicity) is becoming an important agronomic limiting factor throughout the world (Mau and

Porporato, 2015; Sharma et al., 2000; Wong et al., 2010; Yuan et al., 2007). Salt-affected landscapes originate from natural or human-induced processes (Minhas and Dagar, 2007) which respectively affect about 95 million hectares worldwide (Metternicht and Zinck, 2003). In addition, the United Nations Environment Program (UNEP) estimated that about 20% of agricultural land and 50% of cropland in the world has been degraded by salinization (Glenn et al., 1999; Ravindran et al., 2007; Sambou et al., 2010). Excess amounts of salts cause adverse effects on the physical and chemical properties of soil, microbiological processes and crop productivity (Sharma and Sharma, 2008; Tejada et al., 2006).

Accumulation of salts, sodium, or both in these soils have their origin through the weathering and deposition of parent minerals and seawater intrusion which cause primary salinization (Qadir et al., 2008a). In addition, seawater intrusion, evaporation and transpiration processes due to high temperatures and droughts can cause salt movement with capillary action inducing its accumulation in surface soil (Chaiyasit et al., 2016; Ezeaku et al., 2015; Siyal et al., 2002). Secondary salinization is the type of salinity induced due to human activity through different cultural practices, irrigation operations, and crop sequences in the field (Hussain et al.; Rhoades et al., 1997). Applying polluted effluents from industrial waterways and sewage from residential areas can lead to this secondary salinization (Stein and Schwartz, 1990; Tan and Kang, 2009).

Salt-affected soils have been categorized as saline, saline-sodic, and sodic soils (Minhas and Dagar, 2007) based on soil pH, electrical conductivity of the saturated extract (ECe), and sodium adsorption ratio (SAR) (Ghassemi et al., 1995; Rengasamy, 2010; US Salinity Laboratory Staff, 1954). Saline soils contain high concentrations of

soluble salts while sodic soils, formerly called "alkali soils", contain high amounts of exchangeable sodium (SAR > 13) (Bernstein, 1962; Mau and Porporato, 2015; Varallyay and Szabolcs, 1974). These two main types differ not only in their chemical characteristics, but also in their geographical distribution, and their physical and biological properties (Pessarakli, 1991). Saline soils have an ECe greater than 4 dS/m induced by excess of soluble salts and characterized by a sodium adsorption ratio (SAR) less than 13. The detrimental effects of excessive salinity in soils include reduction in water availability to plants due to higher osmotic potential of soil water, a significant change in the hydraulic properties of soil, Na⁺ toxicity to crops, reduced soil fertility due to inhibition of mineral nutrient uptake and ultimately plant death (Dara, 2006; Kumar, 1996; Parida and Das, 2005; Vengosh, 2003). (Romero-Aranda et al., 2001) explored plant-water uptake and plant-water relationships of tomato under saline growth conditions and reported decreased growth and water uptake. A saline-sodic soil has an ECe greater than 4 dS/m and a SAR greater than 13 while sodicity refers to soils for which ECe is less than 4 dS/m and a SAR is greater than 13 (Amini et al., 2016; Minhas and Dagar, 2007; US Salinity Laboratory Staff, 1954). Sodicity can cause breaking of soil aggregates created by physical processes such swelling, and dispersion of clay (Lauchli and Epstein, 1990; Qadir et al., 2008b). This process results in reduction of soil water and air movement, plant-available water holding capacity, and root penetration, while increasing runoff and erosion, and impeding sowing operations (Kumar, 1996).

Occurrence of salt-affected soils is a typical feature in arid and semi-arid areas but regions usually differ in degraded total land area, the degree and chemistry of salinization, and in the distribution of salts in the soil profiles (Barbiero et al., 2004;

Pankova and Konyushkova, 2013; Pessarakli, 1991; Rao and Pathak, 1996). In addition, salt is a serious problem in areas where groundwater with a high salt content is used for irrigation (Sheikh et al., 2007). More than 800 million hectares of soils are salt-affected worldwide (Martinez-Beltran and Manzur, 2005; Rengasamy, 2010). These salt-affected soils occur because of the salts released by weathering of rock or those initially present in the soil-forming materials (Bernstein, 1962) and also by seawater intrusion onto land due to rising sea levels (Rengasamy, 2010). In addition, salt-affected soils occur in these areas because rainfall amounts are insufficient to leach and transport the salts, while the enhanced evaporation characteristic of arid climates, and the pumping of groundwater resources beyond replenishment capacity induce high salt concentration in soil surface layers and surface waters (US Salinity Laboratory Staff, 1954; Vengosh, 2003). Effects of soil salinity are manifested in crop loss, reduced yields due to reduced plant growth, and in severe cases, crop failure (Corwin et al., 2007). Thus food production, in arid and semi-arid world regions, is severely affected due to a decrease in area under cultivation, an increase in area under salinization, and a decrease in overall productivity of food and fertile soils (Sheikh et al., 2007).

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Chapter 2 – EFFECTS OF BIOCHAR APPLICATION ON SOIL FERTILITY OF A TEMPERATE SOIL AND PEARL MILLET (*Pennisetum glaucum* L.) YIELD.

ABSTRACT

The value of biochar for enhancing crop productivity by improving soil nutrient status and simultaneously reducing leaching losses and decreasing the need for fertilizer inputs seems promising; however its potential impacts on temperate agricultural soils still need to be elucidated. To study the effects of biochar amendments on plant-available nitrogen (ammonium NH4⁺ and nitrate NO₃⁻) supply rates, soil fertility, and pearl millet (Pennisetum glaucum L.) yield and growth, a two-year field experiment was conducted under fertilized conditions in a Typic Hapludults in Blacksburg (VA). Biochar treatments consisted of peanut shell (Arachis hypogea L.) and mixed pine (Pinus spp.) wood biochar at three application rates (0, 10, and 20 Mg ha^{-1}) with three replicates per rate in a completely randomized design. Biochar application significantly increased soil total C, total N, and plant available potassium (K) but did not affect soil pH and cation exchange capacity (CEC), available phosphorous (P), ammonium (NH_4^+ -N) or nitrate (NO_3^- -N) concentrations. Millet biomass yields and leaf chlorophyll contents significantly increased under peanut shell treatment at 20 Mg ha⁻¹ over the control by 52% and 13% respectively the first cropping year but were not significantly different between biochar treatments the second cropping season due to growing conditions such as rainfall deficit. Improvement of soil productivity and crop production enhancement with biochar addition may be attributed to its relatively high nutrient content and properties. The results of this study suggest that application of peanut shell and pine wood biochar could improve total

soil C and N, and plant available K and crop productivity in temperate soils. However, limited availability of inorganic N could minimize the beneficial effects of biochar amendment on crop productivity despite considerable accumulation of macronutrients.

INTRODUCTION

Long term application of biochar to cultivated soils has been shown to improve soil fertility and increase crop productivity in *Terra Preta* or Amazonian dark earth soils when compared to the surrounding Oxisols (Lehmann et al., 2003a). The positive effects on these nutrient leached and weathered tropical soils have been attributed to large amounts of stable organic matter and high concentrations of nutrients (Lehmann et al., 2003b). The high amounts of stable organic matter were developed through both natural and anthropogenic burning activities (Glaser et al., 2002; Novotny et al., 2009). In addition, the positive agronomic effects in these tropical, highly weathered soils are mainly attributed to biochar's high pH values (Yamato et al., 2006) which help reduce AI toxicity (Steiner et al., 2008; Van Zwieten et al., 2009; Yang et al., 2013) and its high cation exchange capacity (CEC) (Liang et al., 2006). Biochar high surface charge density and surface area which increase retention of nutrients and reduce leaching losses have been also reported beneficial for crop production (Laird et al., 2010; Lehmann et al., 2003b; Novak et al., 2009a).

Potential agronomic and environmental benefits in tropical soils in response to biochar addition have resulted in research interest in biochar as a soil amendment and its use as a carbon sequestration technology (Chan et al., 2008; Lehmann et al., 2003a; Sohi et al., 2010). In temperate regions, Rogovska et al. (2014) reported an increase in maize grain yield after applying mixed hardwood biochar to a Typic Hapludolls. The mixed hardwood biochar used in this experiment was composed of 78% C, 0.6 % C, 8% ash, and 13% volatile matter with a pH equal to 8.8. Greater productivity was attributed to increased soil pH and organic carbon, and decreased bulk density, along with adsorption

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of allelochemicals by biochar. Brantley et al. (2015) also found higher corn yields when the crop was grown with biochar in combination with fertilizers in a silt loam in the Mid-Southern U.S. The pine woodchip biochar used in this study was alkaline (pH of 8.7) with an electrical conductivity (EC) over 5 dS \cdot m⁻¹ and 24% total C and 0.1 % total N. The increased yield in response to biochar was a function of improved nitrogen use efficiency. The authors reported increased ammonium-N sorption to biochar surfaces and reduced inorganic N leaching. Beech wood biochar (pH of 9.0, 80% C, and 0.4% N) addition to a Mollisol increased spring barley (Hordeum vulgare L.) yield 10% during a prolonged drought, an increase that was attributed to an increase in soil water content (Karer et al., 2013). However, other research suggests biochar may not result in significant improvements of soil fertility and crop growth in a temperate environment (Kloss et al., 2014; Major et al., 2010). Positive effects in temperate regions have been hypothesized to require long term interactions with soils for expression of its potential benefits (Jay et al., 2015). Limited investigations of potential of effects of biochar additions on soil fertility and on crop productivity have been also reported (Atkinson et al., 2010; Karer et al., 2013; Laird et al., 2010; Lehmann et al., 2006; Lehmann and Joseph, 2015; Prommer et al., 2014; Rajkovich et al., 2012) in temperate regions. Of the studies conducted in temperate climate regions, few have determined the agronomic impact of biochar as a soil amendment in field-based experiments.

Soils in temperate regions may be less responsive to biochar application than highly weathered, nutrient-poor tropical soils (Atkinson et al., 2010). In addition, the suitability of the resulting biochar for agronomic and other ecosystem applications (Zhang et al., 2015) depend mainly on the properties of the biomass materials and

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pyrolysis processing conditions (Zornoza et al., 2016) (Jung et al., 2016; Lehmann and Joseph, 2009; Manyà, 2012; Mimmo et al., 2014; Ogawa et al., 2006a; Tripathi et al., 2016). Temperate soils have higher pH values, greater soil organic matter, high-activity clays, lower oxide contents, and higher amounts of plant nutrients compared to highly weathered tropical soils (Brady and Weil, 2008).

