EFFECTS OF BIOCHAR RECYCLING ON SWITCHGRASS GROWTH AND SOIL AND WATER QUALITY IN BIOENERGY PRODUCTION SYSTEMS

A Thesis

by

DEREK HOWARD HUSMOEN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Soil Science

EFFECTS OF BIOCHAR RECYCLING ON SWITCHGRASS GROWTH AND SOIL AND WATER QUALITY IN BIOENERGY PRODUCTION SYSTEMS

A Thesis

by

DEREK HOWARD HUSMOEN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Co-Chairs of Committee,	Donald M. Vietor
	Tony L. Provin
Committee Member,	Clyde L. Munster
Head of Department,	David D. Baltensperger

May 2011

Major Subject: Soil Science

ABSTRACT

Effects of Biochar Recycling on Switchgrass Growth and Soil and Water Quality in Bioenergy Production Systems. (May 2011)

Derek Howard Husmoen, B.S., University of Wisconsin – River Falls

Co-Chairs of Advisory Committee: Dr. Donald M. Vietor
Dr. Tony L. Provin

Intensive biomass production in emerging bioenergy systems could increase nonpoint-source sediment and nutrient losses and impair surface and groundwater quality. Recycling biochar, a charcoal byproduct from pyrolysis of biomass, provides potential sources of mineral nutrients and organic carbon for sustaining biomass productivity and preserving soil and water. Yet, research is needed to verify that recycling of pyrolysis biochars will enhance crop growth and soil and environmental quality similar to black carbon or biochar derived from burning of biomass in tropical or Terra Preta soils. The experimental design of this study consisted of 3 replications and four biochar rates (0, 4, 16, and 64 Mg ha^{-1}) incorporated in both a sandy loam and clay soil with and without fertilizer sources of N, P, and K. The sandy loam and clay soils were studied in separate experiments within a set of 24 box lysimeters seeded with switchgrass. Simulated rain was applied at 50% and 100% establishment of switchgrass for each soil type. Runoff and leachate were collected and analyzed for total and dissolved N, P, K and organic C. After the second rain event, each soil type and the accumulated switchgrass was sampled and analyzed.

In the Boonville soil, biochar applied at 64 Mg ha^{-1} decreased switchgrass emergence from 42% to 14% when compared to soil alone. In the Burleson soil, 64 Mg ha^{-1} biochar had no effect ($P > 0.05$) on biomass production or leaf area index (LAI). Fertilizer N, P, and K had no effect ($P > 0.05$) on switchgrass emergence for either soil, but did increase ($P < 0.001$) N, P, and K uptake, biomass production, and LAI. Increasing rates of biochar increased ($P < 0.001$) runoff concentrations of DRP during each rain event for both the Boonville and Burleson soils. Four rates of biochar receiving supplemental N, P, and K fertilizer also resulted in greater runoff concentrations of DRP. Emergence tests under increased heat showed electrical conductivities of soil-water solutions to be as high as 600 μS cm^{-1}, even after biochar was washed with acetone and water to remove residual oils and tars and soluble salts.

Increasing biochar rates decreased soil bulk density and increased pH and SOC in the 0- to 5-cm depth of soil. As a result of high nutrient recovery during pyrolysis (58 % of total N, 86% of total P and 101% of total K), high rates of biochar applied at 64 Mg ha^{-1} increased mass losses of TN, TP, and TK from both soils. Yet, the mass balance of nutrients showed a surplus of N, P, and K at 64 Mg ha^{-1} biochar, which suggests some nutrient inputs are not plant available and remain in soil. Careful management of biochar, especially at high rates with these high nutrient contents, is critical when trying to improve soil fertility while protecting water quality.

ACKNOWLEDGEMENTS

I would like to thank my committee co-chairs, Dr. Vietor and Dr. Provin, and my other committee member, Dr. Munster, for their guidance and support throughout the course of this research. I want to also thank the Department of Soil and Crop Sciences faculty and staff, as well as my friends and colleagues, for making my time at Texas A&M University a truly enjoyable experience.

I am grateful for financial support of this project from the North Central SunGrant Program (A Sustainable Pyrolysis System for Producing Bio-Crude Oil and Recyclable Byproducts), which is sponsored by the US Department of Energy Office of Biomass Programs, Award # DE-FG36-08GO88073, and the Texas AgriLife Bioenergy Research Initiative (Enhancing the Quality of Marketable Products Derived from Mobile Fast Pyrolysis of Lignocellulosic Biomass), which is directed by Dr. Sergio Capareda.

I also want to extend my gratitude to the Soil, Water, and Forage Testing Laboratory for their help and cooperation with sample analysis during this study. Finally, I would like to thank Bill Allen for his assistance throughout this research in the laboratory and greenhouse.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Increasing energy demands, increased cost of processing fossil fuel resources, and associated climate changes can provide major incentives for the development of renewable, sustainable energy resources; including bioenergy. However, intensive biomass production and harvest of residue in these bioenergy systems can deplete soil nutrients, soil organic carbon, and vegetative cover (Heggenstaller et al., 2008; Laird et al., 2009). Additionally, loss of soil cover can potentially accelerate soil erosion and increase nonpoint-source sediment losses. According to Wilhelm et al. (2004), the quality of our soils would rapidly deteriorate if all aboveground crop residues were removed year after year.

Sustainable cropping systems are needed to conserve resources for future generations while supplying feedstocks for bioenergy production. While economic benefits of new markets for crop biomass conversion to energy are important, environmental and ecological consequences of intensive crop production practices must not be overlooked. It is critical that large-scale generation of energy from crop biomass is balanced with other ecological services that agricultural lands provide, including

---

This thesis follows the style of the Journal of Environmental Quality.

nutrient and water cycling, carbon sequestration, and environmental quality (Anex et al., 2007). Bioenergy systems must also be multifunctional in order to effectively address the complex issues of natural, human, and community resources (Jordan et al., 2007).

Thermochemical conversion is among the technologies available to generate liquid and gaseous fuels from feedstocks, including plant biomass and other biological materials. Pyrolysis, a common thermochemical conversion method, produces three co-products, including a liquid fuel (termed bio-oil), combustible gases (termed synthesis gas or syn-gas), and a carbon-rich charcoal (termed biochar) (Bridgwater, 2003).

Origins of biochar can be traced back thousands of years to the Brazilian Amazon basin. Soils in this region are referred to as ‘Dark Earth’ or ‘Terra Preta’ due to their dark color, high soil organic matter contents, and high fertility resulting from the historic burning of vegetation. These intensively studied soils were under cultivation without fertilization for over 40 years in some instances. Reports describing properties of biochar and beneficial effects on soil properties and crop production for Terra Preta soils have stimulated interest in recycling of biochar from bioenergy production systems back to agricultural land.

A distributed network of mobile pyrolysis systems has recently been proposed to enhance the sustainability of bioenergy and biofuel production in the U.S. and recycle biochar back to soil (Laird, 2008). Mobile pyrolyzers will convert a diverse mix of feedstocks, including crop biomass, wood, manures and composts, and municipal sludge or solids. The bio-oil product of pyrolysis can fuel industrial boilers and furnaces on a local scale or be transported in tankers for upgrading through existing petroleum refineries (Goyal et al., 2008). In addition, locating pyrolyzers proximate to production fields will optimize the logistics for recycling biochar to fields from which the biomass feedstocks are harvested.

The contribution of biochar recycling from mobile pyrolysis systems to ecological services provided by agriculture, including sustained soil, water, and environmental quality, will vary. Biochar yield, composition, and effects on soil and the environment will differ among feedstocks, design and operation of pyrolyzers, and biochar processing and management. Recent research identified potential feedstocks, pyrolysis conditions, and management practices for biochar sources used to recycle both nutrients for crop production and carbon for sequestration in the soil (Gaskin et al., 2008; Gaskin et al., 2010). Yet, crop yield responses to biochar were variable, less than expected, and limited to one soil type. More research is needed to relate properties and composition of biochar to effects on physical, chemical, and biological properties of amended soil. In addition, impacts of recycled biochar and associated fertilization practices on crop establishment and productivity, nutrient cycling or retention, and water runoff and quality need to be evaluated to determine if biochar will yield similar results to those reported in Amazonian soils. A more thorough understanding of biochar physical and chemical properties could explain the inconsistent results reported in the literature.

The purpose of this project was to evaluate effects of biochar recycling on soil physical, chemical, and biological properties and water quality during switchgrass establishment for two different soil types. Biochar was derived from conversion of corn stover biomass through slow pyrolysis. Four rates of biochar, with and without supplemental inorganic fertilizer, were incorporated into box lysimeters for each a sandy loam and clay soil in separate replicated greenhouse experiments. Switchgrass emergence and growth were compared among the eight treatments for each soil type. Two separate simulated rainfall events were applied for each soil type to determine the impacts of biochar rate and inorganic fertilizer on nutrient runoff, sediment loss, and water quality. Soil samples were collected before and after switchgrass establishment for analysis of physical properties and soil pH, organic carbon, and nutrient status. Physical and chemical properties of biochar, including particle density, surface area, and pore size, were quantified to evaluate effects of biochar structure on nutrient and water retention and carbon sequestration. Upon completion of the project, treatment effects and relationships among switchgrass establishment and productivity, nutrient cycling or retention, and water runoff and quality were quantified.

CHAPTER II

EFFECTS OF BIOCHAR-AMENDED SOIL ON SWITCHGRASS ESTABLISHMENT AND RUNOFF LOSS OF NUTRIENTS

Biochar, derived from slow pyrolysis of plant biomass, has the potential to improve soil, water, and environmental quality. When added to soil, biochar has been shown to increase crop productivity and improve soil properties (Gaskin et al., 2008). For biochars derived from anthropogenic sources as well as pyrolysis, effects on soil include increased cation exchange capacity (Liang et al., 2006; Cheng et al., 2008), pH (Novak et al., 2009), and N retention (Gaskin et al., 2008; Steiner et al., 2008). In addition, biochar addition to soil reduced phosphorus loss in runoff (Lehmann, 2007; Novak et al., 2009) and nutrient loss through leaching (Lehmann et al., 2003). For tropical soils in which biochar was deposited and incubated over long periods, improved retention and reduced runoff loss of soil N and P were attributed to increased surface area and surface charge density of the biochar (Liang et al., 2006). Moreover, the chemical structure of aromatic carbon compounds in biochar served as a long-term sink for anthropogenic sources of CO_2 in soil (Lehmann et al., 2006). The recalcitrance of biochar to microbial degradation contributed to mean residence times up to 1000 years in soil. Biochar-sequestered C in soil could offset anthropogenic sources of CO_2 emissions to the environment.

Despite benefits of long-term deposits from anthropogenic sources, properties and soil effects of biochar derived from pyrolysis depend on biomass source, reactor conditions, and processing after pyrolysis (Gaskin et al., 2008). Initially, low surface area and high surface crystallinity of biochar derived from fluidized-bed, fast pyrolysis of switchgrass biomass indicated ion sorption characteristics were poor (Boateng, 2007). Variation of reported crop responses to biochar indicated that integrated studies were needed to relate biochar properties to effects on soils, crops, and the environment. A study by van Zwieten et al. (2010) concluded that increases in soybean biomass occurred only when 10 Mg ha^{-1} biochar was supplemented with N, P, and K fertilizers. In contrast, Rondon et al. (2005) found that biomass production of soybeans under a greenhouse setting increased 60% after charcoal additions of 20 g kg^{-1} of soil without additional fertilizer. Research concerning biochar properties and recycling to soil are needed to complement studies of relationships among properties of feedstocks and co-products of pyrolysis, including biochar, bio-oils, and syn-gas. More specifically, analyses of nutrient conservation and transformations during pyrolysis of biomass and biochar recycling will enable interpretation of crop, soil, and environmental responses.

Objectives

I. Characterize physical and chemical properties of biochar derived from conversion of corn stover biomass through an auger-fed, fixed-bed, slow pyrolysis system.

II. Evaluate effects of biochar rate and supplemental inorganic fertilizer on soil physical, chemical, and biological properties and switchgrass seedling establishment in both a sandy loam and clay soil.

III. Compare runoff and leaching losses of water, sediment, and nutrients during switchgrass establishment with and without incorporation of biochar and supplemental fertilizer nutrients in both a sandy loam and clay soil.

IV. Evaluate the mass balance of nutrient additions in biochar and fertilizer with losses through plant uptake and mass loss in runoff during switchgrass establishment in both a sandy loam and clay soil.

Materials and Methods

Corn stover biomass was collected, dried, and ground to a particle size less than 2 mm. An auger-fed, fixed-bed, slow pyrolysis system was used to convert corn stover biomass to biochar at a reactor temperature of 550 °C. Four rates of the corn stover biochar (0, 4, 16, and 64 Mg ha^{-1}) were incorporated with and without supplemental N, P, and K fertilizer in soil packed within aluminum box lysimeters (44 x 33 x 20 cm) under greenhouse conditions. Granular forms of urea (46-0-0), triple superphosphate (0-46-0), and muriate of potash (0-0-60) were used as sources of supplemental fertilizer nutrients. The respective fertilizer sources were applied to provide 50 kg N ha^{-1}, 100 kg P ha^{-1}, and 200 kg K ha^{-1} and incorporated in the 0- to 15-cm depth of soil. Three replications of the eight treatments comprised a complete randomized design. This experiment was conducted twice; first using topsoil from a Boonville fine sandy loam (fine, smectitic, thermic Chromic Vertic Albaqualfs) and second using topsoil from a Burleson clay (fine, smectitic, thermic Udic Haplusterts) soil. Prior to adding soil, a 5-cm depth of pea gravel was placed in the bottom of each box lysimeter and covered with a sheet of glass microfiber cloth to prevent soil infiltration into the gravel layer. Soil, biochar, and fertilizer were mixed together at calculated rates and packed into the box lysimeters in three 5-cm depth increments to achieve a desired bulk density of 1.5 Mg m^{-3} for the Boonville sandy loam and 1.3 Mg m^{-3} for the Burleson clay soil. In the packing procedure, the mixtures of soil, biochar, and fertilizer for each 5-cm layer were first poured into each lysimeter box and leveled. An 11.4-kg weight was dropped from a height of 30 cm three times on to a 44 x 33 x 2 cm piece of plywood to pack each 5-cm layer. Both soil and biochar were sampled prior to switchgrass seeding to quantify total and extractable forms of N, P, K, and organic C.

