# Biochar for Saline-Sodic Soil Reclamation, Phosphorus Retention, and Crop Growth Improvement

by

Abdelhafid Ahmed Saleh Dugdug

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Soil Science

Department of Renewable Resources
University of Alberta

# ABSTRACT

Biochar incorporation into soils influences many of the soil's physical/chemical properties. The potential of using biochar for reclamation of saline-sodic soils is not well evaluated. Furthermore, how salinity would influence Phosphorus (P) sorption capacity of biochar is not clear. The main goals of this research were to determine the possibility of using biochar on amelioration of a saline-sodic soil and reduce the loss of P from soils, and to evaluate how growth and yield of wheat responses to a biochar amended saline-sodic soil.

The biochars used in this research were produced from wheat straw, hardwood, and willow wood at pyrolysis temperature ranged between 500 and 550 °C. The used soils were sampled from the plow layer (0.1 m) of saline-sodic and non-saline soils of a local farm in Alberta, Canada. The influence of salinity and biochar type on P sorption by biochar was evaluated through a P sorption isotherm experiment. The hardwood biochar was selected as a soil amendment for followed experiments based on its high P sorption capacity. The effect of biochar application at different rates (0, 2, 5 and 8% [w/w]) on reducing salinity and leaching loss of P was evaluated using column leaching experiments. The 0 and 5% of biochar application rates were selected to evaluate the growth and yield of spring wheat in a pot experiment. The responses of the crop to biochar, manure and soil type treatments were evaluated by measuring plant nutrient contents and plant growth and productivity.

Phosphorus sorption by wheat straw and hardwood biochars increased as the P concentration in solution increased, with willow wood biochar exhibiting an opposite trend for P sorption. However, the pattern for P sorption became similar as the other biochars after the willow wood biochar was de-ashed. Willow wood biochar had the highest P sorption followed by hardwood and wheat straw biochars. Salinity in the aqueous solution influenced P sorption by hardwood and willow wood but not by wheat straw biochar.

The electrical conductivity (EC) in leachates from a hardwood biochar amended saline-sodic soil decreased with increasing biochar application rate; however, an opposite trend occurred during sequential events. Biochar addition significantly increased movement of water through the soil and prevented waterlogging of the saline-sodic soil; however, it reduced water retention time in the soil which likely resulted in variation of leachate's EC of the biochar treatments. Generally, biochar addition significantly reduced EC of saturated paste extracts ($EC_e$), exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), and some of the soluble and exchangeable cations. The evaluation of the effectiveness of hardwood biochar for reducing leaching loss of P from a non-saline soil revealed that leaching loss of total P (TP), dissolved reactive P (DRP) and multivalent cations from manured soil was significantly decreased with the increasing biochar application rate. The reduction of leaching losses of multivalent cations in association with increasing soil pH due to biochar application is suggested to be responsible for the large reduction of TP and DRP.

Separate application of biochar and manure increased nutrient availability. However, the nutrient availability was highest when the saline-sodic soil received a combined application of manure and biochar. Nutrient concentrations in the plant tissue were increased by biochar application, but not by manure application. The crop in the treatment with biochar + manure application to the saline-sodic soil had the highest survival rate, nutrient contents, dry matter, and yield. However, manure application without biochar significantly reduced the survival rate in the non-saline soil. The significant response of crops to biochar application, particularly in the saline-sodic soil, was attributed to the role of biochar in improving soil physical/chemical properties, and in facilitating the leaching of salts from the rooting zone.

Hardwood biochar is an effective P sorbent relative to the other two biochars used. Application of hardwood biochar at 5% was the optimal rate for reducing salinity while minimizing

P leaching losses from soils. Also, application of this biochar enhanced general soil quality including soil pH, water holding capacity and infiltration, and fertilization use efficiency by plant and resulted in improvement in plant productivity; therefore, this biochar should be beneficial for saline-sodic soil reclamation as well as for reducing the negative effect on water quality from excessive P input.

# PREFACE

This dissertation is an original work conducted by Abdelhafid Ahmed Saleh Dugdug. A version of Chapter 2 of this thesis has been submitted as Dugdug, A., Chang, S., Ok, Y., Raiapksha, A., Anyia, A. Phosphorus sorption capacity of biochar varies with biochar type and salinity level. Environmental Science & Pollution Research. Versions of chapters 3, 4 and 5 are being prepared for submission to peer reviewed journals. I was responsible for data collection, data analysis and manuscript writing. Chang, S. and Anyia, A. were the supervisory authors and they were involved in research concept formulation and edited manuscripts.

## ACKNOWLEDGMENTS

First and foremost, praises and thanks to **ALLAH**, for His showers of blessings throughout my research work to complete the research successfully.

My special deepest thanks and best wishes go to my advisor: Dr. Scott X. Chang. Your influence on my ability to play a role in this industry and face and conquer challenges is appreciated more than you could know. You are the father of my professional wisdom and my inspiration to overcome all stands in the way of my ideas. Thank you Scott for all that you have done, I'm forever in your debt. Thank you, Dr. Anthony Anyia, for being my co-supervisor; your support, encouragement and guidance during the whole period of my study never allowed me to give up, but motivated me to complete my graduate degree. It was a great privilege and honor to work under the supervision of both of you. My sincere appreciation to my advisory committee: Drs. Tariq Siddique and Guillermo Hernandez Ramirez who gave me an opportunity to work with them as a graduate student. Your encouragement and guidance in all stage of the program are highly appreciated.

The biggest thank you goes to the most important people in my life, my family. Thank you to my parents Ahmed Dugdug and Nwasa Ali, my sibling Khadija Dugdug and my half-sibling elder brother Ali Dugdug. Thank you all for your patience, regular communication that provided me real strength and support to achieve this milestone in my academic and professional life. I would also like to extend my sincerest thanks to my wife, Khadija Alamin. Her patience and unlimited support despite her grief for losing the most cherished family members (my mother and sister in laws) was the source of strength whenever I had a difficult time in the graduate program.

I would like to thank my colleagues in the Forest Soil Laboratory Dr. Yong Sik OK, Dr. Jinhyeob Kwak, Dr. Mihiri Manimel Wadu, Dr. Min Duan, Dr. Ghulam Murtaza Jamro, Dr. Lei Sun, Prem Pokharel, Shujie Ren, Kangyi Lou and Qi Wang for helping in the field and/or in the laboratory. Thanks also go to my best friends Mr. Ali Abdulatif and Riad Issa for assistance in sample collection.

I am really grateful to the Libyan Education Program, Alberta Innovates-Technology Futures (now InnoTech Alberta), the Natural Sciences and Engineering Research Council of Canada (NSERC) and University of Alberta for generous financial support toward my PhD. The cooperation of land owners and farmers for providing soil and manure samples is especially appreciated, as well as the assistance from Tim Anderson and Don Harfield for biochar production.

# TABLE OF CONTENTS

## CHAPTER 3. HARDWOOD DERIVED BIOCHAR REDUCES LEACHING LOSS OF PHOSPHORUS FROM A MANURED SOIL

## CHAPTER 4. RECLAMATION OF A SALINE-SODIC SOIL WITH BIOCHAR: EFFECTS OF BIOCHAR APPLICATION RATE

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF SYMBOLS AND ACRONYMS

BET: Brunauer–Emmett–Teller equation
EC: Electrical conductivity
$CaCl_2$: calcium chloride
CEC: cation exchange capacity
AEC: anion exchange capacity profile
DI: deionized water
$q_e$: amount of the sorbed P
$C_e$: equilibrium P concentration
$k_f$: Freundlich constant
$k_L$: Langmuir constant
$1/n$: sorption intensity
$q_m$: maximum adsorption capacity
$C_i$: P concentration at the initial
$C_t$: P concentration at given time
$K_f$: affinity coefficient
$pH_{zpc}$: zero point of charge
WHC: water holding capacity
IR: soil-water infiltration rate
F.C: field capacity
PV: pore volume
$V_s$: volume of soil in column
$Ø_s$: soil porosity
ESP: exchangeable sodium percentage
SAR: sodium adsorption ratio
ND: not detected
NM: not measured
Bio: Biochar
N: non-saline soil
S: saline-sodic soil
SP: post leaching saline-sodic soil.

P: phosphorus
TP: total phosphorus
AP: available phosphorus
TDP: total dissolved phosphorus
DRP: dissolved reactive phosphorus
DP: dissolved phosphorus
PP: particulate phosphorus
N:P: nitrogen to phosphorus ratio
C to N ratio: carbon to nitrogen ratio
OC: organic carbon
NaCl: sodium cholride
HCl: hydrochloric acid
$NO_3^-$: nitrate
$NH_4$: ammonium
$HCO_3^-$: bicarbonate
$HNO_3$: nitric acid
$HClO_4^+$: perchloric Acid
$SO_4^{3-}$: sulphate
$K_2SO_4$: potassium sulphate
$CaCl_2$: calcium chloride
NH4F: ammonium fluoride
HOAc: acetic acid
NH4OAc: ammonium acetate
TC: total carbon
TN: total nitrogen
HF: hydrofluoric acid
SR: survival rate
RDM: root dry matter
SDM: shoot dry matter
R/S: root to shoot ratio

SI: initial saline-sodic soil

NP: post leaching non-saline soil

NI : initial non-saline soil

LSTP: low soil test phosphorus

HSTP: high soil test phosphorus

# CHAPTER 1. GENERAL INTRODUCTION

## 1. Interoduction

### Biochar production and properties

Biochar is a carbon-rich, solid product of the thermal decomposition of organic matter under a limited supply of oxygen at relatively low temperatures (<700 °C). It is produced with the intent to be applied to soil as a means of improving productivity, carbon storage, or the filtration of percolating water (Lehmann and Joseph, 2015). Biochar porosity (macro-, meso-, and micro-pores) is considered an important factor contributing to biochar's chemical properties (Fukuyama et al., 2001). Biochar generally presents a large surface area (Downie et al., 2009). This in addition to its structure and chemical properties contributes to its great sorption capacity, which has been largely reported for a wide range of organic compounds (Cornelissen et al., 2005; Ping et al., 2006; Chen et al., 2008a; Cao et al., 2009).

Biochar can be produced with a wide variety of properties and applied to a range of soils. Therefore, different biochars have different interactions with soil, depending on their initial chemical and physical characteristics. Moreover, the chemical properties and nutrient compositions of the biochar can vary greatly with the feedstock type. For example, biochars made from poultry manure can have high pH and P content (Chan et al., 2008b; 2009), while biochar made from sewage sludge can have high N and heavy metal concentrations (Liu et al., 2014).

### Cation and anion exchange capacity of biochar

The cation exchange capacity (CEC) of biochar is found to increase as the biochar ages (Cheng et al., 2008), due to an increase in some of the oxygenated functional groups on the biochar surface (Liang et al., 2006; Cheng et al., 2006). Cheng et al. (2008) and Mao et al. (2012) reported that the surface chemistry of biochar is exposed to changes with time, including the development of carbonyl, carboxylate, ether, and hydroxyl surface moieties, which are largely responsible for biochar CEC. In turn, the CEC of biochar governs its activities in biochar-amended soil; its surface charge determines the nature of interaction with other soil particles, such as dissolved organic matter, gases, microorganisms, and water (Joseph et al., 2009).

Biochar increases soil CEC and, consequently, soil sorption capacity (Glaser et al., 2002 ; Laird et al., 2010b; Peng et al., 2011; Sohi et al., 2010; Mao et al., 2012; Wan et al., 2014). However, increases in soil CEC are not always expected from adding biochar (Novak et al., 2009b).

Very little is known about the anion exchange capacity (AEC) of biochar. Most biochar studies, even those that are related to anion retention have included CEC, rather than AEC, in the chemical analysis list. This may be due to a poor adaptability of traditional methods for soils' AEC analysis. Generally, freshly produced biochar has a low CEC (Cheng et al., 2006, 2008; Lehmann, 2007), but it is expected to have a high AEC (Cheng et al., 2008). However, data for biochar AEC is currently very scanty in the literature. Attempts to measure the AEC of biochars generated from oak, pine, and grass was not successful (Mukherjee et al., 2011). Cheng et al. (2008) were also not able to detect AEC for biochar incubated for 12 months at 70 °C, yet they were able to determine the AEC of fresh biochar that they incubated for 12 months at 30 °C. Some other studies have reported varied AEC values for diverse biochars with different stability over a range of pH values (Inyang et al., 2010; Silber et al., 2010). A recent study attributed the high biochar AEC values to many factors, including the lower competition from hydroxide ions for positive sites at low pH, the lower O-containing functional groups of low ash content biochar, and the formation of oxonium structures and pyridinal functional groups (that carry a positive charge at low pH values) during pyrolysis (Lawrinenko and Laird, 2015). Contrary to CEC, the AEC of biochar often decreases with time upon exposing it to biotic and abiotic oxidation (Cheng et al., 2008), especially for biochars produced under low temperature conditions. This indicates that biochars produced at different temperatures oxidize differently (Lawrinenko and Laird, 2015). In low temperature biochar, the oxonium heterocycles that are responsible for AEC convert to pyran- and cyclic ether-like structures through oxidation, resulting in the reduction in AEC. However, biochar produced under higher temperature conditions tends to have more condensed aromatic C, which is more resistant to oxidation (Lawrinenko and Laird, 2015).

## Biochar surface functional groups and pH

Biochar pH plays an important role in the surface charge, which is found to be directly related to the O contents of the functional groups. Many of the functional groups commonly present on the surface of biochars exhibit amphoteric properties, and the reactivity and electronegativity depend on the pH of the environment (Amonette and Joseph, 2009). That functional gropus can either receive or donate a proton ($H^+$) depending on the pH. At a higher pH, the carboxylic acids (-COOH) and some of the hydroxyls (-OH) give up protons and become negatively charged (-COO- and -O-, respectively). At low pH environments, these same groups can accept a proton. Lawrinenko and Laird (2015) reported that carboxylate groups are always in base form at most soil pH values; thus, they are mainly responsible for the CEC of biochar as a function of their formal negative charge. Poultry litter has been reported to produce biochar with a pH range of 8.5–10.3, based on its concentration of Ca and Mg. Furthermore, the pH buffer capacity of biochar expands by increasing its Ca concentrations (Chan and Xu, 2009; Gaskin et al., 2008). Upon the addition of biochar to soil, the reactive surface of biochar allows cations to accumulate and increase soil pH (Mikan and Abrams, 1996).

## 2 The Impacts of Feedstock Type on Biochar Chemical Properties

Many studies have highlighted the importance of feedstock type and production conditions as key factors for managing the properties of biochar to fit its different uses, including the formation of stable soil organic matter and increasing the retention of contaminants and soil nutrients such as N and P. Amonette and Joseph. (2009) and Collison et al. (2009) reported that biochar properties are highly heterogeneous, both within individual biochar particles and among biochars produced from different feedstocks. The feedstock's chemical composition influences the resulting biochar's chemical and structural composition and, therefore, is reflected in its behavior, function, and fate in soils.

Feedstock type refers to the type of biomass used for making biochar. Biochar and its byproducts have been produced from a wide variety of feedstock, such as organic farm waste, waste treatment plant slurry, and woods with high cellulose/lignin content (Chan and Xu, 2009). Only a limited number of pyrolysis studies have been conducted, to compare the influence of a wider range of feedstock types on the chemical properties of the generated biochar (Day et al., 2008; Day et al., 2005). In general, biochars' surface chemistry varies due to their heterogeneous composition, which is inherited from the initial feedstock (Amonette and Joseph, 2009; Collison et al., 2009). Heteroatoms such as Hydrogen, O, N, P and S are found incorporated within the aromatic rings; this is thought to be responsible for the heterogenous surface chemistry and reactivity of biochar (Brennan et al., 2001).

The major chemical constituents of biochar are carbon, volatile matter, mineral matter (ash), and moisture (Antal and Gronli, 2003; McLaughlin et al., 2009). The relative proportion of these components controls the chemical and physical behavior and function of biochar, as well as its transport and fate in the environment (Brown, 2009). Demirbas (2004) found that the majority of the feedstock's mineral content is retained in the produced biochar, where it concentrates due to the gradual loss of C, hydrogen (H), and oxygen (O) during processing.

Generally, feedstock contains elements other than carbon (C), hydrogen, and oxygen; therefore, the amount of ash in biochars reflects the amounts of the mineral elements in the feedstock used. Feedstock with a high content of silica produces biochar with high ash content. For example, chicken-litter biochars are found to contain more than 45% ash (Lima and Marshall, 2005). Agricultural wastes such as nutshells and fruit stones, however, have high lignin and low ash contents (Aygün et al., 2003), sometimes even less than 1% (Kim et al., 2009). The proportion of inorganic components (ash) affects biochars' physical and chemical properties (Rodriguez-Mirasol et al., 1993). Some studies have suggested that high mineral-ash content biochar has a strong ability to adsorb some contaminants in soil, such as heavy metals and pesticides (Swiatkowski et al., 2004; Lima and Marshall, 2005). In another study, ash content was found to have a significant effect on functional groups present on biochars' surfaces (Schnitzer et al., 2007). As well, Schnitzer et al. (2007) and Koutcheiko et al. (2007) have suggested that, in high mineral ash biochar, some of the functional groups may contain metals; they found this to be true in a range of N- and S- based functional groups in chicken manure biochar. More knowledge is required to enable the selection of feedstock type to achieve specific biochar properties and thereby provide the benefits most appropriate for each particular agricultural system and for each purpose.

## 3 Use of Biochar as a Soil Amendment

### 3.1 Salt-affected land

Since ancient times, soil degradation has occurred due to salinization. Today, it is one of the world's major environmental concerns, threatening the sustainability of global agricultural production. It is prevalent in arid and semi-arid regions (Manchanda and Garg, 2008), where rainfall is not sufficient for adequate leaching (Pathak and Rao, 1998). Around 23% of the earth's surface is occupied by salt-affected lands; this has a major negative impact on the productivity of agricultural crops and pastures (NLWRA, 2001; Szabolcs, 1994). Most of these lands are classified as saline-sodic soils, which occupy around 10% of all salt-affected lands worldwide (NLWRA, 2001). In the Canadian prairies (Alberta, Saskatchewan, and Manitoba) more than 80,000 and 2.5 million hectares of irrigated and non-irrigated lands, respectively, are classified as saline or saline-sodic.

Salt-affected soils generally contain high concentrations of dissolved mineral salts, primarily composed of chlorides, sulfates, carbonates, bicarbonates of sodium ($Na^+$), calcium ($Ca^{2+}$), and magnesium ($Mg^{2+}$) (Manchanda and Garg, 2008; Qadir et al., 2000). The concentration and proportions of these salts are commonly varied.

"Salt-affected lands" are defined as groups of soils whose concentration of soluble salt is high enough to restrict the growth of most crops (Paul, 2013), and to degrade the soils' physicochemical properties (Shrivastava and Kumae, 2015). General classification of salt-affected soils is based on their electrical conductivity of saturated paste extracts (ECe), soil sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) (Richards, 1954). Based on these parameters, Richards (1954) and James et al. (1982) divided salt-affected soil into saline soils, sodic soils, and saline-sodic soils. Saline soils are recognized by their high content of soluble salt (Electrical conductivity ($EC_e$) >4, an exchangeable sodium percentage (ESP) < 15 and pH <8.5). Meanwhile, sodic soils are characterized by their high exchangeable sodium ($EC_e$ < 4, an ESP >15 and pH >8.5). Saline-sodic soils, on the other hand, contain both soluble salt and exchangeable sodium at high concentration (EC >4, an ESP >15 and pH >8.5) (James et al., 1982). The accumulation of salts in soils will affect both plant growth and general soil health by altering the soils' physical, chemical, and biological properties (Bernstein, 1974; Lakhdar et al., 2009; Manchanda and Garg, 2008).

The major physical properties of soils that are influenced by elevated levels of exchangeable $Na^+$ in saline-sodic soil are low pore volume and poor relation of soil-water and soil-air (Rengasamy and Olsson, 1991). Sodicity also causes clays to swell, resulting in swelling induced effects such as breakdown of aggregates. This in turn decreases soil hydraulic properties, including hydraulic conductivity and infiltration rate (Rengasamy and Sumner, 1998). Sodium causes the dispersion of soil particles and, consequently, permanent blockage of water navigation pores (Sumner, 1993) and reduction of soil structural stability (Quirk, 1994;

Rengasamy and Olsson, 1991). “Hard setting” is a unique characteristic of saline-sodic soil. It refers to a formation of an impermeable subsoil layer with high bulk density (Qadir and Schubert, 2002), which causes a permanent or frequent condition of poorly aerated, waterlogged soil. These conditions are unfavourable for plant growth and production (Nelson et al., 1998).

The high values of ECe, ESP, SAR, and pH in high salinity and/or sodicity soils affect many morphological, physiological, and biochemical processes in plants. These include increased osmotic pressure of the soil solution (Gadallah, 1996); toxic ion action, such as of boron (Smith et al., 2010b); unbalanced uptake of essential nutrients and/ or the combination thereof (Maas and Hoffman, 1977; Willenborg et al., 2004). Generally, salt-affected soils are highly deficient in their nitrogen (N), phosphorus (P), and potassium (K) contents (Lakhdar et al., 2009). Furthermore, decline in vegetation growth in such soil results in lower C input and further deterioration of the soil’s physical and chemical properties (Wong et al., 2009).

## Mechanisms involved in the effectiveness of biochar for saline-sodic soil reclamation

Until now, few studies have focused on the possibility of using biochar for the reclamation of salt-affected soils, such as a saline-sodic soil. However, the incorporation of biochar into non-saline soils is shown to affect the preexisting soil properties in ways attributed to the physical and chemical properties of biochar (Amonette and Joseph, 2009; Chan and Xu, 2009; Slavich et al., 2013). For example, in recent studies, biochar was found to provide many benefits to amended non-saline soils. These included adding basic cations such as $Ca^{2+}$ and $Mg^{2+}$ (Major et al., 2010; Laird et al., 2010b; Chan et al., 2008b; Gaskin et al., 2010; Novak et al., 2009a), which has been found effective for offsetting the $Na^{+}$ on the exchange sites in a saline-sodic soil (Chaganti et al., 2015). Furthermore, biochar application was found to improve physical soil properties such as bulk density, porosity, and aggregate stability (Herath et al., 2013; Ayodele et al., 2009; Laird et al., 2010b). These, in turn, facilitate water infiltration through soil layers. Biochar also reduces salinity stress through adsorption of $Na^{+}$ (Lashari et al., 2013; Akhtar et al., 2015a; Akhtar et al., 2015b). Therefore, the benefits of biochar for adding divalent cations together with its role in enhancing soil chemical and physical properties could help salt leaching from biochar-amended saline-sodic soil.

## 3.2 High soil test phosphorus soil

The major sources that contribute to phosphorus loading from agricultural watersheds into water bodies include soil phosphorus (P) and phosphorus from fertilizers, manure, and biosolids. The accumulation of P in soil is a function of the characteristics of the P sources added (e.g., solubility), soil properties, and agricultural management practices. Most soils have a high capacity for retaining the P applied as synthetic fertilizers or manure (Brookes et al., 1997). Soluble P forms from these sources react quickly with soil constituents, and P adsorbs to fine mineral particles (clay, Fe and Al oxides, carbonates, etc.); precipitates, as inorganic compounds of low solubility (for example, as calcium and /or iron phosphates); or is retained in complex organic molecules. Thus, in most situations there is little movement of P through the soil profile. This leads to the accumulation of P near the soil surface when it is applied at rates that exceed crop removal (Simard, 2000). However, when the soil becomes enriched in P to a level that exceeds the P retention capacity of the soil, the excess P could potentially move downward through the soil (Koopmans et al., 2007; Lehmann et al., 2005; Ulén et al., 2011; Parvage et al., 2013), causing eutrophication in water bodies (Chen et al., 2008b; Borda et al., 2011; Csathó et al., 2007).