Lack of benefit or even detrimental responses in terms of soil fertility and crop productivity have been reported (Blackwell et al., 2009; Gaskin et al., 2010; Jones et al., 2012; Kloss et al., 2014; Nelissen et al., 2015; Quilliam et al., 2012; Sun et al., 2014) and may reflect different biochar properties which are a function of feedstocks and process conditions (and which are discussed later). Gaskin et al. (2010) observed reduced corn yield after applying peanut hull biochar (73% C, 1.9 % N, pH = 10.12) at 11.2 Mg·ha⁻¹ to Kandiudult soil in the southeastern United States. Significant differences were not found between control soils and biochar-amended soils when 22.4 Mg·ha⁻¹biochar were applied In a study conducted by Rajkovich et al. (2012), biochars produced from dairy manure, paper sludge, or food waste caused a decrease in corn growth when applied at 26 Mg ha⁻¹ to a fine-loamy, mixed, mesic Glossoboric Hapludalf. Jay et al. (2015) explored the effects of sweet chestnut (Castanea sativa Mill.) wood biochar with a pH ranging from 9.0 to 9.2 and composed of 66% C and 0.03% N on crop yield. Chestnut wood biochar applied to a sandy loam soil had no effect on the growth or harvest yield of spring barley (Hordeum vulgare L.), strawberry (Fragaria × ananassa Duch.) and potato (Solanum tuberosum L.), possibly due to limited nitrogen benefits after biochar application. The limited response to biochar application might be also explained by the short time frame (two years) of this field experiment (Jay et al., 2015). , and in some cases long-term

biochar studies in fertile, temperate soils may be required for expression of the potential agronomic benefits (Atkinson et al., 2010). In contrast, Rogovska et al. (2014) reported an increase in maize grain yield after applying mixed hardwood biochar to a Typic Hapludoll at very high rates (96 Mg \cdot ha⁻¹). Greater productivity was attributed to increased soil pH and organic carbon, and decreased bulk density, along with adsorption of allelochemicals by biochar. Brantley et al. (2015) reported higher corn yields when the crop was grown with biochar in combination with fertilizers. This response was a function of improved nitrogen use efficiency by increasing ammonium-N sorption to biochar surfaces and reducing inorganic N leaching. Biochar addition to a Mollisol increased barley (Hordeum sativum) yield 10% during a prolonged drought, an increase that was attributed to an increase in soil water content (Karer et al., 2013). These varied results in temperate cropping systems – due to different soil types, crop investigated, and biochar properties and production processes (Brantley et al., 2015; Kloss et al., 2014) suggest separate investigations are required to better understand and ultimately to achieve the more typically positive effects of biochar application reported in studies in tropical regions (Atkinson et al., 2010; Güereña et al., 2013).

Biochar properties and application rates can induce positive or negative impacts on soil quality and crop productivity (Spokas et al., 2012a). A meta-analysis conducted by Liu et al. (2013) reported that biochar amendment increased crop productivity an average of 11% when applied at rates equal or lower than 30 Mg ha⁻¹. However, little information on biochar addition rates in field studies is available regarding effects of biochar application in temperate regions.

The purpose of this study was to investigate the effects of biochar properties and application rates on fertility and nutrient retention and its effects on crop production in temperate soils. This study had three objectives: (1) to investigate the effects of different biochar concentrations on soil pH, CEC, and nutrient status over two years in a field experiment; (2) to study the influence of different biochar sources and rates on inorganic nitrogen pools and fluxes; and (3) to compare the impacts of biochar sources and rates on pearl millet yields, growth, and leaf chlorophyll concentrations.

MATERIALS AND METHODS

Site conditions

A 2-year field experiment established in July 2014 was conducted at Virginia Tech's Kentland Agricultural Research Farm in Blacksburg, VA (37°11'47.3"N 80°34'49.7"W). The site has a temperate humid climate with the previous 10-year average monthly temperatures of 21, 22, 22, and 18°C during June through September and mean monthly precipitation of 83, 113, 67, and 60 mm. Temperature and precipitation data at the farm were collected with an on-site weather station and all data reported here were acquired from the college farm website (http://www.vaes.vt.edu/college-farm/about/index.html) and used to determine measurements of rainfall, maximum and minimum air temperature.

Soils on the site are very deep, well drained, and moderately permeable, classified as Unison and Braddock loams (fine, mixed semiactive, mesic Typic Hapludults) with 2 to 7 % slopes (Soil Survey Staff, 2014). Prior to the experiment, the site had been under a mixed perennial-annual species vegetative cover under limited management. This cover was killed with glyphosate (2 l ha⁻¹) and plots then were tilled with a tractor and rototiller. Following ground preparation the biochar treatments were applied.

Experimental Design

A completely randomized design with three replications was used to test the effect of two biochar sources (peanut shell and mixed pine wood) applied at three rates (0, 10, and 20 Mg ha⁻¹) on millet production. Biochars used in this study were purchased from a commercial greenhouse which has developed a test pyrolysis facility, and were created

using a top-lit updraft slow pyrolysis system heated to approximately 535°C. Despite the much higher application rates often reported in the literature, moderate biochar application rates were chosen for this study because they were considered at or just above the rates that might be economically feasible at a farm scale. Biochars treatments were applied once at the beginning of the field experiment, i.e., prior to the 2014 growing season. Biochars were weighed and applied to individual $2\text{-m} \times 3\text{-m}$ plots which were separated by a minimum 0.6-m border. Following application, biochars were evenly distributed across each plot with a metal rake and plots were then fertilized by hand. Biochar and fertilizer were incorporated with a rototiller to a depth of 7.5 to 10 cm. Fertilizer (urea, 100 kg N ha⁻¹) was surface applied in 2015 to avoid disturbing the plots and thus minimize losses of char to the border areasN fertilizations rate recommendations often suggest about 70 to 90 kg ha⁻¹ at planting and similar or lower application rates after each cutting (typically two or three). We chose the higher initial fertility rate based on a single application and a single end-of-season harvest.

Crop production and harvest

Hybrid pear millet was grown on the plots to test the effect of biochar source and rate treatments on crop productivity. Millet was seeded into the plots at 13.5 kg ha⁻¹ using a no-till drill (Great Plains Manufacturing, Salina, KS) in 38-cm row widths. Millet seed were drilled into the plots on 18 July 2014 and 26 June 2015 and plants were grown each season under rain-fed conditions. Millet harvests occurred 20 October 2014 and 2 October 2015. Following the 2014 growing season, plots were sown with wheat (*Triticum aestivum* L.) as a winter cover crop. Data on winter wheat yield were collected but are not presented here.

Pearl millet biomass yields were determined by hand harvesting a 1.5-m² area in the center of each plot. After harvest, a subsample of 6 plants was collected and fresh weight was measured in the field. The subsamples were oven dried for 2-3 days at 55°C to constant weight and the fresh and dry weights were used to calculate plant dry matter concentration and plot yields. To determine the effects of biochar on plant components, each plant was separated in inflorescence, leaf, and stem and dry weight was recorded for each parameter.

Measurements of leaf chlorophyll content

Chlorophyll concentrations reported as atLEAF units were made using the atLEAF+ chlorophyll meter (FT Green LLC, Wilmington, USA) on the last fully expanded leaf on each of 6 plants randomly chosen within a plot (Dunn and Goad, 2015; Novichonok et al., 2016). AtLEAF readings were taken at three points (at the tip and on the left and right edges in the longitudinal center) on each leaf, and the mean of the readings was recorded and averaged for each plant to increase the accuracy of the measurements (Dray et al., 2012; Zhu et al., 2012).

Biochar characterization

Biochar properties (ash content, pH, EC, CEC, C:N ratio, elemental composition) are presented in Table 2.1. The moisture content of the biochars was determined by placing approximately 1 g of biochar sample into dry porcelain crucibles and drying in a forced draft oven (Yamato Mechanical Convection Ovens, DKN Series, Yamato DKN600) at 105°C for 2 h. The dried samples were placed in a desiccator for 1 h and then weighed. Moisture content was calculated as the mass loss after heating

Dried char samples in crucibles then were used to determine ash content. Crucibles with char were covered with lids and placed in a muffle furnace (Thermolyne Furnatrol Type 53600 Controller) at 750°C for 6 h. The crucibles were allowed to cool with lids in place in a desiccator for 1 h and weighed (ASTM, 2007a).

Biochar pH and EC values were measured in triplicate by adding water to biochar samples (1 g of biochar : 20 mL deionized water) and agitating at low speed with an Eberbach's E6000 variable-speed mid-range reciprocal shaker for 1.5 h to ensure sufficient equilibration between solution and biochar surfaces. Then, the suspensions were filtered with Whatman 42mm filter paper, and pH and EC were determined respectively with a pH electrode and an EC meter (Rajkovich et al., 2012).

For total C and N, biochar samples were ground and sieved to 1 mm particle size (diameter). Carbon and N were analyzed using dry combustion using a vario MAX CNS Element Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) following the (ASTM, 2007b) procedures.

Available nitrate-N (NO₃⁻ -N) and ammonium-N (NH₄⁺-N) were determined in triplicate with 2M potassium chloride (KCl) extraction (3 g of biochar : 30 mL of 2M KCl), followed by spectrophotometry (Rayment and Higginson, 1992).

To determine the cation exchange capacity of the biochars, 1.0 g of sample was saturated with 50 mL of 1M ammonium acetate at pH 7 and placed on a shaker table overnight to ensure sufficient wetting of the biochar surfaces. After shaking, the initial 50 mL of 1M ammonium acetate were extracted by vacuum with an automatic extractor, and a second dose of 40 mL ammonium acetate was added. The extracted ammonium acetate was used to determine the exchangeable cations in the biochars by inductively coupled

plasma spectrophotometry (ICP-AES, Spectro CIROS, CCD, Germany) (Rajkovich et al., 2012). After extraction of the ammonium acetate, the biochars were washed three times with a total volume of 60 mL of ethanol. After washing the biochars, each sample received 50 mL of 2M KCl and allowed to stand 16 h in order to replace the absorbed NH₄⁺ cations. After extraction of the initial 50 mL, an additional dose of 40 mL of 2M KCL was added and then extracted. The extracted NH₄⁺ was quantified using a continuous flow analyzer (Technicon Auto Analyzer, Chauncey, CT, USA) and was used to determine the CEC of the biochars.