After packing amended soil into box lysimeters, Alamo switchgrass (*Panicum virgatum*) was seeded at a population density of 1240 seeds m^{-2}. Seedling emergence was recorded daily. Mean daily air temperature ranged from 27 °C to 42 °C and midday photosynthetic photon flux density (PPFD) at the soil surface was 1300 μmol m^{-2} s^{-1} during seedling emergence and establishment. Each lysimeter box was watered with 0.5 L deionized water daily using a 1.0 L plastic Ziploc container with small holes punctured into the lid. This was done to reduce the impact of water on the soil surface and to eliminate losses of soil and biochar when watering. At approximately 100% plant coverage of the soil surface, switchgrass biomass was harvested and measured as aboveground dry matter (Mg ha^{-1}). In addition, leaf blades were separated from sheaths and stems and a leaf area meter (LI-3100C Area Meter, LI-COR, Lincoln, NE) was used to measure blade area for leaf area index (LAI) calculations. Total N and mineral nutrients of switchgrass dry matter were determined through nitric acid digestion and subsequent analysis with inductively coupled plasma optical emission (ICP) spectroscopy (McGeehan and Naylor, 1988; Havlin and Soltanpour, 1989).

Simulated rain (~11 cm hr^{-1}) from an oscillating, indoor, multiple intensity rainfall simulator (Birt et al., 2007) was applied to box lysimeters at approximately 50% and 100% switchgrass leaf coverage of the soil surface. Prior to each rainfall, water was treated with a reverse osmosis system (Model No. B-4L Plus, Culligan International Co., Northbrook, IL) and stored in two large 9500 L poly tanks. Lysimeters were mounted in a metal frame beneath the simulator to impose a surface slope of 7%. During each rain event, volumes of runoff were collected for three 8-min. intervals from a flume welded to the downslope wall of each lysimeter and measured. Runoff volumes were composited over the three collection intervals and sampled for each lysimeter. In addition, leachate was collected over the 24-minute duration of the rain event through a manifold of tubes mounted on the bottom of each lysimeter.

Following runoff and leachate collection for each rain event, samples were refrigerated and a subsample was filtered (<0.45 μm) within 24 hours of sampling. An Elementar Rapid LiquiTO$_x$ analyzer (Hanau, Germany) was used to quantify total organic C (TOC) and N (TN) in unfiltered composite runoff samples from each rain event (McGeehan and Naylor, 1988). In addition, ICP spectroscopy was used to quantify total P (TP) and cation concentrations in nitric acid digests of unfiltered runoff and leachate for each rain event (Eaton and Franson, 2005). A microwell plate reader (MRX Microplate Reader, Dynatech Laboratories Inc., Chantilly, VA) was used to measure NO_3-N, NH_4-N, and dissolved reactive phosphorus (DRP) colorimetrically within 24 hr after runoff and leachate samples were filtered (<0.45 µm) (Sims et al., 1995; Lopez and Vargas-Albores, 2003; Pierzynski, 2000). In addition, ICP spectroscopy was also used to measure total dissolved phosphorus (TDP) and cation concentrations in filtrate of runoff and leachate.

After the second rain event and following switchgrass biomass harvest, a golf-cup cutter was used remove to two soil cores (10-cm diameter) from each lysimeter box. Cores were separated into 0- to 5-cm and 5- to 15-cm depth increments and composited within depths for physical and chemical analysis following drying at 60 °C for 3 days. Soil bulk density and water content were computed gravimetrically and pH, electrical conductivity (EC), and nutrient concentrations in Mehlich-3 and water extracts of soil were quantified (Mehlich, 1984). The microwell plate reader was used to measure DRP in filtrate of soil water extracts, as described for runoff. The ICP was used to measure P and cation concentrations in Mehlich-3 extracts.

A one-way ANOVA procedure using JMP 8.0 (SAS Institute Inc., Cary, North Carolina) was used for the analysis of variance among treatments (four rates of biochar, with and without supplemental inorganic fertilizer). Rain events were analyzed separately. Fisher's least significant difference (LSD) test ($P = 0.05$) was used to compare treatment means. Contrasts were made to test the effects of biochar rate and supplemental inorganic fertilizer on soil properties, switchgrass nutrient uptake and biomass production, and nutrient concentrations in runoff and leachate. Mass balance of total N, P, and K nutrients for the four rates of biochar, with and without supplemental inorganic fertilizer nutrients, was calculated by subtracting total nutrient outputs (plant uptake + mass loss in runoff) from total nutrient inputs (biochar + fertilizer).

Results and Discussion

Biochar and Soil

Soil and biochar were sampled and analyzed prior to incorporation in box lysimeters to determine total and extractable nutrients. During pyrolysis of corn stover, 58 % of TN, 86% of TP and 101% of TK in feedstock was conserved in the biochar (Table A-1). Similarly, Gaskin et al. (2008) reported that 27 to 90% of N, 60 to 100% of P, and 60 to 110% of K was conserved in biochar produced from poultry litter, peanut hulls, and pine chips at pyrolysis temperatures of 400 °C and 500 °C. The relatively high recovery of nutrients during pyrolysis suggests that biochar recycling to production fields will reduce inorganic fertilizer requirements needed to sustain biomass productivity in bioenergy systems. Returning and incorporating biochar at rates of 4, 16, and 64 Mg ha^{-1} in this study resulted in significant nutrient additions to soil.

Initial concentrations of soil nutrients were lower in the Boonville sandy loam soil compared to the Burleson clay (Table A-2). Initial TN concentration of the Boonville soil was one half that of the Burleson soil. In addition, TP and total K (TK) concentrations were 75% less for the Boonville than the Burleson soil. Application of 64 Mg ha^{-1} biochar increased soil pH in the Boonville ($P < 0.001$) and Burleson ($P = 0.007$) soils and decreased bulk density in both soils ($P = 0.002$) compared to soil alone at the end of each experiment in the 0- to 5-cm depth (Table A-3 and Table A-4). The

64-Mg rate of biochar raised the Boonville soil pH from 7.7 to 8.6 and the Burleson soil pH from 6.8 to 7.4. Conversely, the 64-Mg rate decreased bulk density from 1.30 to 1.14 g cm^{-3} and 1.22 to 0.99 g cm^{-3} for the Boonville and Burleson soils, respectively. Because bulk density was calculated at the end of each experiment after two rainfall events, means were lower than original targeted values of 1.5 g cm^{-3} for the Boonville sandy loam and 1.3 g cm^{-3} for the Burleson clay due to soil hydration and root growth within box lysimeters. Similar changes to soil properties as the result of biochar application have been reported in previous studies (Novak et al., 2009; Major et al., 2010).

For the Boonville soil, the 64-Mg biochar rate ha^{-1} increased ($P < 0.001$) TN, TP and TK concentrations in the 0- to 5-cm depth compared to soil without biochar. Similarly, incorporation of fertilizer P with biochar increased ($P < 0.001$) soil concentrations (0- to 5-cm depth) of total P and Mehlich-3 extractable P compared to soil amended with biochar only. Significant ($P < 0.001$) increases in Mehlich-3 extractable K for biochar rates ranging from 16 Mg ha^{-1} to 64 Mg ha^{-1}, compared to the Boonville soil alone, reflected the high recovery of biomass sources of TK in biochar. High biochar rates increased concentrations of extractable P and K available for plant uptake in the surface layer, but high soluble P and K concentrations could contribute to runoff losses (Bertol et al., 2007). For soil sampled to the 5- to 15-cm depth, the 64-Mg biochar rate similarly increased soil concentrations of TN, TP, TK, and Mehlich-3 extractable P and K compared to soil without biochar. In addition, Mehlich-3 extractable P and K were greater with than without supplemental N-P-K fertilizer (Table A-5).

Similar effects of increasing biochar rates were observed for the Burleson clay soil. Incorporation of 64 Mg ha^{-1} of biochar in the Burleson clay soil increased TN ($P = 0.006$) and TK ($P = 0.002$), but not TP concentrations ($P > 0.05$) compared to soil without biochar within the 0- to 5-cm depth. In addition, incorporation of fertilizer P with biochar increased ($P = 0.003$) soil concentration of Mehlich-3 extractable P, but not total P, compared to biochar-amended soil without P fertilizer. Without N-P-K fertilizer, Mehlich-3 extractable K was greater ($P < 0.001$) for biochar rates from 16 Mg ha^{-1} to 64 Mg ha^{-1} than for the Burleson soil alone. Compared to the 0- to 5-cm depth, soil TN, TP, and TK concentrations in soil from the 5- to 15-cm depth were more consistently greater for 64 Mg biochar ha^{-1} than Burleson soil alone. Yet, 16 and 64 Mg biochar ha^{-1} increased Mehlich-3 extractable K, but not extractable P, compared to soil without biochar (Table A-6).

Similar to rate effects on K and to previous reports, biochar application increased soil organic carbon in both soils (Novak et al., 2009; Van Zwieten et al., 2009). Concentrations of soil organic carbon (SOC) in the 0- to 5-cm depth increased ($P < 0.001$) 2.4-fold at 16 Mg ha^{-1} of biochar and 6.5-fold at 64 Mg ha^{-1} of biochar compared to Boonville soil without biochar. For the Burleson clay, treatment effects on concentrations of SOC in the 0- to 5-cm depth followed similar trends as in the Boonville soil. Compared to Burleson soil without char, SOC increased ($P < 0.001$) 1.5-fold for 16 Mg ha^{-1} of biochar and 2.6-fold for 64 Mg ha^{-1} of biochar. In addition, soil micronutrient concentrations (Ca, Na, Fe, Zn, S, B, Mn, and Cu) in soil samples from depths 0- to 5-cm and 5- to 15-cm were not different ($P > 0.05$) between 0, 4, 16, and 64 Mg biochar ha^{-1}, with and without N-P-K fertilizer, for either the Boonville or Burleson soils (data not shown).

Switchgrass Growth

Incorporation of fertilizer N, P, and K, with or without biochar, did not affect ($P > 0.05$) switchgrass emergence in either soil. In contrast, biochar applied at 64 Mg ha^{-1} to the Boonville soil decreased ($P < 0.001$) emergence of switchgrass to 14%, which was one third of the percent emergence for soil alone. For the Burleson soil, the 64-Mg biochar rate decreased ($P = 0.02$) emergence to 63%, which was 11% less than soil without biochar (Figure A-1). Rates of 0, 4, and 16 Mg ha^{-1} biochar did not reduce seedling emergence in either soil. In contrast to the inhibitory effect of the 64-Mg rate of biochar on emergence, Van Zwieten et al. (2010) reported a 10-Mg ha^{-1} rate of biochar derived from slow pyrolysis of papermill waste improved emergence of wheat in a ferrosol soil.

Biochar effects on switchgrass biomass production and leaf area index (LAI) differed between the Boonville and Burleson soils. For the Boonville soil, 64-Mg ha^{-1} biochar reduced ($P < 0.001$) dry matter yield 6.4-fold and 16 Mg biochar ha^{-1} reduced yield 1.2-fold compared to soil without biochar (Figure A-2). Similarly, LAI was 4.2-fold lower with than without 64 Mg ha^{-1} biochar in the Boonville soil (Figure A-3). In contrast, both dry matter yield and LAI were similar ($P > 0.05$) among the three biochar rates and soil without biochar for the Burleson soil. Similar to the lack of switchgrass response to biochar rate on the Burleson soil, corn yields did not increase as rates of pine chip biochar were increased to 11 and 22 Mg ha^{-1} (Gaskin et al., 2010). For Burleson compared to Boonville soil, switchgrass yields were two times greater at 0, 4, 16 Mg ha^{-1} of biochar and 10 times greater at 64 Mg biochar ha^{-1}.

Supplemental N, P, and K fertilizer increased ($P < 0.001$) mean switchgrass biomass production and LAI over four biochar rates for both the Boonville and Burleson soils. Mean increases attributed to N-P-K fertilizer were smallest for the Boonville soil at 64 Mg biochar ha^{-1}. At the 64-Mg rate, supplemental N, P, and K fertilizer increased dry matter production 20% for the Boonville soil and 30% for the Burleson soil. Increases in LAI in response to supplemental N-P-K fertilizer were similar to increases in dry matter yield over the four biochar rates.

Nutrient Uptake

Variation of nutrient uptake by switchgrass reflected variation of switchgrass biomass production among biochar rates with or without supplemental N-P-K fertilizer for both soils. Total N, P, and K uptake in aboveground biomass was greater ($P < 0.001$) with than without supplement N-P-K fertilizer for 4 and 16 Mg biochar ha^{-1} and each soil alone. In the Boonville soil without biochar, supplemental N-P-K fertilizer increased N uptake 121%, P uptake 105%, and K uptake 104% (Figure A-4). In contrast to fertilizer responses, uptake of total N, P, or K was similar among biochar rates of 0, 4, or 16 Mg ha^{-1} for the Boonville soil. In addition, total N uptake decreased 3.6-fold, total

P uptake decreased 3.0-fold and total K decreased 4.1-fold at 64-Mg biochar ha^{-1}compared to Boonville soil alone. These decreases in uptake at the 64-Mg biochar rate reflected the small biomass yields of less than 0.5 Mg ha^{-1}.

In the Burleson soil without biochar, supplemental N-P-K fertilizer increased N uptake 15%, P uptake 8%, and K uptake 29%. In contrast to fertilizer responses, uptake of total N or total K was similar ($P > 0.05$) among biochar rates of 4, 16, and 64 Mg ha^{-1} and soil without biochar. Moreover, uptake of total P at 64 Mg biochar ha^{-1} decreased 18% compared to Burleson soil alone (Figure A-5). Similar to these results, Gaskin et al. (2010) reported that responses of N, P, and K uptake in corn tissue were greater for applied inorganic fertilizer nutrients than for pine chip or peanut hull biochar.

To differentiate and quantify the amount of nutrient uptake resulting from biochar only in each the Boonville and Burleson soils, means for soil alone (control) (BC-0) were subtracted from means for treatments receiving 4, 16, and 64 Mg biochar ha^{-1}. Additionally, means for soil amended with N-P-K fertilizer only (BC-0+NPK) were subtracted from treatments receiving 4, 16, and 64 Mg biochar ha^{-1} with supplemental N-P-K fertilizer. In the Boonville soil, nutrient uptake of N, P, and K from 4 and 16 Mg biochar ha^{-1} was slightly higher than soil alone (Table A-7). At the 64-Mg rate, uptake of the same nutrients was dramatically lower than soil alone and was indicative of low biomass production. For treatments receiving N-P-K fertilizer, uptake of N, P, and K from 4, 16, and 64 Mg ha^{-1} biochar was less than Boonville soil with N-P-K fertilizer only. During switchgrass establishment, N, P, and K uptake from biochar was negligible or negative compared to uptake from supplemental N-P-K fertilizer in soil alone.

Compared to the Burleson soil alone, increasing rates of biochar achieved negligible or reduced uptake of N, P, and K (Table A-8). For the Burleson soil supplemented with N-P-K fertilizer, 16 and 64 Mg biochar ha^{-1} increased net increases in uptake of N, P, and K compared to soil with N-P-K fertilizer only. Negative values for N, P, and K applied as biochar and taken up in switchgrass are a result from variation in biomass production between replications within treatments and indicate that nutrient uptake was greater for the soils alone compared to those amended with 4, 16, or 64 Mg biochar ha^{-1}. This suggests that returning biochar back to soil will not maintain sufficient levels of plant available nutrients required for crop production in bioenergy systems.