### 3.2.1 Mechanisms involved in phosphorus retention in biochar and biochar-amended soils

The physical and chemical stabilization mechanisms of biochar in soils determine its effects on soil functions. Two properties of biochar make it a valuable soil amendment: (1) its high stability against decay; and (2) its superior ability to retain nutrients, compared to other soil organic matter (Lehmann, 2007). Its chemical and physical properties such as its high charge density and its particulate nature, along with its specific chemical structure and high microbial and chemical stability all contribute to greater nutrient retention and resistance to microbial decay than that possessed by other organic matter (Atkinson et al., 2010). Historical studies have examined biochar’s effect on the transformation of nutrients, and have found that it clearly has important roles in nutrient retention, availability, and leaching. For instance, pot studies have found a significant reduction in nutrient leaching, upon addition of biochar to soils (Ding et al., 2010; Laird et al., 2010 a; Lehmann et al., 2003; Singh et al., 2010b). In particular, phosphorus concentration in leachate was found to decrease with increasing biochar application due to the great P sorption capacity of biochar (Novak et al., 2009a). The influence of biochar on nutrients depends on its properties, ion of interest, and soil environment. As previously discussed, the type and source of feedstock used to produce biochar are shown to affect the availability of key macronutrients such as N and P, and some metal ions such as $Ca^{2+}$ and $Mg^{2+}$, when incorporated into the soil (Atkinson et al., 2010).

Several studies have reported that the cation exchange capacity (CEC) of biochar is significantly higher than that of the soil alone, clay minerals, or soil organic matter (Sohi et al., 2010; Lehmann et al., 2003). The negatively charged sites (CEC) on biochar surfaces are directly benefiting the retention of positively charged elements. However, they may indirectly contribute to the retention of other elements with a negative charge by holding cations that eventually co-precipitate with those of negatively charged elements, such as that between phosphate and $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, and $Al^{3+}$. The CEC of the biochar also benefit the retention of P directly through increasing the electrostatic adsorption (specific adsorption).

Phosphorus chemistry, reactions, and cycling in the soil and surrounding environment are complex. The fate of P in soil is a function of many soil properties, such as temperature (Barrow, 1974), structure, pH, and clay content (Arai and Sparks, 2007). It has long been known that the major chemical processes controlling solution composition in agricultural soils for phosphorus are adsorption/desorption and dissolution/precipitation (Edwards and Withers, 1998). Inorganic phosphorus in water occurs almost exclusively in the form of orthophosphate. It can be present in soils as $H_2PO_4^-$ (pH 5-6), $HPO_4^{-2}$ (pH 6-8), and in apatites such as Ca (pH < 8) and Al (pH <4) phosphate (Coelho et al., 2012; Ulén et al., 2012). Other speciations of phosphate in soil and water environments are $H_3PO_4$ and $PO_4^{-3}$.

As already discussed, the beneficial characteristics of biochar as a soil amendment are associated with its high cation exchange capacity (CEC; 40 to 80 meq per 100 g); its high surface area (51 to 900 $m^2\ g^{-1}$), which leads to accumulated basic cation and increased soil pH (Mikan and Abrams, 1996); and its affinity for micro- and macro- plant nutrients (Lehmann, 2007; Laird, 2008; Gaunt and Lehmann, 2008; Novak et al., 2009a; Roberts et al., 2009). The high CEC and surface area of the biochar were considered as important chemical characteristics that favor the potential to adsorb P or influence the precipitation of P in insoluble pools (DeLuca et al., 2015). In many studies, the leaching of anions such $NO_3^{-1}$ and phosphate were found to be significantly reduced upon addition of biochar to soils (Laird et al., 2010a; Knowles et al., 2011). The influence of biochar on phosphorus retention in biochar-amended soils varies by biochar type. For example, Yao et al. (2012) found that biochars made from pepperwood caused additional phosphate loss from soil columns. However, the loss was significantly reduced by using peanut hull biochar. Furthermore, soil properties also have an important impact on the amount of phosphorus retention by biochar-amended soils. For example, Xu et al. (2014) reported that sorption of phosphorus by biochar-amended soils is highly influenced by both the biochar application rate and the pH values of the amended soil. The phosphorus sorption increased along with an increasing rate of biochar application in acidic soil, due to the increases in Ca-bounded P that associated with an increasing of soil pH upon the increases of biochar addition. It faintly decreased, however, in alkaline soil. Lawrinenko and Laird (2015) reported that a negative charge is the main charge for both phosphate ions and the biochar surface. Despite this, significant adsorption occurs through an interaction capable of overcoming the electrostatic repulsion (Beaton et al., 1960). This adsorption may be due to biochar AEC (Lawrinenko and Laird, 2015). However, there is limited knowledge about the anion adsorption mechanisms of biochars. Generally, the main mechanisms that are involved in phosphorus retention in soil, biochar, or soil/biochar mixtures are electrostatic adsorption and precipitation. These are discussed in some detail in following section.

#### 3.2.1.1 Electrostatic adsorption (specific adsorption)

Basically, adsorption is a concentration of a liquid or gaseous material on the surface of a solid. This phenomenon is further defined as the net accumulation of matter (adsorbate), in the two-dimensional molecular arrangements at the interface between a solid phase (adsorbent) and an aqueous solution phase (Sposito, 1989). Absorption, on the other hand, is a phenomenon involving the bulk properties of a solid, liquid or gas. It involves atoms or molecules crossing the surface and entering the volume of the material. Sorption includes both adsorption and absorption; this term is used when the exact mechanism of removal is not clear (America, 2008).

Motts (1981) classified anions into two groups: (1) non-specifically adsorbed ions (or outer sphere complexes); and (2) specifically adsorbed ions (or inner sphere complexes). Adsorbed ions (e.g., $Cl^-$ and $NO_3^-$) that are retained on positive sites by simple electrostatic attraction following anion exchange are classified as non-specifically adsorbed ions. These are expected to be influenced by the diffuse layer equilibrium (Arnold, 1978), and therefore easily displaced or exchanged.

Phosphate ions belong to the second group, which generally consists of anions that have a great affinity for soil surfaces against their concentration in solution. These groups of ions are therefore much stronger than the first groups, because they form when ions penetrate the coordination shell of the Fe (or Al) atom and exchange $OH^-$, $H_2O$, or $H^+$ and are retained by covalent bonds. Furthermore, the phosphate form in solution has an important influence on P sorption strength. In one study, adsorption of $H_2PO_4^-$ was found to be greater than that of $HPO_4^{2-}$ or of $PO_4^{3-}$ regardless of their ionic concentration. This was attributed to the greater capacity of $H_2PO_4^-$ for hydrogen bonding, as well as its smaller electrostatic repulsion effect (Beaton et al., 1960).

As already discussed, many chemical properties of biochar are influenced by feedstock and pyrolysis condition. For example, adsorptive capacity for phosphorus was found to increase with increasing pyrolysis temperature (Beaton et al., 1960). Also, biochars with higher surface areas and especially when associated with metal oxides on their surfaces were found to play important roles for phosphorus removal as inner sphere complexes. Yao et al. (2011b) reported that magnesium oxide (MgO) and $Fe^{3+}$ have been shown to be present on the surface of biochars and, depending on pH, have a strong affinity for anions. Phenolic acid groups are mainly responsible for the adsorptive properties of biochar for phosphate (Beaton et al. 1960; Mia et al. 2017). This adsorption occurs via the formation of hydrogen bonds through a protonation and deprotonation process between phenolic groups and $H_2PO_4^-$, respectively (Beaton et al. 1960).

### 3.2.1.2 Chemical precipitation

Precipitation is a chemical process that occurs between liquid material and the surface of a solid, which involves development of a three-dimensional molecular structure (Sposito, 1989). The amount of precipitated P is controlled by the pH of the solution, as well as the abundance of the divalent or trivalent metal salts that precipitate as an insoluble metal phosphate. Phosphorus precipitates with Ca or Mg to form Ca or Mg phosphates in high pH. However, at lower pH, P combines instead with Fe and Al (Morse et al., 1998; Reddy et al., 1980). When biochar is involved, these insoluble pools of precipitated phosphorus could be influenced by biochar addition through alteration of pH, which in turn influences the strength of ionic phosphorus interactions with $Al^{3+}$, $Fe^{2+3+}$ and $Ca^{2+}$ (Lehmann et al., 2003; Topoliantz et al., 2005). For example, Chen et al. (2011) found that co-precipitation of $Fe^{3+}/Fe^{2+}$ creates magnetism in some biochars, which are found to be more effective at P removal than non-magnetic biochars. Biochar also has a high affinity to sorb organic molecules (Smernik, 2005), which may act as chelates of metal ions that precipitate P.

## 4. Biochar Impact on Crop Production

Numerous historical studies have indicated that biochar application into soils enhances the overall soil quality by altering the soil's physical, chemical, and biological properties which in turn increase plant productivity (Asai et al., 2009; Atkinson et al., 2010; Chan and Xu, 2009; Jones et al., 2012; Laird et al., 2010b; Lehmann et al., 2011; Rondon et al., 2007; Solaiman et al., 2010; Spokas et al., 2009; Thies and Rillig, 2009; Van Zwieten et al., 2010). Biochar often has high concentrations of available nutrients (e.g., $NH_4$, $PO_3$, $Ca^{2+}$, and $Mg^{2+}$) on its surfaces, which can have fertilization effects over short time-scales (Jeffery et al., 2011; Pluchon et al., 2014). However, Amonette and Joseph (2009) reported that, during pyrolysis of the biomass, the majority of the potassium (K), chlorine (Cl), and N vaporizes at relatively low temperatures, while calcium (Ca), magnesium (Mg), phosphorus (P), and sulphur (S) vaporize at relatively higher temperatures due to increased stability. The availability of the remaining minerals in biochar, for plants' and soil microbes' consumption, is considered limited. For example, Bagreev et al. (2001) found that by increasing pyrolysis temperatures N forms pyridine-like complexes that reduce its availability. Biochar addition to soil was found to have a continuous effect on the soil's physical and chemical properties, contributing to long-lasting positive effects on soil fertility that, in turn, reduce the need for fertilizer (Gavin et al., 2003; Gouveia et al., 2002; Pessenda et al., 2010). For instance, the Terra Preta soils of the Amazon Basin are still fertile 800 years after charcoal application (Glaser et al., 2002; Lehmann et al., 2003). However, negative yield responses to biochar have also been found, particularly in neutral to basic soils. This is due to micronutrient deficiencies at high soil pH values, which are often associated with biochar addition (Lehmann et al., 2003; Rondon et al., 2007; Vaccari et al., 2011).

## 5. Thesis Structure

The main objectives of this thesis were to determine the effectiveness of biochar on (1) amelioration of a saline-sodic soil, (2) mitigation of P leaching from a soil with high soil test P, and (3) to evaluate the effect of biochar amendment on crop production. Four experiments were conducted, including three laboratory experiments and one greenhouse experiment, to test the following hypotheses.

- The phosphorus sorption capacity of biochar would vary, based on P concentration in solution and biochar properties. Thus, to some extent, the sorption capacity would increase with increasing P in solution, as well as with increasing CEC, and surface area of the biochar as.
- The feedstock type used to produce the biochar would also influence its P sorption capacity, through its influence on the generated biochar's properties such as ash and associated metal elements, CEC and surface area.
- Removing ash from the biochar could increase on its P sorption capacity.
- The phosphorus sorption capacity of biochar would decrease under saline conditions, due to increasing in ionic strength of the solution.
- Biochar application to saline-sodic soil could enhance the leaching of salt, by releasing divalent cations such as Ca and Mg that are necessary for offsetting $Na^+$ from the exchangeable sites of soil.
- Biochar could also facilitate the leaching of salt from saline-sodic soil by improving soil physical properties such as water infiltration.
- The addition of cations such as Ca and Mg contained in biochar increases soil pH could facilitate P retention, resulting in a reduction of P leaching losses.
- The increases of water-infiltration rate with an increasing biochar application rate could be associated with proportional increases of P leaching losses. Therefore, there may be an optimal rate of biochar application that could minimize the associated losses of P.
- Biochar application to saline-sodic soil could increase plant growth and productivity, as a result of its expected roles in reducing salinity and improving soil quality including water infiltration rate, and water holding capacity. The expected increase of soil pH, due to biochar addition, could also contribute to the retention of soil nutrients in an available form for plant uptake.

This thesis consists of six chapters. Figure 1-1 describes the relationships among the chapters. Each of chapters 2 to 5 constitutes a manuscript that has been submitted or will be submitted for publication.

Chapter 1 provides background information and an overview of the thesis.

Chapter 2 focuses on the effects of biochars derived from different feedstock types on P sorption capacity under non-saline and saline conditions. A manuscript entitled "Phosphorus sorption capacity of biochar varies with biochar type and salinity level" was submitted to Environmental Science & Pollution Research.

Chapter 3 focuses on effects of biochar application rates on P leaching losses from soil with high and low soil test P. Dry cattle manure was used as a source of P in the involved treatment.  A manuscript entitled "Hardwood derived biochar reduces leaching losses of phosphorus from manure amended soil" is being developed for submission for publication.

Chapter 4 focuses on effects of biochar application rates on leaching of salt from non-saline and saline-sodic soils. A manuscript entitled "Reclamation of a saline-sodic soil with biochar: effects of biochar application rate" is being developed for submission for publication.

Chapter 5 focuses on effects of an investigated biochar optimal rate and nutrients addition from manure on growth and productivity of wheat crop in the non-saline and saline sodic soils under greenhouse condition. A manuscript entitled "Biochar application improved soil quality, wheat growth and yield in a manured saline-sodic soil" is being developed for submission for publication.

Chapter 6 provides a summary of research findings and suggests future research.

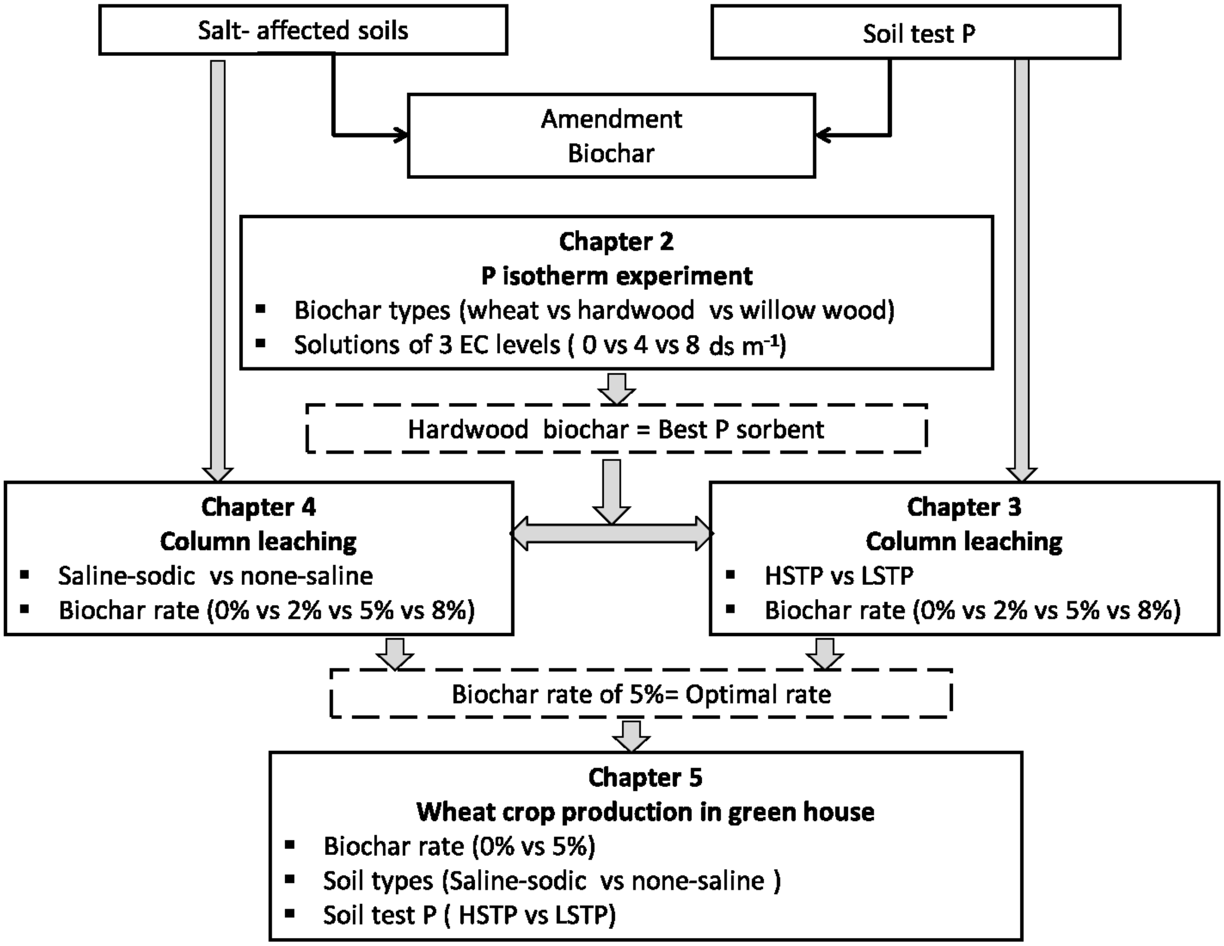

**Figure 1.1**: Flow chart showing the relationship between thesis chapters. Boxes with a solid border indicate an experiment. Boxes with broken border indicate a selected treatment. *Abbreviations: HSTP= High soil test phosphorus, LSTP= Low soil test phosphorus, EC= Electrical conductivity, P= Posphorus.

# CHAPTER 2. PHOSPHORUS SORPETION CAPACITY OF BIOCHAR VARIES WITH BIOCHAR TYPE AND SALINITY LEVEL

## 1. Introduction

Phosphorus (P) is an essential nutrient for plant growth and often needs to be applied to achieve optimal crop yield. Phosphorous is required for many critical plant functions including photosynthesis, respiration, seed production and root growth. However, land application of supplemental P in the form of animal manure, mineral fertilizer, and plant residues can also increase the risk of P loss to surface water to cause eutrophication (Ngatia et al., 2014); this is well known as one of the main factors for causing water quality degradation (Gartley and Sims, 1994; Sims et al., 2000, 2002; Kronvang et al., 2005; Karunanithi et al., 2015).

The eutrophication of surface waters has become a significant environmental problem in many countries and agriculture has been identified as a significant source of P (Kronvang et al., 2005; Csatho et al., 2007). There have been many historical efforts to reduce the loss of P from soils; most of these efforts aimed to improve the soil's capacity for P retention which was considered as an important mechanism controlling the release of P from the soil to water (Karunanithi et al., 2015).Sorption is one of the common mechanisms for P retention in the soil (Villapando et al., 2001; Berg and Joern, 2006).

Biochar is one of the organic amendments that has been evaluated for P sorption and has been considered as an environment friendly sorbent that can adsorb P from aqueous solutions through precipitation of P with $Ca^{2+}$ and $Mg^{2+}$ from biochar materials (Chen et al., 2011; Yao et al., 2011b; Sarkhot et al., 2013; Shepherd et al., 2016; Shepherd et al., 2012; Wang et al., 2016), and reduce P leaching from soils (Lehmann et al., 2003; Laird et al., 2010a; Yao et al., 2012). Understanding P retention and release mechanisms of biochar will provide crucial information for the effective management of P to enhance crop production and sustain soil and water quality. Biochar is a carbonaceous material produced by thermal degradation of organic material during pyrolysis (Keiluweit et al., 2010; Novak et al., 2015). The utilization of biochar as a chemical sorbent in agroecosystems has both economic and environmental benefits. Recently, biochar has been used widely as an amendment for improving soil chemical and physical properties including the soil's P retention capacity. Biochar has been found to increase P availability in the soil by minimizing P leaching loss through increased P sorption (DeLuca et al., 2009;

Thangarajan et al., 2015) and to enhance the availability and plant uptake of P due to biochar's high anion exchange capacity (AEC) and surface area (Deluca et al., 2009; Farrell et al., 2014; Lehmann et al., 2015).

Saline soils are defined as soils that have an electrical conductivity (EC) above 4 dS $m^{-1}$ based on water-saturated soil paste extraction (Chinnusamy et al., 2005; US Salinity Laboratory Staff, 1954). However, the threshold value at which negative effects of salinity occur depends on many factors including plant type (Roy et al., 2014). Generally, soil salinity poses a huge threat to soil productivity in agricultural land (Masoud and Koike, 2006; Yoon et al., 2009; Zhang et al., 2012). In Alberta, for example, there are more than 3 million hectares of saline land under agricultural use (Sommerfeldt and Rapp, 1982; Sommerfeldt, 1988). There have been attempts to use biochar to mitigate salt stress in agricultural lands to improve crop production; for example, Lashari et al. (2013) used a wheat straw biochar as an amendment in salt stressed soils and found that application of a poultry manure compost with biochar and the pyroligneous solution from crop straw significantly reduced the negative effect of salinity on crop productivity. However, salinity could differently affect P sorption and desorption of biochars based on the type of biochar used. Also salinity and P levels could interact to affect P reactions in a system with particular properties. For example, salinity and temperature are found to influence P sorption on marine sediments; thus, P sorption was found to increase with increasing temperature or decreasing salinity (Zhang and Huang, 2011). Therefore, the influence of salinity on P sorption and desorption on the biochar applied as a soil amendment has to be well understood for the purpose of maximizing P retention and decrease its leakage under this condition.

Comparing the P sorption capacity of various biochars under non-saline and saline conditions is useful in understanding biochar characteristics that may contribute to reduce P leaching from soils receiving P fertilizer. Generally, the benefit of using biochar for soil reclamation is highly related to the chemical characteristics of both the biochar and the soil in question. Biochar characteristics are variable due to feedstock type, pyrolysis temperature, heating rate and other conditions (Antal and Gronli, 2003; Guo and Rockstraw, 2007). One of those chemical characteristics of biochar is its sorption capacity, particularly for P. Understanding how P sorption by different biochar is influenced by salinity conditions will help producing biochars that are effective in reclaiming salt affected soils. In this study, three biochars were produced from the slow pyrolysis of wheat straw, hardwood and willow wood feedstock.

The overall goal of this study was to narrow down the available biochars to the most likely to have positive and measurable results under saline and non-saline conditions. The specific objectives of this study were 1) to compare the influence of feedstock type (wheat straw, hardwood, and willow wood) on the P sorption capacity of biochars. We hypothesize that biochar's P sorption capacity would increase with increasing P concentration in the solution, and increasing biochar cation exchange capacity (CEC) and total surface area will facilitate sorption. These biochar properties would be influenced by the feedstock type used for making biochar; 2) to investigate the effects of biochar de-ashing and de-ashing methods on the P sorption efficiency of biochars. We hypothesize that removing ash could increase P sorption capacity of biochars;, and 3) to investigate the effects of salinity on P sorption by the three biochars. We hypothesize that ionic strength would increase with increasing salinity of solution and that would reduce the P sorption capacity of biochars.

## 2. Materials and Methods

Two experiments are reported in this paper that deal with different aspects of sorption by biochar. The first experiment was focused on P sorption characteristics of the biochars before and after de-ashing using acid and water. The second experiment was focused on the influence of salinity on P sorption characteristics of biochars made with different feedstock types.

### 2.1 Biochar production

For this study, biochars were produced from wheat straw, hardwood, and willow wood by Alberta Innovates - Technology Futures (AI-TF) at Vegreville, Alberta, Canada. The willow wood and hardwood biochars were produced in an auger retort carbonizer (ABRI- Tech, 1 tonne retort system, Alberta Biochar Initiative- AI-TF Vegreville) and the wheat straw biochar was produced in a batch carbonizer (AI-TF, Prototype 1.0), both units were built locally. The batch carbonizer had a much slower heating rate than the continuous auger retort carbonizer. The pyrolysis temperature ranged between 500- 550 °C for wheat straw and hardwood biochars, and it was 500-560 °C for willow wood biochar. Heating rate was 85-100 °C minute$^{-1}$ for hardwood and willow wood biochars, and 9-10 °C minute$^{-1}$ for wheat straw biochar.