Total P, Ca, Mg, K, and Na of the biochars were determined after a complete digestion using a MARS Xpress Microwave Digestion System (MARS 5, CEM Corporation, Mathews, NC, USA). To each sample digestion vessel, 0.5g of sample and 8 mL of nitric acid (HNO₃) were added and this was allowed to stand open in a hood overnight to predigest the samples. Two (2) mL of hydrogen peroxide ($H_2O_2 - 30\%$) were then slowly added to the samples and allowed to stand in the open vessels for 45 minutes. The vessels were sealed and samples were digested using 55-mL MARS Xpress vessels heated at 1600W at 75% power and putting the tubes (12 samples) in the machine's inner row. Samples were held at 200°C for 20 min and held 15 min at 200°C. Vessels were removed from the block and allowed to cool before diluting with deionized water to achieve 8% acid concentration. The samples were then allowed to stand overnight and filtered. Total elemental composition was measured using Inductively Coupled Plasma Spectroscopy- Mass Spec (ICP-MS) analysis (Enders and Lehmann, 2012; Rajkovich et al., 2012). All biochar analyses were conducted at the laboratory facilities of Crop and Soil Environmental Sciences Department, Virginia Tech (Blacksburg, VA).

Soil sampling and analysis

Soil samples (0 to 15cm depth) were collected before biochar application and after harvest each season. Three subsamples per plot (6 m²) were taken using a soil probe, composited, and crushed gently. Soil samples were air dried and pH was determined using a 1:1 soil: deionized water mixture. Buffer pH was determined by mixing Mehlich buffer solution with the soil- deionized water mix from the water pH determination in a 1:1 (volume/volume) ratio (Maguire and Heckendorn, 2011). Estimates of soil cation exchange capacity and exchangeable bases were made following extraction with Mehlich 1 buffer containing 0.05N HCl in 0.025N H₂SO₄ (Maguire and Heckendorn, 2011). Plant available Ca, Mg, P, and K were extracted with a Mehlich 1 solution (Maguire and Heckendorn, 2011; Mehlich, 1953) and measured by inductively coupled plasma spectrometry (ICP, Thermo Jarrell-Ash model 61E, Thermo Fisher Scientific, Waltham, MA). Total C and N were analyzed by dry combustion using vario MAX CNS Element Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

Nitrate and ammonium in soil solution

Anion and cation exchange membranes (IEMs) were used to assess temporal changes in soil inorganic nitrogen concentrations (Bowatte et al., 2008; Gibson et al., 1985; Huang and Schoenau, 1996; Johnson et al., 2005; Qian and Schoenau, 2002). The IEMs (GE Power and Water, Trevose, PA, USA) were cut into 5 cm x 10 cm rectangles and a 6.3-mm diameter hole was punched through each membrane so that a nylon string could be attached to the resin to facilitate recovery. The total single-membrane surface area was 43.7 cm². The IEMs were thoroughly washed with deionized water twice, washed for 10 min in 5% HCl solution, rinsed with deionized water twice, and placed in a

saturated solution of 1M NaCl for at least 24 h to load the cation and anion-exchange sites with Na^+ and Cl^- ions respectively for exchange with NH_4^+ (ammonium) and NO_3^- (nitrate) in the soil.

In each plot, two pairs of cation and anion exchange membranes were carefully inserted vertically (0-10 cm depth) into the soil without further disturbance for adsorption of NO₃⁻-N and NH₄⁺-N (Cooperband and Logan, 1994). The IEMs were removed and replaced at 4-week intervals for 3 successive periods, allowing a total of 12 weeks of cumulative nutrient supply to be recorded. Upon removal, freshly charged replacement IEMs were placed in the same hole. The retrieved membranes were rinsed with deionized water to wash any soil residues, and placed in zip-lock bags upon return to the laboratory. Once in the laboratory, the IEMs were placed in 500-mL Nalgene bottles containing 50 mL 1M KCl, and shaken for 1 h on an oscillating shaker to desorb NH₄⁺_N and NO₃⁻ N from IEMs into HCl solution. After harvesting, approximately 3 g of soil from a composite soil sample taken in each plot was placed in 50 mL centrifuge tube containing 30 mL 2 M KC1, and shaken for 30 min. The concentrations of NH_4^+ -N and NO_3^{-} -N in soil and IEM extracts (expressed in μ g-N / cm²) were determined using Lachat QuikChem AE flow-injection autoanalyzer and ion chromatography. After extraction, the IEMs were cleaned and recharged following the procedure described previously.

Data processing and statistical analysis

The statistical analyses were performed with JMP Pro version 12.0.1 statistical software (SAS Institute Inc., Carey, NC). Two-way analysis of variance (ANOVA) was used to test the effects of year, treatment and year x treatment interaction and differences were considered significant at $\alpha = 0.05$ level of probability. When treatment effects were

significant, means were separated using Tukey's honestly significant difference (HSD) test.

RESULTS

Precipitation during the 2014 (July through September) and 2015 (June through August) growing seasons was below the previous 10-year average (144 mm vs. 263 mm in 2014 and 99 vs. 240 mm in 2015) (Figure 2.1). Average monthly temperatures during the 2014 and 2015 growing seasons were 20°C and 22°C whereas the previous 10-year average were 21°C and 21°C respectively (Figure 2.1).

Biochar Analysis

Peanut shell (PS) biochar had slightly higher pH and about 33% greater EC than the pinewood (PW) biochar (Table 2.1). The higher EC value of peanut shell biochar likely was a function of the greater concentration of salts, which often were twice as high in the peanut shell biochar.

The peanut shell biochar in this study had similar properties to that of the char used by Gaskin et al. (2010) in terms of pH (10.2 vs. 10.1) and C:N ratio (31 vs. 38). However, char used in our study was produced at higher temperature (535 vs. 400°C) and without steam. Our char had low C (19 vs. 739%) and N (0.6 vs. 1.9%) concentrations. and moderate ash (6.0%) The C and N in the peanut shell biochar used by Gaskin et al. (2010) and in this study may reflect the potential range, as Chang et al. (2016) reported a peanut biochar produced under 350°C had 44.0% C, 1.0% N, ash content of 27.9% for a pH equal to 8.6.

The mixed pine wood biochar used in this field study had pH of 9.6 and was composed of 5.1% ash, 16% C, 0.3% N, corresponding to a C:N ratio of 60. The C and N contents of the mixed pine wood biochar is less than the pine wood biochar used by Chintala et al. (2014), which was produced from fast pyrolysis at 650°C. Their charhad

pH of 5.8, 83% C, and 0.4% N. Sika and Hardie (2014) also reported a pine (*Pinus radiata* L.) wood biochar with a greater C (83%), N (0.5%) for C:N ratio of 156 with a pH of 9.4. The pine wood biochar was produced from sawmill waste and was slow-pyrolyzed at approximately 450°C.

Effect of biochar on soil nutrients status

Soil pH and CEC were numerically greater in year 2 than in year 1, but neither parameter was significantly affected by biochar treatment. Soil C concentrations were greater in year 1 than in year 2 and levels were strongly correlated ($r^2 = 0.702$ PS and $r^2 = 0.730$ PW) with increasing rates of biochar application with both peanut shell and mixed pine wood biochars (Table 2.2). Soil N was increased by peanut shell char at the highest rates of application (Table 2.2), but levels were not affected by mixed pine wood char application (Table 2.2).

Biochar tended to increase soil P (P = 0.0825) above that in the control plot soils. As with N, soil K was increased with levels of peanut shell char but was unaffected by mixed pine wood char application (Table 2.2). Neither soil Ca nor Mg concentrations were affected by biochar treatment, although levels of these minerals consistently were greater in year 2 (Table 2.2).

Effect of biochar on nitrogen supply rates

Application of biochar to soils had no significant effect on NH_4^+ -N (Figure 2.2) and NO_3^- -N (Figure 2.3) supply rates in either year (Table 2.3). In addition, total NH_4^+ and NO_3^- -N pools were much lower in 2015 compared to 2014 in the surface soil (0-10 cm depth) for biochar treatments. Analysis of total inorganic N showed that NO_3^-

concentrations accounted for more than 94% and 98% of soil inorganic N for biochar treatments, while NH_4^+ proportion was lower than 4% and 2% in 2014 and 2015, respectively (Table 2.3).

The differences in the concentration and temporal patterns of NH_4^+ and NO_3^- supply rates were dissimilar after biochar application. Following the initial N fertilization, NH_4^+ extracted from the IEMs concentrations were lower at the 4- and 8- week sampling times but 4 to 5 times greater at the end of the growing season (12 weeks) in 2014 (Figure 2.2). A similar pattern was observed in 2015, although the available NH_4^+ was several-fold lower than in 2014 (Figure 2.2). In contrast, NO_3^- content peaked at a much higher concentration and reached an average of 177 µg cm⁻² in 2014 and 111 µg cm⁻² in 2015 at the first sampling date (4 weeks) following N fertilizer application (Figure 2.3). Extracted NO_3^- -N levels were much lower at the 8-wk measurement period but tended to increase by 12 weeks, reaching an average 66 µg cm⁻² in 2014 and 10 µg cm⁻² in 2015 (Figure 2.3).

Effect of biochar on millet yield

Year × treatment interactions were significant (P < 0.0077) thus data were analyzed and are presented by year. Millet dry biomass yields were significantly different (P < 0.0025) among biochar treatments in 2014 but were not significant (P < 0.6125) in 2015 (Table 2.4). A maximum value of millet dry biomass of 9.26 Mg ha⁻¹ was observed when peanut shell biochar was applied at 20 Mg ha⁻¹ compared to 4.43 Mg ha⁻¹ in the control, corresponding to a 109 % yield increase in 2014 (Table 2.4). In contrast, the yield of millet was not significantly affected by biochar amendments in 2015.

Similar to the millet dry biomass, year × treatment interactions were only significant for leaf (P < 0.012) and stem (P < 0.020 component yields, largely due to declines in millet dry biomass yields from year 1 to year 2. Inflorescence, leaf, and stem component yields were higher (P < 0.002) in the biochar-amended plots compared to that of the control in 2014 (Table 2.4). Among treatments applied, 20 Mg ha⁻¹ of peanut shell had the greatest effect on biomass components, nearly doubling inflorescence biomass and more than doubling leaf, and stem growth (Table 2.4). Component yield responses were intermediate with the 10 Mg ha⁻¹ of peanut shell treatment. Total and component yields were less responsive to mixed pine wood biochar application and not different between treatment rates, averaging about a 40% increase across components and mixed pine wood char treatment rates (Table 2.4). In 2015, as with millet dry biomass yield, there was no visible impact of the peanut shell and mixed pine wood biochars on the total inflorescence, leaf, and stem production compared to the control plots (Table 2.4).