Runoff

Mean runoff volumes were similar ($P > 0.05$) among four rates of biochar with or without supplemental fertilizer nutrients for both soils. Mean runoff volumes for the Boonville soil across all treatments were 46.0 L m^{-2} for the first rain event and 38.5 L m^{-2} for the second rain event. Similarly, mean runoff volumes for the Burleson soil were 40.9 L m^{-2} and 38.7 L m^{-2} for first and second rainfall events, respectively.

Analysis of runoff water from each of two rain events for both soils indicated both biochar and fertilizer sources of P contributed to increases in runoff concentration of DRP. During the first rain event on the Boonville soil, increasing rates of biochar without supplemental N-P-K fertilizer increased runoff concentrations of DRP (Table A-9). Biochar at 64 Mg ha^{-1} increased runoff concentration ($P < 0.001$) of DRP 3.2-fold compared to soil alone. Runoff concentrations of DRP were lower for the second than first rain event for the Boonville soil. Yet, DRP concentration remained 6.2-fold greater for 64 Mg biochar ha^{-1} than Boonville soil without biochar.

Biochar effects on runoff were similar for the Burleson soil. Runoff concentration of DRP for 64 Mg biochar ha^{-1} was 2.1-fold greater during the first rain event and 1.8-fold greater during the second rain event than runoff concentrations for soil alone (Table A-9). Similar to the Boonville soil, mean DRP concentration in runoff from the Burleson soil was lower during the second than first rain event. For both soils, DRP comprised between 50-75% of TDP lost in two runoff events (Table A-10). In contrast to runoff losses of DRP from biochar-amended soil in this study, high biochar rates (2% w/w) reduced P leaching losses compared to the control soil in a previous study (Novak et al., 2009). The DRP lost in runoff from biochar-amended soil is a potential nonpoint P source for aquatic microorganisms and eutrophication in lakes and streams (Sharpley et al., 1992).

Supplemental N-P-K fertilizer increased ($P < 0.001$) runoff concentrations of DRP compared to soil without inorganic fertilizer for both Boonville and Burleson soils. For both soils, DRP concentrations in runoff were reduced from the first to second rain due to switchgrass uptake and mass runoff loss of P from the first rainfall event. Yet, effects of supplemental N-P-K fertilizer on runoff concentration of DRP were evident during both rain events. For the Boonville soil, incorporated P fertilizer increased runoff concentration of DRP 3.7-fold during the first rain event and 3.4-fold during the second rain event compared to treatments without N-P-K fertilizer. Similarly, runoff concentrations of DRP from the Burleson soil were 1.2-fold greater for both the first and second rainfall events for treatments with compared to without inorganic N-P-K fertilizer. Pote et al. (1996) similarly reported P fertilizer amendments increased runoff losses of DRP and soil concentrations of water extractable P and Mehlich-3 extractable P.

The highest biochar rate increased ($P < 0.001$) mass loss of TP compared to soil alone over two rain events for both soils. Incorporation of 64 Mg ha^{-1} biochar without N-P-K fertilizer in the Boonville soil increased cumulative mass runoff loss to 1.67 kg TP ha^{-1}, which compared to 0.72 kg TP ha^{-1} in runoff from soil alone. Similarly for 64 Mg biochar ha^{-1} applied to the Burleson soil without N-P-K fertilizer, cumulative mass TP loss in runoff was 0.57 kg TP ha^{-1} or more than 2 times the TP loss (0.27 kg ha^{-1}) from soil alone. Supplemental N-P-K fertilizer increased ($P = 0.04$) cumulative mass loss of TP in runoff for three of four biochar rates applied to the Boonville, but not the Burleson soil ($P > 0.05$).

Incorporation of 64 Mg biochar ha^{-1} increased ($P < 0.001$) cumulative mass loss of total K over two rain events for each the Boonville and Burleson soils. Mass loss of TK was 71.4 kg ha^{-1} for 64 Mg biochar ha^{-1} without supplemental N-P-K fertilizer as compared to 21.5 kg TK ha^{-1} for the Boonville soil alone (Figure A-6). For the Burleson soil, mean mass loss for 64 Mg ha^{-1} biochar and no N-P-K fertilizer was 11.3 kg TK ha^{-1} as compared to 2.6 kg TK ha^{-1} for soil alone (Figure A-7). Supplemental inorganic fertilizer amendments did not increase ($P > 0.05$) cumulative mass loss of TK for either soil type. For the Boonville soil, dissolved K (DK) comprised only a small percentage of TK in runoff, whereas DK comprised nearly half of the TK lost in runoff for the Burleson soil. Higher concentrations of Mehlich-3 extractable K in the Burleson clay soil could have contributed to higher proportions of dissolved K in runoff. Runoff losses of K, as well as N and P, could adversely affect water quality and nutrient balances required to maintain sustainable crop production.

Mass Balance

The mass balance of TN for both Boonville and Burleson soils amended with four rates of biochar, with and without supplemental N-P-K fertilizer, was strongly influenced by initial N content in biochar. Biochar rates of 4, 16, and 64 Mg ha^{-1} supplied 76, 300, and 1198 kg N ha^{-1}, respectively. Low switchgrass uptake of TN, especially at 64 Mg biochar ha^{-1}, reflected variation of biomass production for the Boonville soil. For Boonville soil without biochar or N-P-K fertilizer, a deficit of -60 kg TN ha^{-1} was observed. Addition of supplemental N-P-K fertilizer without biochar reduced the deficit to -43 kg TN ha^{-1} (Figure A-8). At rates of 4, 16, and 64 Mg ha^{-1} biochar without supplemental N-P-K fertilizer, respective surpluses were 0.5, 235, and 1142 kg TN ha^{-1}.

Increasing biochar rates similarly affected TN mass balance of the Burleson soil. Deficits were -96 and -12 kg TN ha^{-1} for 0 and 4 Mg biochar ha^{-1}, respectively, without N-P-K fertilizer (Figure A-8). In contrast, surpluses totaling 213 and 1113 kg TN ha^{-1}

occurred for respective biochar rates of 16 and 64 Mg ha^{-1} without N-P-K fertilizer. Mineralization of biochar TN sources could provide nutrients for plant uptake, but leaching and runoff loss of NO_3-N are potential concerns. Addition of supplemental N-P-K fertilizer increased TN surpluses of biochar-amended Boonville or Burleson soils only slightly.

Similar to mass balance of TN, mass balance total P was strongly influenced by TP rates applied in biochar. Biochar rates of 4, 16, and 64 Mg ha^{-1} supplied 8, 33, and 130 kg TP ha^{-1}, respectively. Total P outputs (from switchgrass uptake and mass loss of TP in runoff over two rain events) across all treatments were less than 8 kg ha^{-1} for the Boonville soil and less than 15 kg ha^{-1} for the Burleson soil. For the Boonville soil without biochar or N-P-K fertilizer, a slight deficit occurred (-3.0 kg TP ha^{-1}). In contrast, surpluses of 4.5, 19, and 128 kg TP ha^{-1} were observed for soil mixed with 4, 16, and 64 Mg ha^{-1} biochar, respectively. In addition, incorporation of 100 kg P ha^{-1} as inorganic fertilizer in the Boonville soil achieved TP surpluses for all three biochar rates and soil without biochar (Figure A-9).

During the period of switchgrass establishment on the Burleson soil, TP deficits were -11 and -2.0 kg TP ha^{-1} for 0- and 4-Mg biochar ha^{-1} without supplemental N-P-K fertilizer. Increasing biochar rates to 16 and 64 Mg ha^{-1} achieved respective surpluses of 23 and 122 kg TP ha^{-1}. The surpluses indicate biochar rates of 16 and 64 Mg ha^{-1} will provide establishment requirements of switchgrass, but surpluses of dissolved P forms are a potential nonpoint source for runoff losses of P.

Although increases in biochar rate increased soil concentrations of TK and Mehlich-3 K, larger mass losses of K contributed to greater deficits for TK than TN and TP during switchgrass establishment. The respective biochar rates (4, 16, and 64 Mg ha^{-1}) supplied 12, 49, and 196 kg K ha^{-1}. Yet, respective deficits were -54, -56, and -13 kg TK ha^{-1} for the three biochar rates incorporated in the Boonville soil (Figure A-10). A TK surplus (115 kg ha^{-1}) occurred for 64 Mg ha^{-1} only. A large portion of the TK deficits were attributed to runoff losses. Mean mass losses in runoff over two rain events for the Boonville soil ranged from 21 kg TK ha^{-1} without biochar to 71 kg TK ha^{-1} with 64 Mg ha^{-1} biochar. Similarly, 64 Mg ha^{-1} biochar yielded the only TK surplus (89 kg ha^{-1}) for the Burleson soil. Deficits of TK were greater for the Burleson than Boonville soil due to higher switchgrass biomass production and uptake of K for the Burleson soil (Figure A-10). Even if biomass K is largely recovered in biochar during pyrolysis (101%), 64 Mg ha^{-1} was the only biochar rate that provided a surplus of K. Over time, crop biomass yield could decline as a result of crop biomass removal of K or excess losses of K through runoff. Management of K nutrient sources, including biochar, will be necessary to sustain the productivity of bioenergy systems.

CHAPTER III

CARBON AND NITROGEN MINERALIZATION AND SEEDLING EMERGENCE FOLLOWING BIOCHAR PRE-TREATMENT

Consistent increases in soil organic carbon (SOC) have been reported following application of pyrolysis biochar at various rates (Novak et al., 2009; Major et al., 2010). Yet, observed biochar effects on soil fertility and crop productivity have been both negative and positive. Despite potential negative effects, biochar recycling to soil could enhance C sequestration and mitigate increasing atmospheric CO_2 concentrations across the globe (Laird, 2008). Biochar comprises two types of C structures: aromatic rings and aliphatic/oxidized carbon forms (Schmidt and Noack, 2000). In highly recalcitrant aromatic rings, C atoms are bound tightly to one another, which limit microbial attack and decomposition of biochar. Cheng et al. (2005) reported mean residence times (MRT) of 1335 years for aged hardwood biochar in soil and 1300 years for fresh grass biochar. In contrast, aliphatic and oxidized C forms are more vulnerable to microbial degradation, which allows eventual biochar mineralization to CO_2 similar to other sources of organic matter in soil.

Biochar composition and structure are dependent on the original feedstock or plant biomass source and pyrolysis temperature. Chemical and physical characterizations of biochar will, in turn, be used to interpret biochar effects on physical, chemical, and biological properties of amended soil. The absence of positive responses of switchgrass biomass and leaf area accumulation to increasing biochar rate in the previous lysimeter study indicated slow mineralization limited availability of N and other nutrients in Boonville and Burleson soils. Mineralization rates need to be quantified to evaluate the fate of biochar C and nutrient sources in varying soil textures. Additionally, research is needed to evaluate the inhibitory effect of 64 Mg ha^{-1} biochar on switchgrass emergence in the Boonville soil.

Objectives

I. Compare C and N mineralization rates without and with increasing rates of biochar and with and without N-P-K fertilizer during a 96-day incubation in each a sandy loam and clay soil.

II. Relate variation of chemical properties of biochar and soil to variation of switchgrass seedling emergence in response to high biochar rates in the Boonville sandy loam soil.

Materials and Methods

At the conclusion of switchgrass biomass harvest from sandy loam and clay soils treated with or without biochar and N-P-K fertilizer, a 6-cm diameter core was removed from the top 5 cm of soil in each box lysimeter. Cores at approximately field moisture capacity from each replication of eight treatments were placed into 1-L jars, covered with lids, and incubated for 96 days at 25 °C. Similar to the arrangement of box lysimeters from which soil cores were sampled for analysis, 24 jars comprised a complete randomized design within a laboratory incubator. Alkali traps containing 10 mL of 1.0 N NaOH were inserted within jars to absorb CO_2 and were changed and titrated with acid (1.0 N HCl) at 1, 3, 6, 12, 24, 48, and 96 days. Rates of CO_2 evolution were used to quantify C mineralization rates during specified incubation periods (Haney et al., 2004). In addition, colorimetric inorganic N concentrations (NH_4-N + NO_3-N) of non-incubated soil samples collected at the end of the box lysimeter experiment for each treatment were subtracted from soil inorganic N concentrations after 96 days of subsequent incubation to quantify N mineralization (Sims et al., 1995).

In addition to incubations, switchgrass seedling response to high biochar rate was re-evaluated in replicated pot experiments under laboratory and greenhouse conditions. It was hypothesized that oil and tar residues from pyrolysis remained on biochar particles after cooling and storage. In addition, K, Ca, and Na salts were potential components of the biochar derived from slow pyrolysis of corn stover. To test these initial hypotheses, biochar was washed with varied solvents to remove organic residues and inorganic salts before biochar effects on switchgrass seedling emergence were re-evaluated in the Boonville soil amended with 64 Mg biochar ha^{-1}. Three extraction treatments comprised: 1) biochar washed with water only to dissolve and extract soluble salts, 2) biochar washed with acetone only to remove oil and tar residues, and 3) washing of biochar with acetone, then water, to remove oils/tars and soluble salts. Thirty grams of biochar were measured into a 1-L jar with either water or acetone to create a 10:1 solution to biochar ratio. A reciprocal shaker (6010 Benchtop Fixed-Speed, 180 osc min^{-1}, Eberbach Corporation, Ann Arbor, MI) was used to agitate biochar extraction mixtures for 24 hours. After shaking, extraction solutions were filtered (20 μm) and biochar was dried (60 °C for 3 days).

Under laboratory conditions (25 °C), previously washed and unwashed biochars were mixed in triplicate with Boonville soil at 64 Mg ha^{-1} and compared to controls of soil alone in small 4 x 4 x 6 cm peat pots. Treatments comprised Boonville soil alone, soil with unwashed biochar, soil with water-washed biochar, soil with acetone-washed biochar, and soil with biochar washed with both acetone and water. Twelve switchgrass seeds were sown at a 0.5-cm depth in each pot and watered daily with 50 mL deionized water. Switchgrass emergence was recorded daily until all seeds emerged in one or more treatments. Under greenhouse conditions, emergence was re-evaluated for the same biochar treatments (64 Mg ha^{-1} rate) in 10-cm diameter, plastic pots (12 cm deep) under greenhouse conditions. Twenty seeds were seeded in each pot, pots were watered daily with 100 mL deionized water, and switchgrass emergence was recorded daily until all seeds emerged in one or more treatments.

A third test was conducted to examine effects of washed and unwashed biochar on seedling emergence from the Boonville soil under high temperature and irradiance. Topsoil samples of Boonville soil, which were amended with unwashed biochar and with three corn stover biochars washed with acetone or water as described previously, were compared to soil alone. In addition, pot size and seeding practices were the same as the previous greenhouse experiment. Two heating lamps, each containing a 200-Watt incandescent light bulb, were placed approximately 0.5 m above the surface of pots after seeding. Thermocouples were inserted into the soil surface of one pot in each of the five replicated treatments and connected to a data logger for continuous monitoring of surface temperature (data not shown). Switchgrass emergence was recorded daily until all seeds emerged for one or more treatments. At the conclusion of emergence observations, soil in the 0- to 2-cm depth was collected from each pot for measurements of soil pH and electrical conductivity in extraction solutions (2:1 solution to soil) (Schofield and Taylor, 1955).