### 2.2 Chemical analyses

The biochars were homogenised and ground to < 2 mm for use for most of the analyses. For total elemental analysis, biochar samples were ground to < 1 mm. At least 3 replicates were used for each analysis. Surface areas of biochars were measured from $N_2$ isotherms at 77 K using a gas sorption analyzer (NOVA-1200; Quantachrome Corp. Boynton Beach, FL, USA). The samples were degassed for 6 h under vacuum at 473 K prior to conducting the gas adsorption measurements. The $N_2$ adsorbed per g of biochar was plotted versus the relative vapor pressure (P/Po) of $N_2$ ranging from 0.02 to 0.2, and the data were fitted to the Brunauer–Emmett–Teller equation (BET) to calculate surface area. Total pore volume was estimated from $N_2$ adsorption at P/Po ~0.5. The Barret–Joyner–Halender method was used to determine the pore size distribution from the $N_2$ desorption isotherms (Park and Komarneni, 1998). The pH and EC of biochars were determined in a suspension of 1:5 (w:v) biochar to deionized water using an Orion digital pH meter (Thermo Electron Corp., Waltham, MA, USA) and an Orion EC meter (Thermo Electron Corp., Waltham, MA, US/555A Orion 3 Star Conductivity meter) after shaking for 1 h following Lou et al. (2016) and Li et al. (2013) for the pH and EC, respectively.

Exchangeable cations of the biochar samples were measured using 1 M ammonium acetate (pH 7) following Dume et al. (2016). The elemental composition of biochars including C, H, N, S and O were determined by dry combustion using an elemental analyzer (EA1110, CE Instruments, Milan, Italy); these data were used to calculate molar ratios of H/C, O/C, (O+N)/C, and (O+N+S)/C (Ahmad et al., 2014; Rajapaksha et al., 2014).

In order to investigate the effect of ash and associated metal elements on the sorption of P by biochars, all biochars were washed by two methods: 1) acid wash, biochars were washed by adding 1 M HCl and 0.05 mol $L^{-1}$ HF at a 1:5 solid to liquid ratio and shaking at 140 rpm (40 °C) for 5 days (Sun et al., 2013a). After that, the mixture was rinsed with de-ionized water and centrifuged at 4500 rpm (2240 g) for 30 minutes and the supernatant was removed. This treatment was repeated for six times to get samples with increased % organic carbon (OC), then, the washed samples were freeze-dried (Sun et al., 2013a); and 2) water wash, biochars were washed by packing them in a polyethylene plastic column and leaching by deionized water. This treatment was repeated until the EC of the leachate was < 20 $\mu s\ cm^{-1}$ (Xu et al., 2011), then the biochar samples were air dried before running the sorption isotherm experiment.

The P retention capacity is often determined in the laboratory by equilibrating soil with a range of P concentrations for a set period of time. The amount of P sorbed is calculated as the difference between the amount of P added and the P remaining in the solution at equilibrium. The data obtained are then fitted to different sorption models and various indices of P sorption capacity are calculated (Barrow and Carter, 1978; Chien and Clayton, 1980; Kinniburgh, 1986). Phosphorus sorption was determined according to the procedure outlined in Nair et al. (1984). All glassware was acid washed in a HCl bath (1 M) and rinsed with deionized water prior to use. Preliminary sorption experiments were performed using all three types of biochars to evaluate the biochar to liquid ratio and to obtain preliminary sorption results for P (results not shown). The sorption experiments were performed by using three replicates of each biochar sample. A 0.5 g sample of each biochar was transferred to 50 mL centrifuge tubes. Then 40 mL solutions containing 0, 1.25, 2.5, 6.25, 12.5, 18.75, and 25 mg P $L^{-1}$ were added to centrifuge tubes with biochar samples. The added P was equivalent to 0, 100, 200, 500, 1000, 1500, and 2000 mg P $kg^{-1}$ of biochar. Two drops of chloroform were added to each centrifuge tub to inhibit microbial growth. Samples were equilibrated on a reciprocal shaker (Eberbach E 6010) at 180 oscillations per minute for 24 h at room temperature and then centrifuged for 10 minutes at 5200 rpm (3000 g) to collect the supernatant. The supernatant was filtered through 0.45 µm filter papers. Inorganic P remaining in the filtrate was measured by the ammonium molybdate–antimony potassium tartrate ascorbic acid method of Murphy and Riley (1962). For the purpose of tracking any possible influence of the described experimental procedure on the initially added P, a control treatment run by repeating that procedure but without addition of a biochar sample to the centrifuge tube. A constant P concentration at the final measurement for each level of the added P means that no influence occurred on the added P due to the procedure.

For assessing the influence of salinity and pH on biochar's capacity for P sorption, the sorption experiment was repeated twice. First, an experiment was done by using solutions with EC values of 0, 4 and 8 dS $m^{-1}$ to represent a wide range of salinity conditions. Sodium chloride was used to make the saline solutions. Second, an experiment was carried out by controlling pH of the equilibrium solution to between 3 and 11, with one pH unit interval. However, since the chemical form of phosphate is pH sensitive, we conducted the other sorption experiments without controlling pH.

Sorbed P was calculated as the difference between the initial P concentration and the P concentration at equilibrium. The Freundlich and Langmuir isotherm models were used to describe the sorption of phosphate onto the biochars, which are expressed as follows (Gerente et al., 2007):

The Freundlich equation; $$q_e = K_F {C_e}^{1/n} \quad (1)$$

which can be expressed as: $$Log\ (q_e) = Log(K_F) + \frac{1}{n} Log(C_e)\,. \quad (2)$$

and the Langmuir equation: $$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where $q_e$ is the amount of the sorbed P (mg kg$^{-1}$), $C_e$ is the equilibrium P concentration (mg L$^{-1}$) in the supernatant after shaking, $k_F$ (mg g$^{-1}$) and $k_L$ (L mg$^{-1}$) are the Freundlich and Langmuir constants, respectively. 1/n is sorption intensity and $q_m$ is maximum adsorption capacity (mg kg$^{-1}$). The parameters for both isotherms are listed in Tables 2-3 and 2-4.

The P sorption ratio and sorption amount were calculated using the following relationships:

$$\text{Sorption ratio (\%)} = \frac{C_i - C_t}{C_i} \times 100 \quad (4)$$

$$\text{Amount of P sorbed } (q_e) = \frac{V}{M}(C_i - C_t) \quad (5)$$

where $C_i$ and $C_t$ are the corresponding P concentration (mg L$^{-1}$) at the initial time and a given time, respectively, $M$ (g) is the mass of adsorbent and $V$ is the volume of P solution (L).

### 2.3 Statistical analysis

Statistical analysis of variances (ANOVA) was performed using PROC MIXED in the Statistical Analysis Systems software (SAS) package (SAS 9.4). Before performing the ANOVA analysis, the normality of distribution and homogeneity of variance were tested. All assumptions were met and no transformation of the datasets was required. Two-way ANOVAs were conducted to test the effect of de-ashing methods and salinity conditions on P sorption by biochar as well as to test the effect of biochar type and initial P concentration on P sorption by water-washed biochars. Tukey's HSD ($P \leqslant 0.05$) was used to compare treatment means, and to test the statistical differences of the sorped P (%) between initial P concentration and biochar types.

## 3. Results and Discussion

### 3.1 Phosphorus sorption on biochars

The biochars derived from different feedstocks had different chemical and physical properties (Table 2-1). The pH, EC, CEC, surface area and pore volume were the highest in willow wood biochar followed by wheat straw and hardwood biochars, except that surface area was higher in hardwood than in wheat straw biochar. The CEC value was around 11-fold higher in willow wood biochar than in hardwood and wheat straw biochars, with respective values of 196, 18 and 17.6 cmol $kg^{-1}$. However, surface area was around 7-fold lower in wheat straw biochar than in hardwood and willow wood biochars, with respective values of 55.2, 324 and 380 $m^2$ $g^{-1}$. Consistent with many other studies (Amonette and Joseph, 2009; Collison et al., 2009), feedstock type had a marked influence on the properties of the biochars produced.

In this study, P sorption was significantly higher with the willow wood biochar (1.93 mg $g^{-1}$ in a 25 mg $L^{-1}$ P solution) than with the other two biochars, indicating that the willow wood biochar has a large P sorption capacity (Figure 2-1). However, the P sorption trend of willow wood biochar was in opposite direction to that of the other biochars as shown in Figure 1. There is a dynamic equilibrium between release and surface precipitation of P on the adsorbent as calcium and magnesium phosphates ( Philip, 1988; Lai and Lam, 2009). Therefore, high sorption rate of P could be expected if surface precipitation of P on biochar is greater than its release and versa vice. However, the reason for the opposite trend of P sorption by willow biochar is not clear but its higher initial P content (Table 2-2) might have influenced the P sorption.

Elemental concentration was higher in willow wood than in the other two biochars (Table 2-1). The concentrations of Ca and Mg in willow wood biochar were 19.6 and 2.14 mg $g^{-1}$, respectively. However, the concentrations of these two elements were markedly lower in the hardwood (1.7 and 0.18 mg $g^{-1}$ for Ca and Mg, respectively) and wheat straw biochar (1.4 and 0.18 mg $g^{-1}$ for Ca and Mg, respectively). We hypothesize that the greater P sorption by willow wood biochar in comparison to the other two biochars could be also due to the high Ca and Mg concentrations in the former biochar (Table 2-1) that has been known for a long time as a favored formation for the surface precipitation of P (Morse et al., 1998; Reddy et al., 1980). Also, in a recent study, elements such as Fe, Al, Ca and S in the biochar material were found to play important roles for P retention (Shepherd et al., 2017). The high sorption rate of P by biochars was previously shown to be the result of high surface precipitation (Yao et al., 2011b; Qian et al., 2013; Zeng et al., 2013). It has been reported that biochar surfaces are often negatively charged, repelling negatively charged ions such as phosphate (Eberhardt et al., 2006; Yao et al., 2011c; Lee et al., 2010; Lawrinenko, 2014). Therefore, sorption of phosphate from aqueous solutions is emphasized to be mainly controlled by the surface area of the adsorbent and formation of metal-ion complexes (Zeng et al., 2013). Moreover, P release and retention processes such as sorption/desorption, ion exchange, and precipitation/dissolution are known to be controlled by the availability of aluminum, iron, and other divalent cations such as Ca and Mg in the soil (Reddy et al., 1999) as well as in biochar material (Hale et al., 2013; Mukherjee and Zimmerman, 2013).

Another potential mechanism of high P sorption by willow wood biochar was the salinity effect. Willow wood biochar had a significantly higher salt content (higher EC), which was approximately three times greater than the other biochars (Table 2-1), indicating the existence of water soluble salts that can cause extra sorption of P. The concept of salinity effect on P sorption was proposed by Jun et al. (2013) who found that the amount of P sorbed by artificial saline soils was up to three times higher than that by the control soil. The mechanism for that action is not clear but can likely be attributed to the possible precipitation of $PO_4$-P with $Ca^{2+}$ and $Mg^{2+}$ in the saline condition.

Hardwood and wheat straw biochars showed the same trend of P sorption but opposite to that of the willow wood biochar. However, hardwood biochar sorbed more P than wheat straw biochar in a non-saline aqueous solution, but at a very high P concentration in equilibrium solution (> 18 mg P $L^{-1}$), P sorption by wheat straw biochar exceeds that of hardwood biochar (Figure 2-1). Generally, these two biochars showed different sorption capacity, with 1.20 and 1.06 mg $g^{-1}$ in a 25 mg $L^{-1}$ P solution, for hardwood and wheat straw biochars, respectively. However, both biochars had comparable chemical properties including EC, pH, and Ca and Mg concentrations (Table 2-1), which provide no clear reason for the observed differences on their P sorption. On the contrary, in willow wood biochar, formation of ion complexes could be the primary reaction affecting P sorption. That is because all biochars' properties are relatively comparable except their CEC value and the concentrations of $Ca^{2+}$ and $Mg^{2+}$, which were at least 10-fold higher in the willow wood as compared to the other biochars (Table 2-1). Also, analysis of water that collected after washing biochar indicated that $Al^{3+}$ concentration in willow wood biochar was about 7-fold higher than that in the other biochars (Table 2-2). Existence of these cations at high concentration together with high CEC could facilitate formation of ion complex with P.

### 3.2 Phosphorus sorption on washed biochars

Unwashed and both acid and water washed hardwood and wheat straw biochars showed a similar trend of P sorption; however, unwashed biochars generally showed a tendency to have a higher but not significant P sorption ($p = 0.14$) at most of the equilibrium concentrations measured for P sorption (Figure 2-2). Also, water washed biochar tended to have a relatively higher but not significant P sorption capacity ($p = 0.14$) than that of acid washed biochar for all three studied biochars (Figure 2-2). Even though, these results showed non-significant p values, they indicate that acid washing tended to increase the capability to leach Ca and other elements from the biochars and tended to reduce P sorption efficiency than the water washing method. The affinity coefficient ($K_F$) values for wheat straw biochars with different washing methods were very similar (Table 2-3), with values of 0.29, 0.351 and 0.321 mg kg$^{-1}$ for unwashed, water and acid washed biochar, and with $R^2$ of 0.99, 0.99 and 0.98 for the three biochars, respectively. These parameters indicate that the P sorption capacity of that biochar was not highly influenced by washing. However, P sorption capacity of unwashed hardwood is significantly higher than that of water or acid washed biochar ($K_F$ values were 0.37, 0.29, and 0.25 mg kg$^{-1}$, and with $R^2$ values of 0.99, 0.94 and 0.98, respectively). Also, P sorption capacity of unwashed willow wood biochar was significantly higher than that of water or acid washed biochar ($p < 0.01$), their $K_F$ value were 3.49, 0.40 and 0.40 mg kg$^{-1}$, and with $R^2$ values of 0.83, 0.99 and 0.99, respectively. As mentioned above, the reduction of P sorption efficiency for washed biochars may coincide with a loss of calcium (Ca) due to leaching during pre-treatment (Table 2-2). Zheng et al. (2010) reported similar results, noting that the sorption capacity of biochar for P was significantly reduced for deionized water washed biochar in comparison to that of the unwashed biochar. On the contrary, Ji et al. (2011) suggested that removing ash by washing biochar with acid or deionized water could eventually create additional sites on the biochar surface and facilitate more sorption of anions.

The pattern of P sorption by the washed (with acid or water) willow wood biochar became the same as that of other biochar types with or without washing. The change of the pattern for P sorption for the willow wood biochar before and after being washed could be due to the release of the P from the biochar (Table 2-2) through the washing process. The release of P from biochar has been reported a long time ago (Toyron, 1948) and recently the mechanism of that release is considered to be simple; charring organic materials volatilizes organic C, cleaves organic P bonds, and makes P releasable from the charred material (Deluca et al., 2015). Also, removing ash from willow wood biochar through washing could reduce the concentration of associated elements (particularly Ca and Mg) and open up more pores on the biochar material, which in turn cause the pattern of P sorption to become similar to that of other biochar types.

### 3.3 Effects of pH on P sorption capacity by biochars

In this research, the pH value of the aqueous solution was higher for the willow wood than that of hardwood and wheat straw biochars, indicating the existence of suitable conditions for P to interact and precipitate with other ions, such as Ca and Mg. This could be another explanation for why the willow wood biochar had the highest P sorption capacity. The high pH values of willow wood biochar may be due to the hydrolysis of carbonates and bicarbonates of the present base cations such as Ca, Mg, Na, and K, which existed in high concentrations in the biochar materials (Table 2-1). The linkage between hydrolysis and pH value of biochar was also reported by Gaskin et al. (2008). High CEC and surface area of willow wood biochar could be additional factors leading to high pH reported for different biochar types, causing the soil pH to increase in biochar applied soils (Mikan and Abrams, 1996; Liang et al., 2006; and Cheng et al., 2008). The % ash in willow wood biochar was much greater than that of other biochars (Table 2-1) and this is another reason for the high pH of this biochar. High ash content and high pH occur together commonly in biochars made from plant biomass (Glaser et al., 2002; and Singh et al., 2010a).

The P sorption capacity of hardwood biochar increased sharply with increasing pH up to about 7 and then became constant or decreased slightly, suggesting the existence of an optimum pH for maximum phosphate sorption. The wheat straw and willow wood biochars had a higher capacity for P sorption at low pH values as compared to the hardwood biochar. However, pH seemed to have no or a negligible effect on P sorption by willow wood biochar, while P sorption by wheat straw biochar followed the same trend as hardwood biochar at pH values between 6 and 11 and both had the same optimum pH (~7) (Figure 2-3A). A similar range of optimum pH was found in a study of the pH effect on P sorption from aqueous solutions by other carbon-based adsorbents (Kumar et al., 2010). The fluctuation of P sorption by wheat straw and hardwood biochars based on solution pH was identical to a study by Yao et al. (2011c) who found the sorption of P by biochar was increased as solution pH rose from 2.1 to 4.1. However, no further increases were observed beyond that pH value. Conversely, Jung et al. (2015) found that P sorption capacity decreased as pH increased to 7 and then eventually increased as pH rose to 12. In our study, in the range of pH values between 3 and 11 studied, pH showed no remarkable effect on P sorption of the willow wood biochar. This biochar showed high and stable sorption of P when solution pH was low and tended to decrease after pH 7.

The influence of pH dependent charges on the sorption of P from solution seems to be negligible because the $pH_{zpc}$ (zero point of charge) of biochar in general reported to be in a range between 2.0 and 3.5 depending on the biochar type (Mukherjee et al., 2011), which means that biochar surfaces will have no charge between these values but will be negatively charged when the solution pH is greater than the ZPC. In another study, biochar surface was suggested to be negatively charged at pH larger than 3 (Shepherd et al., 2017). Also, the anion exchange capacity on the biochar surface is mainly at the acid pH range (Cheng et al., 2008). Thus, by increasing the pH of the solution beyond 3, the adsorbent is supposed to carry more negative charges, which, in turn, repulse the negatively charged solute in the solution (Singh et al., 2005; Yang et al., 2006) and reduce their sorption; however, this was not supported by the P sorption by biochars results found in this study. The result suggests that high pH encourages surface precipitation of Ca and Mg with P on the biochar more than repulses negatively charged phosphates. At optimum pH, all phosphate exists in the form of $H_2PO_4^-$; however, at pH levels higher than that, polynuclear components may compete for adsorption sites, resulting in a significant reduction in P sorption on the biochar surface (Yao et al., 2011c).

### 3.4 Effectiveness of Biochar for P Sorption

Both the Freundlich and Langmuir models fit the sorption data for wheat straw and hardwood biochars, and the Freundlich but not the Langmuir model fit the data for willow wood biochar. Therefore, only the Freundlich sorption isotherms are discussed here. The Freundlich model assumed that the sorption of ions occurs on a heterogeneous sorbent surface; however, the Langmuir model assumed the sorption to occur on a homogenous sorbent surface (Zheng et al., 2010). Biochar usually contains carbonized and non-carbonized fractions, making its surface heterogeneous (Chen et al., 2008a; Cao et al., 2009).The highly non-carbonized fraction (ash) content in willow wood biochar (Table 2-1) likely resulted in a severely heterogeneous surface, causing the Langmuir model to fail to fit the data.

The Freundlich equation satisfactorily described P sorption by the three biochars, as shown by the high $r^2$ values (Table 2-3). The sorption intensity was higher for wheat straw and hardwood biochars than for willow wood biochars (0.757, 0.658, and -0.352, respectively) (Table 2-3), suggesting that the first two biochars did not reach their saturation point. A potential explanation for the low sorption intensity of willow wood biochar is that its high capacity for P sorption (based on the slope of the curve) causes a large portion of the available sites for P sorption to be saturated. Also, based on the model affinity coefficient ($K_F$), willow wood biochar had a higher affinity for P sorption than wheat straw and hardwood biochars whether it's unwashed or washed with water or acid. This result is consistent with the intensity values as indicator for saturation states that, in all described biochar washing treatments, the highest affinity for P sorption of willow wood biochar was associated with the lowest intensity values (Table 2-3). This relation occurred because as more P is sorped, fewer sorption sites remained available for P sorption. This indicates that biochars made with different feedstock type have different adsorption intensities and affinities. Studies have shown that feedstock type and pyrolysis condition affect chemical properties, including the specific surface area of the char (Lehmann and Joseph, 2009), which is one of the main factors affecting P sorption.

### 3.5 Effects of initial P concentration on P sorption by water- washed biochars

As only washed biochars had a similar trend for P sorption, water-washed biochars were used to study the effects of initial P concentration and biochar type on P sorption. The results showed that there were inconstant patterns of P sorption based on the initial concentration of P and the biochar type (Figure 2-3B). However, P sorption of washed biochars was significantly affected by initial P concentration ($p= <0.001$) and biochar type ($p= <0.001$) with no significant interaction between them. At high initial P concentrations (12.5 to 25 mg P $L^{-1}$), sorption of P by willow wood biochar was significantly higher than that of the other biochars; however, its sorption was similar to the other biochars at very low initial P concentrations (1.25, 2.5 and 6.25 mg $L^{-1}$). These results indicate that the sensitivity of P sorption based on biochar type increases with increasing P concentrations. The proportion of sorbed P increased as the initial P in the solution increased, depending on the biochar type. Similar results were obtained through comparing P sorption capacity of corn stover, ponderosa pine wood residue, and switchgrass biochars (Chintala et al., 2014).

### 3.6 Phosphorus sorption under saline condition

Very little work has focused on the effect of salinity on the P sorption capacity of biochar. This study showed that higher salt concentration in the biochar materials associated with increases in P sorption capacity of biochar. Also, the amount of P sorped by biochars gradually increased with increasing P concentration in each of the three solutions with different salinity levels (EC of 0, 4 and 8 dS $m^{-1}$), however, the P sorption trend of willow wood biochar was opposite to that of the former two biochars (Figure 2-4). Statistically, the two-way ANOVA results showed that the salinity factor had no significant effect on P sorption capacity of wheat straw biochar ($p = 0.71$). The P sorption capacity of hardwood followed the order EC4 > EC8 > EC0 (their $K_F$ values were 0.45, 0.28, and 0.12mg $kg^{-1}$, respectively; $p=0.006$). The P sorption capacity of willow wood biochar was higher in the salinity condition of 8 than 0 ds $m^{-1}$ (the $K_F$ values were 2.44 and 1.56 mg $kg^{-1}$, respectively; $p=0.027$). The Freundlich equation did not satisfactorily describe P sorption by willow wood biochar under EC4, as shown by a low $r^2$ (Table 2-4, Figure 2-4).

Generally, the P sorption capacity of the three biochars was higher under saline than under non-saline condition, similar to results in Jun et al. (2013), who attributed that to precipitation of P with Ca- and Mg-containing minerals in the saline solution. The result for P sorption by the studied biochars is inconsistent with Clavero et al. (1990), who found that P sorption in soil sediments decreases as salinity increases. The differences of the examined material, reaction time and solution dynamic cycle in the current study may be responsible for the observed dissimilarity in the results. For most P concentrations in the equilibrium solution tested in this study, the maximum P sorption was in EC4 and the minimum was in EC0 (Figure 2-4). The observed reduction of the P sorption capacity of biochar at EC8 as compared to EC4 could be related to the changes in ionic strength and associated changes in ionic double layer thickness. Diffusion rate of P toward the sorbent surface reported to reduce with the increases of both ionic strength (Huang et al., 2015) and double layer thickness (Bar-Yosef et al., 1988). Therefore, the increase of these two parameters with the increases of EC could be responsible for that reduction of P sorption at EC8. The sorption of some monovalent ions such as $Cl^-$ classified as non-specifically adsorbed ions (forming outer sphere complexes), which means that these ions are weakly retained on positive sites on the sorbents surface by simple electrostatic attraction (Motts, 1981) under the influence of diffuse layer equilibrium (Arnold, 1978). Therefore, in saline solution these ions could occupy a high portion of the positive sites of the biochar surface. But, the phosphate ions added to the saline solution could be more effective for displacing majority of $Cl^-$ ions when existed in relatively low concentration, which resulted in increased P sorption capacity of biochar in EC4 compared to that in EC8. The displacment of ions happens because the phosphate ions are specifically adsorbed ions (or ions in inner sphere complexes) that have a stronger affinity for sorption sites than non- specifically adsorped ions (Motts, 1981). However, the reason that caused the P sorption capacity in EC0 to be the lowest is not known. Therefore, how changes in the salinity level affect the chemical and physical properties of biochars that control P sorption has to be examined more mechanistically in order to clearly understand the behaviour of P sorption by biochar under these conditions.