Effect of biochar on leaf chlorophyll content

Leaf chlorophyll concentrations were significantly different among biochar treatments in 2014 (P < 0.020) but were not significant (P < 0.272) during 2015 (Table 2.5). In 2014, highest average AtLEAF values (55.6) were observed in millet grown in plots treated with peanut shell biochar applied at 20 Mg ha⁻¹ and lowest (51.0) with millet grown on plots treated with 10 Mg ha⁻¹ of mixed pine wood biochar (Table 2.5). Leaf chlorophyll concentrations were not significantly affected by biochar amendments in 2015. However, although treatment differences were not observed, the lowest numeric AtLEAF reading (37.7) occurred with the lowest rate (10 Mg ha⁻¹) of mixed pine wood biochar application.

DISCUSSION

Biochar amendments to temperate soils often increase soil pH and cation exchange capacity, total soil C and N, and plant available nutrient concentrations. In this study, however, biochar application had no significant effect on soil pH or CEC of amended plots in both 2014 and 2015 when compared to the control plots. Increases in soil pH have been observed in response to peanut biochar addition under greenhouse conditions (Chang et al., 2016; Jiang et al., 2014; Novak et al., 2009b; Wang et al., 2014; Yuan and Xu, 2011) and in response to pine biochar (Robertson et al., 2012; Wang et al., 2016). However, peanut hull and pine chip biochar also have been reported to decrease soil pH, which was attributed to crop uptake and leaching losses of the base cations in a sandy soil (Gaskin et al., 2010). Although biochar can act as a liming agent (Glaser et al., 2002; Lehmann and Rondon, 2006; Van Zwieten et al., 2009) and our biochars were alkaline, the lack of effect on soil pH likely reflects the moderate starting pH (6.41) and relatively high buffering capacity of the soils in this study.

Addition of peanut shell and mixed pine wood biochars did not induce remarkable differences in soil CEC. Lack of CEC response to poultry litter biochar application to Frederick silt loam (fine, mixed, semiactive, mesic, Typic Hapludults) soils in Virginia was also observed by Revell et al. (2012). In studies in which biochar application increased soil CEC, greater negative charge on biochar particle surfaces was measured and this was induced by the presence of functional groups (e.g. carboxyl and hydroxyl) (Liang et al., 2006; Mao et al., 2012; Yuan et al., 2011; Zheng et al., 2013b). It may be that significant increases in soil CEC with biochar application will require more time and

particle weathering, because aging and oxidation of biochar surfaces over time are reported to increase cation adsorption (Atkinson et al., 2010; Cheng et al., 2008).

Biochar application to soils significantly increased total soil C and N compared to un-amended soils. Xu et al. (2015) found that addition of peanut shell biochar increased total soil C and N while Wang et al. (2016) observed similar results after application of pine biochar. The increases in total soil C in biochar-amended soils are readily explained by the large addition of C with biochar treatments. High inputs of C also may limit the decomposition of native soil organic matter because of change in C/N ratio, contributing to the greater concentrations of C in soil (Krapfl et al., 2014; Lehmann et al., 2006). Increased soil N may in part be explained by addition of N from biochar (Table 2.1). Greater total soil N in biochar-amended soils also could be a result of N immobilization (Lehmann et al., 2003b; Rajkovich et al., 2012; Wang et al., 2015b) due to the high C/N ratio of the peanut shell and mixed pine wood biochars inducing enhanced microbial biomass and activity (Brantley et al., 2015).

Peanut shell biochar application resulted in increased plant available K, but had little effect on plant available P, Ca, and Mg. Wang et al. (2014) reported that addition of peanut shell biochar resulted in decreased soil exchangeable acidity and Al saturation and also increased in exchangeable cations. In contrast, wood biochar had no discernible effects on soil cations, which is similar to the results of Brantley et al. (2015), who found limited effects of pine biochar on soil nutrients and corn yield in a silt loam in the midsouthern U.S. The increase in plant available K is explained by the high content of K in peanut shell biochar. However, the lower nutrient concentrations in the mixed pine wood biochar resulted in no measurable effects on soil nutrients. Variations in the types of

biomass feedstocks (Spokas and Reicosky, 2009; Voorde et al., 2014; Wu et al., 2016; Yao et al., 2012) and pyrolysis processes (Bruun et al., 2012a; Cross et al., 2010; Gaskin et al., 2008; Kloss et al., 2014) have been proven to result in differences on the elemental compositions of the resulting biochar (Naeem et al., 2014). These variations could also induce differences on its potential effects on soil properties and crop productivity (Biederman and Harpole, 2013; Jeffery et al., 2011).

Biochar application to soils significantly increased pearl millet aboveground biomass (Table 2.4) and leaf chlorophyll content (Table 2.5) the first year after application, but no significant differences were observed the second year between biochar treatments and control plots. The significant increase of millet growth and AtLEAF values in 2014 on biochar-amended soils could be explained by enhancement of nutrient availability and retention through biochar's intrinsic elemental and compositional nutrients especially N (Atkinson et al., 2010; Biederman and Harpole, 2013; Crane-Droesch et al., 2013; Jeffery et al., 2011; Liu et al., 2013; Spokas et al., 2012a). For the 2015 growing season, there was no evidence of beneficial effects of biochar addition on millet growth and AtLEAF values and IEM measures were indicative of lower N availability. The lower N availability in second year of the experiment could be explained by possible N losses due to surface application of urea in order to limit the disturbance of biochar amended plots.. Gaskin et al. (2010) reported small yield responses after application of peanut hull and pine chip biochar in a low C, low inherent fertility soil due to low rainfall conditions during a 2-year field study. In addition, higher available C as a result of biochar addition may enhance microbial biomass and activity (Bruun et al., 2012a; Kolb et al., 2009). This increase in microbial community and activity could

induce greater N demand by the microbes (Burger and Jackson, 2003) therefore leaving less N available to plants (Nelson et al., 2011).

Reduced rainfall during the first two months of the 2015 growing season (188 mm in 2015 vs. 297 mm in 2014) resulting in less available inorganic N could explain the reduced millet growth in the second year. Temporary decrease in soil NH₄⁺-N concentrations is consistent with the results from the sorption experiments conducted by Yao et al. (2012). As a consequence, lower soil NO_3^- -N concentrations in biocharamended soils may be observed due to less NH_4^+ to be nitrified. Decrease in crop yields of aboveground biomass the second year after biochar application could also be explained by the observed presence of competing weedy vegetation for nutrients and water resources could partly explained as reported by Major et al. (2003). Similar results have been reported by Khairwal et al. (2007) who observed up to 70% decrease in pearl millet yield due greater ability of weeds to compete for nutrients and moisture in agricultural soils under water stress conditions.

CONCLUSIONS

Biochar additions of peanut shell and mixed pine wood were conducted to study their effects on soil nutrients, pearl millet yield and growth, and leaf chlorophyll concentrations in a Typic Hapludults soil during a 2-year field experiment. Biocharamended soils generally increased soil C, N, and plant available K, largely due to high rates of peanut shell char application. A numeric pattern of decreased NH4⁺ -N and NO3⁻ -N concentrations with char application also was observed. Peanut shell biochar significantly stimulated pearl millet growth compared to control plots the first growing season but had no effects on crop yields the following year. Peanut shell biochar's ability to improve soil fertility and enhance pearl millet growth in the first season could be attributed to increased soil nutrient contents through its application. The inconsistent differences in soil and crop responses to biochar application in the second cropping year likely reflect limitations in water availability and inorganic N supply along with presence of competitive weedy vegetation. The results of this experiment in a Typic Hapludults soil demonstrates potential benefits of biochar soil amendment for improving soil productivity and crop growth in temperate soils.

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http://dx.doi.org/10.1016/j.chemosphere.2015.08.046.

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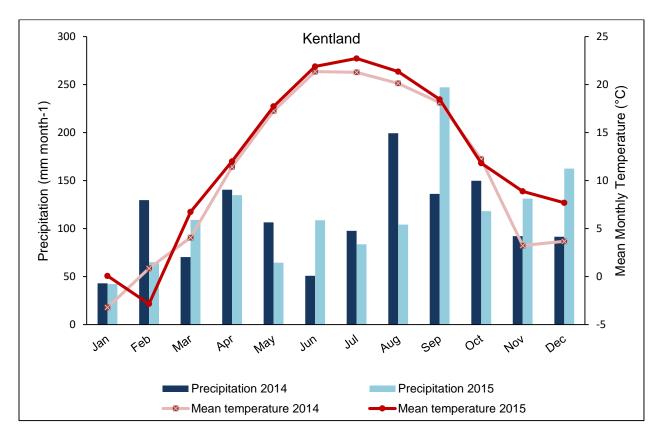


Figure 2.1. Mean monthly precipitation (mm) and temperature (°C) during 2014 and 2015 at Kentland Farm (Blacksburg, VA).

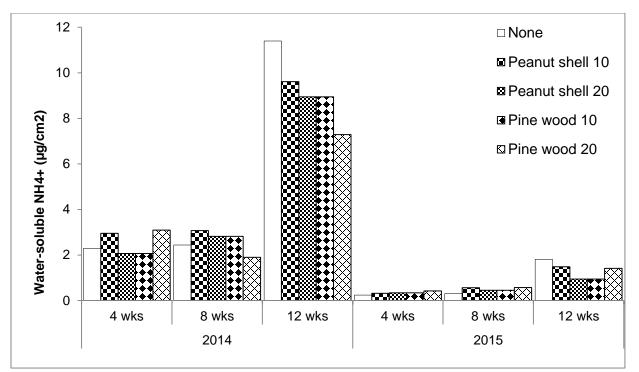


Figure 2.2. Effects of biochar application on soil solution NH4+ -N measured with ion exchange membranes.

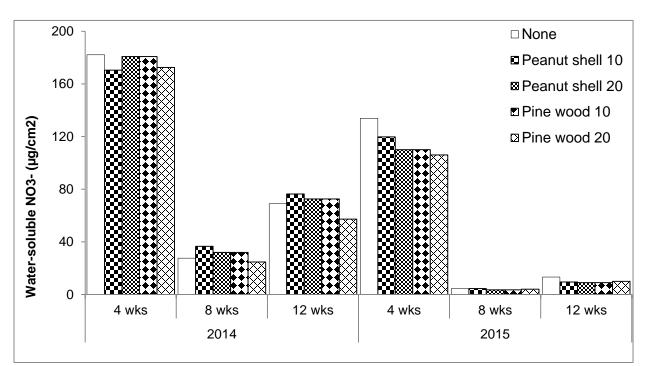


Figure 2.3. Effects of biochar application on soil solution NO3- -N measured with ion exchange membranes.