Results and Discussion

Mineralization Study

Mean cumulative CO_2 evolution over 96 days was greatest for 64 Mg biochar ha^{-1} in the Boonville soil cores, but variation among biochar rates was not statistically significant ($P > 0.05$) for either soil type (Figure B-1 and Figure B-2). After 96 days, cumulative CO_2-C evolution for four biochar rates ranged from 100 to 140 mg for the Boonville sandy loam and from 180 to 200 mg for the Burleson clay. Supplemental N-P-K fertilizer did not increase ($P > 0.05$) C mineralization rates with or without biochar for either soil (data not shown). Greater CO_2-C evolution in the Burleson clay than the Boonville sandy loam was attributed to a higher initial concentration of SOC for the Burleson soil. Clay-textured soils tend to enhance soil aggregation, which could reduce microbial access to antecedent SOC and increase SOC available during the incubation period.

To differentiate and quantify the percent of mineralizable carbon resulting from biochar only in each the Boonville and Burleson soils, means for soil alone (control)

(BC-0) were subtracted from means for treatments receiving 4, 16, and 64 Mg biochar ha^{-1} and divided by the total amount of biochar carbon in the incubated soil core. Additionally, means for soil amended with N-P-K fertilizer only (BC-0+NPK) were subtracted from treatments receiving 4, 16, and 64 Mg biochar ha^{-1} with supplemental N-P-K fertilizer and divided by the total amount of biochar carbon in the incubated soil core. It was assumed that the difference between mineralizable-C, as measured by CO_2 evolution, in each soil between each of the three biochar rates resulted from biochar and not other carbon sources in the soil. Even at the high 64-Mg biochar rate in both soils, biochar-C mineralized was less than 1% for treatments without fertilizer (Table B-1). Negative values for percent biochar-C mineralized resulted from variation in CO_2 evolution measurements and indicates C mineralization was greater in the soil alone compared to those treatments amended with 4, 16, or 64 Mg biochar ha^{-1}.

For both soil types, these relatively low values for C mineralization suggest that corn stover biochar, similar to other ‘black carbon’ materials, is relatively stable in soil. Major et al. (2010) reported that over two years after application, only 2.2% of black carbon applied to an Oxisol at 23.2 Mg ha^{-1} was lost through respiration. Recycling of biochar similar to that generated from slow pyrolysis in this study could enhance soil organic C storage, benefit soil quality, and sustain productivity of biomass crops.

For the Boonville soil, 64 Mg ha^{-1} biochar increased ($P < 0.001$) mineralization of TN to NH_4-N and NO_3-N compared to soil without biochar during the 96-day incubation period (Figure B-3). In contrast, cumulative mineralization of TN was similar among 0, 4, and 16 Mg biochar ha^{-1}. For the Burleson soil, cumulative mineralization of TN was similar ($P > 0.05$) among the three biochar rates and soil without biochar. Surprisingly, incorporation of supplemental N-P-K fertilizer with or without biochar did not significantly affect ($P > 0.05$) N mineralization for the Boonville or Burleson soil. Incubated soil cores were collected after switchgrass establishment and two simulated rainfall events. A large portion of labile N forms in biochar could have been mineralized during switchgrass establishment with or without supplemental N fertilizer in box lysimeters and taken up in plants or lost through runoff.

Switchgrass Emergence

Under greenhouse and controlled conditions in the laboratory, seedling emergence from the Boonville soil was similar ($P > 0.05$) without and with washed or unwashed biochar (Figure B-4). Although mean percent emergence under greenhouse conditions was lowest for biochar washed with both acetone and water, emergence under laboratory conditions was highest for the same treatment. Under both greenhouse and laboratory conditions, emergence percentages across all treatments ranged from 58 to 75%. In contrast, switchgrass emergence was only 14% in Boonville soil amended with 64 Mg ha^{-1} unwashed biochar under greenhouse conditions in box lysimeters.

The third emergence test under greenhouse conditions evaluated effects of high irradiance and temperature, which could have limited switchgrass emergence for the 64-Mg biochar rate in the previous lysimeter study. Under the lamps in the greenhouse, switchgrass emergence was highest in the Boonville soil alone and decreased ($P = 0.002$) with additions of unwashed and washed biochar (64 Mg ha^{-1}) (Figure B-5). Emergence from soil amended with unwashed char (18%) under the lamps was comparable to that for the Boonville soil amended with 64 Mg ha^{-1} biochar in the box lysimeters under greenhouse conditions. In addition, emergence rates were even lower for soil amended with biochar washed with acetone, water, or both. Mean surface temperatures of soil in pots under the lamps was 42 °C and ranged from 37 °C to 54 °C over the period of switchgrass emergence. In addition, incorporation of 64 Mg ha^{-1} unwashed and washed biochar increased ($P < 0.001$) electrical conductivity (EC) and pH in water extracts of the 0- to 2-cm layer of Boonville soil (Table B-2). Even after washing raw biochar with acetone and water to remove oils, tars, and salts, E.C. readings were 622 $\mu S\ cm^{-1}$, which was highest among all five treatments and 4.5 times greater than Boonville soil alone. Furthermore, pH readings jumped to over 9.5 in treatments with biochar, washed or unwashed, compared to a pH of 8.1 in the Boonville soil alone.

High evaporative loss under the lamps and high EC in biochar-amended treatments of Boonville soil indicated salt added through biochar could have increased soil pH and limited switchgrass seedling emergence. Even the highest biochar rate did not affect switchgrass emergence from the Burleson clay in box lysimeters under greenhouse conditions, which indicates fine soil texture and high surface area could mitigate effects of cations or salts in biochar. Biochar responses of sorghum, corn stover, and other biomass crops need to be evaluated under a range of soil textural classes and environmental conditions. In addition, chemical characterization is needed to determine what salts are present in biochar. Previous biochar research has not evaluated this hypothesis and further tests are needed to substantiate the soil and biochar properties limiting seedling emergence. However, a recent study by Gell et al. (2011) examining phytotoxic effects of ten biochars (from green waste, animal manure, and bamboo at various pyrolysis temperatures) on lettuce, radish, and wheat seeds found low yield responses. Although the exact mechanism triggering these responses was uncertain, the phytotoxicity was attributed to high EC or water-soluble phytotoxic organic compounds in the biochar.

CHAPTER IV

CONCLUSIONS

Development of renewable and sustainable energy resources, including bioenergy, could offset rising costs of fossil fuels and improve soil, water, and environmental quality. Recycling biochar, a co-product from pyrolysis, to biomass production fields could maintain soil fertility and prevent erosion and runoff of sediment and nutrients. The goal of recycling biochar back to soil is to create a sustainable crop production system in which feedstocks are supplied for bioenergy production without compromising valuable ecological resources that cropping systems provide.

Production and quality of biochar varies among feedstocks, pyrolysis conditions, and operations. In the present study, biochar derived from corn stover biomass was generated, characterized, and incorporated in a Boonville sandy loam and Burleson clay soil at 4, 16, and 64 Mg ha^{-1} with and without supplemental N-P-K fertilizer. During pyrolysis, 58% of total N, 86% of total P, and 101% of total K in feedstock was conserved in biochar. Increasing application rates of biochar increased concentrations of soil organic carbon (SOC) in both soil types. Compared to soil alone, incorporation of 64 Mg ha^{-1} biochar increased SOC 6.5-fold in the Boonville soil and 2.5-fold in the Burleson soil. In the Boonville soil, biochar increased concentrations of total N, P, and K and Mehlich-3 extractable K in the 0- to 5-cm depth. Similarly, biochar increased concentrations of total N, K, and Mehlich-3 extractable K in the Burleson soil at the 0- to 5-cm depth, but not concentrations of total P. In both soils, supplemental N-P-K fertilizer increased concentrations of Mehlich-3 extractable P with and without biochar at 0- to 5-cm and 5- to 15-cm depths, but did not affect micronutrient concentrations at either depth. Increased concentrations of extractable nutrients following the additions of biochar can contribute to nonpoint-source losses through runoff or leaching from production fields.

Switchgrass emergence and dry matter production was dramatically different between Boonville and Burleson soils. Boonville soil amended with 64 Mg biochar ha^{-1} reduced percent emergence of switchgrass to 14 %. In contrast, percent emergence was 63% for Burleson soil amended with the same biochar rate. For all biochar rates, aboveground biomass production and leaf area after establishment was greater for the Burleson than Boonville soil. Although mineral nutrients were conserved in recycled biochar, supplemental N-P-K fertilizer increased mean biomass production on both soils with or without biochar.

Variation of nutrient uptake reflected variation of switchgrass biomass production among treatments with and without biochar and N-P-K fertilizer. Similar to variation of biomass yield, switchgrass nutrient uptake was not directly related to biochar rate. Total N, P, and K uptake was similar among treatments without biochar and soil mixed with 4 and 16 Mg biochar ha^{-1}. For Boonville soil, N, P, and K uptake in switchgrass biomass was lower at 64 Mg biochar ha^{-1} than other biochar rates or soil alone. Similarly, P uptake was lower at 64 Mg biochar ha^{-1} than other treatments for the Burleson soil. In contrast to biochar effects on nutrient uptake, supplemental N-P-K fertilizer increased uptake of total N, P, and K in aboveground biomass compared to treatments without N-P-K fertilizer. For treatments receiving N-P-K fertilizer in the Boonville soil, uptake of N, P, and K from 4, 16, and 64 Mg ha^{-1} biochar was less than the control (BC-0+NPK). In the Burleson soil, however, rates of 16 and 64 Mg biochar increased uptake of N, P, and K compared to the control soil (BC-0+NPK). Greater switchgrass biomass production and nutrient uptake for the Burleson than Boonville soil was indicative of the mitigating effect of clay texture on the negative impacts of the highest biochar rate (64 Mg ha^{-1}). Negative values of N, P, and K uptake in switchgrass applied as biochar suggests returning biochar back to bioenergy production fields may not maintain sufficient levels of plant available nutrients required for crop production.

Mean runoff volume for the Boonville soil across all treatments was 46.0 L m^{-2} for the first rain event and 38.5 L m^{-2} for the second rain event. Similarly, Burleson soil mean runoff volumes were 40.9 L m^{-2} and 38.7L m^{-2} for first and second rainfall events, respectively. Analysis of runoff water from each of two rain events for both soils indicated biochar and fertilizer sources of P contributed to increases in runoff concentration of dissolved reactive P (DRP). In the first runoff event for the Boonville soil, 64 Mg biochar ha^{-1} increased runoff concentration of DRP 3.2-fold compared to soil without biochar. For the Burleson soil, 64 Mg biochar ha^{-1} increased runoff concentrations of DRP 2.1-fold compared to soil without biochar. In both soils, mean DRP concentration in runoff was reduced during the second rainfall event due to switchgrass uptake of P and mass loss of total P in runoff during the first rainfall event. For both soils, supplemental N-P-K fertilizer increased runoff concentrations of DRP compared to soil alone or amended with three biochar rates. Runoff losses of DRP increased due to increases in water- and Mehlich-3- extractable P in soil after N-P-K fertilizer additions.

Mass loss of total P (TP) and total K (TK) from Boonville and Burleson soils was greater for 64 Mg ha^{-1} biochar than soil without or with lower biochar rates. Supplemental N-P-K fertilizer increased mass loss of TP in runoff from the Boonville but not the Burleson soil and mass loss of TK was similar with or without N-P-K fertilizer for both soils. The contribution of biochar to a positive mass balance for N, P, and K was greater at 64 Mg ha^{-1} than other biochar rates. Runoff losses of K, as well as N and P, reduced nutrient amounts recovered in both soils after harvest of switchgrass biomass. Low to moderate rates of biochar application (4 or 16 Mg ha^{-1}) were not sufficient to offset K loss from the soil system during switchgrass establishment.

Recycling of biochar derived from pyrolysis could achieve net removal of CO_2 from the atmosphere and sequester C in soil. A 96-day incubation study indicated C mineralization was not affected by biochar rates up to 64 Mg ha^{-1} and low values of percent biochar-C mineralized support the concept that biochar is very recalcitrant in soils. For the Boonville soil, 64 Mg biochar ha^{-1} increased N mineralization. In contrast, incorporation of biochar did not affect N mineralization rate in the Burleson soil. Surprisingly, supplemental N-P-K fertilizer did not increase N mineralization rates in either soil. Complex, aromatic structures of biochar could have constrained microbial breakdown and C mineralization in amended soils. In addition, recycling of C through biochar may have increased the C:N ratio in soil to a point where mineralizable N was limited. In addition, N mineralization during switchgrass establishment could have reduced the N pool size available for mineralization during incubation of soil cores sampled after establishment.

Finally, switchgrass emergence tests revealed potential detrimental effects of salt accumulations in biochar applied to sandy soils. Emergence tests under high irradiance and temperature indicated accumulation of salts and increases in pH near the surface could inhibit seed germination and seedling emergence. Even after washing biochar with acetone and water to remove excess oils or tars and salts, switchgrass emergence was strongly diminished. Further investigations are needed to quantify salts present in biochar and other physical or chemical biochar properties that could affect plant emergence.

Overall, recycling biochar back to soil in bioenergy cropping systems remains a viable option to recycle nutrients to the soil, sequester carbon, and sustain biomass productivity. Additional research is needed to evaluate pyrolyzer design and operation in relation to biochar composition effects on soil properties and plant growth. Large scale field experiments need to approximate application rates that have the most beneficial impact on soil and environmental quality and determine the fate of biochar once applied to a variety of soils. Finally, biochar nutrients need to be properly managed to maintain an effective, efficient, sustainable cropping production system.

REFERENCES

Anex, R. P., L. R. Lynd, M.S. Laser, A. H. Heggenstaller, and M. Liebman. 2007. Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. Crop Science 47: 1327-1335.

Bertol, I., F. Engel, A. Mafra, O. Bertol, and S. Ritter. 2007. Phosphorus, potassium, and organic carbon concentrations in runoff water and sediments under different soil tillage systems during soybean growth. Soil and Tillage Research 94: 142-150.

Birt, L., R. Persyn, and P. Smith. 2007. Evaluation of an indoor nozzle-type rainfall simulator. Applied Eng. Agric. 23: 283-287.

Boateng, A. 2007. Characterization and thermal conversion of charcoal derived from fluidized-bed fast pyrolysis oil production of switchgrass. Ind. Eng. Chem. Res. 46: 8857-8862.

Bridgwater, A. V. 2003. Renewable fuels and chemicals by thermal processing of biomass. Chemical Engineering J. 91: 87-102.

Cheng, C. H., J. Lehmann, and M. H. Engelhard. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochim Cosmochim Acta 72: 1598-1610.

Eaton, A., and M. Franson. 2005. Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC.