### 3.7 Effects of pH on P sorption capacity of biochars under saline condition

The pH values of the aqueous solutions after adding the three biochars are consistent with the first part of this experiment with the solution with willow wood biochar having higher pH than the other two biochars. The pH values for solutions with 8, 4 and, 0 dS $m^{-1}$ were 8.5, 8.7, and 8.6, respectively, for those added with willow wood biochar. The corresponding pH values were 6.8, 6.7, and 6.6, respectively, for solutions added with hardwood biochar, And 6.8, 6.4, and 6.6, respectively, for solutions added with wheat straw biochar. Solution pH among the biochars was uncontrolled due to the sensitivity of phosphate forms to pH. The uncontrolled pH might limit the comparison of sorption capacity between biochar types under different salinity conditions. But for each individual biochar, the consistency of the pH values among the three salinity levels indicates that no changes in solution pH occurred due to salinity effect. These results conclude that the variation of P sorption capacities of hardwood and willow wood biochars across the studied salinity conditions was not related to the pH effect.

## 4. Conclusions

We conclude that 1) feedstock type had a strong influence on biochar properties that control their P sorption capacity. Willow wood biochar had a higher P sorption capacity than the other two biochars and P sorption by willow wood biochar mainly occurred due to precipitation of P with cations such as Ca and Mg contained in the biochar; 2) solution pH influenced the sorption of P by the wheat straw and hardwood biochars, but had negligible influence by the willow wood biochar in non-saline solutions; 3) willow wood biochar released P when exposed to a solution with a low P concentration which caused the unique sorption trend observed, and which limited its benefit as a P sorbent; and 4) salinity conditions played an important role on the P sorption, depending on the biochar type. High salinity increased P sorption by hardwood and willow wood biochars, but not by wheat straw biochar. The results from this study suggest that hardwood biochar can be an effective sorbent for removing P from aqueous solutions as compared to the other two biochars studied under both non-saline and saline conditions. Further study in column tests using saline soils with high soil test P is necessary before using this biochar for field applications.

**Table 2-1**: Selected physicochemical properties of the three studied biochars.

| Property | Wheat straw | Hardwood | Willow wood |
|---|---|---|---|
| pH (1:20 w:v) | 10.13±0.02 | 9.96±0.01 | 10.5±0.004 |
| C (%) | 86.97 | 89.22 | 86.74 |
| H (%) | 2.64 | 2.67 | 2.17 |
| O (%) | 8.85 | 7.90 | 10.25 |
| N (%) | 1.32 | 0.20 | 0.83 |
| S (%) | 0.22 | 0.01 | 0.01 |
| EC (1:5) (dS $m^{-1}$) | 0.53±0.01 | 0.27±0.01 | 2.27±0.02 |
| CEC (cmol $kg^{-1}$) | 17.6 | 18 | 196 |
| Surface area ($m^2$ $g^{-1}$) | 55.24 | 324.6 | 380.0 |
| Pore volume ($cm^3$ $g^{-1}$) | 0.03 | 0.02 | 0.04 |
| Pyrolysis temperature (°C ) | 500 - 560 | 500 - 550 | 500 - 550 |
| Ash content (%) | 31.84±1.9 | 35.8±1.4 | 37.7±0.8 |
| Mobile matter (%) | 28.20±0.8 | 16.62±0.8 | 19.91±0.9 |
| Fixed Matter (%) | 18.09 | 35.94 | 30.04 |
| Pore size (nm) | 26.11 | 17.44 | 17.60 |
| Extracted elemental concentration, mg $g^{-1}$ | | | |
| Ca | 1.4±0.18 | 1.7±0.23 | 19.6±4.8 |
| Mg | 0.18±0.03 | 0.18±0.01 | 2.14±0.38 |
| Na | 0.27±0.03 | 0.38±0.06 | 0.66±0.08 |
| K | 3.3±0.41 | 2.7±0.24 | 33.7±1.24 |
| $NH_4$-N | 2.04±0.16 | 3.13±0.34 | 6.97±0.85 |

Mean of some parameters expressed with standard error [± SE], n = 3.

**Table 2-2**: Elemental concentration in water collected after washing biochar

| Biochar type | Na | Mg | Al | P | K | Ca | Fe | Mn | Ni | Cu | Zn | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | µg $L^{-1}$ | | | | | | |
| Wheat straw | 2248±15 | 187±26 | 209±24 | ND | 8572±68 | 1176±43 | ND | 0.8±0.1 | ND | ND | 12±2.9 | 24± 0.1 |
| Hardwood | 2513±30 | 248±12 | 106±9 | ND | 2255±22 | 1025±67 | ND | 8.5±0.5 | ND | ND | 47±8.2 | 39±0.8 |
| Willow wood | 6887±40 | 1492±19 | 4964±78 | 90±6 | 57298±320 | 1593±70 | ND | 4.1±0.1 | ND | 2.4±0.4 | 40±0.3 | 83±3.6 |

Mean elemental concentrations are expressed with standard error [± SE], n = 3. (ND) Not detected.

**Table 2-3**: Parameters obtained from Freundlich isotherms for P sorption by three biochars under three washing conditions

| Parameter | Wheat biochar |  |  | Hardwood biochar |  |  | Willow biochar |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Un-washed | Water | Acid | Un-washed | Water | Acid | Un-washed | Water | Acid |
| $K_F$ (mg $kg^{-1}$) | 0.290 | 0.351 | 0.32 | 0.375 | 0.292 | 0.25 | 3.493 | 0.407 | 0.404 |
| 1/n | 0.757 | 0.674 | 0.69 | 0.658 | 0.747 | 0.76 | -0.353 | 0.545 | 0.495 |
| $R^2$ | 0.99 | 0.99 | 0.98 | 0.99 | 0.94 | 0.98 | 0.83 | 0.99 | 0.99 |

$K_F$ is the Freundlich constant, 1/n is sorption intensity and $R^2$ is the correlation coefficient

**Table 2-4**: Parameters for the Freundlich model that describe P sorption by three biochars under three salinity levels

| Parameter | Wheat straw biochar | | | Hardwood biochar | | | Willow wood biochar | | |
|---|---|---|---|---|---|---|---|---|---|
| | EC 0 | EC 4 | EC 8 | EC 0 | EC 4 | EC 8 | EC 0 | EC 4 | EC 8 |
| $K_F$ (mg kg$^{-1}$) | 0.06 | 0.16 | 0.07 | 0.12 | 0.45 | 0.28 | 1.56 | 0.92 | 2.44 |
| 1/n | 1.09 | 0.78 | 1.04 | 0.90 | 0.47 | 0.61 | -0.37 | -0.49 | -0.49 |
| $R^2$ | 0.97 | 0.94 | 0.98 | 0.98 | 0.84 | 0.97 | 0.97 | 0.23 | 0.80 |

$K_F$ is the Freundlich constant, 1/n is sorption intensity, $R^2$ is the correlation coefficient, and EC is electrical conductivity.

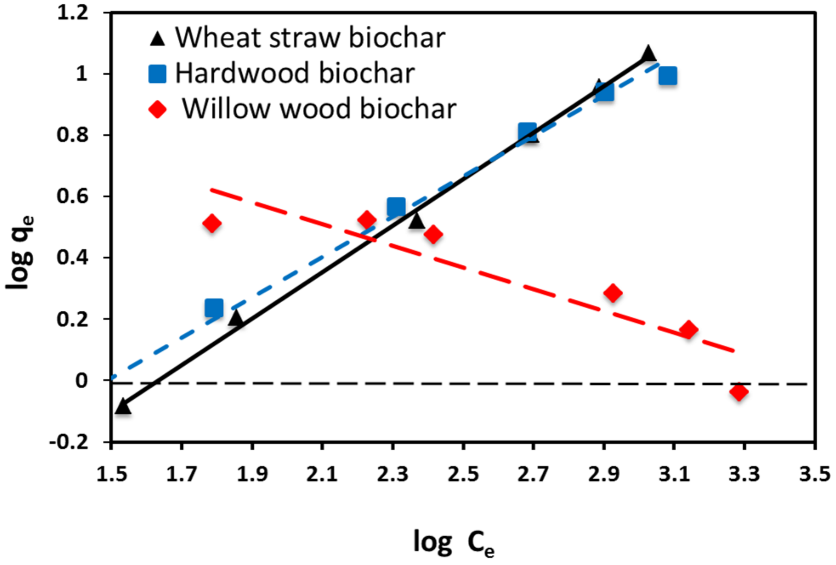

**Figure 2-1**: Linearized Freundlich isotherm for phosphorus adsorbed to unwashed (U) biochars. Phosphorus (P) concentration in an aqueous solution ($C_e$) and sorbed P ($q_e$**)**.

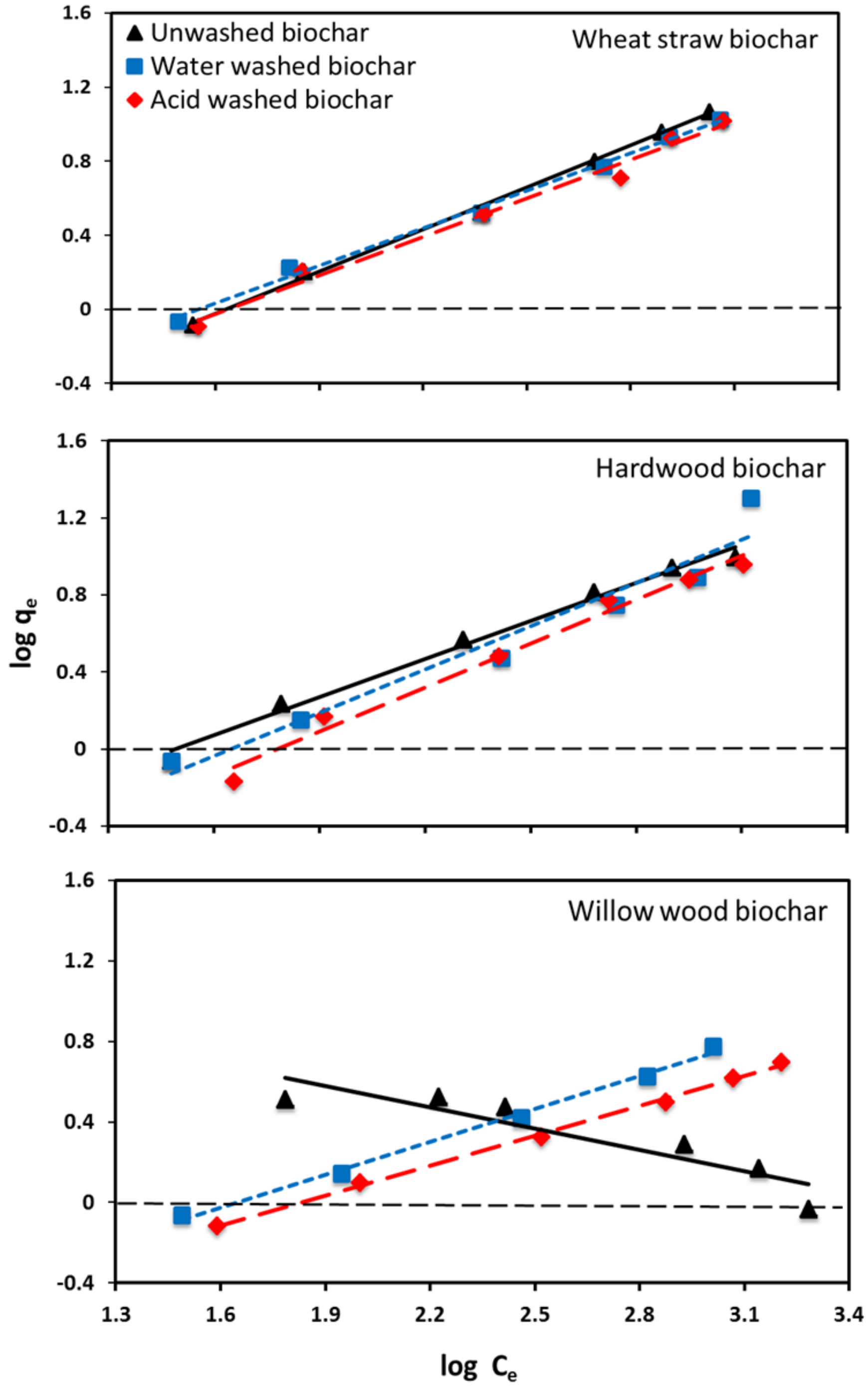

**Figure 2-2**: Linearized Freundlich isotherm for phosphorus sorbed to unwashed and washed biochars. Phosphorus (P) in the aqueous solution ($C_e$) and sorbed P ($q_e$).

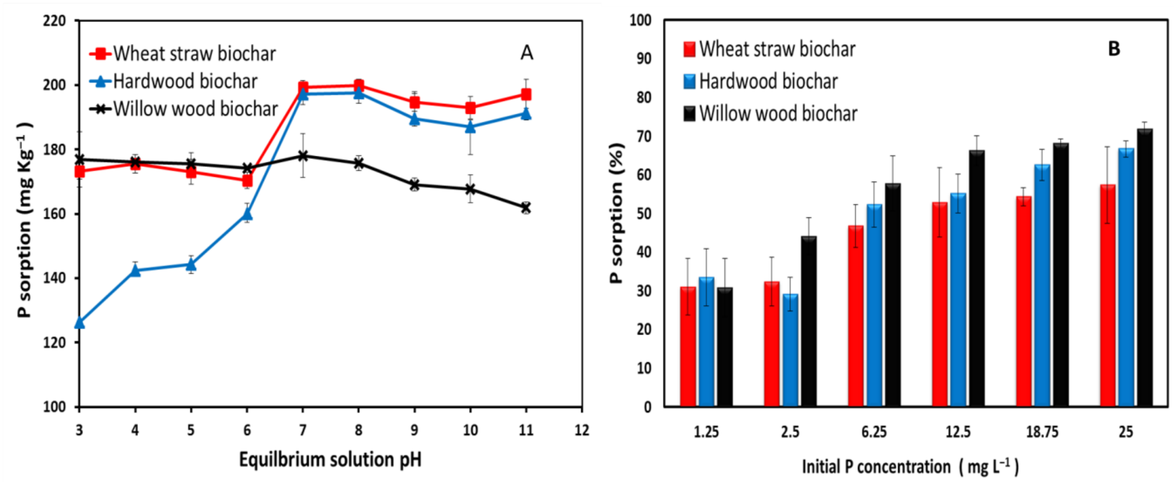

**Figure 2-3**: a) Effect of pH on phosphate (P) sorption isotherms by three biochars; and b) Effect of initial phosphorus (P) concentration and water -washed biochars on % P sorption. Vertical bars are standard deviations (n=3)

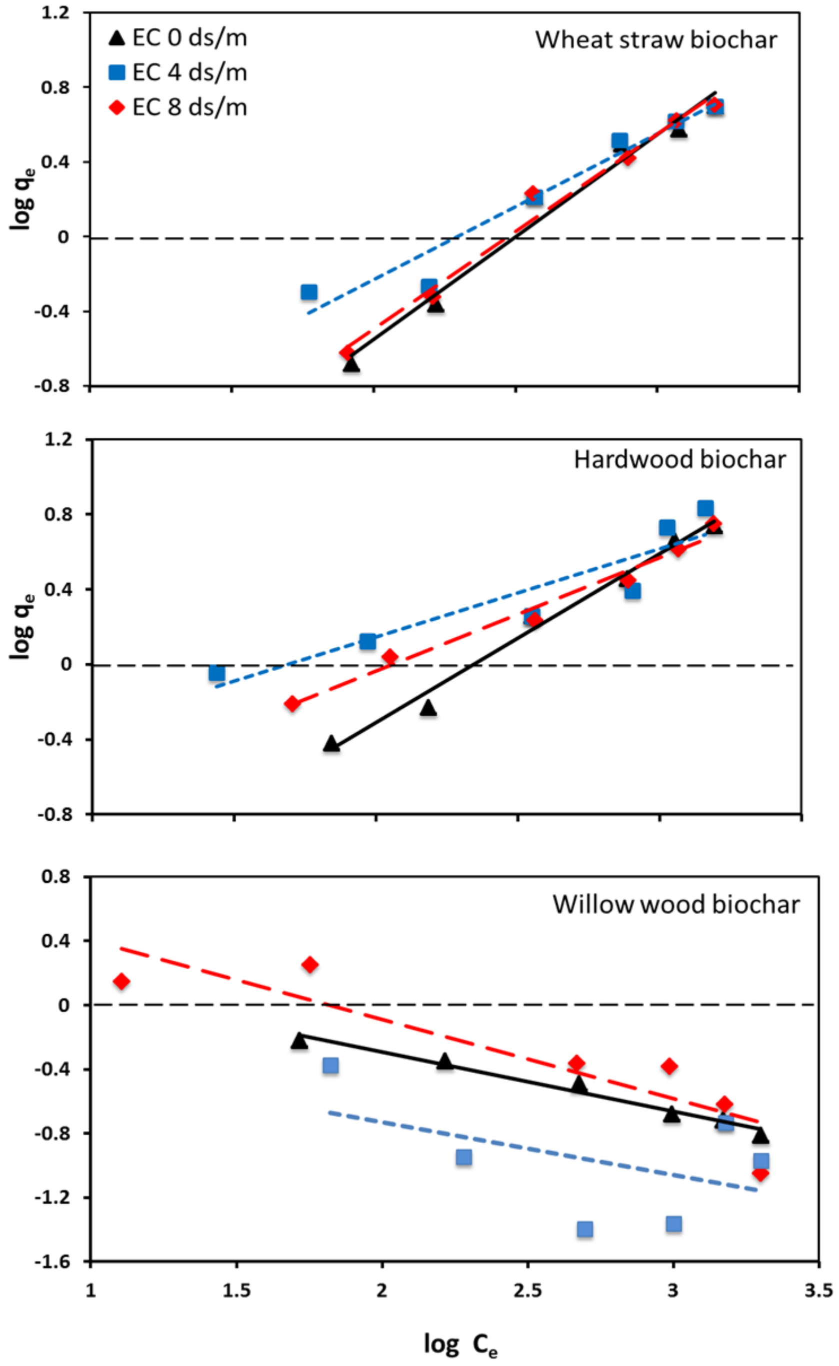

**Figure 2-4**: Linearized Freundlich isotherm for phosphorus sorbed to biochars under different salinity levels. Phosphorus (P) concentration in the aqueous solution ($C_e$) and sorbed P ($q_e$)

# CHAPTER 3. HARDWOOD DERIVED BIOCHAR REDUCES LEACHING LOSS OF PHOSPHORUS FROM A MANURED SOIL

## 1. Introduction

Phosphorus (P) is an essential macronutrient for profitable crop and animal production and manure is commonly being applied as a source of P in crop production. However, land application of manure can increase the risk of P loss and negatively impact surface water quality, since manure is considered a direct source of P in leaching and runoff due to its high soluble P concentration (Mueller et al., 1984; Sharpley et al., 1994). When soil P exceeds the P sorption capacity of the soil, the excess P can move downward through the soil (Koopmans et al., 2007; Lehmann et al., 2005; Ulén et al., 2011; Parvage et al., 2013), causing eutrophication in water bodies (Chen et al., 2008b; Borda et al., 2011). Since P is the most limiting nutrient in many water bodies, increased P input can cause eutrophication at concentrations as low as 0.02 to 0.035 mg $L^{-1}$ (Canadian Council of Ministers of the Environment, 2004). Hence even a small, agronomically insignificant loss of soil P can adversely affect water quality (Correll, 1999; Brookes et al., 1997). Conversely, high concentrations of P in the soil help to improve crop production (Sharpley, 1994).

Phosphorus concentrations in most agricultural soils were initially very low, and P has been added to enhance crop yield. However, the addition of P from manure and fertilizers over many years and in excess amounts has increased soil P concentration beyond what is needed for optimum crop production (Bergström et al., 2005). A significant increase in the soil P concentration from 34 to 48 mg $kg^{-1}$ in soils used for vegetable production was attributed to long term application of synthetic P fertilizers in Wisconsin during the period of 1967-1990 (Sharpley et al., 1994). Increasing animal production in certain areas can result in a large amount of manure (more than the P requirement of crops) being applied to the agricultural land, resulting P surpluses on farms and high P concentration in the percolation water (Chardon et al., 2007) and in the surrounding watershed (Sharpley et al., 2001). Applying manure on the basis of crop N requirement often results in the accumulation of P in the soil and increased P loss via erosion, overland flow and leaching (Schoumans and Groenendijk, 2000; Bai et al., 2013; Edwards and Daniel, 1994), with much of the P lost as dissolved P (Kleinman et al., 2005). The concentration of dissolved P (DP) in subsurface flow increased (up to 28-fold) after the broadcast application of dairy manure near the study site (Kleinman et al., 2009).

Most of past efforts to reduce nutrient loading in waterbodies were focused on point sources rather than non-point agricultural sources, which provide a large amount of P to cause eutrophication in receiving waterbodies (Sharpley et al., 1994; Andersson et al., 2013). There are three pathways of P movement to water bodies, including leaching and runoff of DP, as well as erosion of particulate P (PP). Leaching of DP is generally greater in coarse-textured soils than in fine textured soils due to high infiltration rates in the former. In the Canadian prairie, the combination of a flat landscape and an increasing amount of manure being applied to the land favors the loss of P as DP (Glozier et al., 2006). Input of DP into the aquatic environment is more harmful than that of PP, due to DP's immediate and high biological availability to cyanobacteria (Regan et al., 2014). Adsorption/desorption and dissolution/precipitation are main chemical processes that control the concentration of P in the soil solution (Edwards and Withers, 1998); which in turn control the movement of P to waterbodies (Campbell and Edwards, 2001). Therefore, increasing soil's P sorption capacity could reduce P loss and help mitigate its harmful impact on water bodies.

Recently, biochar is recognized as an important soil amendment that can enhance soil chemical and physical properties (Gaskin et al., 2010; Atkinson et al., 2010; Brockhoff et al., 2010; Singh et al., 2010a) and increase the soil's capacity to retain and recycle nutrients (Verheijen et al., 2010), including P (Yao et al., 2012; Chintala et al., 2014). Biochar is produced from the pyrolysis of organic feedstocks in the absence of oxygen (Sanghi and Singh, 2012; Novak et al., 2016a) and has a great ability to adsorb P from solutions (Yao et al., 2011b; Sarkhot et al., 2013) and reduce P leaching losses from soils (Lehmann et al., 2003; Laird et al., 2010a). The large surface area and porosity, and high charge density of biochar are important to enhance P retention (Farrell et al., 2014; Lehmann et al., 2015). The existence of carboxylate groups on biochar's surface helps increase the cation exchange capacity (CEC) of biochar-amended soils (Novak et al., 2009b); this increase of negatively charged sites may indirectly help retain P by holding cations that precipitate with P, such as Ca, Mg, Fe and Al. Alteration of soil pH, due to biochar addition, could influence the type of co-precipitating cations and the strength of ionic P interaction with these cations (Lehmann et al., 2003; Topoliantz et al., 2005). For example, magnesium oxide (MgO) and $Fe^{3+}$ on the surface of biochars is found to have a strong affinity for anions, depending on the pH (Yao et al., 2011b). Biochar also has high affinity for organic molecules (Smernik, 2005) that may act as chelates for metal ions that precipitate P. Given the above P retention properties biochar could be potentially used to reduce P leaching from manured soils (Laird et al., 2010a). However, other factors such as the rate of biochar application; the initial concentration of soil test P (STP) and the quality and quantity of other elements in manure might affect P retention by biochar.

The objective of this study was to evaluate the effect of biochar addition on P leaching, and to compare the influence of biochar application rates on the concentration of P in the leachates. We hypothesized that: 1) biochar improve the soil P sorption capacity and reduce P loss by leaching, and 2) biochar addition increase soil pH that facilitates P precipitation reaction with Ca and Mg in biochar, manure and soil. We also hypothesized that continuous increases in soil-water infiltration rate, accompanying increased biochar addition, could impose a negative impact on soil capacity for P retention. Therefore, we aimed at finding the optimal rate of biochar application with maximum P retention that overrides the leaching of P due to increased infiltration.