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Table 2.1. Mean soil (prior to treatment) and peanut shell and mixed pine wood biochars pH, electrical conductivity (EC), total carbon (C), total nitrogen (N), C:N, cation exchange capacity (CEC), plant available nutrients, and total recoverable mineral concentrations (n = 3).

	Soil	Peanut shell char	Mixed pine wood char
Parameter			
Moisture (g kg ⁻¹)		0.618	0.597
Ash (g kg ⁻¹)		0.595	0.512
pH water	6.41	10.2	9.6
EC (dS/m)	0.23	0.82	0.62
C (%)	1.2	19	16.1
N (%)	0.15	0.6	0.3
C:N	10.3	31	60
NO ₃ ⁻ -N (µg/g)	5.92	0.55	0.05
NH_4^+ -N ($\mu g/g$)	2.38	0.02	0.01
CEC (meq/100g)	4.7	22	19
P plant available (mg/kg)	118	145	81
K plant available (mg/kg)	246	9730	6720
Caplant available (mg/kg)	2110	2400	1400
Mg plant available (mg/kg)	566	558	295
Na plant available (mg/kg)		276	137
Total P (mg/kg)		9560	6790
Total Ca (mg/kg)		60930	60830
Total K (mg/kg)		88900	76580
Total Mg (mg/kg)		18090	16930
Total Na (mg/kg)		4970	5840

pH: soil (1:1 soil: deionized water mixture on a volumetric basis) and biochar (1 g of biochar : 20 mL deionized water)

Total carbon (C) and total nitrogen (N): vario MAX CNS Element Analyzer

Inorganic NO3⁻-N and NH4⁺-N: 2M KCl extraction

CEC: soil (Acidity + Ca + Mg + K (in the units of meq/100 g soil or cmol/kg); biochar (1M ammonium acetate +ethanol +2M KCl)

Plant available nutrients: soil (Mehlich 1 solution); biochars (1M ammonium acetate) Biochars total recoverable mineral concentrations: nitric acid (HNO₃) and hydrogen peroxide ($H_2O_2 - 30\%$) digest

Year	Treatment	рН	CEC	С	Ν	Р	К	Ca	Mg
	Mg ha ⁻¹		meq/100g		g kg ⁻¹		mg kg	-1	
2014	Control	6.59	5.35	17.6 d	1.64 bc	122	364 b	2500	709
	PS 10	6.60	5.34	26.3 bc	1.79 ab	148	505 ab	2470	681
	PS 20	6.64	5.14	33.0 a	1.88 a	148	617 a	2350	643
	PW 10	6.60	5.35	25.2 c	1.62 bc	153	361 b	2500	688
	PW 20	6.63	5.14	30.7 ab	1.55 c	145	366 b	2420	691
	S.E.	0.03	0.05	0.90	0.03	1.50	5.49	8.40	2.98
		ns	ns			ns		ns	ns
2015	None	6.73	5.50	12.1 b	1.14 b	125	393 b	2580	759
	PS 10	6.70	5.51	14.9 b	1.17 ab	152	520 ab	2550	724
	PS 20	6.76	5.35	19.7 a	1.27 a	149	572 a	2500	701
	PW 10	6.71	5.48	15.3 b	1.13 b	163	411 b	2550	728
	PW 20	6.72	5.45	19.4 a	1.15 ab	151	407 b	2560	751
	S.E.	0.03	0.07	0.54	0.01	1.83	4.43	11.40	3.66
		ns	ns			ns		ns	ns

Table 2.2. Mean pH, CEC, total C and N, Mehlich I extractable nutrient concentrations in soil (0–15 cm) as affected by peanut shell and mixed pine wood biochar during the 2014 and 2015 growing seasons.

S.E. standard error. Peanut shell (PS) and pine wood (PW) biochars were added at rates of 10 and 20 Mg ha⁻¹. Different letters in a column indicate significant differences (Tukey test (P<0.05) between biochar source and rate (0, 10, 20 Mg ha⁻¹) treatments in a single year. ns: not significant at p < 0.05.

Table 2.3. Total extractable NH_4^+ -N and NO_3^- -N ($\mu g \text{ cm}^{-2}$) in soil amended with peanut shell and mixed pine wood biochar during the 2014 and 2015 growing seasons

Year	Treatment	$\mathrm{NH_{4}^{+}}$	NO ₃ -
	${ m Mg}~{ m ha}^{-1}$	μg c	m^{-2}
2014	None	16.1 ± 1.9 a	279 ± 44 a
	Peanut shell 10	$15.6 \pm 1.4 \text{ a}$	283 ± 40 a
	Peanut shell 20	$13.8 \pm 2.5 \text{ a}$	$285 \pm 56 a$
	Pine wood 10	12.3 ± 2.0 a	255 ± 58 a
	Pine wood 20	$16.1 \pm 1.8 \text{ a}$	261 ± 55 a
	S.E.	0.86	21.90
2015	None	2.36 ± 0.5 a	152 ± 27 a
	Peanut shell 10	2.37 ± 0.4 a	134 ± 23 a
	Peanut shell 20	1.74 ± 0.3 a	123 ± 26 a
	Pine wood 10	2.40 ± 0.8 a	120 ± 24 a
	Pine wood 20	2.20 ± 0.3 a	100 ± 29 a
	S.E.	0.23	11.53

S.E. standard error. Values represent arithmetic mean. Different letters indicate a significant difference among the biochar treatments in a single year, which was determined by the Tukey test (P<0.05).

Table 2.4. Mean of millet dry biomass yield (Mg ha⁻¹), inflorescence, leaf, and stem as affected by peanut shell and mixed pine wood biochar during the 2014 and 2015 growing seasons

Year	Treatment Mg ha ⁻¹	Millet dry biomass Mg ha ⁻¹	Inflorescence Mg ha ⁻¹	Leaf Mg ha ⁻¹	Stem Mg ha ⁻¹
2014	None	4.43 b	0.87 b	1.56 b	2.01 b
	Peanut shell 10	6.69 ab	1.14 ab	2.13 ab	2.86 ab
	Peanut shell 20	9.20 a	1.61 a	3.15 a	4.17 a
	Pine wood 10	6.12 ab	1.15 ab	2.16 ab	2.81 ab
	Pine wood 20	6.45 ab	1.19 ab	2.3 ab	2.97 ab
	S.E.	0.40	0.07	0.13	0.19
2015	None	3.60 a	0.75 a	1.37 a	1.40 a
	Peanut shell 10	3.92 a	0.85 a	1.60 a	1.51 a
	Peanut shell 20	3.80 a	0.87 a	1.55 a	1.59 a
	Pine wood 10	3.53 a	0.70 a	1.46 a	1.37 a
	Pine wood 20	3.20 a	0.73 a	1.29 a	1.28 a
	S.E.	0.15	0.04	0.06	0.07

S.E. standard error. Different letters indicate a significant difference among the biochar treatments in a single year, which was determined by the Tukey test (P<0.05).

Year	Treatment Mg ha ⁻¹	AtLEAF Readings		
2014	None	52.0 ab		
	Peanut shell 10	54.3 ab		
	Peanut shell 20	55.6 a		
	Pine wood 10	51.0 b		
	Pine wood 20	52.0 ab		
	S.E.	0.50		
2015	None	38.4 a		
	Peanut shell 10	42.3 a		
	Peanut shell 20	41.9 a		
	Pine wood 10	37.7 a		
	Pine wood 20	41.2 a		
	S.E.	0.84		

Table 2.5. Mean of AtLEAF values as affected by peanut shell and mixed pine wood biochar during the 2014 and 2015 growing seasons.

S.E. standard error. Different letters indicate a significant difference among the biochar treatments in a single year, which was determined by the Tukey test (P<0.05).

Chapter 3 – EFFECTS OF BIOCHAR AND MANURE APPLICATIONS ON SOIL FERTILITY OF A TROPICAL, SANDY, SALT-AFFECTED SOIL AND PEARL MILLET (*Pennisetum glaucum* L.) YIELD.

ABSTRACT

Projected increase of the world's population is occurring at the same time that salt-affected lands and saline-contaminated water resources are expanding. Finding means to reclaim and effectively use salt-affected soils could be key to improving soil nutrient status and increasing world crop productivity, especially in semi-arid and food insecure regions. Biochar amendment could be an effective option for alleviating salinity stress in sandy, salt-affected croplands given its potential water and nutrient retention capacity. This study investigated potential of two biochar sources to decrease salinity and improve fertility of a salt-stressed soil. A two-year field experiment tested the effects of a one-time application of peanut shell (Arachis hypogaea L.) and eucalyptus (Eucalyptus *camaldulensis*) wood biochars to a tropical, sandy, and salt-affected soil in Senegal. Biochars were applied at 0, 10, and 20 Mg ha⁻¹ with or without cattle manure. Peanut shell biochar applied at 10 Mg ha⁻¹ in combination with manure significantly increased soil carbon (C) and calcium (Ca) in year 1, but statistical differences were not seen in soil pH, electrical conductivity (EC), sodium adsorption ration (SAR), soil nitrogen (N), and available phosphorous (P), potassium (K) and magnesium (Mg). No treatment effects on soil chemical properties in the second cropping year were observed. Biochar treatment had a moderate effect on salinity reduction and nutrient concentration increases in the salt-stressed soil. Overall, the results suggested that addition of peanut shell and

eucalyptus wood biochars did not significantly reduce soil salinity, improve soil fertility, or increase crop yields compared to control plots in the salt-affected croplands.However, research challenges from this study and successful results in other studies suggest, further investigation should be carried out to design suitable biochar treatments to alleviate salinity stress and enhancesoil fertility in arid climates.

INTRODUCTION

Widespread occurrences of salt-affected lands and future projections for their extensive use in agriculture as demands for food and energy are expected to increase (Pitman and Läuchli, 2002; Qadir et al., 2008b) suggest the need for their reclamation and effective utilization (Amini et al., 2016; Diacono and Montemurro, 2015). Thus, efforts to promote sustainable farming practices, protect cultivated soils from degradation, and to reclaim salt-affected soils which have lost their productivity as well as to develop marginal lands should be top priorities (Lakhdar et al., 2009; Pessarakli, 1991) and different approaches have been hypothesized to improve the properties of these soils (Ahmad and Chang, 2002; Gupta et al., 1985; Rengasamy, 2010; Sharma and Minhas, 2005).