Gaskin, J., C. Steiner, K. Harris, K. Das, and B. Bibens. 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Trans. ASABE 51: 2061-2069.

Gaskin, J., R. Speir, K. Harris, K. Das, R. Lee, L. Morris, and D. Fisher. 2010. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agronomy J 102: 623-633.

Gell, K., J. Van Groenigen, and M. L. Cayuela. 2011. Residues of bioenergy production chains as soil amendments: Immediate and temporal phytotoxicity. Journal of Hazardous Materials 186: 2017-2025.

Goyal, H., D. Seal, and R. Saxena. 2008. Biofuels from thermochemical conversion of renewable resources: A review. Renewable and Sustainable Energy Reviews 12: 504-517.

Haney, R. L., A. J. Franzluebbers, E. B. Porter, F. M. Hons, and D. A. Zuberer. 2004. Soil carbon and nitrogen mineralization: Influence of drying temperature. Soil Sci. Soc. Am. 68(2): 489-492.

Havlin, J. L., and P. N. Soltanpour. 1989. A nitric acid and plant digest method for use with inductively coupled plasma spectrometry. Commun. Soil Sci. Plant Anal. 14: 969-980.

Heggenstaller, A. H., R. P. Anex, M. Liebman, D. N. Sundberg, and L. R. Gibson. 2008. Productivity and nutrient dynamics in bioenergy double-cropping systems. Agronomy J 100: 1740-1748.

Jordan, H., G. Boody, W. Broussard, D. Glover, D. Keeny, B. McCown, G. McIsaac, M. Muller, H. Murray, J. Neal, C. Pansing, R. Turner, K. Warner, and D. Wyse. 2007. Sustainable development of the agricultural bio-economy. Science 316: 1570-1571.

Laird, D. A. 2008. The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agronomy J 100: 178-181.

Laird, D. A., R. C. Brown, J. E. Amonette, and J. Lehmann. 2009. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioproducts, and Biorefining 3: 547-562.

Lehmann, J. 2007. Bio-energy in the black. Front. Ecol. Environ 5: 381-387.

Lehmann, J., J. P. da Silva Jr., C. Steiner, T. Nehls, W. Zech, and B. Glaser. 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertilizer, manure, and charcoal amendments. Plant Soil. 249: 343-357.

Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems: A review. Mitigation and Adaptation Strategies for Global Change 11: 403-427.

Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J. O. Skjemstad, J. Thies, F. J. Luizao, J. Petersen, and E. G. Neves. 2006. Black carbon increases cation exchange capacity in soils. Soil Sci. Soc. Am. J. 70: 1719-1730.

Lopez, J. H. and F. Vargas-Albores. 2003. A microplate technique to quantify nutrients (NO_2^-, NO_3^-, NH_4^+, PO_4^{-3}) in seawater. Aquacult. Res. 35: 1201-1204.

Major, J., J. Lehmann, M. Rondon, and C. Goodale. 2010. Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. Global Change Biology 16: 1366-1379.

Mehlich, A. 1984. Mehlich-3 soil test extractant: A modification of Mehlich-2 extractant. Commun. Soil Sci. Plant Anal. 9(6): 477-492.

McGeehan, S. L., and D. V. Naylor. 1988. Automated instrumental analysis of carbon and nitrogen in plant and soil samples. Commun. Soil Sci. Plant Anal. 19: 493-505.

Novak, J. M., W. J. Brusscher, D. L. Laird, M. Ahmedna, D. W. Watts, and M. A. S. Niandou. 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Science 174: 105-112.

Pierzynski, G. 2000. Methods of phosphorus analysis for soils, sediments, residuals, and waters. Southern Cooperative Series Bulletin, vol. 396. North Carolina State Univ., Raleigh, pp. 91-93.

Pote, D. H., T. C. Daniel, P. A. Moore, Jr., D. J. Nichols, A. N. Sharpley, and D. R. Edwards. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. Soil Sci. Soc. Am. J. 60: 855-859.

Rondon, M., J. A. Ramirez, and J. Lehmann. 2005. Charcoal additions reduce net emissions of greenhouse gases to the atmosphere. *In* Proceedings of the 3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration. 21-24 March 2005, Baltimore, MD.

Schmidt, M. and A. Noack. 2000. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14: 777-794.

Schofield, R. K and A. W. Taylor. 1995. The measurement of soil pH. Soil Sci. Soc. Am. Proc. 19: 164-167.

Sharpley, A., S. Smith, O. Jones, W. Berg, and G. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. Journal of Environmental Quality 21: 30-35.

Sims, G. K., T. R. Ellsworth, and R. L. Mulvaney. 1995. Microscale determination of inorganic nitrogen in water and soil extracts. Commun. Soil Sci. Plant Anal. 26: 303-316.

Steiner, C., B. Glaser, W. G. Teixeira, J. Lehmann, W. E. H. Blum, and W. Zech. 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian ferralsol amended with compost and charcoal. J. Plant Nutrition Soil Sci. 171: 893-899.

Van Zwieten, L. S. Kimber, S. Morris, K. Chan, A. Downie, J. Rust, S. Joseph, and A. Cowie. 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 327: 235-246.

Wilhelm, W. W., J. M. F. Johnson, J. L. Hatfield, W. B. Voorhes, and D. R. Linden. 2004. Crop and soil productivity response to corn residue removal: A literature review. Agronomy J 96: 1-17.

APPENDIX A

Table A-1. Physical and chemical properties of corn stover feedstock and biochar generated from slow pyrolysis through a fixed-bed, auger-fed system.

	Total N	Total P	Total K	Total C	Water Extractable P (WEP)	BET Surface Area
	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	m^2 g^{-1}
Feedstock	11.8	876	1120	419		
Biochar	18.7	2037	3060	639	108	12.0
% Nutrients Conserved from Feedstock	58%	86%	101%			

Table A-2. Chemical properties of the Boonville and Burleson soils prior to incorporation of biochar and N-P-K fertilizer in box lysimeters.

	pH	Total N	Total P	Total K	Total C	Mehlich-3 P	Water Extractable P (WEP)	Mehlich-3 K
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Boonville Soil	7.8	577	71.5	277	2.8	18	0.94	106
Burleson Soil	6.6	1140	270	980	11.2	114	1.43	421

Table A-3. Physical and chemical properties of the Boonville soil (0-5 cm depth) alone and mixed with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Soil was sampled after switchgrass establishment. Numbers given represent mean value of each treatment. Letters indicate mean separation using LSD (P = 0.05).

	Bulk Density	pH	E.C.	Total N	Total P	Total K	SOC	Mehlich-3 P	Mehlich-3 K
Treatment	g cm^{-3}		µS cm^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
BC-0	1.30 a	7.7 bc	76 cd	486 b	80 c	298 c	2.5 d	20 c	75 e
BC-4	1.32 a	7.9 b	95 cd	458 b	84 c	333 c	3.8 d	20 c	93 de
BC-16	1.28 a	8.0 b	104 cd	535 b	90 c	510 b	6.1 c	23 c	176 bc
BC-64	1.14 b	8.6 a	159 ab	802 a	129 b	1158 a	15.8 b	34 c	643 a
BC-0+NPK	1.32 a	7.6 c	58 d	443 b	121 b	325 c	2.7 d	49 b	89 de
BC-4+NPK	1.32 a	7.7 bc	113 bc	553 b	121 b	348 c	3.2 d	55 ab	129 cd
BC-16+NPK	1.33 a	7.9 b	171 a	483 b	127 b	525 b	6.1 c	49 b	186 b
BC-64+NPK	1.17 b	8.6 a	105 cd	868 a	167 a	1256 a	17.7 a	65 a	657 a
Prob > F	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Table A-4. Physical and chemical properties of the Burleson soil (0-5 cm depth) alone and mixed with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Soil was sampled after switchgrass establishment. Numbers given represent mean value of each treatment. Letters indicate mean separation using LSD (P = 0.05).

	Bulk Density	pH	E.C.	Total N	Total P	Total K	SOC	Mehlich-3 P	Mehlich-3 K
Treatment	g cm^{-3}		µS cm^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
BC-0	1.22 a	6.8 c	381 a	1238 c	281 a	997 b	12.7 d	84 e	293 d
BC-4	1.26 a	7.0 bc	447 a	1245 c	270 a	1052 b	14.6 d	87 de	329 d
BC-16	1.16 a	7.0 bc	382 a	1434 bc	289 a	1300 b	18.3 c	91 cde	483 bc
BC-64	0.99 c	7.4 a	392 a	2139 a	369 a	2643 a	39.5 a	97 bcd	1056 a
BC-0+NPK	1.24 a	6.9 c	414 a	1248 c	289 a	1007 b	13.1 d	100 abc	347 d
BC-4+NPK	1.21 a	7.0 bc	386 a	1359 c	309 a	1188 b	14.6 d	105 ab	384 cd
BC-16+NPK	1.13 ab	7.0 bc	370 a	1577 bc	251 a	1076 b	19.8 c	107 ab	516 b
BC-64+NPK	1.00 bc	7.2 ab	394 a	1842 ab	244 a	1547 b	27.6 b	109 a	976 a
Prob > F	0.002	0.007	n.s.	0.006	n.s.	0.002	< 0.001	0.003	< 0.001

Table A-5. Chemical properties of the Boonville soil (5-15 cm depth) alone and mixed with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Soil was sampled after switchgrass establishment. Numbers given represent mean value of each treatment. Letters indicate mean separation using LSD (P = 0.05).

	pH	E.C.	Total N	Total P	Total K	SOC	Mehlich-3 P	Mehlich-3 K
Treatment		µS cm^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
BC-0	7.4 e	86 e	503 de	77 c	296 c	3.9 d	19 d	75 f
BC-4	7.8 d	88 e	645 c	84 c	393 bc	4.3 cd	20 cd	110 ef
BC-16	8.1 c	141 de	608 cd	91 c	583 b	7.9 b	24 cd	232 c
BC-64	8.6 a	268 b	1010 a	136 b	1672 a	20.1 a	32 c	776 b
BC-0+NPK	7.0 f	188 cd	480 e	131 b	417 bc	3.5 d	50 b	120 e
BC-4+NPK	7.4 e	203 bcd	514 de	123 b	438 bc	4.6 cd	61 ab	172 d
BC-16+NPK	7.9 d	217 bc	572 cde	118 b	593 b	7.1 bc	49 b	264 c
BC-64+NPK	8.4 b	354 a	844 b	183 a	1573 a	18.7 a	68 a	853 a
Prob > F	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Table A-6. Chemical properties of the Burleson soil (5-15 cm depth) alone and mixed with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Soil was sampled after switchgrass establishment. Numbers given represent mean value of each treatment. Letters indicate mean separation using LSD (P = 0.05).

	pH	E.C.	Total N	Total P	Total K	SOC	Mehlich-3 P	Mehlich -3 K
Treatment		µS cm^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
BC-0	6.9 c	454 b	1537 ab	274 e	1022 d	12.7 d	89 bc	318 c
BC-4	7.0 bc	410 b	1250 b	294 cde	1090 d	14.7 cd	85 c	337 c
BC-16	7.1 b	421 b	1243 b	290 de	1357 c	18.9 bc	95 bc	526 b
BC-64	7.3 a	666 a	1867 a	340 b	2580 a	34.9 a	109 ab	1117 a
BC-0+NPK	6.8 d	480 b	1189 b	321 bcd	1148 d	13.1 d	122 a	360 c
BC-4+NPK	6.8 cd	548 ab	1204 b	336 bc	1186 d	14.2 d	121 a	403 c
BC-16+NPK	6.9 cd	686 a	1256 b	339 b	1553 b	19.9 b	126 a	603 b
BC-64+NPK	7.3 a	703 a	1806 a	396 a	2721 a	36.7 a	126 a	1199 a
Prob > F	< 0.001	0.003	0.02	< 0.001	< 0.001	< 0.001	0.001	< 0.001

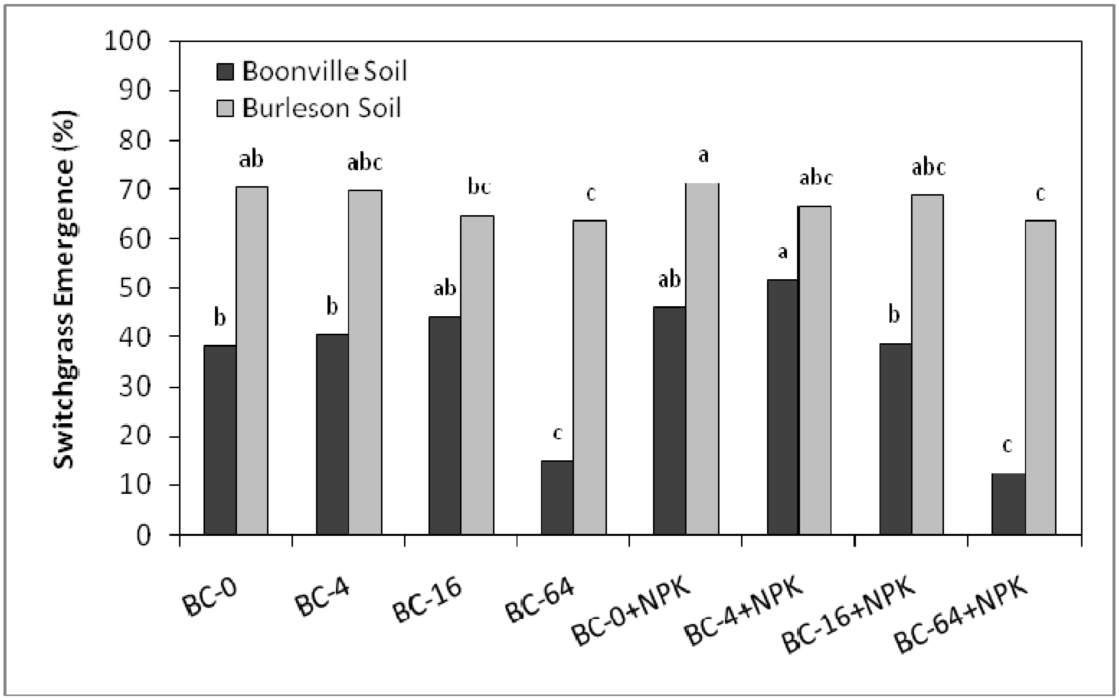

Figure A-1. Switchgrass emergence for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD ($P = 0.05$).