## 2. Materials and Methods

### 2.1 Soil and biochar

Soil was sampled from the plow layer (between 0.1 to 0.2 m) of an agricultural field in Holden, County of Beaver; 100 km east of Edmonton, Alberta, Canada. The majority of the soil types in the sampling site are belong to Chernozemic and Solonetzic orders (Kjearsgaard et al., 1983).

A hardwood biochar was selected for the soil column leaching study due to its best overall P sorption performance among the biochars tested (chapter 2). The biochar was produced by Alberta Innovates - Technology Futures, Vegreville, Canada. Spruce, Pine and Fir mixtures feedstocks were slowly pyrolyzed in an auger retort carbonizer (ABRI- Tech, 1 Tonne retort system, Alberta Biochar Initiative- AI-TF Vegreville) at temperature ranged between 500 and 550 °C (heating rate, 85-100 °C/min). The properties of the biochar and soil are given in Table 3-1; however, their preparation discussed in detail in chapter 2 and 4.

### 2.2 Preparation and leaching of soil columns

The experiment included four biochar application rates, and two manure treatments (i.e., manured and unmanured soils). The manured and unmanured soils are abbreviated as HSTP and LSTP indicating high and low soil test P, respectively. To ensure equal P content in all different biochar treatments, HSTP soil was prepared by mixing manure at application rate of 5.17 t $ha^{-1}$ with the entire volume of soil before biochar addition. Biochar then mixed with the entire soil mass to bring the final biochar content to 0, 2, 5, and 8% (w/w). Then soil of each treatment was mixed with acid- washed sand at 20% (v/v) to improve the infiltration in the control without biochar, and each treatment was triplicated.

The columns are acrylic tubes with an inner diameter of 10 cm and15 cm high (1178 $cm^3$ volume). The columns were sealed at the base with a perforated PVC plate to allow for the outflow of leachates. The perforated plate was designed to allow the collection of leachates by gravity flow. Three vertical channels with diameter of 3 mm were joined at the column base, and two holes were drilled in each channel plus one hole in the joint center for water drainage, which eventually flowed out through one outlet (Figure 3-1). A fine-screen mesh was installed in the base of the column to prevent the blockage of the leachate outlet. A coarse, acid-washed sand layer (to a height of 1.5 cm) was placed at the bottom of each column, ensuring that the soil remained free draining.

To ensure a uniform bulk density and that the soil was restored to the initial values of 1.13 to 1.16 g $cm^{-3}$, soil mass was added to the columns in batches and gently compacted with a wooden plate until the top of the soil columns sank no further. This packing procedure also helps to prevent the formation of preferential flow pathways. The treatments were pre-wetted with deionized water to 60% of water holding capacity (WHC), and incubated for two weeks at room temperature (25 ±1 °C). The WHC of the treated soils was determined using plastic containers (10 cm in diameter) in which the bottom was perforated and fitted with a fine screen mesh. The containers were filled with 100 g of soil to a uniform compaction and leached three times with deionized water to ensure maximum saturation. Excess water was drained until no more drainage was observed. After half an hour, saturated soils were weighed to determine the WHC. By the end of the incubation period, all columns were leached six times every other day with deionized water that is equivalent to pore volume at each time. Leachate was collected during following 24-h period and stored in 250 mL polyethylene bottles and kept refrigerated until the time of analyses. The pore volume for each treatment was calculated using the following equation according to Kirkham (2014):

$$PV = V_s \text{ x } Ø_s \tag{1}$$

where ($V_s$) is the volume of soil in the column, and ($Ø_s$) is associated porosity. The pore volume of the biochar treatments of 0 and 2 was 500 $cm^3$ whereas other two biochar treatments (i.e., 5 and 8) had a pore volume of 650 $cm^3$.

The net change in soluble elements due to the interaction between manure and biochar was determined by the difference between soluble element concentration in respective biochar treatments in manured and unmanured soils. The percent of P that was added with the manure and recovered in the leachate was estimated using the following equation of Laird et al. (2010a):

$$R_{xi} = ((X_{mci} - \bar{X}c) * 100) / X_{mi} \tag{2}$$

where $R_{xi}$ is the percent recovery of element X for column i; $X_{mci}$ is the mass of X that leached from a specific column (i), at a particular manure application rate (m) and biochar treatment (c); $\bar{X}c$ is the average mass of X that leached from control columns (i.e., without manure addition) for the biochar treatment (c); and $X_{mi}$ is the mass of element X in the manure that was added to column (i).

### 2.3 Leachate analysis

All leachate samples were subjected to several chemical analyses. The pH and EC of the leachate samples were measured using an AP75 portable waterproof conductivity/TDS meter (Thermo Fisher Scientific Inc., Waltham, MA, US) and an Orion pH meter (Thermo Fisher Scientific Inc., Beverly, MA, US), respectively. The leachates were filtered using Whatmann # 40 filter paper and analyzed for $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$, $Fe^{3+}$, and $SO_4^{3-}$ ions using Perkin Elmer Optima 3000 DV inductively coupled plasmamass spectrometer (ICP-MS) (PerkinElmer Inc., Shelton, CT). The unfiltered leachate samples were tested for TP after digestion in a nitric acid–perchloric acid mixture (Olsen et al., 1982). Sub-samples of leachate were filtered using 0.45-µm filters to remove particulates and then analyzed for dissolved reactive P (DRP) colorimetrically according to Murphy and Riley (1962). The P load in leachate was calculated by multiplying the leachate volume per event, by the corresponding volume-weighted concentrations (mg $L^{-1}$) of the respective P form since the total volume of leachate varied depending on the treatment.

### 2.4 Soil and manure analysis

Sub-samples of air-dried after the two weeks of incubation were analyzed to determine soil chemical and physical properties. The particle size distribution of the original soil was determined using the hydrometer method (Gavlak et al., 2003). The sand content was 22% and the clay content was 34% (equivalent to a clay loam). Chemical analyses were conducted after sieving sub-samples of soil using 2 mm mesh. Electrical conductivity (EC) measured on the original soil using saturated paste extracts, (Richards, 1954), using an AP75 portable waterproof conductivity/TDS meter (Thermo Fisher Scientific Inc., Waltham, MA, US). Soil pH was measured for the original and final soils; both measurements were done at soil: water ratio of 1:1 (m:v) using an Orion pH meter (Thermo Fisher Scientific Inc., Beverly, MA, US). Soluble cations were analyzed after extracting incubated soil with deionized water at 1:1 (m:v) ratio by inductively coupled plasma molecular absorption spectrophotometry (ICP-MS) using a Perkin Elmer ELAN 6000 spectrophotometer (PerkinElmer, Inc.MA). Total phosphorus (TP) in incubated soil was extracted by digestion of 2 g of finely ground soil using $HClO_4$ + $HNO_3$ (Olsen et al., 1982). Incubated soil samples also analyzed for available P (AP) using the modified Kelowna extraction method (0.015 *M* NH4F, 1.0 *M* HOAc, 0.5 *M* NH4OAc) (Ashworth and Mrazek, 1995).

Dry cattle manure was obtained from a farm in Edmonton, Canada. Manure collection, handling and preparation were done according to the guidelines of A&L Canada Laboratories Inc. Dry matter content of the manure was determined by drying five sub-samples of manure at 105 °C and chemical properties of the manure (Table 3-2) were determined using following procedures. Organic matter content was estimated by heating manure samples to a temperature of 550 °C for 24 h. (Navarro et al., 1993). Total P content was determined by digesting 2 g of dried manure at 105 °C using agua regia digestion (3:1, v/v, $HCl/HNO_3$). Water-extractable P in the manure was determined by mixing 20 g of manure with 200 mL deionized water, and shaking horizontally at 150 strokes (3000g) for 20 minutes (Kleinman et al., 2007). The mixture was then filtered through a 0.45-μm membrane filter, and DRP/TRP were determined in the filtrate. All P analyses were conducted using the ascorbic acid molybdate blue method (Murphy and Riley, 1962).

### 2.5 Data analysis

Statistical analysis of variances (ANOVA) was performed using PROC MIXED in the Statistical Analysis Systems software (SAS) package (SAS 9.4). Before performing the ANOVA analysis, the normality of distribution and homogeneity of variance were tested. A two-way factorial design was used to test the degree of significance of effect of biochar rates; the effect of STP level; and the interaction between these factors at $\alpha = 0.05$. A one-way factorial design was used only for the HSTP soil to test the degree of significance of the biochar rates effect on the percentage of P recovered in leachate and the initial and net changes of soil-soluble elements due to manure addition. Significant differences between the treatment means were analyzed using Tukey's test at 95% significance level ($P < 0.05$). Analyses of variances for the two- and one-way factorial designs were performed according to the following equations, respectively:

$$Y_{ijk}=\mu+A_i+B_j+(AB)_{ij}+\varepsilon_{ijk}; \quad (3)$$

$$Y_{ik}=\mu+A_i+\varepsilon_{ik}; \quad (4)$$

where $Y_{ijk}/Y_{ik}$ are dependent variables, $\mu$ is the overall mean, $A_i$ and $B_j$ are the effects of $i^{th}$ and $j^{th}$, biochar rate, STP, respectively, and $\varepsilon_{ijk}/\varepsilon_{ik}$ are the random variable error within the experiment.

## 3. Results and Discussion

### 3.1 Changes in leachate composition due to manure and biochar addition

The reported alkaline pH of biochar (Table 3-1) is common for thermally-produced biochar (Lehmann and Joseph, 2009). The high pH of biochar was expected to facilitate P precipitation along with other cations in soil and biochar material. The oxygen and hydrogen contents of biochar were 7.9% and 2.6%, respectively (Table 3-1). These elements are expected to be present in organic functional groups on the biochar surface (Uchimiya et al., 2011; Inyang et al., 2011) and known as polar groups, which have a great influence on biochar chemistry and its interactions with soil and solutes (Lawrinenko and Laird, 2015).

In general, biochar effect on the leachate composition was identified only when biochar was applied at high rates (5 and 8%). At the first leaching event, the biochar treatment of 8% applied to LSTP soil caused a significant increase in the pH of leachate compared to the control treatment likely due to the higher pH of biochar than the soil (Table 3-1). In consistent with our results, a recent study showed an increase in the pH of the leachate that was collected from an acidic soil after treated with different biochar types (Buecker et al., 2016). However, biochar had no significant influence on leachate pH of the subsequent leachate events. The pH of the leachate gradually increased during the subsequent leaching events probably due to the reduction in leached sulfate across the leaching events (Table 3-3). Even though the concentration of basic cations in the leachate was reduced during the leaching events (Table 3-3), the sulfate releases seemed to have a stronger influence on the leachate pH than the releases of basic cations.

The highest concentration of $Ca^{2+}$ and $Mg^{2+}$ was observed in the leachate collected during the first leaching event but markedly decreased thereafter showing 8- and 10-fold reduction in the concentration of $Ca^{2+}$ and $Mg^{2+}$, respectively (Table 3-3). In the first event, the concentrations of these cations in the leachate from the 8% biochar treatments were significantly lower than that from the control. Element valency was shown to have an important influence on element concentration in the leachate of the three selected leachate events. In the most cases, the concentration of multivalent cations such as $Ca^{2+}$ and $Mg^{2+}$ significantly decreased; however, the concentration of monovalent cations such as $K^+$ and $Na^+$ significantly increased with the increasing biochar application rate. That indicating the ability of biochar to adsorp the $Ca^{2+}$ and $Mg^{2+}$ over the $K^+$ and $Na^+$, which are essential for P retention in the high pH soil. Similar results have been reported in a previous study and the difference in ion retention strength per cation type was attributed to the proportional relationship between the charge of the ion and the distances between the biochar surface (sorbent) and sorbate (Novak et al., 2009a).

The removal of $Al^{3+}$ and $Fe^{3+}$ with the leachate was opposite to that of basic cations. During the first leaching event the concentration of $Al^{3+}$ was significantly lower in all biochar treatments than the control whereas $Fe^{3+}$ concentration was lower than the detection limit in all samples. The concentration of $Al^{3+}$ and $Fe^{3+}$ increased during the subsequent leaching events probably due to the influence by soil pH and the associated P sorption/ desorption activities. In the first leaching event, the pH of the leachate was neutral and relatively low compared to the subsequent leaching events suggesting the relatively low pH in soil at the beginning of the leaching. Adsorption of phosphate to the surfaces of iron (III) and aluminum oxide and hydrated oxide is long been known to be important for P retention in acid and neutral soils (Bromfield, 1965; Syers et al., 1971; Torrent, 1987). Therefore, at the beginning of leaching, most of the hydrous oxides of the $Al^{3+}$ and $Fe^{3+}$ were tightly retained through phosphate adsorption especially for the HSTP soil. However, removal of sulfate and other acidic sources during the leaching events increased the soil pH (Table 3-3). The increase of soil pH is favored for P retention by precipitation with $Ca^{2+}$ and $Mg^{2+}$ than through the oxide and hydrated oxide of $Al^{3+}$ and $Fe^{3+}$. That favourable reaction might facilitate the removal of these trivalent cations with leachate (Table 3-3).

### 3.2 Influence of manure and biochar on soluble elements and phosphorus leaching

Understanding the changes in soil elements due to biochar and manure interaction during incubation is helpful to improve our understanding on benefits of biochar application for P retention in soil. The changes of the soluble elements in the incubated soil that were treated with manure and biochar are presented in figure 3-2. Since manure was distributed homogenously in the soil, the concentration of elements introduced with the manure considered equal in all biochar treatments. Significant changes in the contents of soluble elements, particularly for the multivalent cations were observed at the end of incubation. Such findings indicated possible reactions between soluble elements added with manure and the specific effects of biochar application rates on the soluble element content (Figure 3-2).

The initial soluble $Na^{+}$ in the soil was not influenced by biochar addition; also the amount of soluble $Na^{+}$ that introduced with the manure application (net change of soluble $Na^{+}$) was not influenced by the reaction between manure and biochar (Figure 3-2). It is well known that divalent cations are preferred at the exchange site than monovalent cations (Phongikaroon et al., 2006) and the competition by multivalent cations for the exchange sites of the biochar might have resulted in similar soluble $Na^{+}$ content among different biochar treatments. However, the initial soluble $K^{+}$ content in soil was significantly higher in the 5 and 8% biochar treatments in comparison to that of the control but when biochar and manure interaction was considered, net change of soluble $K^{+}$ content was higher in the control than in these biochar treatments (Figure 3-2). Biochar was found to release a significant amount of soluble $K^{+}$ when applied to soil at a high rate as it appeared for the LSTP soil (Table 3-3). This is due to the higher $K^{+}$ concentration in the biochar compared with soil; the difference was about 8-fold as found for the same biochar and same un-manured soil (Table 3-1). Also, in other study a significant release of K and P from a biochar-amended soil compared to that un-amended soil has been reported (Buecker et al., 2016; Laird et al., 2010a). The high solubility of $K^{+}$ probably has resulted from the ash in the charred material, which is considered be a source of available nutrients (Glaser et al., 2002). The soluble $K^+$ that was added with the manure may be high enough to make the order of K content in manured soil to be opposite to that was initially found between biochar treatments of the un-manured soil. Concurrently the $K^+$ added with the manure may be adsorbed to the high rate of biochar treatments in higher intensity than that adsorbed to the control (0% biochar) in order to keep an equilibrium balance of K content between the solid and the liquid form. As a result, soluble $K^+$ in the control treatment became higher than that in the other biochar treatments when a comparison was made of the net changes of the $K^+$ due to manure addition.

The initial soluble $Ca^{2+}$ and $Mg^{2+}$ contents in soil varied in a similar way among different biochar treatments, compared with the net changes of each element due to manure addition and reaction with biochar (Figure 3-2). In both cases, $Ca^{2+}$ and $Mg^{2+}$ were found to decrease as biochar application rate increased. The 8% biochar treatment released significantly lower concentrations of soluble $Ca^{2+}$ and $Mg^{2+}$ than the control treatment and difference between the two treatments was about 50% for both elements. Such finding indicates the high potential of biochar to adsorb these divalent cations and reduce their removal as soluble ions. However, affinity of biochar to adsorb $Ca^{2+}$ was higher than that for $Mg^{2+}$ when these cations were added at high amounts along with the manure addition as shown for their net changes (Figure 3-2). There was no significant difference between the different biochar treatments when the net change of soluble $Mg^{2+}$ was considered. In contrast, net change in soluble $Ca^{2+}$ was about 50% lower in the 8% biochar treatment than in the control (Figure 3-2).

Initial soluble $Al^{3+}$ and $Fe^{3+}$ contents in soil increased with the increasing biochar rate. The two elements were significantly higher in the 5 and 8% biochar treatments when compared with the control and 2% biochar treatment indicating that biochar could be an important source of these elements. However, the net changes of these elements were negative after manure treatment (Figure 3-2). For example, the average concentrations of $Al^{3+}$ and $Fe^{3+}$ in the 0% biochar and without manure were 30 and 23, respectively. After manure was added, the concentrations dropped to 24 and 19.5 mg column$^{-1}$ (data not showed). The reduction in the net change of these elements was found to increase as biochar addition rate was increased may be ascribe to the soil pH changes. The soil with 0% biochar had an average initial pH value of 7.1. Adding manure to soil with such a neutral pH was expected to encourage P to adsorb on the surface of $Al^{3+}$ and $Fe^{3+}$ hydrous oxides in insoluble form. The adsorption reaction likely consumed a large quantity of the soluble $Al^{3+}$ and $Fe^{3+}$ elements, both from those that were added and from those initially presented in the soil. This adsorption of P with Al and Fe hydrous oxides may also be responsible for the reduction of their leachate losses in the first leaching event, which was discussed in 3.1 and presented in table 3-3. However, saturation of soil during leaching events could resulted in increased solubility of $Fe^{3+}$ and $Al^{3+}$ through the reduction that convert them from trivalent to divalent species with high potential to be leached out from soil during substantial events.

### 3.3 Effects of biochar addition on soil pH and phosphorus leaching

The soil pH measured at the end of the leaching experiment showed that pH increased with increasing biochar rate (Figure 3-3). The pH of the control soil was 7.3 and while the pH of 8% biochar treatment was 8.9. The pH change created by biochar addition was greater in HSTP soil than that in LSTP soil. This may be due to the additional base cations that were introduced with manure treatment. Furthermore, the relatively higher pH of the manure in comparison to that of soil (Manure pH was 8.5, Table 3-2) could be another reason for the raised pH of the HSTP soil. The pH of the biochar used in the current study was about two degrees higher than the pH of two soils (Table 3-1) and increase in soil pH was expected. Our results are in agreement with Laird et al. (2010b); Yao et al. (2011a); Chintala et al. (2014). A significant reduction in soil pH has been also noted in a biochar-amended saline soil, and was attributed to the lower pH of biochar than the soil (Wu et al., 2014).

The solubility of orthophosphate is affected by the pH and the presence of other ions: $Al^{3+}$, $Fe^{3+}$, $Ca^{2+}$ and $Mg^{2+}$. In low-pH conditions, P precipitates mostly through formations of insoluble compounds, such as $Fe_3 (PO_4)_2.8H_2O$ and $AlPO_4.2H_2O$. However, the high soil pH created by biochar, is expected to help precipitate P along with basic cations (i.e., formation of Ca-P / Mg-P species), resulting in a considerable reduction of P leaching. The leaching losses of $Ca^{2+}$ and $Mg^{2+}$ are found to be lower in the biochar-amended soil in comparison with that of the control (Table 3-3), resulting in the lowest DRP in the 8% biochar treatment (Figure 3-4). Soil-soluble P concentration found to decrease with an increase in the biochar application rate, which coincided with associated increases in soil pH; that reduction attributed to a reaction between P and the added $Ca^{2+}$ and $Mg^{2+}$ with biochar (Parvage et al., 2013).

### 3.4 Effects of soil test phosphorus and biochar addition on phosphorus leaching

A comparison of the DRP in the leachate from HSTP and LSTP soils treated with different biochar rates showed that the biochar treatments affected DRP in the leachate from the HSTP soil but not the LSTP soil (Figure 3-4). The DRP losses decreased significantly with the increasing biochar application rate. However, for the LSTP soil, although not statistically significant, the DRP in the leachate decreased with increasing biochar application rate from 0 to the 5% biochar treatment and increased with the 8% biochar treatment (Figure 3-4). In comparison with the control, the 2, 5 and 8% biochar treatments released about 26, 47 and 23% less DRP, respectively.

In most of the leaching events, as well as in the calculated cumulative amount, similar loss patterns were observed for DRP and TP. A significant effect of biochar application on the P losses was identified only in the HSTP soil (Table 3-4 and Fig 3-4). Since removal of dissolved P from soil is immediately available for organisms in the water, the losses of DRP from the HSTP soil will be discussed in more detail.

For the HSTP, the losses of DRP from control increased to a level of around 1.05 mg column$^{-1}$, and after 4 events decreased down to a level of 0.5 mg column$^{-1}$ at the end of the leaching period (Table 3-4). The highest losses of DRP occurred in event 3 and were 0.8, 0.7 and 0.55 mg column$^{-1}$ for 2, 5 and 8% biochar treatments, respectively, and then continuously decreased after that to end up with values of 0.6, 0.6 and 0.66 mg column$^{-1}$$_{,}$ for 2, 5 and 8 biochar treatments, respectively. Regardless of the soil P level, the losses of DRP from the two soils very comparable in the first event indicating the P retention ability in the HSTP soil against losses by leaching. Even though the losses of P from the two soils in this event were the lowest, the two factors of soil P level and biochar had significant influence on the DRP losses. However, there was no interaction between them (p=0.085). The influence of biochar on reducing P losses was obvious even in the soil of LSTP; thus, in the first event the losses of DRP from the 8% biochar treatments were significantly lower than those from the control (0% biochar) for both soils. In the second and third events, the DRP losses were higher from the control and 2% biochar treatments than from the 5 and 8% biochar treatments of the HSTP. Also the fourth and fifth events of HSTP followed similar described trend of the DRP losses except that the losses from the 2 and 5% biochar treatments were not significantly different during these events. Nonetheless, in the last event the difference between treatments in the DRP losses was the opposite to that of the previous events. Here, the DRP losses increase with the increases of biochar, until the losses from 8% biochar became significantly higher than that from the control treatment. These differences were due to the variation between the treatments with respect to P sorption and desorption capacities during the whole leaching period. The 5 and 8% biochar treatments may have sorbed high P, released some part of it gradually over the time. However, the control and 2% biochar treatments sorbed less P, and simultaneously released it quicker compared to the other two treatments. Phosphorus leaching losses increased rapidly after the first leaching event as indicated by the high increase in the DRP concentration. The increase in P losses may have resulted from the increased solubility of P due to the reduction of $Fe^{3+}$ to $Fe^{2+}$ under saturated soil conditions (Zhang et al., 2010).

The changes in cumulative DRP with different biochar treatments agreed with the DRP lost during most of the individual leaching events. The result for the HSTP soil showed that biochar application at high rates (5 and 8%) caused significant reduction in both TP and DRP in comparison to that from the control treatment with average reduction of 26 and 33% for the two P forms, respectively. The high concentration of cations such as $Ca^{2+}$, $Mg^{2+}$ are important for P retention in the biochar-amended soil due to the binding to positively charged metal complexes formed on biochar surfaces (Novak et al., 2009a; DeLuca et al., 2015), or through precipitation with $Ca^{2+}$ (Ulén and Snäll, 2007) and $Mg^{2+}$ (Rahaman et al., 2008). Furthermore, it has been long known that the P precipitation with the divalent or trivalent ions is controlled by the pH of the soil solution (Morse et al., 1998; Reddy et al., 1980). Thus, the associated increase of soil pH in the biochar-amended soil encouraged P- Ca and Mg precipitation.