In order to effectively reclaim salt-affected soils, their nature and formation must be taken into consideration. Saline and sodic soils differ in their physical and chemical characteristics, the effects and interactions of varying edaphic, geographic, and hydrologic factors (soil permeability, water table depth, salinity of perched groundwater, soil parent material), management factors (irrigation, drainage, tillage, cropping practices), as well as climate-related factors (rainfall amount and distribution, temperature, relative humidity, wind) (Pessarakli, 1991; Rhoades et al., 1997). The reclamation of salt-affected soils is a practice that has been in use prior to scientific knowledge on the nature and properties of the soils (Abbas et al., 1994; Irshad et al., 2007). The maintenance of adequate soil physical and chemical properties in salt-affected lands may be achieved by using good quality water to accelerate soil desalinization processes by leaching salts through the profile (at least where leaching is possible)

(Abbas et al., 1994; Corwin et al., 2007; Häfele et al., 1999; Prasad et al., 1995; Sisodia et al., 2013; Tan and Kang, 2009). Brunet (1994) explored the effect of an anti-salting dam in reclaiming saline soils in Casamance (Senegal) and reported an increase in rice yield due to water management. In addition, physical approaches such as deep plowing, sub-soiling, profile inversion between the lower layer material and the salt-stressed soil layer, and water application have been proposed as means to reclaim salt-affected soils (Sheikh et al., 2007; Wong et al., 2009) by decreasing salt concentration in the soil profile occupied by the root zone to reclaim salt-effected soil.

Chemical treatments such as amendment with gypsum, calcium chloride, and limestone have been used as reclamation methods for salt-affected soils (Gharaibeh et al., 2010; Ilyas et al., 1997; Mzezewa et al., 2003). Gypsum application to salt-affected soils has been reported to increase wheat yield due to due to enhanced soil infiltration rate, pH, EC_e, and SAR (Ghulam et al., 2015). Greater rice and millet biomass and grain yields also were observed due to improvements in soil physicochemical properties (Ezeaku et al., 2015). Selection of salt-tolerant species coupled with crop rotation and diversification is another major approach to prevent or even reclaim salt-affected soils (Qadir et al., 2008a; Rao and Pathak, 1996; Ravindran et al., 2007; Rengasamy, 2010; Sadiq et al., 2007; Tejada et al., 2006). Application of manure and organic material, notably in the form of crop residues, are common practices on salt-affected areas and can reduce surface evaporation, improve soil aggregation, increase soil organic carbon stocks, increase water infiltration, and improve water holding capacity (Al-Busaidi et al., 2014; Kumar, 1996; Lal, 2001). (Sall et al., 2015) explored the effects of the "camel's foot" (*Piliostigma reticulatum*) residues on microbial response in a Senegalese tropical sandy soil and

reported greater structure and an increase in microbial biomass. A significant decrease in bulk density and increase in hydraulic conductivity from organic amendments in salt-affected soils was reported by (Shendurse et al., 2014); however, changes in soil pH, electrical conductivity and cation exchange capacity were not observed. Furthermore, the application of organic matter has been shown to increase soil microbial biomass and some soil enzymatic activities, and to favor plant cover (Tejada et al., 2006). Integration of physical, chemical, and biological methods can be more effective and also enhance crop productivity and fertilizer use efficiency (Ezeaku et al., 2015). (Ullah et al., 2015) reported maximum increase in rice grain yield under salt-affected soils after application of wheat residue along with phosphorus fertilizer due to improvement of the availability of soil P, K, and Ca to plant roots.

Renewable energy sources such as biomass-sourced energy accounted for 11% of global energy consumption and 38% of the world's population relies on biomass as their primary fuel for cooking (IEA, 2015). In Sub-Saharan Africa, about 50% of all primary energy comes from biomass sources. In Senegal, biomass is the major energy source and constitutes about 47% of the country's primary energy supply (Hrubesch, 2011). Senegalese agriculture is characterized by a small average size of farms and a decline in real income of farmers, leading to the sharp reduction in the use of agricultural inputs. Forms of biomass resources, other than wood, include agricultural residues such as millet stalks, and rice hulls; agro-industrial residues such as peanut shells, and cotton (*Gossypum* spp.) stalks; and aquatic plants such as cattails (*Typha australis*) (Table 3.1) (Peracod, 2009).

Senegalese agriculture is challenged to meet the production needs of the country in the face of land degradation by salinization. The reclamation of salt-affected soils, despite having promising beginnings, has not produced the expected results. Proper and cost-effective measures for reducing salt stresses on crop growth are thus a high priority need for technology development in Senegal's agricultural sector. Although there is information available on the physicochemical properties of crop residues and organic manures and their effects on plant growth, very few attempts have been made to study the effect of residue-based biochars as amendments to improve soil fertility and increase crop productivity on salt-affected soil (Sisodia et al., 2013; Thomas et al., 2013). The main objective of this research was to investigate the potential of biochar resources for improving soil quality and crop production in salt-affected soils. Added potential benefits include use of available resources, improved environmental quality and crop production, and alleviation of poverty in rural Senegal. Specifically, we determined the efficacy of biochar as a soil amendment in ferruginous tropical sandy and salt-affected soils. We hypothesized that biochar would improve the physical and chemical properties of a sandy and saline-sodic soil. To test this, we implemented a two-year field experiment with three rates of peanut shell and eucalyptus wood biochars on a ferruginous tropical sandy and salt-affected cropland and examined the effects on soil and pearl millet (Pennisetum glaucum) yield.

MATERIALS AND METHODS

Site location and experimental design

The field experiment was conducted in Ndoff (Figure 3.2.), in the Fatick region of Senegal (14°21′29″N / 16°35′08W). The climate is a Sahelo-Sudanian and Coastal Sudanian characterized by a mean annual temperature of 27 °C to 28 °C and mean annual rainfall values ranging between 400-800 mm, most of which occurs during a three-month rainy season. Weather data collected by Agence Nationale de l'Aviation Civile et de la Météorologie (ANACIM) were used to determine measurements of rainfall (Figure 3.3)

Situated in the West Central Agricultural Region or "Peanut Basin" (25,915km²), the soil types in Ndoff are iron-rich tropical sandy soils, slightly leached from a flat to gently rolling eolian sands overlying a sandstone plateau of the continental sedimentary basin (Tappan et al., 2004).

The study was conducted as a randomized complete block design with nine fertility treatments each replicated three times. Two biochar sources at three application rates (0, 10, 20 Mg ha⁻¹) were tested with and without cattle (*Bos indicus*) manure (0, 100 kg ha⁻¹ of N). Treatments (Table 3.2) were evenly applied on 28 August 2014 by hand to 3-m x 5-m plots and tilled into the soil at 15-cm depth using farm animals.

Following treatment application, millet (cv 'IBMV 8401') was sown on all plots and grown under rainfed conditions. Sowing and harvesting were conducted in mid-August and early November in year 1 and mid-July and early October, respectively. In each plot, eighteen (18) plants per plot were maintained at a 90-cm x 90-cm spacing.

Biochar production and characterization

Biochar produced peanut shell was made using a traditional slow pyrolysis method using hand mixing with shovels during the heating process. Eucalyptus wood biochar was made with an "Adam kiln" in which a fire at one end of the wood-filled kiln is used to force hot air through a series of channels (Diatta and Fall, 2010). The vent gases from the wood were burned from a flue at the opposite end of the kiln. Strict temperature controls were not possible with either method, but it is estimated that peanut shells were pyrolyzed at 350°C (residence time 1 to 5 h) and eucalyptus wood was pyrolyzed at 600 to 750°C with a 28-h residence time (Diatta and Fall, 2010). The eucalyptus biochar used for this study was comprised of screenings that remained after the larger charcoal pieces were removed for sale as an energy source for cooking. The eucalyptus char screenings were piled and weathered for about a year before being collected for this study.

The moisture content of the biochars was determined by adding approximately 1 g of biochar sample to the porcelain crucibles. The crucibles with samples were then placed in a forced draft oven (Yamato Mechanical Convection Ovens, DKN Series, Yamato DKN600) at 105°C for 2 h and the dried samples were placed in a desiccator for 1 h and weighed to determine moisture content.

Ash content was determined by covering the crucibles with lids and placing in the muffle furnace (Thermolyne Furnatrol Type 53600 Controller) at 750°C for 6 h. The crucibles were allowed to cool with lids in place in a desiccator for 1 h and weighed (ASTM, 2007a).

Biochar pH and EC values were measured in triplicate by adding water to biochar samples (1 g of biochar : 20 mL deionized water) and agitating at low speed with an Eberbach's E6000 variable-speed mid-range reciprocal shaker for 1.5 h to ensure sufficient equilibration between solution and biochar surfaces. Then, the suspensions were filtered with Whatman 42mm filter paper, and pH and EC were determined respectively with a pH electrode and an EC meter (Rajkovich et al., 2012).

For total C and N, biochar samples were ground and sieved to 1 mm particle size (diameter). Carbon and N were analyzed using dry combustion using a vario MAX CNS Element Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) following the (ASTM, 2007b) procedures.

Available nitrate-N (NO₃⁻ -N) and ammonium-N (NH₄⁺-N) were determined in triplicate with 2M KCl extraction (3 g of biochar : 30 mL of 2M KCl), followed by spectrophotometry (Rayment and Higginson, 1992).

To determine the cation exchange capacity of the biochars, 1.0 g of sample was saturated with 50 mL of 1M ammonium acetate at pH 7 and placed on a shaker table overnight for a sufficient wetting of the biochar surfaces. After shaking, the initial 50 mL of 1M ammonium acetate were extracted by vacuum with an automatic extractor, and a second dose of 40 mL ammonium acetate was added. The extracted ammonium acetate was used to determine the exchangeable cations in the biochars by inductively coupled plasma spectrophotometry (ICP-AES, Spectro CIROS, CCD, Germany) (Rajkovich et al., 2012). After extraction of the ammonium acetate, the biochars were washed three times with a total volume of 60 mL of ethanol. After washing the biochars, each sample received 50 mL of 2M KCl and allowed to stand 16 h in order to replace the absorbed

NH₄⁺ cations. After extraction of the initial 50 mL, an additional dose of 40 mL of 2M KCL was added and then extracted. The extracted NH₄⁺ was quantified using a continuous flow analyzer (Technicon Auto Analyzer, Chauncey, CT, USA) and was used to determine the CEC of the biochars.