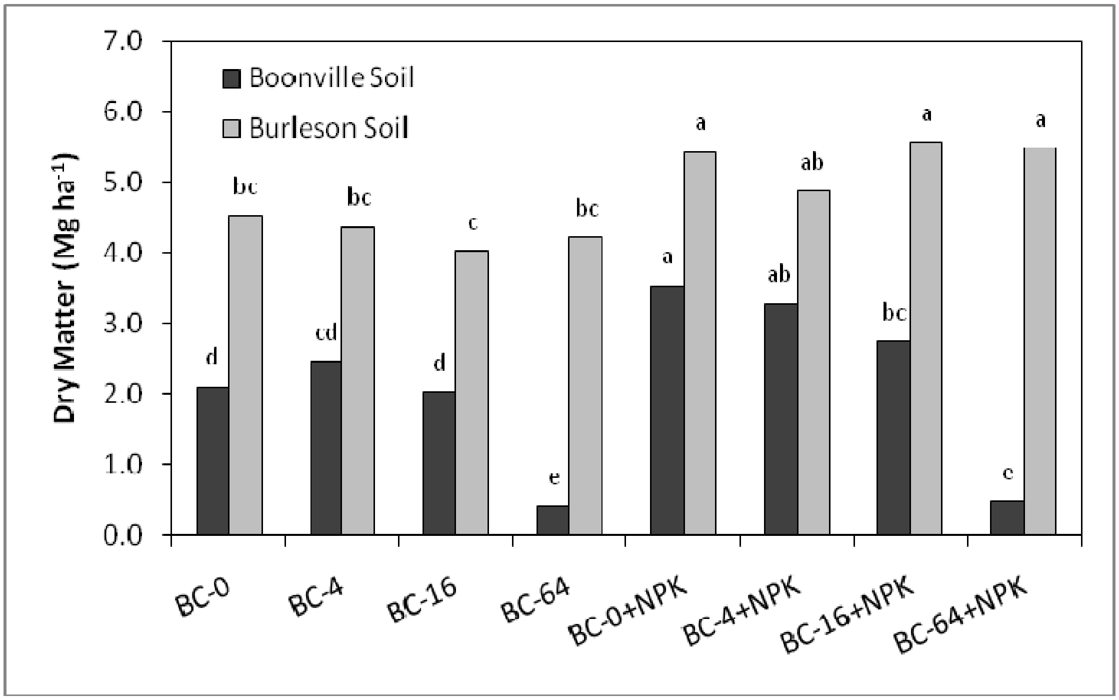

Figure A-2. Mean dry matter production of switchgrass for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

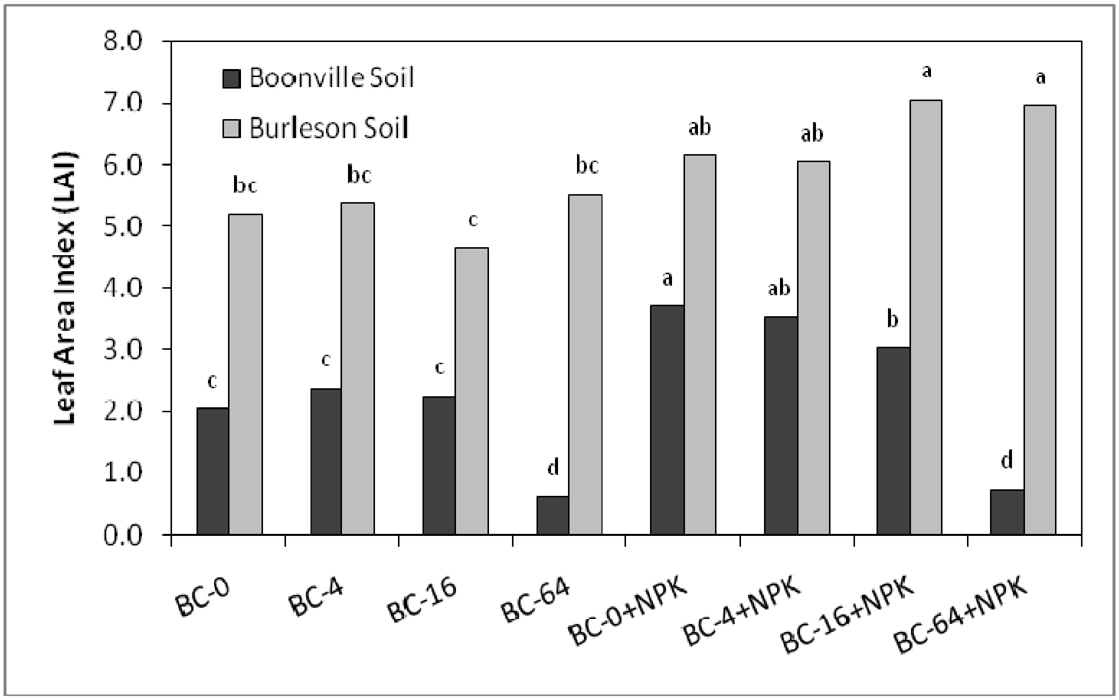

Figure A-3. Mean leaf area index (LAI) of switchgrass for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

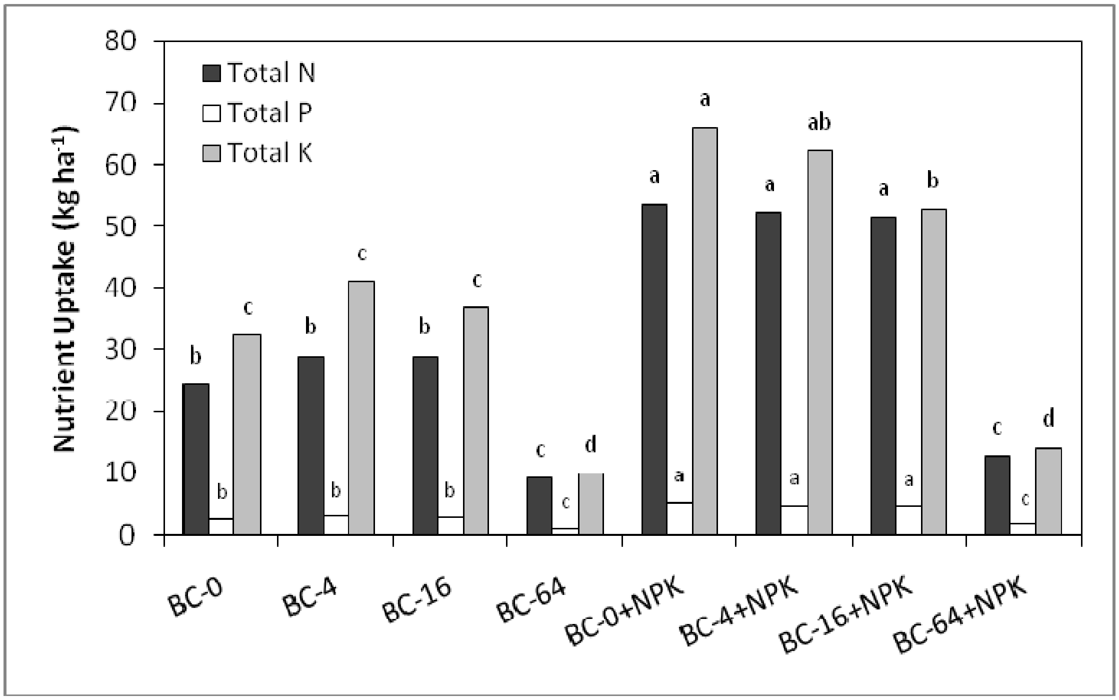

Figure A-4. Uptake of total N, P, and K in aboveground switchgrass biomass for the Boonville soil alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

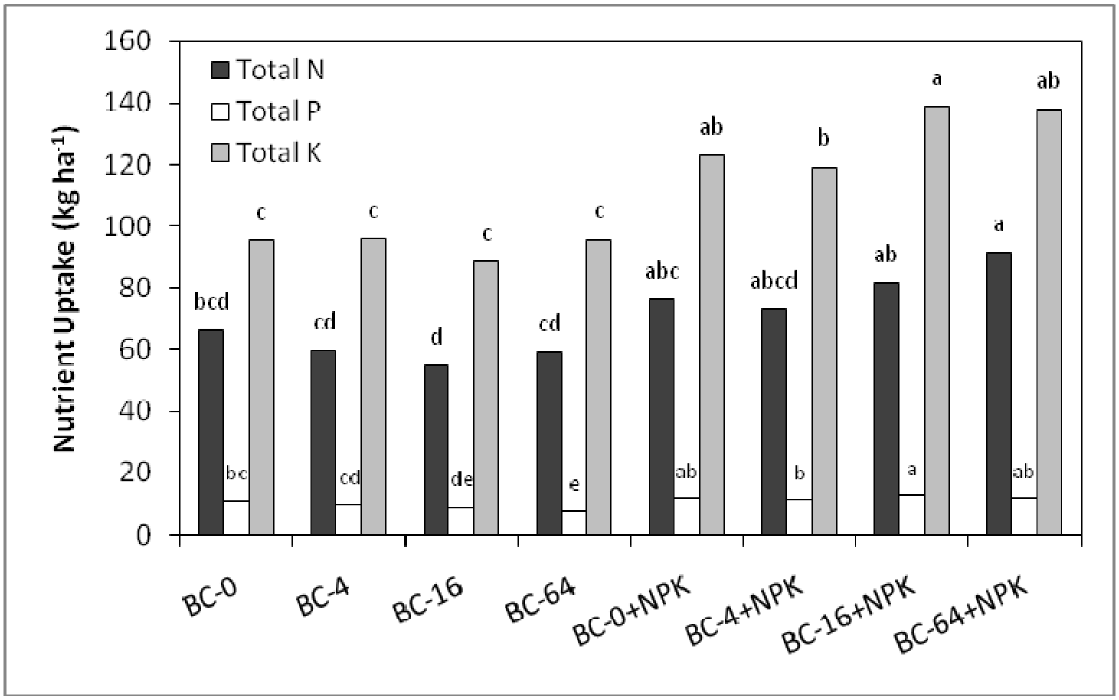

Figure A-5. Uptake of total N, P, and K in aboveground switchgrass biomass for the Burleson soil alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

Table A-7. Percent N, P, and K applied as biochar at 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer, taken up by switchgrass in the Boonville soil. BC -N, -P, and -K taken up in switchgrass is calculated as the difference in plant uptake between control treatments (BC-0 or BC-0+NPK) and 4, 16, or 64 Mg BC ha^{-1} (with or without supplemental N-P-K fertilizer), divided by the N, P, and K rate applied as biochar.

	Total N			**Total P**			**Total K**		
	Applied as BC	Plant Uptake	BC-N Taken up in Switchgrass	Applied as BC	Plant Uptake	BC-P Taken up in Switchgrass	Applied as BC	Plant Uptake	BC-K Taken up in Switchgrass
Treatment	kg ha^{-1}	kg ha^{-1}	%	kg ha^{-1}	kg ha^{-1}	%	kg ha^{-1}	kg ha^{-1}	%
BC-0	0	24.3	0.0	0	2.6	0.0	0	32.3	0.0
BC-4	76	29.0	6.2	8	2.8	2.5	12	41.0	72.5
BC-16	300	28.9	1.5	33	2.8	0.6	49	36.7	9.0
BC-64	1198	9.1	-1.3	130	1.0	-1.2	196	10.0	-11.4
BC-0+NPK	0	53.6	0.0	0	5.3	0.0	0	66.1	0.0
BC-4+NPK	76	52.2	-1.8	8	4.7	-7.5	12	62.1	-33.3
BC-16+NPK	300	51.4	-0.7	33	4.6	-2.1	49	52.7	-27.3
BC-64+NPK	1198	12.7	-3.4	130	1.6	-2.8	196	14.0	-26.6

Table A-8. Percent N, P, and K applied as biochar at 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer, taken up by switchgrass in the Burleson soil. BC -N, -P, and -K taken up in switchgrass is calculated as the difference in plant uptake between control treatments (BC-0 or BC-0+NPK) and 4, 16, or 64 Mg BC ha^{-1} (with or without supplemental N-P-K fertilizer), divided by the N, P, and K rate applied as biochar.

	Total N			**Total P**			**Total K**		
	Applied as BC	Plant Uptake	BC-N Taken up in Switchgrass	Applied as BC	Plant Uptake	BC-P Taken up in Switchgrass	Applied as BC	Plant Uptake	BC-K Taken up in Switchgrass
Treatment	kg ha^{-1}	kg ha^{-1}	%	kg ha^{-1}	kg ha^{-1}	%	kg ha^{-1}	kg ha^{-1}	%
BC-0	0	66.0	0.0	0	10.9	0.0	0	95.5	0.0
BC-4	76	59.5	-8.6	8	9.7	-15.0	12	96.0	4.2
BC-16	300	54.5	-3.8	33	8.9	-6.1	49	88.5	-14.3
BC-64	1198	59.1	-0.6	130	7.6	-2.5	196	95.8	0.2
BC-0+NPK	0	76.3	0.0	0	11.8	0.0	0	122.9	0.0
BC-4+NPK	76	73.3	-3.9	8	11.3	-6.3	12	119.1	-31.7
BC-16+NPK	300	81.4	1.7	33	12.8	3.0	49	139.0	32.9
BC-64+NPK	1198	91.4	1.3	130	11.7	-0.1	196	137.9	7.7

Table A-9. Mean concentration of dissolved reactive phosphorus (DRP) in runoff during each of the two simulated rain events for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters indicate mean separation using LSD (P = 0.05).

	Boonville Soil				**Burleson Soil**			
	1st Rain DRP		2nd Rain DRP		1st Rain DRP		2nd Rain DRP	
Treatment	---------- mg L^{-1} --------				-------- mg L^{-1} --------			
BC-0	0.004	c	0.009	c	0.129	bc	0.088	d
BC-4	0.013	c	0.017	c	0.122	c	0.113	cd
BC-16	0.043	c	0.027	c	0.158	bc	0.132	bcd
BC-64	0.254	b	0.173	b	0.302	a	0.170	ab
BC-0+NPK	0.246	b	0.098	bc	0.172	bc	0.122	bcd
BC-4+NPK	0.174	bc	0.071	bc	0.171	bc	0.146	bc
BC-16+NPK	0.184	bc	0.101	bc	0.210	b	0.158	bc
BC-64+NPK	0.545	a	0.494	a	0.337	a	0.210	a
Prob > F	< 0.001		< 0.001		< 0.001		< 0.001	

Table A-10. Cumulative mass loss of total P, total dissolved P (TDP), and dissolved reactive P (DRP) in runoff from two simulated rainfall events for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters indicate mean separation using LSD (P = 0.05).