Phosphorus may be held much more tightly through Fe oxides than through $Ca^{2+}$ and $Mg^{2+}$ precipitation (Green et al., 1978). Therefore, the lowest concentration of $Al^{3+}$ and $Fe^{3+}$ in the leachate during the first event may confirm the retention of these elements with P in insoluble form (Table 3-3), resulting in a highly comparable quantity of P losses between the HSTP soil and the other LSTP soil. The increase of soil pH is linked with breakdown of the P bond with $Al^{3+}$ and $Fe^{3+}$, resulting in increased losses of P and the associated $Fe^{3+}$ and $Al^{3+}$ elements (Table 3-3). The influence of increased soil pH on a reduction in P adsorption on oxide mineral surfaces with pH-dependent charge, and on an increase in its movement in soil, was also reported by Kang et al. (2011). On the other hand, the high removal of $Ca^{2+}$ and $Mg^{2+}$ with leachate in the first event reduced their benefit in terms of holding much P through precipitation when the soil pH increased. Despite the fact of higher removal of $Ca^{2+}$ and $Mg^{2+}$ in the first leaching event, in comparison to the average removal from the sequential events (8- and 2-fold, respectively), there was significantly less removal of $Ca^{2+}$ and $Mg^{2+}$ from the 8% biochar treatment when compared to the other biochar treatments (Table 3-3). This fact, especially when combined with the noticeable increase in soil pH, could be responsible for the consistent lowest leaching losses of P from the 8% biochar treatment among all different biochar treatments (Table 3-4). Another possible reason for this result is that colloidal soil P may be flocculated due to elevated levels of $Ca^{2+}$, $Mg^{2+}$, and $K^{+}$ in the high biochar treatments (Parvage et al., 2013). Some of the soil colloids that are formed may be large and unable to pass through the 0.45 μm filter that is used to separate this form of P (Koopmans et al., 2005). The result of that could be a low concentration of the measurement of DRP in the leachate from the 8% biochar treatment, whereby highest cations are added and retained. However, in our study, the influence of soil colloids on the accuracy of DRP measurement could be negligible as indicated by the obtained similar leaching losses pattern of the TP and DRP (Table 3-4), where the TP representing all P forms.

The percentages of recovered P in the leachates that were initially introduced with manure to the different treatments were evaluated using a mass balance analysis technique adopted from Laird et al. (2010a). A summary of these results is given in table 3-5. As expected, the manure added a substantial amount of AP to the soil and the added amount was about 8-fold higher than the average amount that was added with the biochar. Simultaneously, more P was added due to the increase in the biochar application rate. It has been reported that significant increases of soil-soluble P up to 253% with addition of 1% of wheat straw biochar have been reported (Parvage et al., 2013). In the current study, even with the addition of more P as the biochar application rate increased, the recovered P in the leachate as DRP decreased significantly (Table 3-5). This was consistent with the result obtained by Laird et al. (2010a) and Beck et al. (2011). However, the 8% biochar was the only treatment that significantly reduced the leachate losses of TP among the examined treatments (Table 3-5). This indicates that biochar is more effective in reducing the losses of the reactive form of P than the other P forms. In addition to the already discussed effects of biochar on leaching losses of DRP, the soil-water infiltration rate (IR) was also found to be influenced by biochar application. Our finding is consistent with the results from many recent studies (Ayodele et al., 2009; Novak et al., 2016b), where the IR was found to rise along with increases in biochar addition (Figure 3-5). However, the leaching losses of DRP showed opposite trend and decreased as biochar addition increased (Figure 3-4). Overall the IR for each individual treatment started with relatively high IR and dropped significantly over the leaching period, except for the control treatment which started with an initial low IR that remained constant during all leaching events. Movement and precipitation of small soil particles, particularly with the high IR in the biochar amended soil is expected to be responsible for the eventual reduction of IR. The explanation of the effect of biochar in increasing IR and the associated leaching loss of P is a bit more complex. Overall P movement in soil is controlled physically through water infiltration rate, and chemically through the sorption intensity of biochar. As shown in figure 3-5, both infiltration rate and P retention by biochar increased as the rate of biochar increased. In general, we can conclude that the reduction of DRP losses when biochar addition is increased, even with the associated increases of IR, can indicate a tight retention of DRP in the biochar material against leaching losses.

## 4. Conclusions

The efficiency of biochar on minimizing leachate removal of basic cations increase with the increasing of the valency of the cation; however, that efficiency decline with the increasing of the elemental concentration in the biochar material. The retention of divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ is essential for P retention in biochar-amended soil. Thus P losses generally decrease with increase of biochar application rate. That decreases perhaps due to a combination of reactions that include: 1) adsorption and precipitation by Ca, Mg-phosphates, which could be facilitated by the associated increase of soil pH due to biochar addition; 2) adsorption of $PO_4^{3-}$ by Fe and Al oxides and hydroxides. Soil infiltration rate increased significantly due to biochar addition. However, the increased soil infiltration rate appeared to have no or only minor influence on the biochar's capacity to retain P. The results obtained from the current column leaching study suggests a great potential for hardwood biochar as soil-amendment for minimizing the potential environmental pollution problems due to leaching of P to water bodies when it present at high concentrations in manured soil.

**Table 3-1**: Selected physical and chemical properties of used soils and biochar.

| Characteristic | LSTP soil | HSTP soil | Biochar |
|---|---|---|---|
| Surface area ($m^2$ $g^{-1}$) | nm | nm | 324.6 |
| Pore volume ($cm^3 g^{-1}$) | nm | nm | 0.02 |
| Pyrolysis temperature (°C ) | nm | nm | 500 - 550 |
| Ash content (%) | nm | nm | 37.74 |
| Sand (%) | 22 | nm | nm |
| Silt (%) | 44 | nm | nm |
| Clay (%) | 34 | nm | nm |
| Texture | Clay loam | nm | nm |
| Bulk density (g $cm^{-3}$) | 1.13 | 1.0 | nm |
| C (%) | 3.39±0.3 | 3.5±0.1 | 89.22 |
| N (%) | 0.36±0.06 | 0.31±0.02 | 0.20 |
| CEC (cmol $kg^{-1}$) | 34 | 36 | 18 |
| pH (w/v) | 7.07(1:1) | 7.37(1:1) | 9.96(1:2) |
| $EC_e$ (ds $m^{-1}$) | 1.8±0.05 | 2.4±0.1 | 0.27±0.01 |
| $Na^+$ (mg $kg^{-1}$) | 21±4 | 53±3 | 380± 60 |
| $Ca^{2+}$( mg $g^{-1}$) | 1.8±0.08 | 2.1±0.2 | 1.7±0.23 |
| $Mg^{2+}$( mg $g^{-1}$) | 0.28±0.02 | 0.32±0.01 | 0.18±0.01 |
| $K^+$ (mg $g^{-1}$) | 0.38±0.01 | 0.68±0.02 | 2.7±0.24 |
| Total P (g $kg^{-1}$) | 0.51±0.03 | 0.61±0.04 | nm |
| Available P(mg $kg^{-1}$) | 32±2 | 80±5 | nm |

Mean of some parameters expressed with standard error [± SE], n=3.

nm= not measured;CEC= cation exchange capacity; $EC_e$ = Electrical conductivity of the soil; P= Phosphorus; LSTP and HSTP= Low and high soil test phosphorus, respectively.

**Table 3-2**: Selected characteristics of manure used in the study.

| Properties | Mean | Standard deviation |
|---|---|---|
| Moisture content (%) | 65.3 | 1.9 |
| Dry matter content | 34.7 | 1.2 |
| Total P (g $kg^{-1}$) | 5.89 | 0.08 |
| DRP* in 200:1 extract (mg $L^{-1}$) | 3.94 | 0.02 |
| TDP in 200:1 extract (mg $L^{-1}$) | 4.07 | 0.1 |
| pH | 8.5 | 0.05 |

DRP* = Dissolved reactive phosphorus, TDP= Total dissolved phosphorus.

**Table 3-3**: Leachate composition of manured (HSTP) and unmanured (LSTP) soils with different biochar application rates during three selected leaching events in soil column experiment.

| Treatment$^z$ | Leaching time | pH | K$^+$ (mg L$^{-1}$) | Na$^+$ (mg L$^{-1}$) | Ca$^{2+}$ (mg L$^{-1}$) | Mg$^{2+}$ (mg L$^{-1}$) | Al$^{3+}$ (mg L$^{-1}$) | Fe$^{3+}$ (mg L$^{-1}$) | SO$_4^{2-}$ (mg L$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| HSTP-Bio 0% | Event 1* | 7.14±0.04 c$^y$ | 220±1 b | 114±6.5 a | 585±24 ab | 163±6.7 a | 0.14±0.03 a | ND | 156±23 a |
| HSTP-Bio 2% | | 7.20±0.1 c | 241±15 b | 124± 13 a | 626±48 a | 165±17 a | 0.03±0.001 b | ND | 127±30 a |
| HSTP-Bio 5% | | 7.5b±0.06 bc | 279±1 a | 134±5.4 a | 453±30 abc | 139±0.9 ab | 0.04±0.001 b | ND | 100±3.1 a |
| HSTP-Bio 8% | | 7.7±0.06 ab | 295±6 a | 138±7.8 a | 327±50 cd | 106±4.1 b | 0.04±0.01 b | ND | 99±4.7 a |
| LSTP-Bio 0% | | 7.3±0.1 bc | 69±0.9 d | 34±6.9 b | 385±4.6 bc | 97±2.4 bc | 0.02±0.01 b | ND | 85±1.4 a |
| LSTP-Bio 2% | | 7.4±0.07 bc | 81±3.3 cd | 43±13 b | 337±20 cd | 87±11 bc | 0.03±0.006 b | ND | 95±1.5 a |
| LSTP-Bio 5% | | 7.4b±0.03 bc | 110±1 c | 58±11 b | 354±27 cd | 92±8.4 bc | 0.02±0.01 b | ND | 92±17 a |
| LSTP-Bio 8% | | 8.0±0.1 a | 100±6.2 cd | 42± 2.1 b | 167±36 d | 45±15 c | 0.02±0.01 b | ND | 67±23 a |
| Prob>F | | **0.37** | **0.03** | **0.71** | **0.16** | **0.48** | **0.03** | | **0.37** |
| HSTP-Bio 0% | Event 3 | 7.8±0.09 a | 80 ±0.9 bc | 25±0.6 abc | 65±8.5 a | 14.1±1.5 a | 0.12±0.03 a | 0.30±0.03 a | 9.8±1.6 a |
| HSTP-Bio 2% | | 8.2±0.1 a | 103±8.4 ab | 30±1.7 a | 66±0.4 a | 15.2±1.4 a | 0.10±0.07 a | 0.1±0.01 a | 8.9±2.9 a |
| HSTP-Bio 5% | | 8.3±0.2 a | 119±2 a | 28±0.2 ab | 64±2.2 a | 15.1±0.1 ab | 0.08±0.02 a | 0.1±0.01 a | 8.2±2.6 a |
| HSTP-Bio 8% | | 8.4±0.2 a | 122±13 a | 24±1.8 abc | 54±5.7 a | 13.3±1.2 ab | 0.14±0.04 a | 0.05±0.01 a | 9.8±1.2 a |
| LSTP-Bio 0% | | 7.7±0.02 a | 25±5.3 d | 9.1±3.3 d | 58±11 a | 8.2±2.2 b | 0.12±0.04 a | 0.51±0.2 a | 8.9±3.4 a |
| LSTP-Bio 2% | | 7.9±0.1 a | 34±0.7 d | 11±2.4 d | 62±4.6 a | 8.5±0.1 ab | 0.08±0.02 a | 0.1±0.01 a | 11±2.4 a |
| LSTP-Bio 5% | | 8.2±0.1 a | 43±0.2 d | 14±1.9 cd | 51±3.8 a | 8.4±0.1 ab | 0.09±0.05 a | 0.1±0.01 a | 14±2.0 a |
| LSTP-Bio 8% | | 8.0±0.2 a | 60±7.3 cd | 17±3.0 bcd | 42±2.2 a | 9.3±1.1 ab | 0.07±0.06 a | 0.02±0.01 a | 17±3.0 a |
| Prob>F | | **0.82** | **0.48** | **0.11** | **0.87** | **0.66** | **0.51** | **0.86** | **0.37** |
| HSTP-Bio 0% | Event 6 | 8.1±0.05 a | 71±6.3 a | 10.2±0.9 a | 69±1.8 a | 21±1.1 a | 0.02±0.01 a | 0.12±0.02 a | 9.8±0.3 a |
| HSTP-Bio 2% | | 8.5±0.08 a | 76±1.0 a | 10.3±0.65 a | 59±3.1 ab | 13.8±0.2 b | 0.05±0.03 a | 0.07±0.01 a | 8.8±0.4 a |
| HSTP-Bio 5% | | 8.7±0.1 a | 70±0.4 a | 8.8±0.2 ab | 48±1.0 abc | 10b±0.1 cd | 0.05±0.001 a | 0.05±0.01 a | 8.5±0.6 a |
| HSTP-Bio 8% | | 8.8±0.2 a | 71±1.1 a | 7.9±1.0 ab | 40±2.5 bc | 8.6±0.5 cde | 0.09±0.01 a | 0.03±0.01 a | 8.4±0.6 a |
| LSTP-Bio 0% | | 8.0±0.04 a | 26±0.1 c | 4.9±1.1 b | 53±2.6 abc | 11.0±1.1 bc | 0.04±0.009 a | 0.11±0.01 a | 9.8±0.7 a |
| LSTP-Bio 2% | | 8.4±0.2 a | 32±2.2 bc | 6.5±1.4 ab | 52±5.9 abc | 8.3±1.3 cde | 0.05±0.02 a | 0.04±0.01 a | 8.2±0.6 a |
| LSTP-Bio 5% | | 8.7±0.2 a | 41±2.1 b | 7.5±0.3 ab | 44±5.0 bc | 5.98±0.4 de | 0.05±0.002 a | 0.06±0.01 a | 8.3±0.8 a |
| LSTP-Bio 8% | | 8.7±0.1 a | 45±0.5 b | 8.1±0.1 ab | 33±1.9 c | 5.03±0.2 e | 0.11±0.05 a | 0.05±0.01 a | 7.0±0.6 a |
| Prob>F | | **0.93** | **0.01** | **0.06** | **0.56** | **0.01** | **0.98** | **0.9** | **0.95** |

* Data from each leaching event was analysed spereately.

[y] Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test).

[z] HSTP = high soil phosphorus, LSTP= low soil phosphorus; Bio 0%, Bio 2%, Bio 5%, and Bio 8% denote biochar application rate based on weight.

**Table 3-4**: Phosphorus concentration in leachates from manured (HSTP) and unmanured (LSTP) soils with different biochar application rates during leaching events and cumulative leaching loss of P over the experimental period.

| Treatment[z] | Event 1[*] | | Event 2 | | Event 3 | | Event 4 | | Event 5 | | Event 6 | | Accumulative | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DRP | TP | DRP | TP | DRP | TP | DRP | TP | DRP | TP | DRP | TP | DRP | TP |
| | mg column$^{-1}$ | | | | | | | | | | | | | |
| HSTP-Bio 0% | 0.12a[y] | 0.58a | 0.82 a | 1.39 a | 1.06a | 1.71 a | 1.05 a | 1.78 a | 0.98 a | 1.45 a | 0.51 b | 0.83 bc | 4.52a | 7.78a |
| HSTP-Bio 2% | 0.07b | 0.43b | 0.71 a | 1.38 a | 0.84ab | 1.60 b | 0.78 b | 1.55 b | 0.81 ab | 1.49 a | 0.60ab | 0.72 c | 3.82b | 7.18b |
| HSTP-Bio 5% | 0.045bc | 0.28c | 0.57 b | 1.22 b | 0.71b | 1.44 c | 0.67 bc | 1.35 c | 0.70 b | 1.31 ab | 0.62ab | 1.22 a | 3.33c | 6.81b |
| HSTP-Bio 8% | 0.026 c | 0.17d | 0.40 c | 0.68 c | 0.55 b | 1.15 d | 0.59 c | 1.18 d | 0.72 b | 1.13 b | 0.66a | 1.01 ab | 2.99c | 5.34c |
| LSTP-Bio 0% | 0.07b | 0.18d | 0.10 d | 0.22 d | 0.15 c | 0.28 e | 0.17 d | 0.27 e | 0.19 c | 0.31 c | 0.23c | 0.31 d | 0.93d | 1.63d |
| LSTP-Bio 2% | 0.05bc | 0.11de | 0.09 d | 0.16 d | 0.12 c | 0.19ef | 0.12 d | 0.18 e | 0.12 c | 0.18 c | 0.13c | 0.16 d | 0.65d | 1.02e |
| LSTP-Bio 5% | 0.042bc | 0.06ef | 0.08 d | 0.14 d | 0.09 c | 0.15f | 0.11 d | 0.17 e | 0.11 c | 0.17 c | 0.10c | 0.14 d | 0.55d | 0.86e |
| LSTP-Bio 8% | 0.026c | 0.02 f | 0.09 d | 0.10 d | 0.10 c | 0.12 f | 0.15 d | 0.15 e | 0.16 c | 0.17 c | 0.16c | 0.17 d | 0.70d | 0.76e |
| Prob>F | **0.08** | **<0.01** | **<0.01** | **<0.01** | **0.01** | **<0.01** | **<0.02** | **<0.01** | **0.03** | **<0.03** | **<0.01** | **<0.01** | **<0.01** | **<0.01** |

[*] A separate analysis was done for each of the leaching events and also for total cumulated P.

[y] Mean values followed by the same letter within a column are not significantly different ($p<0.05$, Tukey's test).

[z] HSTP = high soil test phosphorus, LSTP= low soil test phosphorus, DRP= dissolved reactive phosphorus, TP= total phosphorus. Bio 0%, Bio 2%, Bio 5%, and Bio 8% denote biochar application rate based on weight

**Table 3-5**: Mass of cumulative P added with manure and biochar treatments to soil columns and recovered percentages in leachates.

| Mass of phosphorus added to the columns with the manure and biochar (mg column$^{-1}$) | | |
|---|---|---|
| Component | Available P | Total P |
| Manure (87g) | 83 | 105 |
| 2% Biochar (34 g) | 9 | 20 |
| 5% Biochar (85 g) | 11 | 40 |
| 8% Biochar (135 g) | 14 | 50 |
| Total mass of P leached during events 1–6 (mg column$^{-1}$) | | |
| Treatment[z] | | |
| HSTP-Bio 0% | 4.52±0.09 a[y] | 7.78±0.13 a |
| HSTP-Bio 2% | 3.82±0.16 b | 7.18±0.13 b |
| HSTP-Bio 5% | 3.33±0.09 c | 6.81±0.10 b |
| HSTP-Bio 8% | 2.99±0.15 c | 5.34±0.11 c |
| LSTP-Bio 0% | 0.93±0.03 d | 1.63±0.05 d |
| LSTP-Bio 2% | 0.65±0.02 d | 1.02±0.02 e |
| LSTP-Bio 5% | 0.55±0.02 d | 0.86±0.02 e |
| LSTP-Bio 8% | 0.70±0.01 d | 0.76±0.01 e |
| Prob>F | **<0.01** | **<0.01** |
| Percent of P added with the manure recovered in the leachate | | |
| Treatment | | |
| HSTP-Bio 0% | 4.326±0.15 a[y] | 5.82±0.17 a |
| HSTP-Bio 2% | 3.814±0.23 ab | 5.83±0.14 a |
| HSTP-Bio 5% | 3.355±0.12 bc | 5.63±0.11 a |
| HSTP-Bio 8% | 2.764±0.20 c | 4.33±0.09 b |
| Prob>F | **<0.02** | **0.01** |

The calculation methodology is detailed in Laird et al. (2010).

[y] Mean values followed by the same letter within a column are not significantly different ($p<0.05$, Tukey's test). [z] HSTP = high soil test phosphorus, LSTP= low soil test phosphorus, Bio 0%, Bio 2%, Bio 5%, and Bio 8%= % denote biochar application rate based on weight.

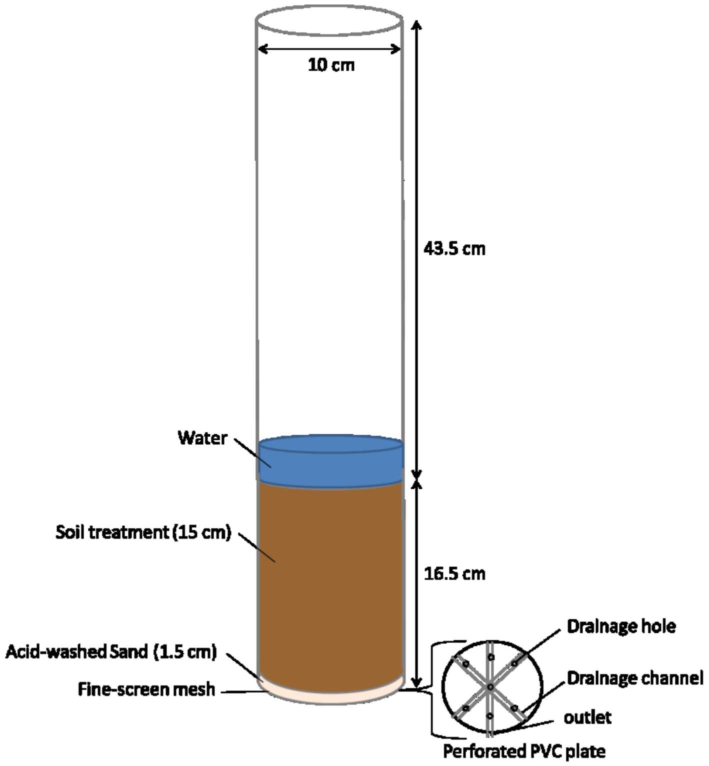

**Figure 3-1:** Soil column made from acrylic tube used in the leaching experiment.

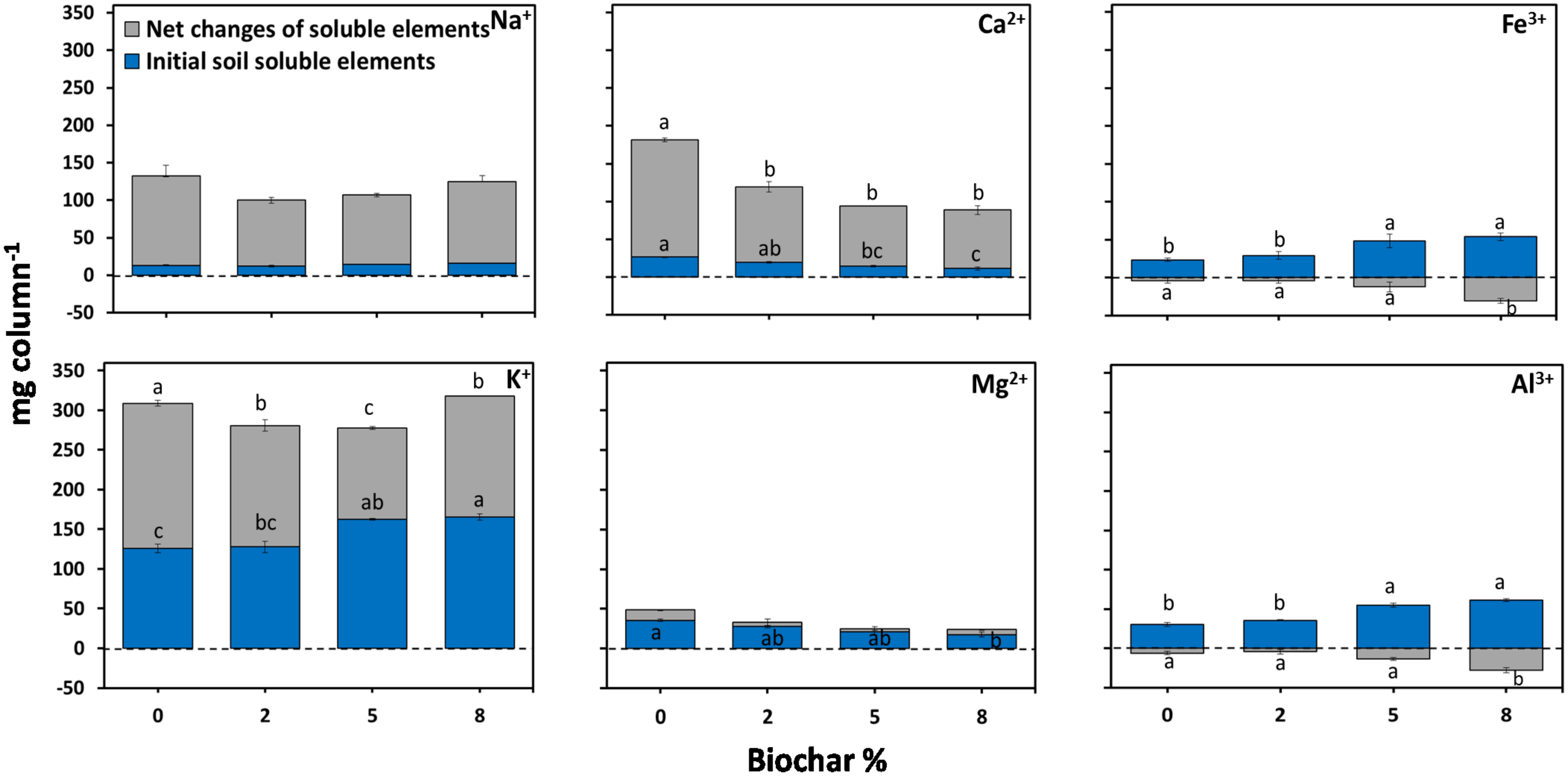

**Figure 3-2**: Concentration of initial and net changes of soluble elements in incubated soil due to soil, manure and biochar interaction. Blue bars represent soluble elements in un-manured soil; Gray bars represent net change of soluble elements after manure addition. Each bar illustrates the mean (n=3). Vertical error bars indicate standard error of the means (SEM).