Total P, Ca, Mg, K, and Na of the biochars were determined after a complete digestion using a MARS Xpress Microwave Digestion System (MARS 5, CEM Corporation, Mathews, NC, USA). To each sample digestion vessel, 0.5g of sample and 8 mL of nitric acid (HNO_3) were added and this was allowed to stand open in a hood overnight to predigest the samples. Two (2) mL of hydrogen peroxide (H₂O₂ - 30%) were then slowly added to the samples and allowed to stand in the open vessels for 45 minutes. The vessels were sealed and samples were digested using 55-mL MARS Xpress vessels heated at 1600W at 75% power and putting the tubes (12 samples) in the machine's inner row. Samples were held at 200°C for 20 min and held 15 min at 200°C. Vessels were removed from the block and allowed to cool before diluting with deionized water to achieve 8% acid concentration. The samples were then allowed to stand overnight and filtered. Total elemental composition was measured using Inductively Coupled Plasma Spectroscopy- Mass Spec (ICP-MS) analysis (Enders and Lehmann, 2012; Rajkovich et al., 2012). All biochar analyses were conducted at the laboratory facilities of Crop and Soil Environmental Sciences Department, Virginia Tech (Blacksburg, VA).

Soil sampling and treatment

Soil samples (0 to 15cm depth) were collected before biochar application and after harvest each season. Three subsamples were taken from each 15-m² plot using a soil probe and composited. Soil samples were air dried and pH was determined using a 1:1

soil:water mixture. Buffer pH was determined by mixing Mehlich buffer solution with the soil-water mix from the water pH determination in a 1:1 (vol/vol) ratio (Maguire and Heckendorn, 2011). Soil cation exchange capacity and extractable base cations were determined following extraction with Mehlich 1 solution containing 0.05N HCl in 0.025N H₂SO₄ (Maguire and Heckendorn, 2011). The measured soil pH, EC, and SAR (1) were used to determine the type of salinity of our field plots (US Salinity Laboratory Staff, 1954) (Brady and Weil, 2008) (Rengasamy, 2010). SAR was calculated as follows:

SAR =
$$[Na^+] / [Ca^{2+} + Mg^{2+}]^{\frac{1}{2}}$$
 (1)

where Na⁺, Ca²⁺, and Mg²⁺ are soluble cation concentrations measured in mmol L⁻¹ from saturated paste extractions. Extractable Ca, Mg, P, and K were extracted with a Mehlich I solution (Mehlich, 1953) and measured by inductively coupled plasma spectrometry (ICP, Thermo Jarrell-Ash model 61E,Thermo Fisher Scientific, Waltham, MA). Total C and N were analyzed by dry combustion using a vario MAX CNS Element Analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

Data processing and statistical analysis

Two-way analysis of variance (ANOVA) was used to test the effects of year, treatment and year x treatment interaction and differences were considered significant at $\alpha = 0.05$ level of probability. When treatment effects were significant, means were separated using Tukey's honestly significant difference (HSD) test using JMP Pro version 12.0.1 statistical software (SAS Institute Inc., Carey, NC.

RESULTS

Biochar Analysis

The basic soil and biochar characterizations are summarized in Table 3.3. Peanut shell biochar had higher pH, EC, degradable organic and total carbon concentrations, and greater total nitrogen. However, eucalyptus wood biochar had higher CEC, nitrate, and available calcium but lower available potassium, magnesium, and sodium concentrations (Table 3.3). The low concentration of these exchangeable minerals in the eucalyptus biochar corresponds to lower total calcium and higher total potassium, magnesium, and sodium concentrations compared to peanut shell biochar.

The peanut shell biochar used in this study was composed of 58% ash, 17% C, 1.4% N corresponding to a C:N ratio of 12 with a pH of 8.2, suggesting the traditional synthesis process resulted in a high degree of combustion. In contrast, Debarati et al. (2016) prepared thermally activated peanut shell at $300 \pm 5^{\circ}$ C in a closed muffle furnace for 2 h and reported a 3.3% ash, 56% C, and 0.9% N. Similar to their results, Xu et al. (2015) processed peanut shell at 550 °C and reported 67% C, 1.3% N with an alkaline pH of 10.1. The weathered eucalyptus wood biochar produced using an "Adam kiln" was also of low quality relative to other char processing methods. The char had a pH of 7.6 and contained 68% ash, 16% C, 0.2 N corresponding to a C:N ratio as high as 104. Sun et al. (2013a) produced eucalyptus wood biochar using a homemade midscale low-temperature rotary furnace (up to 400°C) in an oxygen-depleted environment. They reported a greater elemental composition with a 77.8% C and 0.41% N and a pH of 7.5. Dempster et al. (2012) also found that eucalyptus wood pyrolysed using a Lambiotte carbonization reactor at 600°C for 24 h had a pH of 7.4, 75% C, and 0.3% N. Overall, the

low C content of the peanut shell and eucalyptus wood biochars used in our field experience in Ndoff (Fatick, Senegal) could be explained by limitations in controlling strict temperature and oxygen availability during the pyrolysis process.

Effect of biochar on soil nutrients status

With a soil pH < 6, ECe > 4 dS/m, and SAR > 13, the soils of the experimental study are categorized as saline-sodic soils (Table 3.4) (Brady and Weil, 2008) (Rengasamy, 2010). Soil pH was numerically greater while soil EC and SAR were numerically lower in year 2 than in year 1, but not any of these soil parameters were significantly affected by biochar treatment during this field experiment. Soil C concentrations were significantly greater only in year 1 by eucalyptus wood biochar at the lowest rate combination with manure (Table 3.4). Soil N was not increased by any treatment (Table 3.4).

Similar to soil C, Ca concentrations were affected (P < 0.0068) by treatments in year 1 (Table 3.4), but not in year two. Soil Ca was increased with levels of peanut shell at the lowest rate of application in association with manure but was unaffected by eucalyptus wood char application at any rate or combination. In the first cropping year, a significant increase of 1004 Mg ha⁻¹ in soil Ca corresponding to a 44% increase in PS 10-M was reported over the control soils (Table 3.4). As with N, soil P, K, and Mg concentrations were unaffected by biochar treatment, although levels of these minerals consistently were lower in year 2 (Table 3.4).

Millet production

Differences in millet production in response to treatment were not observed. However, several challenges were faced in collecting millet biomass and grain data.

Delayed start of the rainy season in 2014 resulted in a very late start to planting while stands were destroyed by livestock late in the growing season. In 2015, stand variability associated with excessive rain resulting in standing water in millet plots limited ability to make meaningful interpretation. Thus, millet production responses are not discussed.

DISCUSSION

Addition of biochar for the reclamation of salt-affected soils has been reported to increase soil pH, EC, and SAR (Amini et al., 2016). In our study, biochar amendments in conjunction with manure did not significantly increase soil pH. Similar to our findings, Hammer et al. (2015) reported no changes in soil pH after biochar amendment to saltstressed soils due to a contrasting effect of biochar and salt additions on soil pH. Lashari et al. (2013) applied biochar mixed with poultry manure compost in combination with pyroligneous solution ("wood-vinegar" or "liquid by-product of pyrolysis of crop biomass") to an abandoned salt-affected soil and observed a significant decrease in soil pH by 0.3 compared to the control plots. They reported that enhancement in soil physical properties resulted in increased leaching of salts which in turns could be responsible for the observed decrease in soil pH. Chaganti and Crohn (2015) reported lower EC and SAR of saline-sodic soils treated with wood chip biochar after leaching under greenhouse conditions. They concluded that the lower soil EC and SAR could be explained by the increased salt leaching facilitated by soil aggregation as a result of organic matter addition and addition of divalent cations such as Ca^{2+} and Mg^{2+} in the soil solution from biochar amendments. The decrease in soil EC and SAR was similar to the findings of Lashari et al. (2015), Hammer et al. (2015), Akhtar et al. (2015a) and Akhtar et al. (2015b) who reported that biochar addition to soil reduced Na⁺ concentrations from soil solution due to its adsorption to biochar surfaces and increased K⁺, Ca⁺⁺, Mg⁺⁺ concentrations. The reduction of Na⁺ in the soil solution also increased crop yields under saline conditions. The direct sorption of NaCl salts onto the biochar surfaces was supported by a glasshouse experiment conducted by Thomas et al. (2013)

who found strong increases in biochar EC after salt addition. This increase in biochar EC could be explained by enhanced CEC (Liang et al., 2006) as result of aging and oxidation processes of biochar (Cheng et al., 2006). However, Usman et al. (2016) showed that biochar addition at higher rates can increase EC values due to the concentration of soluble salts in the ash, and Subhan et al. (2015) reported increased SAR due to high concentrations of Na⁺ in the biochar produced from cotton stalks.

The eucalyptus biochar at the lowest rate of application in combination with manure had the highest soil C concentration in year 1 but biochar treatments did not induce significant differences compared to untreated soils the following year. In a shortterm incubation study, Bhaduri et al. (2016) reported higher total soil C in saline soils amended with peanut shell biochar at the highest rate of application due to decreased C mineralization therefore improving C sequestration potential of these salt-affected soils. Wong et al. (2010) reported that reductions in soil organic mineralization in saline and sodic soils could be explained by limited accessibility to substrates by microbial populations. Although peanut shell and eucalyptus wood biochars used in our study had relatively low concentrations of C, biochar amendments to soil could result in fertilization effects due to addition of mineral nutrients from biochar weathering. The decrease in soil C is partly due to higher mineralization and loss of soil organic matter through the increased solubility of organic matter in the presence of Na⁺ (Usman et al., 2016). Lashari et al. (2013) reported no significant differences in total N between plots applied with biochar manure compost in combination with pyroligneous solution and untreated plots the first year of the experiment but there was a 69% increase in total N in year 2.

Biochar amendment had significant effects on soil Ca in year 1 but this did not persist the following year. Amended soils soil P, K, or Mg levels were not significantly different than to the control soils in either year though their concentrations decreased at the end of the study. This decrease in base cation concentrations by the end of the second growing season is probably due to crop uptake and leaching losses in this sandy and saline-sodic soil. Lashari et al. (2013) observed a 100% increase in soil phosphorus availability under combined amendment of poultry manure compost with biochar and the pyroligneous solution compared to the control soils due to biochar high content of available P.