	Boonville Soil						**Burleson Soil**					
	Total P		TDP		DRP		Total P		TDP		DRP	
Treatment	----------------- kg ha^{-1} ---------------						--------------- kg ha^{-1} ---------------					
BC-0	0.72	cd	0.13	c	0.00	d	0.27	b	0.15	c	0.09	d
BC-4	0.91	cd	0.14	c	0.01	cd	0.27	b	0.20	bc	0.10	cd
BC-16	0.71	cd	0.17	c	0.03	cd	0.39	b	0.20	bc	0.12	bcd
BC-64	1.67	ab	0.33	b	0.18	b	0.57	a	0.27	ab	0.17	ab
BC-0+NPK	1.24	bc	0.27	bc	0.15	b	0.26	b	0.21	bc	0.12	bcd
BC-4+NPK	0.66	d	0.21	bc	0.10	bcd	0.31	b	0.20	bc	0.12	bcd
BC-16+NPK	1.08	cd	0.27	bc	0.13	bc	0.37	b	0.24	bc	0.15	bc
BC-64+NPK	2.18	a	0.62	a	0.46	a	0.56	a	0.35	a	0.22	a
Prob > F	< 0.001		< 0.001		< 0.001		< 0.001		0.01		0.004	

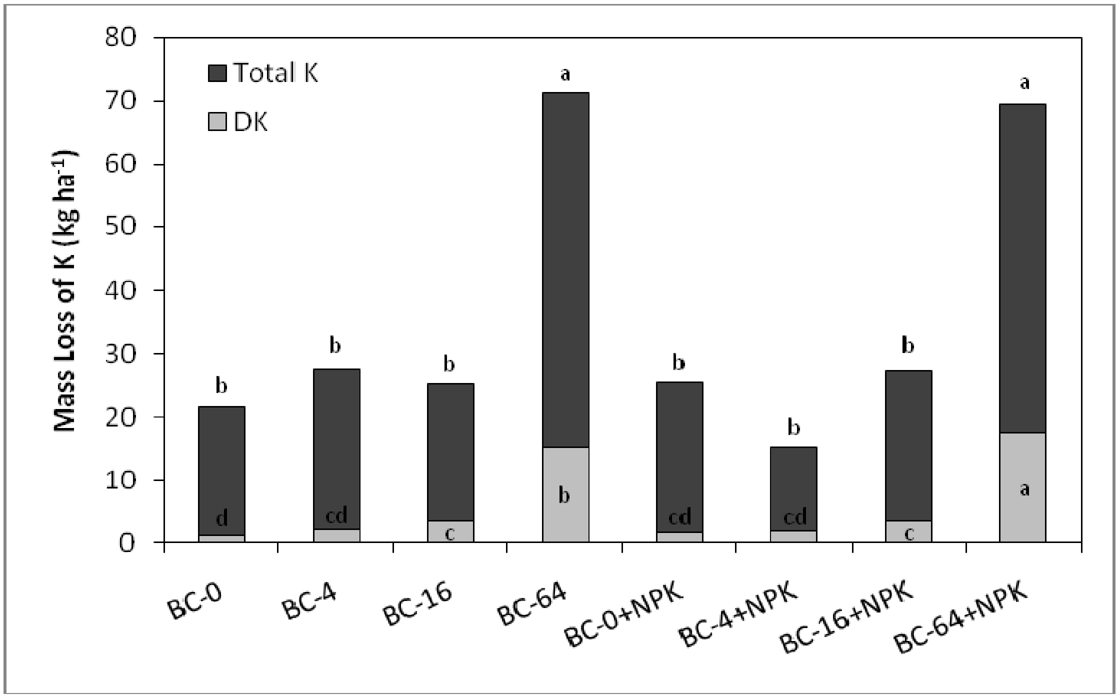

Figure A-6. Cumulative mass loss of total K and dissolved K (DK) in runoff from two simulated rainfall events for the Boonville soil alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

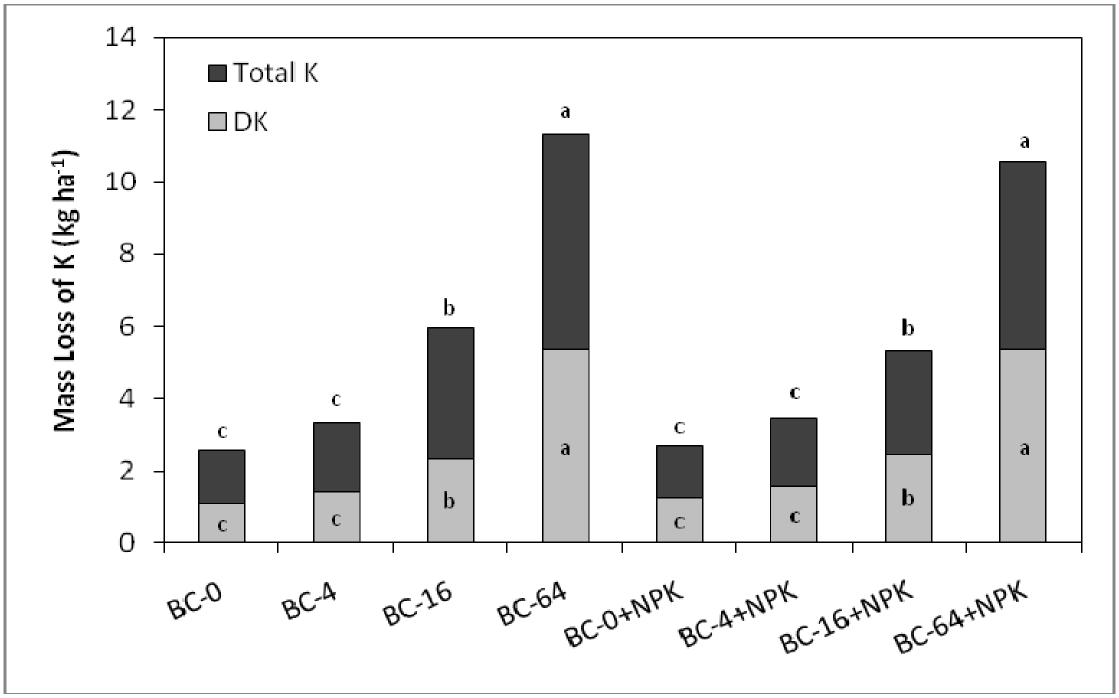

Figure A-7. Cumulative mass loss of total K and dissolved K (DK) in runoff from two simulated rainfall events for the Burleson soil alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Letters above bars indicate mean separation using LSD (P = 0.05).

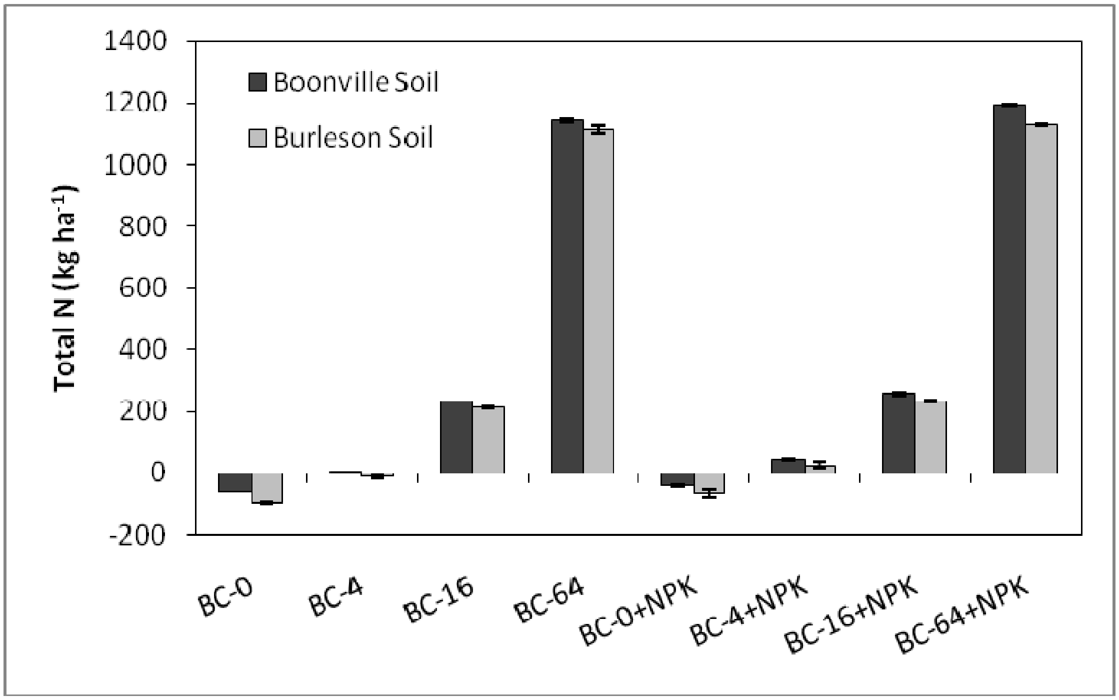

Figure A-8. Mass balance of nitrogen (total N inputs – total N outputs) for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Error bars indicate standard error of the mean.

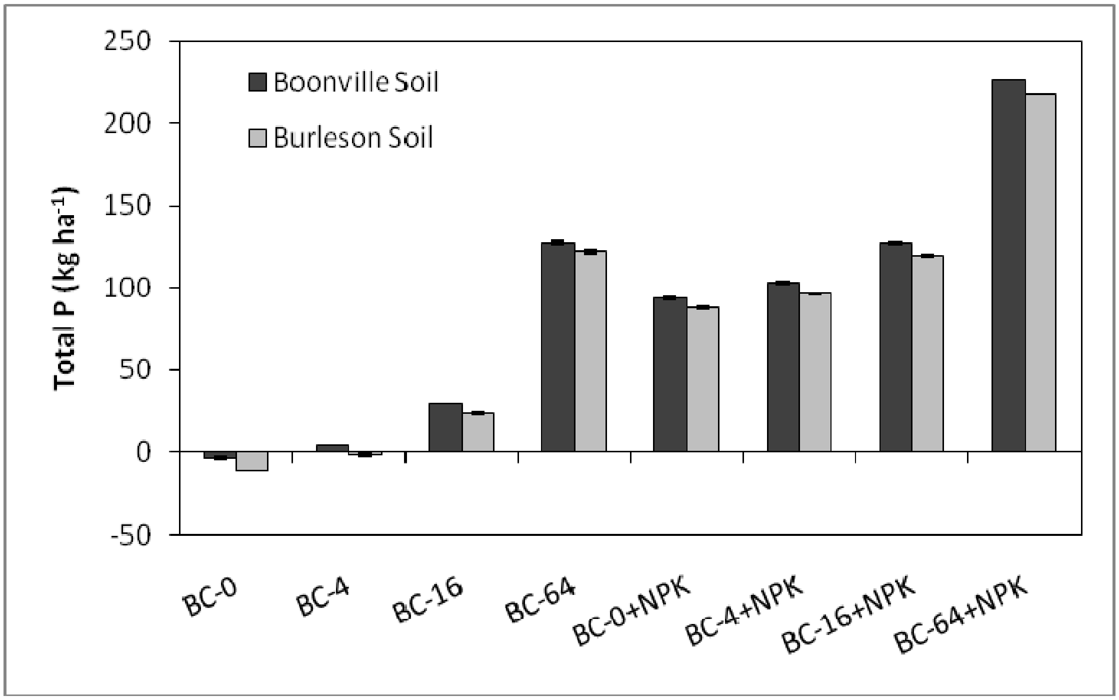

Figure A-9. Mass balance of phosphorus (total P inputs – total P outputs) for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Error bars indicate standard error of the mean.

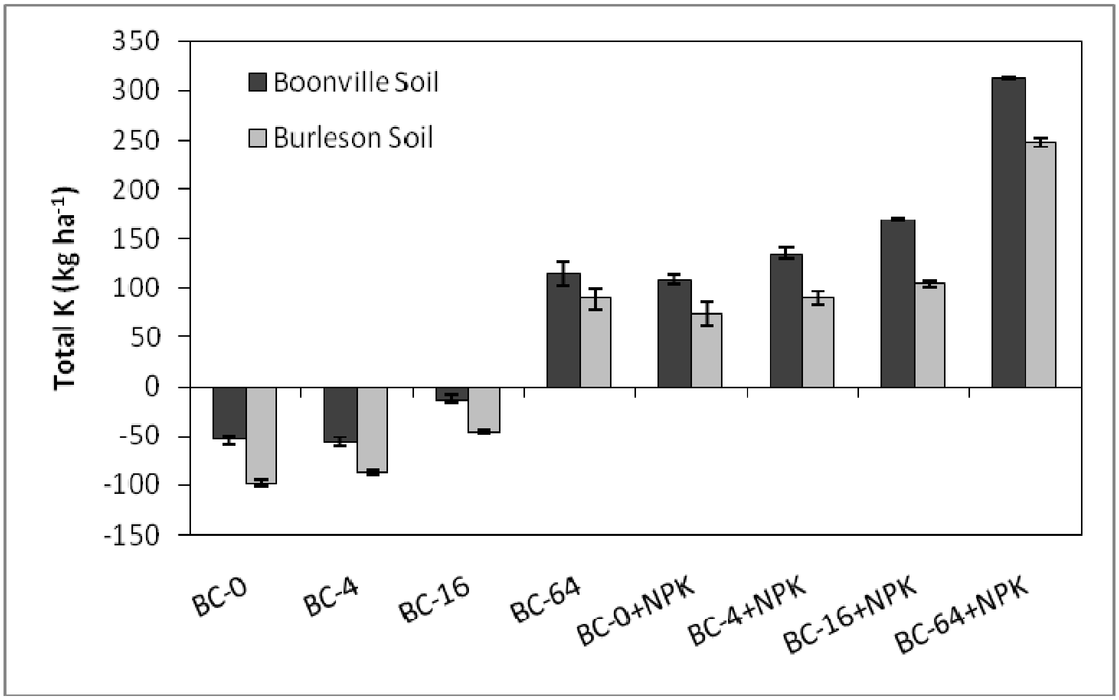

Figure A-10. Mass balance of potassium (total K inputs – total K outputs) for Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer. Error bars indicate standard error of the mean.

APPENDIX B

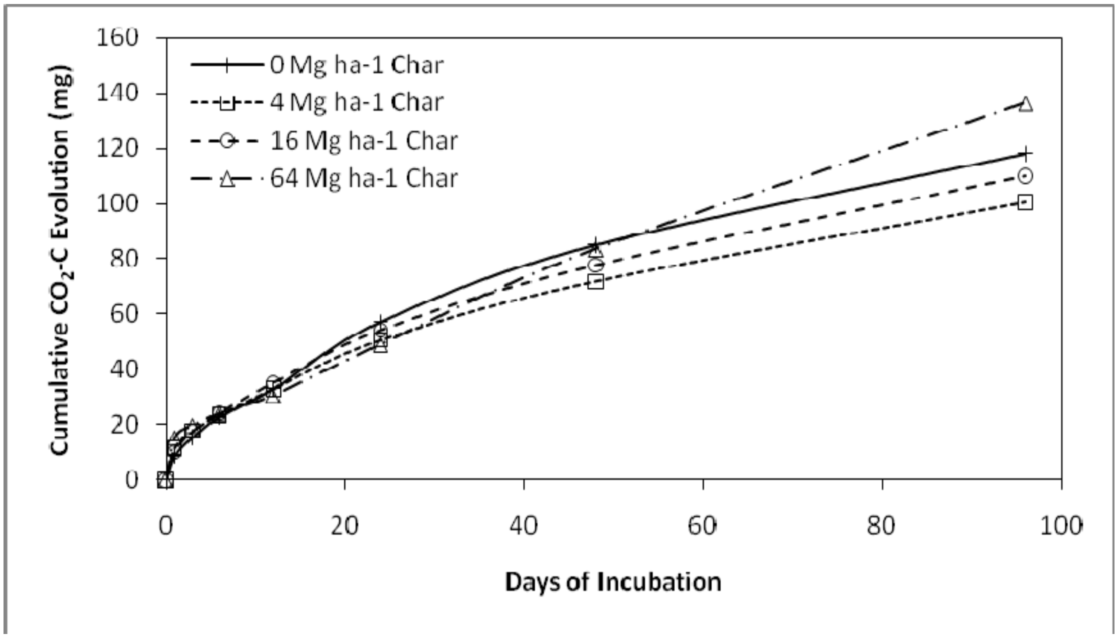

Figure B-1. Mean cumulative CO_2-C evolution from Boonville soil alone and with 4, 16, and 64 Mg ha^{-1} of biochar during a 96-day incubation.