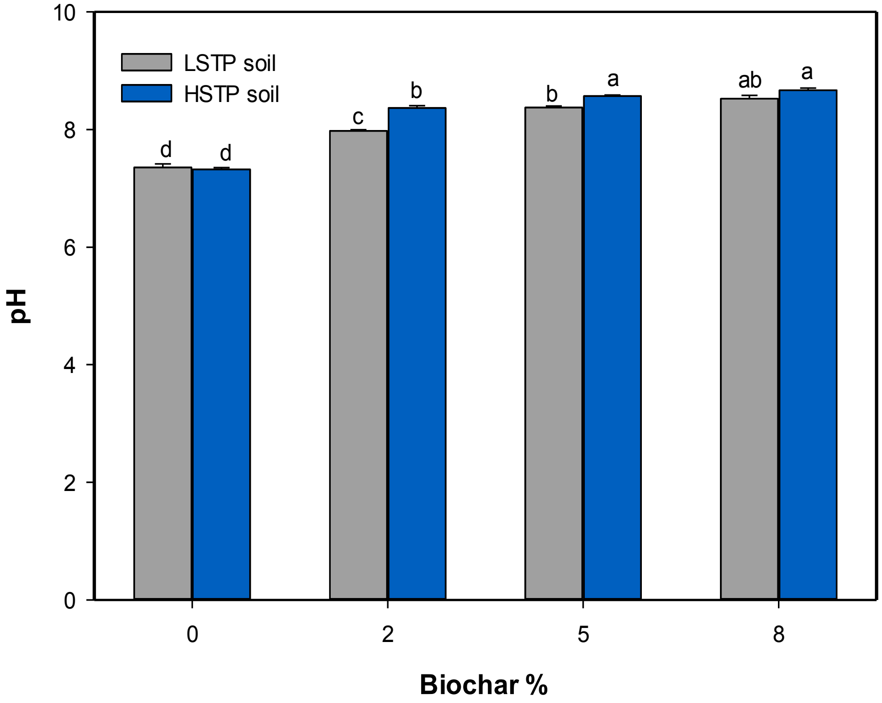

**Figure 3-3**: Effects of biochar application rate on soil pH at the end of the leaching experiment of manured (HSTP) and unmanured (LSTP) soils. HSTP = high soil test phosphorus, LSTP= low soil test phosphorus. Each bar illustrates the mean (n=3).Vertical error bars are standard error of the means (SEM).

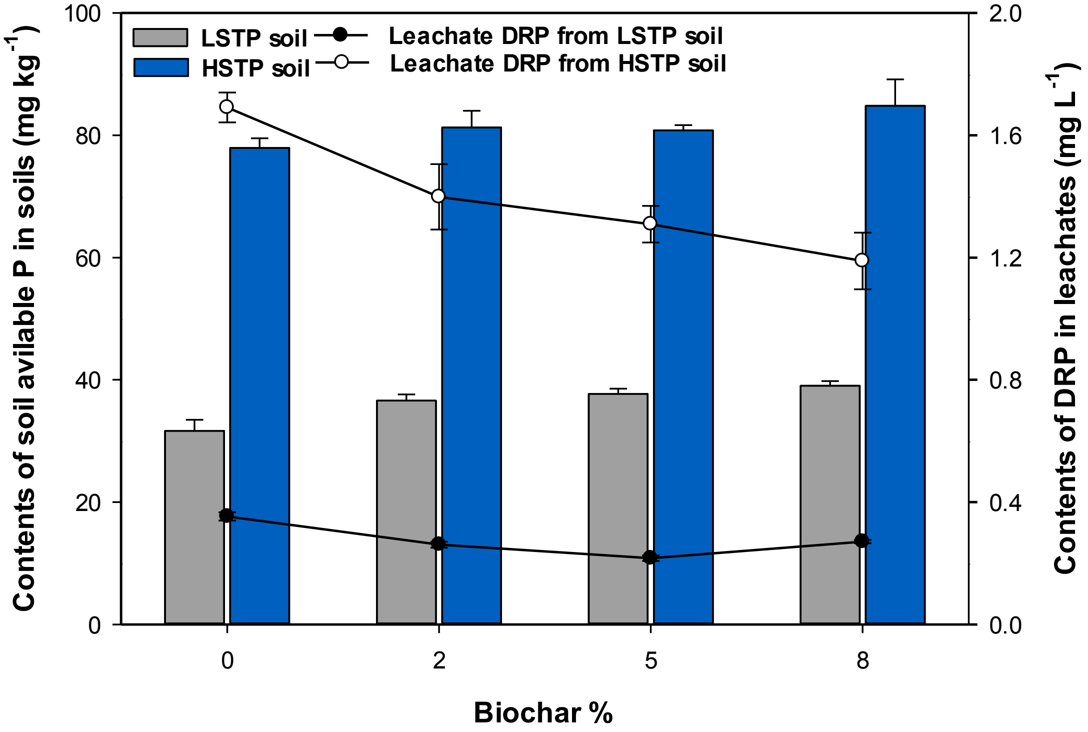

**Figure 3-4**: Comparison of soil P level (bars) of incubated soil and cumulative leachate loss of dissolved reactive P. Each bar illustrates the mean (n=3). Vertical error bars are standard error of the mean (SEM). HSTP = high soil test phosphorus, LSTP= low soil test phosphorus, DRP= dissolved reactive phosphorus.

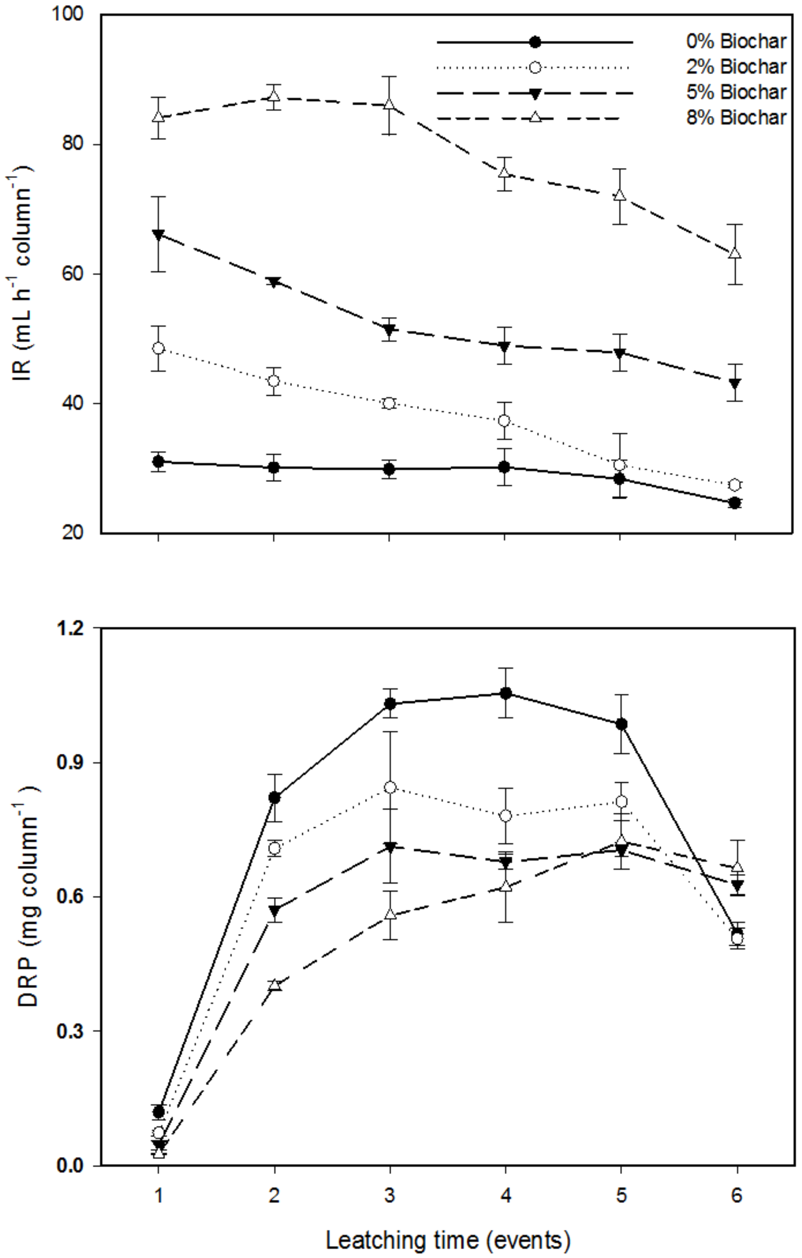

**Figure 3-5**: Changes in soil water infiltration rate and leached dissolved reactive P in different treatments during the six leaching events for manured (HSTP) soil. IR is infiltration rate, DRP is dissolved reactive phosphorus. Vertical error bars are standard error of the mean (n=3).

# CHAPTER 4. RECLAMATION OF A SALINE-SODIC SOIL WITH BIOCHAR: EFFECTS OF BIOCHAR APPLICATION RATE

## 1. Introduction

Soil salinity poses a serious threat to soil productivity in agricultural land (Lobell et al., 2007; Rengasamy, 2006; Wong et al., 2009). The salts are mainly carbonates, chlorides, sulfates, and bicarbonates of calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), and sodium ($Na^+$) (Manchanda and Garg, 2008). Salt-affected soils are estimated to occupy around 831 million hectares, representing more than 23% of the earth's land surface (NLWRA, 2001; Szabolcs, 1994; Martinez-Beltran and Manzur, 2005). Around 10% of salt-affected land is saline-sodic (NLWRA, 2001). High levels of exchangeable $Na^+$ in saline-sodic soils cause poor soil physical properties (Rengasamy and Olsson, 1991) such as low hydraulic conductivity and infiltration rate due to the breakdown of aggregate as a result of slaking, clay swelling and soil particle dispersion (Rengasamy and Sumner, 1998). The majority of saline soils are in semiarid and arid regions, where the rainfall is not sufficient for adequate leaching (Pathak and Rao, 1998). More than 80,000 hectares of irrigated lands and 2.5 million hectares of non-irrigated lands in Alberta, Saskatchewan, and Manitoba are classified as saline or saline-sodic lands. The major salts in these areas are sodium, magnesium, calcium and potassium sulfates, and with small amounts combined with chloride, bicarbonate, and carbonates (Sommerfeldt et al., 1988). Most of these soils contain sufficient precipitated gypsum and lime, therefore, soil reclamation can be achieved by drainage and leaching (Sommerfeldt et al., 1988).

Removal of the soluble salts from the rooting zone is required to restore productivity of saline soils. Leaching is the only feasible method for reducing soluble salts in the rooting zone. But the effectiveness of leaching for reducing salinity is highly dependent on the soil structure, which is usually poor or weak for most salt-affected soils with high exchangeable $Na^+$. Reclamation of saline-sodic soils involves replacing $Na^+$ in exchange sites by divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ (Gupta and Abrol, 1990). The replaced $Na^+$ has to be removed from the rooting zone by sufficient leaching in order to avoid re-sodification. Numerous studies have been conducted over decades for the use of chemical amendments such as gypsum ($CaSO_4 . 2H_2O$), as a source of $Ca^{2+}$, also the use of sulfur and sulfuric acid to react with calcium carbonate in soil and provide soluble $Ca^{2+}$ to replace $Na^+$ on the exchange sites of saline-sodic soils (Qadir et al., 2002; Ghafoor et al., 2001; Mace and Amrhein, 2001; Oster et al., 1996). Recently, phyto-remediation has examined and considered as an alternative technique to chemical amendments for reclamation of calcareous saline-sodic soils (Qadir et al., 2007; Qadir and Oster, 2004). This technique provides soluble calcium through influencing plants to change partial pressure of $CO_2$ in root zone for facilitating the remediation. Organic amendments such as dry sludge, farmyard manure, chicken manure (Rehman et al., 1996) and composts (Chaganti et al., 2015) have been studied for their effectiveness in improving soil properties such as soil structure, aggregate stability, hydraulic conductivity, and in turn on their effectiveness in saline- sodic soil reclamation.

Biochar, a carbon-rich, solid product from thermal decomposition of organic matter under a limited supply of oxygen at relatively low temperatures (<700 °C) (Lehmann, 2009), is well known as a source of divalent cations (Tsai et al., 2012; Laird et al., 2010b). For instance, Major et al. (2010) found that availability of $Ca^{2+}$ and $Mg^{2+}$in an Oxisol increased significantly after addition of biochar at a rate of 20 tones $ha^{-1}$. The availability of these cations in soils could help improve soil structure due to their role for replacing the exchangeable $Na^+$ for leaching. Furthermore, biochar application was found to improve soil physical properties such as reducing bulk density, and increasing porosity and aggregate stability (Herath et al., 2013; Ayodele et al., 2009; Laird et al., 2010b), which in turn facilitates water infiltration through the soil. In another study, Barzegar et al. (1997) observed that addition of pea straw to a saline-sodic soil significantly reduced clay dispersion regardless of SAR value of the soil resulting in the enhancement of soil structural stability.

Biochar application can improve crop production through enhancing soil chemical, physical and biological properties, with most research conducted on soils that are not affected by salt (Gaskin et al., 2008; Gaskin et al., 2010; Atkinson et al., 2010; Brockhoff et al., 2010; and Singh et al., 2010a). However, much less attention has been paid to the potential role of biochar for the reclamation of saline and sodic soils. Therefore, the objective of this study is to evaluate the effect of biochar addition to a saline-sodic soil for reducing soil exchangeable $Na^+$ and enhancing salt leaching. We hypothesize that 1) adding biochar to saline-sodic soils could enhance the releases of $Na^+$ due to the high concentration of divalent cations ($Ca^{2+}$ and $Mg^{2+}$) contained in the biochar that replace $Na^+$ on the exchange sites, and 2) biochar can improve soil's physical properties, such as water infiltration which in turn could lead to more salt being washed out with the percolation water.

## 2. Materials and Methods

### 2.1 Soil sampling and preparation

A saline-sodic soil and a non-saline soil were collected to a 0.1 m depth from a farm located in Holden, Beaver County, which is 100 km east of Edmonton in Alberta, Canada. Most soils in the sampling site are classified in Cernozemic and Slonetzic orders.

Plant residues and coarse fragments were removed from the soil samples before they were air-dried at room temperature (18-25 ºC). The soils were sieved twice through a 10 mm mesh to ensure the soil thoroughly mixed. Sub-samples were used to analyze the soil chemical and physical properties. Air dried samples were ground into fine powder using a ball mill (MM200, REtsch GmbH, Haan, Germany) and analyzed for total C and N concentrations. Soil texture analysis was conducted using the hydrometer method (Gavlak et al., 2003). This analysis indicated that both soils have a clay loam texture. The $EC_e$ measurements of the soils were evaluated on a saturated paste, following the method described in Richards (1954) using an AP75 portable waterproof conductivity/TDS meter (Thermo Fisher Scientific Inc., Waltham, MA, US) and soil pH was measured in a 1/1 soil weight to deionized water volume ratio using an Orion pH meter (Thermo Fisher Scientific Inc., Beverly, MA, US). Soluble cations were also analyzed in a 1/1 soil weight to deionized water volume ratio by inductively coupled plasma molecular absorption spectrophotometry (ICP-MS) using a Perkin Elmer ELAN 6000 spectrophotometer (PerkinElmer, Inc.MA). Soil cation exchange capacity (CEC) was estimated according to the $Na^+$ saturation method (Polemio and Rhoades, 1977). Extractable cations ($K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$) were measured by rinsing soils with excess of 1 M ammonium acetate solution buffered at pH 8.5 (Normandin et al., 1998). Exchangeable cations were then determined by subtracting soluble cations from total extractable cations following the method described in Chaganti et al. (2015). The properties of the saline soil (Table 4-1) showed that $EC_e$, and ESP values exceeded the maximum for crop production ($EC_e$ >4 ds $m^{-1}$, and ESP >15 %), indicating that the soil is saline-sodic, and sodium sulfate was the dominant salt in this soil.

### 2.2 Biochar production and properties

The hardwood biochar produced by Alberta Innovates - Technology Futures, Vegreville, Canada, by using an auger retort carbonizer (ABRI- Tech, 1 Tonne retort system, Alberta Biochar Initiative-AI-TF Vegreville). More details about the biochar production along with chemical and physical properties were presented in study done by Dugdug et al. (Submitted).

### 2.3 Soil treatments and incubation

The experimental design consisted of two soil types (saline-sodic and non-saline soils) and four rates of biochar treatments: control, no biochar (0%), and biochar application at rates of 2, 5 and 8% [w/w]. The experiment was set up in a completely randomized design with three replicates, resulting in a total of 24 soil columns. Soil infiltration for each treatment improved by mixing the soil with acid-washed sand at 20% [v/v] to facilitate the collection of leachates from control soils.

Soil columns were acrylic tubes with a diameter of 10 cm and a length of 15 cm (1178 $cm^3$ volume) and closed with perforated PVC plates in the bottom to allow the outflow of leachates. Three vertical channels were drilled through the perforated plate, and two holes were drilled into each channel plus one hole in the joint center. The design of the used soil column was descriped in detals in chapter 3.

Biochar were thoroughly mixed into the soil, and then the mixture was placed into the columns with repeated tapping, followed by gently pressing the soil material with a wooden pestle until the top of the soil columns sank no further. This procedure ensured a restored the bulk density to the range of the initial values in the field that ranged between 1.13 to 1.16 g $cm^{-3}$ for the two soils; it also prevented the formation of preferential flow pathways. The soils in the columns were pre-wetted with deionized water to bring the moisture content to 60% water holding capacity (WHC). The WHC of the treated soils was determined by the method described in chapter 3. All columns were then incubated for two weeks at room temperature (25 ±1 °C).

## 2.4 Leaching experiment

By the end of the incubation period, the columns were leached with deionized water equivalent to six times the soil pore volume (PV) in the packed columns. Leaching occurred every other day over a 12-day period. The PV of each soil column was calculated using the following equation (Kirkham, 2014):

$$PV = V_s \times Ø_s \qquad (1)$$

where ($V_s$) is volume of the soil in the column, and ($Ø_s$) is associated porosity. Porosity values were very close for the control and 2% biochar treated soil columns; therefore, they had a mean initial PV of 500 $cm^3$. Similarly, the 5 and 8% biochar treatments had a mean initial PV of 650 $cm^3$ due to their close values of soil porosity. However due to waterlogging after third leaching event, the added water was not equal among all treatments. Full PV was added to the 5 and 8% biochar treatments; however, for other treatments, water was added based on the required volume to refill the treatments back and attain a full PV.

The leachate from each column was collected in polyethylene bottles and stored in a refrigerator until analysis. The leachates were analyzed for $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, and $SO_4^{3-}$ concentrations using an ICP as described above. Leachate EC was measured using an AP75 portable waterproof conductivity/TDS meter (Thermo Fisher Scientific Inc., Waltham, MA, US). After completion of the leaching phase, all columns were allowed to drain freely. Soils from the columns were carefully removed, air-dried, and crushed to pass through a 2 mm sieve. Some soil samples collected after incubation and before leaching were also air dried and sieved. These air dried soil samples were analyzed to determine their respective chemical properties, including ECe, pH, ESP, SAR, soluble and exchangeable cations ($Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$), and CEC using the same methods and equipment described above.

## 2.5 Data analysis

Data on leachate EC, infiltration volume as well as leachate losses of elements were analyzed separately for each leaching event using a two-way factorial analysis of variance (ANOVA). Exchangeable cations were also analyzed separately for initial and post leaching soils using a two-way ANOVA. Data on soil pH was analyzed using a two-way ANOVA. In order to get the effects of leaching and its interaction with other main factors, data on soil $EC_e$, ESP, as well as SAR were analyzed for initial and post leaching soils using a three-way ANOVA. All analyses were done using PROC MIXED model of Statistical Analysis System (SAS) software package (SAS 9.4). to test the degree of the significance of the biochar effect, soil effect and the interaction between these factors ($\alpha<0.05$), and to compare between initial and post leaching soils, leaching effect was included in the analyses that were involved in a three- way ANOVA. Residual was evaluated if ANOVA assumptions of normality and equal variance were fulfilled. Only data on leachate $EC_e$ of second and third events, soil $EC_e$, ESP, and SAR were non-normally distributed; therefore, log-transformation was applied to these data before further analysis; however, original data are presented. Significant differences between the treatment means were analyzed using Tukey's test at 95% significance level ($P < 0.05$). Two- and three-way analysis of variances was performed according to linear models (2) and (3), respectively:

$$Y_{ijk}=\mu+A_i+ B_j+ (AB)_{ij}+ \varepsilon_{ijk;} \qquad (2)$$

$$Y_{ijkl}=\mu+A_i+ B_j+ C_k+ (AB)_{ij}+ (AC)_{ik}+(BC)_{jk} +(ABC)_{ijk} + \varepsilon_{ijkl;} \qquad (3)$$

where $Y_{ijk}$ and $Y_{ijkl}$ are dependent variables, $\mu$ is the overall mean, $A_i$ and $B_j$ and $C_k$ are the effects of ith and jth and kth salinity level, biochar rate, and leaching, respectively, and εijk and $\varepsilon_{ijkl}$ are the random error terms within the experiment.

## 3. Results and Discussion

### 3.1 Effects of biochar on soil physical properties and salinity

### 3.1.1 Effects of biochar application on infiltration and percolation volume

The amount of leachates collected at the end of the first event from the 5 and 8% biochar treatment was significantly lower than that from the control and 2% biochar treatment (Figure 4-1). These results indicate the biochar's ability to increase the soil's water-holding capacity (Novak et al., 2009b; Chan et al., 2008a; Laird et al., 2010b; Brockhoff et al., 2010; and Thomas et al., 2013). In the second event, the amount of leachate from different biochar treatments was not significantly different ($p > 0.05$) which could be due to the stability in water movement in the treatments after saturated during the first event. There was no significant difference in the leachate volume between the 0 and 2%, and also between the 5 and 8% biochar treatments after the second event. However, the amount of leachates from 5 and 8% treatments was significantly higher than that from the control and 2% biochar treatments. Moreover, the leachates from the 5 and 8% biochar treatments were relatively stable during most events, but the leachate volume from the other two treatments was reduced considerably after the second leaching event (Figure 4-1). The observed low infiltration volumes from the 2 and 5% biochar treatments could be due to soil particle dispersion caused by high $Na^+$ concentration in these treatments. However, high $Ca^{2+}$ and $Mg^{2+}$ concentration in the biochar material helped reduce the levels of $Na^+$ from the saline-sodic soil in the 5 and 8% biochar treatments.