CONCLUSIONS

This field experiment evaluated the use of biochar amendment as a management approach for reclaiming sandy and salt-stressed soils in Ndoff (Fatick, Senegal). Amendment of peanut shell and eucalyptus wood biochars in association with manure did not significantly improve the soil chemical conditions of the sandy and salt-stressed soils. Soil pH, EC, SAR, and nutrient concentrations were not significantly affected by biochar and manure additions compared to the control plots. This could be attributed to the limited benefits of biochar application on reducing Na⁺ concentrations and increasing base cations (K⁺, Ca⁺⁺, Mg⁺⁺) in the soil solution. Although the results of our 2-year field experiment suggest limited potential of biochar-manure amendment for alleviating salt stress in croplands, they must be considered in the context of the study's limitations. First and foremost, the char sources used in this study would be considered low quality relative to chars used in other research. Low C and high ash contents in our chars suggest the materials were subject to some level of combustion during processing. This may have affected the character of the char surfaces in addition to reducing the total surface area of the char. Such changes would have limited the capacity of the char to hold water and nutrients and support greater crop growth.

Other factors may have included the variable weather events – drought in year 1 and flooding in year 2 – which affected both the planting and harvest seasons. Addition of plot borders also may be been helpful in maintaining char in the appropriate plots and in identifying the correct plot layout. These factors, in combination with the fact that data from other studies suggest biochar amendment for reclaiming salt-affected soils and sustaining crop production in arid and semi-arid areas is possible, suggest that it is too

soon to declare biochar application infeasible for salt-affected soils in Senegal. Therefore, for biochar to be successful in improving soil fertility and decreasing soil salinity in Ndoff (Fatick, Senegal), further research will be required.

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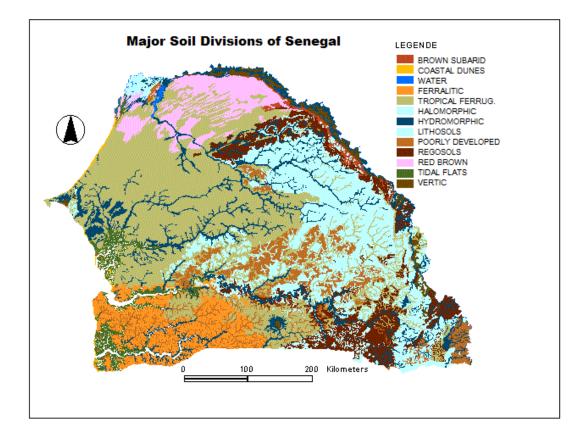


Figure 3.1. Major Soil Divisions of Senegal. This map was generalized from the "Morpho-Pedology Map of Senegal" originally published at 1:500,000 scale of Stancioff et al. (1986), (USGS, 2016).

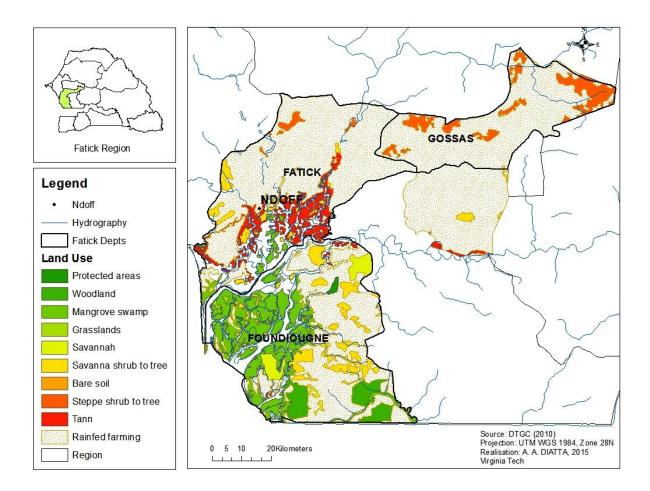


Figure 3.2. Fatick (Senegal) land use and land lover and location of the experimental site (Ndoff).

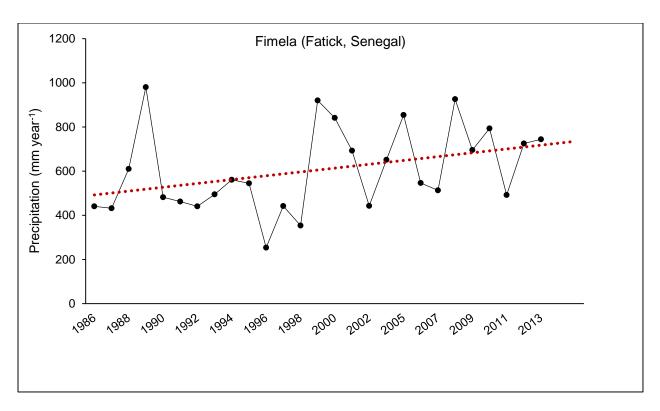


Figure 3.3. Mean yearly precipitation (mm) 1986-2013 in Fimela (Fatick, Senegal). Red line represents trend line of the average yearly precipitation. Source: "Agence Nationale de l'Aviation Civile et de la Météorologie (ANACIM)".

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Agricultural and agro-industrial residues	Annual production (1000 Mg)	Char yield (%)	Biochar potential (1000 Mg)
Cattails	<u> </u>	29	
			65
Rice hull (Senegal River Delta)	13	50 25	0 72 5
Peanut	175	25	73.5
Millet, sorghum and maize \tilde{a}	4,500	30	1,600
Cotton	45	33	18

Table 3.1. Agricultural and agro-industrial residues in Senegal (Hrubesch, 2011).

Table 3.2. Treatment inputs for study of char source and rate effects and manure application on soil quality and millet yield in Senegal.

Char source	Char rate, Mg/ha	Manure N, kg/ha
Eucalyptus wood	0	0
	10	100
Peanut shell	20	

	Soil	Peanut shell char	Eucalyptus wood char
Parameter			
Moisture (%)		3.3	4.3
Ash (%)		58.3	67.7
Total Sand (%)	90	—	—
Total Silt (%)	6	—	—
Total Clay (%	4		—
pH water	4.2	8.2	7.6
EC (dS/m)		0.46	0.12
C (%)	0.6	17	16
N (%)	0.1	1.43	0.16
C/N	6	12	104
CEC (meq/100g)	7	19	44
P plant available (mg/kg)	2	680	135
K plant available (mg/kg)	247	9610	1410
Ca plant available (mg/kg)	199	7690	24110
Mg plant available (mg/kg)	435	1360	980
Na plant available (mg/kg)		400	260
Total P (mg/kg)		710	1730
Total Ca (mg/kg)		26090	9040
Total K (mg/kg)		1415	9090
Total Mg (mg/kg)		1330	2280
Total Na (mg/kg)		140	460

Table 3.3. Mean soil (prior to treatment) and peanut shell and mixed pine wood biochars pH, electrical conductivity (EC), total carbon (C), total nitrogen (N), C:N, cation exchange capacity (CEC), plant available nutrients, and total recoverable mineral concentrations (n = 3).

pH: soil (1:1 soil: deionized water mixture on a volumetric basis) and biochar (1 g of biochar : 20 mL deionized water)

Total carbon (C) and total nitrogen (N): vario MAX CNS Element Analyzer

Inorganic NO₃⁻-N and NH₄⁺-N: 2M KCl extraction

CEC: soil (Acidity + Ca + Mg + K (in the units of meq/100 g soil or cmol/kg); biochar (1M ammonium acetate +ethanol +2M KCl)

Plant available nutrients: soil (Mehlich 1 solution); biochars (1M ammonium acetate)

Biochars total recoverable mineral concentrations: nitric acid (HNO₃) and hydrogen peroxide (H₂O₂ - 30%) digest

Year	Treatment	pН	EC	SAR	С	Ν	Р	K	Ca	Mg
	Mg ha ⁻¹		dS m ⁻¹		g kg ⁻¹	g kg ⁻¹	mg kg ⁻¹	g kg ⁻¹	g kg ⁻¹	g kg ⁻¹
2014	None	4.7	11	53	5.15 ab	0.44	19	0.97	1.27 b	1.47
	Manure	4.6	10	51	5.98 ab	0.48	21	0.99	1.53 ab	1.49
	EW 10	4.6	9	48	8.40 ab	0.57	23	1.06	1.26 ab	1.38
	EW 10 - M	4.8	11	54	9.35 a	0.60	33	0.93	2.28 a	1.50
	EW 20	4.8	9	50	6.66 ab	0.52	21	1.32	1.76 ab	2.23
	EW 20 - M	4.5	11	51	5.99 ab	0.45	16	0.69	0.93 b	0.68
	PS 10	4.6	9	46	6.04 ab	0.50	25	1.32	1.57 ab	2.05
	PS 10 - M	4.9	9	47	4.56 ab	0.38	13	0.74	1.09 b	1.09
	PS 20	4.6	10	50	4.43 b	0.40	12	0.72	0.83 b	1.02
	PS 20 - M	4.5	8	51	5.75 ab	0.45	17	0.88	1.14 ab	1.14
	S.E.	0.04	0.57		0.35	0.02	1.56	0.07	0.09	0.14
		ns	ns			ns	ns	ns		ns
2015	None	5.0	2.1	23	4.06	0.37	4.5	0.11	0.18	0.08
	Manure	5.0	1.8	22	3.20	0.28	2.6	0.12	0.14	0.07
	EW 10	4.9	1.4	16	3.94	0.35	2.5	0.08	0.18	0.06
	EW 10 - M	5.0	1.5	17	4.93	0.41	2.7	0.10	0.17	0.06
	EW 20	5.2	1.3	16	7.06	0.41	2.5	0.10	0.15	0.63
	EW 20 - M	4.8	3.8	25	4.14	0.33	3.8	0.12	0.18	0.11
	PS 10	5.0	0.9	13	3.95	0.33	1.1	0.07	0.11	0.05
	PS 10 - M	4.7	1.8	18	5.38	0.47	1.5	0.10	0.14	0.07
	PS 20	4.9	1.3	15	4.79	0.38	3.0	0.08	0.16	0.06
	PS 20 - M	4.8	2.1	22	4.60	0.40	1.5	0.11	0.12	0.08
	S.E.	0.04	0.27		0.30	0.02	0.48	0.01	0.01	0.01
		ns	ns		ns	ns	ns	ns	ns	ns

Table 3.4. Mean pH, , EC, SAR, total C and N, Mehlich I extractable nutrient concentrations in soil (0–15 cm) as affected by eucalyptus wood and peanut shell biochars in association with manure during 2014 and 2015 growing seasons.

S.E.: standard error. EW: eucalyptus wood biochar; PS 10: peanut shell biochar; 10 and 20: biochar was added at a rate 10 or 20 Mg ha⁻¹; M: manure was added at a rate 100 kg ha⁻¹. Different letters indicate significant difference in a single year with Tukey test (P<0.05). ns: not significant at p < 0.05.