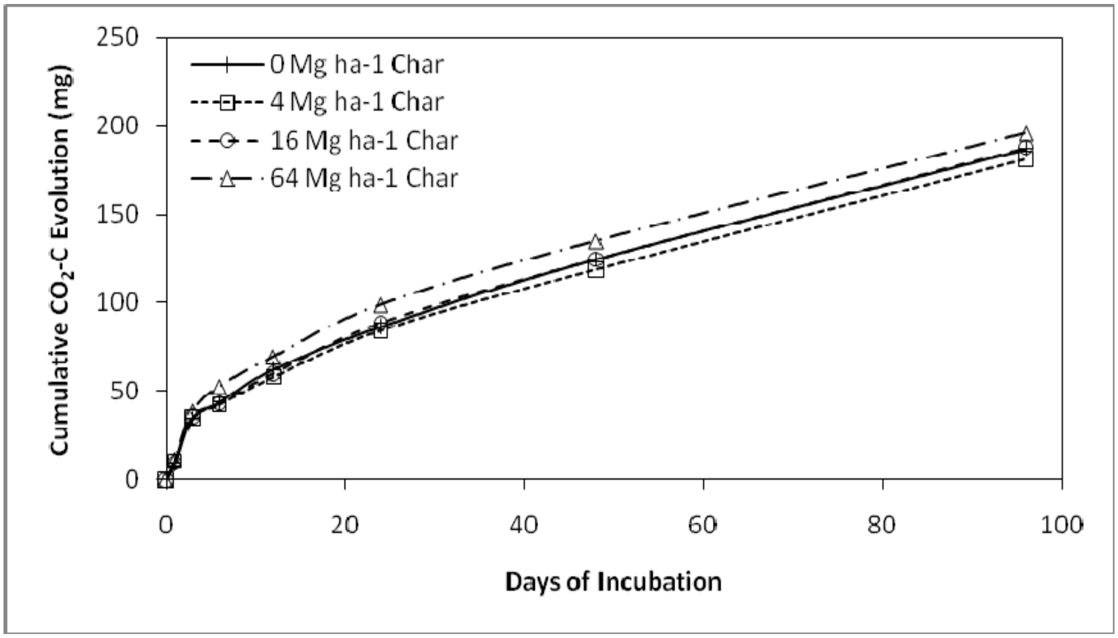

Figure B-2. Mean cumulative CO_2-C evolution from Burleson soil alone and with 4, 16, and 64 Mg ha^{-1} of biochar during a 96-day incubation.

Table B-1. Percent of biochar carbon mineralized for each treatment in both the Boonville and Burleson soils during a 96-day incubation. Percent biochar-C mineralized is calculated as the difference between control treatments (BC-0 or BC-0+NPK) and 4, 16, or 64 Mg BC ha^{-1} (with or without supplemental N-P-K fertilizer), divided by the total biochar-C in the incubated soil core.

	Boonville Soil			**Burleson Soil**		
	Cumulative CO_2 over 96 days	Biochar-C in Incubated Core	Biochar-C Mineralized	Cumulative CO_2 over 96 days	Biochar-C in Incubated Core	Biochar-C Mineralized
Treatment	mg	mg	%	mg	mg	%
BC-0	118.1	0.0	0.0	187.0	0.0	0.0
BC-4	100.5	184.0	-9.6	181.1	437.7	-1.3
BC-16	110.0	602.6	-1.3	187.7	749.1	0.1
BC-64	136.4	2052.0	0.9	195.8	3361.3	0.3
BC-0+NPK	96.8	0.0	0.0	161.3	0.0	0.0
BC-4+NPK	125.4	168.9	16.9	178.9	186.6	9.4
BC-16+NPK	113.7	564.4	3.0	152.5	702.9	-1.3
BC-64+NPK	141.1	2388.5	1.9	171.6	1606.8	0.6

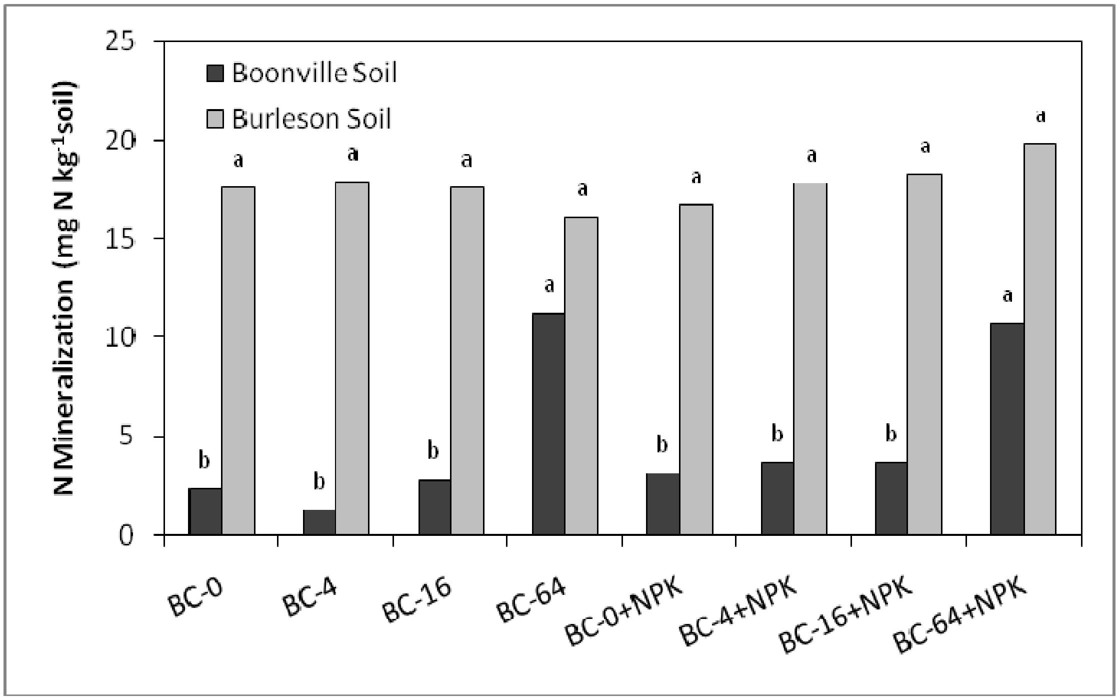

Figure B-3. Cumulative mineralization of TN to NH_4-N + NO_3-N in Boonville and Burleson soils alone and amended with 4, 16, and 64 Mg biochar (BC) ha^{-1}, with and without supplemental N-P-K fertilizer, during a 96-day incubation. Letters above bars indicate mean separation using LSD ($p = 0.05$).

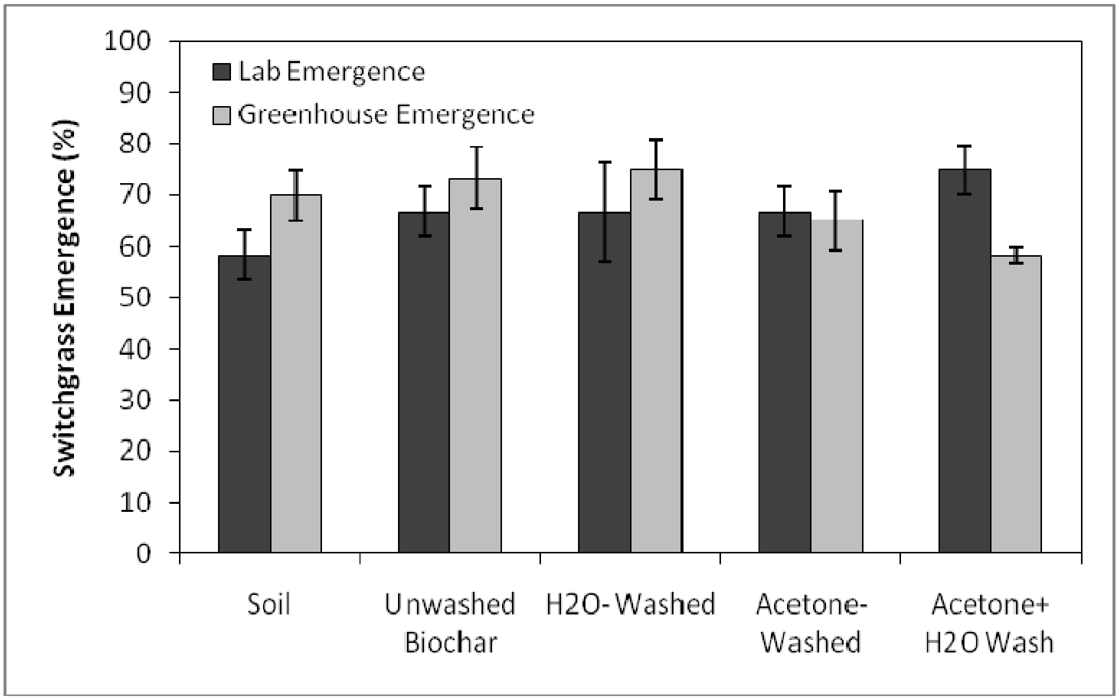

Figure B-4. Switchgrass emergence from Boonville soil alone and amended with 64 Mg ha^{-1} washed and unwashed biochar under laboratory and greenhouse conditions. Error bars indicate standard error of the mean.

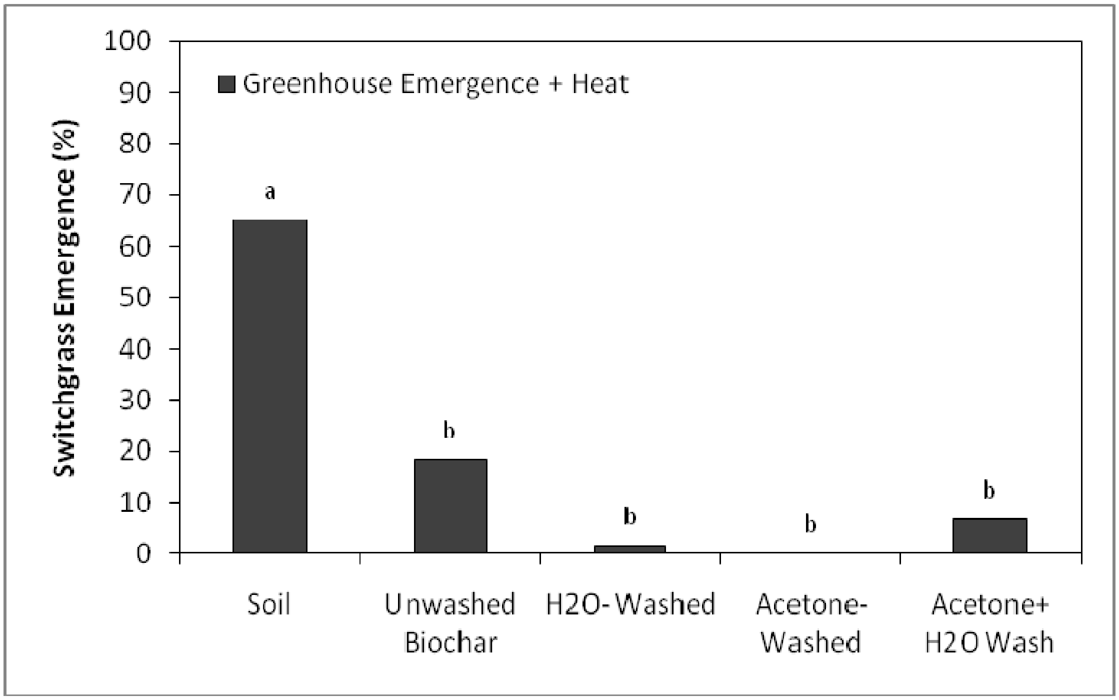

Figure B-5. Switchgrass emergence from Boonville soil alone and amended with 64 Mg ha^{-1} of washed and unwashed biochar. Incandescent lamps contributed to high irradiance and soil temperature under greenhouse conditions. Letters above bars indicate mean separation using LSD (p = 0.05).

Table B-2. Percent switchgrass emergence and electrical conductivity (EC) and pH of extracts of Boonville soil mixed with 64 Mg ha^{-1} of unwashed or washed biochar. Letters indicate mean separation using LSD (p = 0.05).

	Switchgrass Emergence		Electrical Conductivity		pH	
Treatment	%		µS cm^{-1}			
Boonville Soil	65.0	a	135.9	c	8.1	c
Unwashed Biochar	18.3	b	464.0	b	9.8	a
H2O-Washed Biochar	1.7	b	415.9	b	9.7	a
Acetone-Washed Biochar	0.0	b	495.3	b	9.5	b
Acetone + H_2O Washed Biochar	6.7	b	622.3	a	9.5	b
Prob > F	0.002		< 0.001		< 0.001	

VITA

Derek Howard Husmoen
Department of Soil and Crop Sciences
Heep Center
Texas A&M University
College Station, TX 77843-2474
derekhusmoen36@tamu.edu

Education:

M.S., Soil Science, Texas A&M University, 2011
B.S., Agricultural Engineering Technology, University of Wisconsin- River Falls, 2008

Professional Memberships:

- American Society of Agronomy
- Crop Science Society of America
- Soil Science Society of America
- Alpha Zeta

Awards:

- Texas Water Resources Institute (TWRI) Mills Scholarship Recipient, 7/2010
- 2008 Outstanding Senior in the College of Agriculture, Univ. of Wisconsin-River Falls, 3/2009
- 2007-2008 ASABE Wisconsin Section Agricultural Engineering Technology Student of the Year, 12/2008

Abstracts and Presentations:

- Husmoen, D., S. Capareda, T. Provin, C. Munster, R. Schnell, J. Wise, and D. Vietor. 2010. Biochar effects on switchgrass establishment and water quality. ASA-CSSA-SSSA Annual Meetings, Long Beach, CA. 11/2010.
- Husmoen, D., D. Vietor, F. Rouquette, Jr., S. Abernathy, and T. Cothren. 2010. Comparative water stress responses between bermudagrass cultivars. Texas A&M AgriLife Annual Conference. 1/2010.