In general, biochar application had a positive effect on percolation during measured eight hours of leaching, and as a result, the water retention time decreased with an increasing biochar application rate (Figure 4-2). The water retention time was 4 to 6 hours and more than 24 hours for high (5 and 8%) and low (0 and 2%) biochar treatments, respectively. All treatments showed a decrease in percolation over a short period (hours), reflecting the reduction of water volume on the soil surface. The decrease of percolation for soil with 0 and 2% biochar treatments occurred gradually during each leaching event, but this decrease of percolation occurred rapidly when a comparison was made across sequential events. Because of this rapid decrease, the 0 and 2% biochar treatments reached the water-logged stage in the third leaching event, which markedly reduced percolation during the following leaching events. An opposite trend occurred in the 5 and 8% biochar treatments; the decrease was relatively stable and gradual during all leaching events, resulting in no soil waterlogging. These results suggest that biochar amendment has the ability to improve the water infiltration rate of the studied saline-sodic soil, which is normally prone to waterlogging due to its high $Na^+$ concentration. Generally, biochar application to soil is more efficient for improving soil aggregation and the associated water infiltration than for enhancing the soil's water-retention capacity (Ayodele et al., 2009; and Novak et al., 2016b). Our results agreed with Xiao et al. (2015), who found the influence of biochar on water infiltration to be dependent on soil type and the biochar application rate. They found that biochar addition to Aeolian and Loessial soil reduced water infiltration and increased water holding capacity when applied at a high rate (5%, w/w). This could be due to different soil texture. Thus, biochar could increase infiltration in fine-textured soils and decrease infiltration in course-textured soils (Tseng and Tseng, 2006).

### 3.1.2 Effects of biochar treatment on leaching and leachate EC

The majority of the salts were leached from both soil types in the first leaching event, and regardless of the biochar treatment, there was a significant difference in leachate EC between saline-sodic and non-saline soils, which reflected the initial salt content in each soil type (Table 4-2). Biochar treatments significantly affected leachate EC of the saline-sodic soil only; therefore, the discussion in this study will be focused mainly on this soil. In the first leaching event, the leachate EC of the saline-sodic soil has the following order: 0 > 2 >5 > 8% biochar, which is consistent with the net volume of water that infiltrated through these treatments (Figure 4-1 and Table A-1). In the second and third leaching events, the leachate EC of the 8% biochar treatment was significantly higher than that of other treatments. This trend also corresponded with the net volume of percolated water especially for the third leaching event, where the collected volume from the 5 and 8% biochar treatment was higher than that from other treatments (Figure 4-1). After the third leaching event, the saline-sodic soil became waterlogged, in which the volumes of leachate collected from the control and the 2% biochar treatment were 4 to 6 times lower than those collected from the other biochar treatments. At the waterlogging stage, the EC measurement may not accurately represent salt loss from treatments (0 and 2%) that were waterlogged due to the influence of the dilution factor, and, as a result, reducing further salt leaching in those treatments. The other two biochar treatments (5 and 8%) maintained the rate of leaching with a continuous decrease in EC until equilibrium was reached between the EC of the leachate and that of soil solution at the fifth and sixth events as indicated by consistency of leachate EC during these events.

Water retention time was longer in the control and 2% biochar treatment (> 24 hours) than in the 5 and 8% biochar treatment (4 to 8 hours). The differences in water retention time may also have influenced the amount of salt leached by the percolated water, that is, the longer the retention time, the more salt was dissolved and released. The higher porosity of the biochar amended soil in comparison to that of the control soil could have allowed water to move through faster. In other words, the improvement of soil permeability due to biochar application facilitated the movement of water through the soil by creating larger pores. Based on this improved permeability, we can conclude that the contact time between salts and percolating water was short for the biochar treatments. Therefore, fluid in the small pores cannot be easily replaced in comparison to that in the large pores, so there is no complete displacement of the effluent in small pores (Gharaibeh et al., 2011). These concepts could explain the trend observed in the first event, in which the mean leachate EC decreased with the increasing biochar application rate. This trend occurred because the salts came mainly from large pores under the influence of fast percolation, which made less contact with salts in the small pores. Our results agree with Sika and Hardie (2014) who found the leachate EC from a 10% biochar treatment was lower than that from the control at the beginning of leaching; however, the leachate ECs followed the opposite trend with time. In another study, Buecker et al. (2016) compared the leachate EC from soils treated with four biochar types that applied at 0, 1 and 3% (w/w); they found only wheat straw biochar amended soil leached a greater amount of salt in comparison to the other treatments.

### 3.2 Effects of biochar treatments on soil's chemical properties and salinity

In addition to the described effect of biochar on salt removal by altering the soils' physical properties, biochar could also influence salt removal by altering soils' chemical properties. The observed trend of releasing salt from biochar treatments (0 > 2 >5 > 8%) in this study was also reported by Thomas et al. (2013), who found that salt washed quickly through the control and low biochar treatment (5 t $ha^{-1}$), but it washed slowly and gradually through the high biochar treatment (50 t $ha^{-1}$). This result was attributed to biochar's high initial sorption of salt with gradual desorption over time, but the high ionic concentration in the control or low biochar treatments forced quick and large releases of salt. Our results contrast with Chaganti et al. (2015), who found that the amount of salt leaching from organic amended soils, including biochar, was higher than that from the control soil. These differences can likely be attributed to the chemical quality of the supplied water as Chaganti et al. (2015) used reclaimed water with moderate SAR. This reclaimed water may not have been as effective as deionized water in dissolving and, hence, replacing the existing $Na^+$ and other salt ions in the soil.

### 3.2.1 Soil pH

Biochar addition at 5 and 8% increased soil pH of post-leaching soils more than the 2% treatment, with no difference between the two high rates (Figure 4-3). The biochar pH was around two units higher (data not shown) than the soil (Table 4-1). Our results agree with the results obtained by Chan et al. (2008a) and Laird et al. (2010b); however, they contrast with Chaganti et al. (2015), who reported a decrease in soil pH upon biochar addition to a saline-sodic soil. They assumed leaching of $Na^+$ salt from biochar-amended soils contributed to the reduction of soil pH. Also, Wu et al. (2014) found that the addition of furfural biochar into saline soil caused the reduction of soil pH. They attributed that reduction to the acidification from the biochar used, which had a much lower pH relative to that of the soil; the pH of their biochar and soil were 4.5 and 8.3, respectively.

### 3.2.2 Soil $EC_e$

All biochar treatments of both soil achieved significant reductions in soil $EC_e$ after leaching due to the effective salt removal in the examined leaching events (Figure 4-4A). However, the release of salt was relatively higher from saline-sodic soil than that from non-saline soil that caused the EC of the former soil to be within the average value for the non-saline soil. The post-leaching soil $EC_e$ of saline-sodic soils with 5 and 8% biochar treatments was significantly lower than that of the control and 2% biochar treatments. After 6 leaching events, the $EC_e$ values of these two treatments (5 and 8%) became even lower than those of the non-saline soil with the same biochar application rate. The decreased $EC_e$ in the high biochar treatment (5 and 8%) was due to facilitated leaching of ions through the soil as a result of the great improvements in the soil's physical properties made by biochar. Similar reductions of soil $EC_e$ upon biochar addition to saline-sodic soils were reported by Chaganti et al. (2015). Correspondingly, Rehman et al. (1996) obtained a substantially decreased $EC_e$ of saline-sodic soils treated with various organic amendments including dry sludge, farmyard and chicken manure.

### 3.2.3 Soil ESP and SAR

As a result of the low initial $Na^+$ concentration in non-saline soil, no changes occurred to the ESP of this soil type due to biochar addition and soil leaching. On the contrary, biochar addition and leaching held a significant influence on the ESP of saline-sodic soil (Figure 4-4B). Post-leaching soil with 2, 5 and 8% biochar treatments showed a significantly lower ESP in comparison to the control, but the 8% biochar treatment was also significantly lower than the 2 and the 5% biochar treatments regarding the ESP value. After 6 leaching events, the ESP values were 9, 4, 2, and 1.5 for the 0, 2, 5, and 8% biochar treatments, respectively. The adsorption of divalent cations at the exchange site is preferred over monovalent cations (Phongikaroon et al., 2006), and it is well known that biochar is an important source of these cations in biochar-amended soils (Tsai et al., 2012; Laird et al., 2010b). Therefore, the reduction of soil ESP in the high biochar treatment was expected as a result of the biochar's replacement of $Na^+$ on the exchange site by $Ca^{2+}$ and $Mg^{2+}$. Similar results were reported by other studies that compared the influence of gypsum and other organic amendment applications including biochar on the ESP value of saline-sodic soils (Chaganti et al., 2015; Gharaibeh et al., 2011; Jalali and Ranjbar, 2009; Tejada et al., 2009).

Leaching caused no changes to the SAR of the non-saline soil, but biochar addition at a rate of 8% caused significant increases of SAR in comparison to the control treatment (Figure 4-4 C). The sodium concentration of biochar is notably higher than that of the original soil; the concentrations were 0.38 and 0.034 mg $g^{-1}$ for biochar (not presented) and soil (Table 4-1), respectively. Therefore, the application of biochar at a high rate could be the main reason for the increases of the SAR in the soil with low initial $Na^+$ concentration. The situation differed completely for the saline-sodic soil, in which the biochar $Na^+$ concentration is negligible relative to that in the soil. Overall, the heavy removal of $Na^+$ through leaching from saline-sodic soil caused significant reductions in the SAR for all treatments in comparison to their initial values; the reduction reached an average of 95% for all treatments. In contrast, biochar addition at high rate (5 and 8%) caused a significant reduction in the SAR for post-leaching saline-sodic soils relative to the control and 2% biochar treatments. The release of $Ca^{2+}$ and $Mg^{2+}$ from biochar into the soil solution helped offsite and replace $Na^+$ on exchange sites of the saline-sodic soil. The reduction of SAR after leaching due to biochar addition to saline-sodic soil was also reported by Chaganti et al. (2015). Also, significant reduction observed in the SAR after leaching when soil was treated with organic amendments (Shaaban et al., 2013; Tazeh et al., 2013). This reduction attributed to either an increase in $Ca^{2+}$ and $Mg^{2+}$ or a decrease in $Na^+$ (Paraguarí and Simpson, 2012).

### 3.2.4 Effects of biochar treatments on exchangeable cations

Initial soil analysis showed that no changes occurred in the exchangeable $Na^+$ and $Mg^{2+}$ cations of both soil types after the biochar application during incubation time. Furthermore, the interaction between soil type and biochar was significant only for the $Mg^{2+}$ and $Na^+$ of the post-leaching soils (Table 4-3). In the post-leaching saline-sodic soil, the exchangeable $Na^+$ was the only cation that decreased in concentration as the biochar application rate increased (Table 4-3). Thus, the exchangeable $Na^+$ concentration of the control treatment was significantly higher than the other biochar treatments. Relative to the initial measurements, the average decrease in exchangeable $Na^+$ after leaching were 60, 79, 88, and 90% for the control, 2, 5, and 8% biochar treatments, respectively. Van de Graaff and Patterson (2001) reported that $Na^+$ could be easily replaced by divalent cations because $Na^+$ was less effective in neutralising the negative charge at the soil exchange site. Therefore, the decreased $Na^+$ concentration with a high biochar application could be attributed to the release of divalent cations from the biochar, which displaced the $Na^+$ from the exchange sites in the soil.

The concentration of exchangeable $K^+$ in soils increased significantly after application of biochar. However, no significant differences between the 5% and the 8% biochar treatments were observed (Table A-3). This could be attributed to the higher $K^+$ concentration in the biochar material compared with the concentration in the soil. When the concentration in post-leaching soil compared with the initial measurements, the exchangeable $K^+$ concentrations decreased, as was observed for the $Mg^{2+}$ concentrations. The average decreases were 2.6, 10, 12.5, and 18% for the control, 2, 5, and 8% biochar treatments, respectively. Walker and Bernal (2008) found that $K^+$ competed strongly with $Na^+$ at the exchange site of the sodic soil. Therefore, the increase in exchangeable $K^+$ concentration with the increases in biochar application to post-leaching soil could partially help replace $Na^+$ from the soil's exchange site.

The exchangeable $Ca^{2+}$ concentration found to increase with the increase of biochar addition (Table A-3). There were also relative increases observed in the $Ca^{2+}$ concentrations in the post-leaching saline-sodic soil compared with the initial values before leaching; the average increases were 1.5, 1, 2, and 5.7% for the control, 2, 5, and 8% biochar treatments, respectively. The increase in exchangeable $Ca^{2+}$ concentration after biochar application and after leaching was likely due to the replacement of $Na^+$ in the soil exchange sites, which resulted in an important release of $Na^+$ with the percolation of water especially with the enhancement in the soil structure of biochar- amended soils (Chaganti et al., 2015). This result confirmed that biochar was an important source of $Ca^{2+}$ in biochar-amended soils.

Exchangeable $Mg^{2+}$ concentration in post-leaching of saline-sodic soil was significantly lower for the control treatment in comparison with the biochar treatments, although the concentrations were not significantly different between the biochar treatments themselves (Table 4-3). The average concentration of $Mg^{2+}$ in post-leaching soil of control treatment was 27% lower than the concentrations in the other biochar treatments. However, the exchangeable $Mg^{2+}$ concentration in post-leaching soil decreased compared to the initial measurements before leaching; the average decreases were 38, 27, 25, and 20% for the control, 2, 5, and 8% biochar treatments, respectively. Similar results were found by Chaganti et al. (2015) who compared the changes in exchangeable cations upon treating saline-sodic soil with organic amendments, including biochar. Jalali and Ranjbar (2009) attributed the decrease in exchangeable $Mg^{2+}$ to the increase in $Ca^{2+}$, which was favored more at the soil exchange sites. Our results confirmed that the percentage decrease in $Mg^{2+}$ was found to be consistent with the percentage increase in $Ca^{2+}$.

### 3.3 Effect of biochar treatments on leachate losses of soil cations

In the most of the three selected leaching events, there were no significant differences between the different biochar treatments on the leached cations from the non-saline soil (Figure 4-5). Therefore, the discussion focused mainly on the saline-sodic soil. As expected, the losses of saline cations during the studied events coincided with the EC of the leachates. In general, the average losses of these cations were extremely high in the first leaching event relative to the losses of cations during the following sequential events. Furthermore, $Na^+$ was the dominant cation in the leachate, followed by $Mg^{2+}$, $Ca^{2+}$, and $K^+$, respectively.

The average leachate loss of $Na^+$ from all treatments in the first event was up to 15 times higher relative to the average losses of the other measured cations. Therefore, the EC values of the leachate were likely controlled by the concentration of the $Na^+$ in the leachates, especially in the first event. In the first event, the biochar treatments leached significantly different amounts of $Na^+$ in the order $0 > 2 > 5 > 8$% of biochar treatments (Figure 4-5). This result could be related to the variation in the outcome of leachate volume and water retention time, as was previously discussed. In the third event, the biochar treatment of 8% leached significantly higher amounts of Na than did the other treatments. This result could be due to the accumulative effect from the first event in which the loss of $Na^+$ from the 8% biochar treatment was lower compared with the huge intensive releases from the control and the other biochar treatments. In the sixth event, the 5 and 8% biochar treatments leached significantly higher amounts of $Na^+$ than did the control and the 2% biochar treatments. Although the accumulative effect could be partially responsible for this result, the main reason for the results could be the waterlogged stage that occurred for the control and the 2% biochar treatment after the third event and continued until the end of the experiment. There were not many differences in the leachate losses of $Mg^{2+}$ during the studied events, except for some minor variation in the degrees of significance between treatments, these variations were not vital for generating a new concept. Similar results were reported by Akhtar et al. (2015a) who found that the addition of biochar had no effect on the $Na^+$ concentration in non-saline soils. However, the $Na^+$ concentration was significantly reduced in the biochar-amended saline soil because higher levels of $Na^+$ were adsorbed by the biochar relative to the levels adsorbed by the control.

The leachate loss of $K^+$ was significantly higher with the 5 and 8% biochar treatments compared with the 0 and 2% biochar treatments (Figure 4-5). The chemical composition of biochar (Dugdug et al., submitted) revealed that the biochar concentration of $K^+$ is up to 90% higher than the other measured elements. Therefore, the soluble $K^+$ could be released mainly from the biochar material in the 5 and 8% biochar treatments, reflecting the equilibrium roles in balancing soluble and exchangeable elements in the biochar-amended soil. In the third and sixth events, no significant difference in the leachate loss of $K^+$ was observed between treatments.

## 4. Conclusions

Hardwood biochar application at high rate (5 and 8%) was vital for improving the physical properties of the soils, including water infiltration. However, these physical improvements had a negative impact on salt removal by 1) reducing the contact between the soil, water, and salt, and 2) reducing the water retention time. Both factors reduced the amount of salt that dissolved and was released from the saline-sodic soil. The majority of the salt was released in the first leaching event and even with the decreased salt losses that found as the percentage of biochar application increased in this event, the $EC_e$, ESP, and SAR of saline-sodic soil treated with high rate of biochar application (5 and 8%) were lower than those of the control treatment and in some cases even lower than the values in the non-saline soil. We conclude that biochar plays an important chemical role in reducing salt by adsorbing $Na^+$ from the soil and/or by adding divalent cations ($Ca^{2+}$ and $Mg^{2+}$), that help replace and release $Na^+$ from the soil exchange site. The results obtained from this study suggest great benefits of biochar for saline-sodic remediation. The maintained infiltration rate due to the biochar treatments particularly could help with the continuous release of salts and prevent re-salinization and re-sodification of this type of soil in the long term.

**Table 4-1**: Physical and chemical properties of the two soils

| Soil characteristics | Saline-sodic soil | Non-saline soil |
|---|---|---|
| Sand (%) | 23±0.4 | 22±0.1 |
| Silt (%) | 39±0.1 | 44±0.3 |
| Clay (%) | 38±0.2 | 34±0.1 |
| Texture | Clay loam | Clay loam |
| Bulk density (g $cm^{-3}$) | 1.15±0.07 | 1.13±0.1 |
| TC (%) | 2.56±0.03 | 3.39±0.54 |
| TN (%) | 0.26±0.09 | 0.36±0.02 |
| CEC (cmol $kg^{-1}$) | 30±2.0 | 34±2.5 |
| pH | 7.18±0.01 | 7.07±0.5 |
| $EC_e$ (ds $m^{-1}$) | 28±0.2 | 1.8±0.05 |
| ESP | 18.5±1.5 | 1.06±0.02 |
| Soluble $Na^+$ (mmol $L^{-1}$) | 41.4±0.6 | 0.3±0.02 |
| Soluble $Ca^{2+}$( mmol $L^{-1}$) | 2.66±0.01 | 0.39±0.01 |
| Soluble $Mg^{2+}$( mmol $L^{-1}$) | 6.42±0.6 | 0.17±0.01 |
| $SO_4$-S (mmol $L^{-1}$) | 7.9±0.92 | 0.09±0.03 |
| $HCO_3$(mmol $L^{-1}$) | 1.79±0.20 | 1.34±0.16 |

Values are means and standard errors (± SE, n=3).

**Table 4-2**: Mean leachate EC$_e$ for non-saline and saline-sodic soils with different biochar application rate during six leaching events in a soil column leaching experiment.

| Treatment $^z$ | 1st event$^*$ | 2nd event | 3rd event | 4th event | 5th event | 6th event | Mean |
|---|---|---|---|---|---|---|---|
| | | | | ds m$^{-1}$ | | | |
| N-0% Bio | 3.6±0.07 e$^y$ | 0.53±0.01 d | 0.37±0.03 c | 0.40±0.04 | 0.42±0.01 c | 0.42±0.01 c | 0.80±0.01 e |
| N-2% Bio | 2.6±0.03 e | 0.57±0.01 d | 0.44±0.01 c | 0.41±0.03 | 0.42±0.02 c | 0.43±0.03 c | 0.80±0.01 e |
| N-5% Bio | 2.6±0.10 e | 0.64±0.01 d | 0.46±0.01 c | 0.39±0.01 | 0.37±0.01 c | 0.36±0.01 cd | 0.81±0.01 e |
| N-8% Bio | 1.9±0.13 e | 0.68±0.05 d | 0.52±0.04 c | 0.42±0.02 | 0.37±0.02 c | 0.33±0.01 d | 0.69±0.01 e |
| S-0% Bio | 63±0.31 a | 6.1±0.29 b | 0.80±0.03 b | 0.58±0.01 | 0.73±0.01 a | 0.73±0.02 a | 12.2±0.12 a |
| S-2% Bio | 61±0.23 b | 5.2±0.18 c | 0.81±0.01 b | 0.55±0.01 | 0.51±0.01 b | 0.57±0.02 b | 11.4±0.06 b |
| S-5% Bio | 55±0.18 c | 6.1±0.14 b | 0.87±0.01 b | 0.49±0.01 | 0.37±0.01 c | 0.32±0.01 d | 10.6±0.03 c |
| S-8% Bio | 51±0.47 d | 7.1±0.13 a | 1.28±0.06 a | 0.54±0.01 | 0.39±0.01 c | 0.31±0.01 d | 10.1±0.11 d |
| Prob>F | **<0.01** | **<0.04** | **<0.07** | **0.25** | **<0.01** | **<0.01** | **<0.01** |

[*] A separate analysis was done for each event and also for the mean across six events.

[y] Mean values followed by the same letter within a column are not significantly different ($p<0.05$). [z] N = non-saline soil; S= saline-sodic soil; 0% Bio, 2% Bio, 5% Bio and 8% Bio denote biochar application rate based on weight.

**Table 4-3**: Soil exchangeable cations of non-saline and saline-sodic soils before and after leaching.

| Treatment$^z$ | $Na^+$ | | $Ca^{2+}$ | | $Mg^{2+}$ | | K+ | |
|---|---|---|---|---|---|---|---|---|
| | | | | cmol $kg^{-1}$ | | | | |
| | Initial | Post leaching | Initial | Post leaching | Initial | Post leaching | Initial | Post leaching |
| N- 0% Bio | 0.4±0.02 $^y$ | 0.25±0.02 d | 27.7±0.5 | 26.4±0.5 | 4.9±1.6 | 5.6±0.03 b | 1.8±0.4 | 2.1±0.02 |
| N-2% Bio | 0.4±0.01 | 0.30±0.01 d | 29.7±0.4 | 27.1±0.8 | 6.3±0.02 | 5.9±0.06 b | 2.4±0.1 | 2.5±0.04 |
| N-5% Bio | 0.5±0.01 | 0.25±0.02 d | 29.9±0.1 | 27.5±0.9 | 6.3±0.01 | 6.0±0.1 b | 2.8±0.3 | 2.8±0.09 |
| N-8% Bio | 0.5±0.01 | 0.25±0.01 d | 28.7±0.9 | 27.7±0.6 | 6.5±0.06 | 5.9±0.02 b | 3.5±0.04 | 3.0±0.2 |
| S-0% Bio | 5.5±0.3 | 2.2±0.1 a | 11.1±0.2 | 12.9±0.4 | 11.9±2.0 | 7.4±0.4 b | 1.2±0.01 | 0.9±0.06 |
| S-2% Bio | 6.4±0.5 | 1.3±0.1 b | 12.9±0.4 | 15.8±0.1 | 13.4±1.9 | 9.8±0.7 a | 1.6±0.08 | 1.2±0.02 |
| S-5% Bio | 7.5±0.3 | 0.85±0.2 bc | 13.1±0.6 | 16.1±0.2 | 13.8±1.7 | 10.4±0.6 a | 2.1±0.1 | 1.4±0.09 |
| S-8% Bio | 8.2±1.3 | 0.8±0.1 c | 13.2±0.6 | 16.5±0.1 | 13.0±1.9 | 10.4±0.2 a | 2.2±0.1 | 1.7±0.03 |
| Prob>F | **0.17** | **<0.01** | **0.61** | **0.17** | **0.98** | **0.02** | **0.28** | **0.56** |

$^y$Mean (± SE, n=3) followed by the same letters within a column indicate no significant differences among treatments ($p<0.05$). $^z$N = non-saline soil; S= saline-sodic soil; 0% Bio, 2% Bio, 5% Bio and 8% Bio denote biochar application rate based on weight.

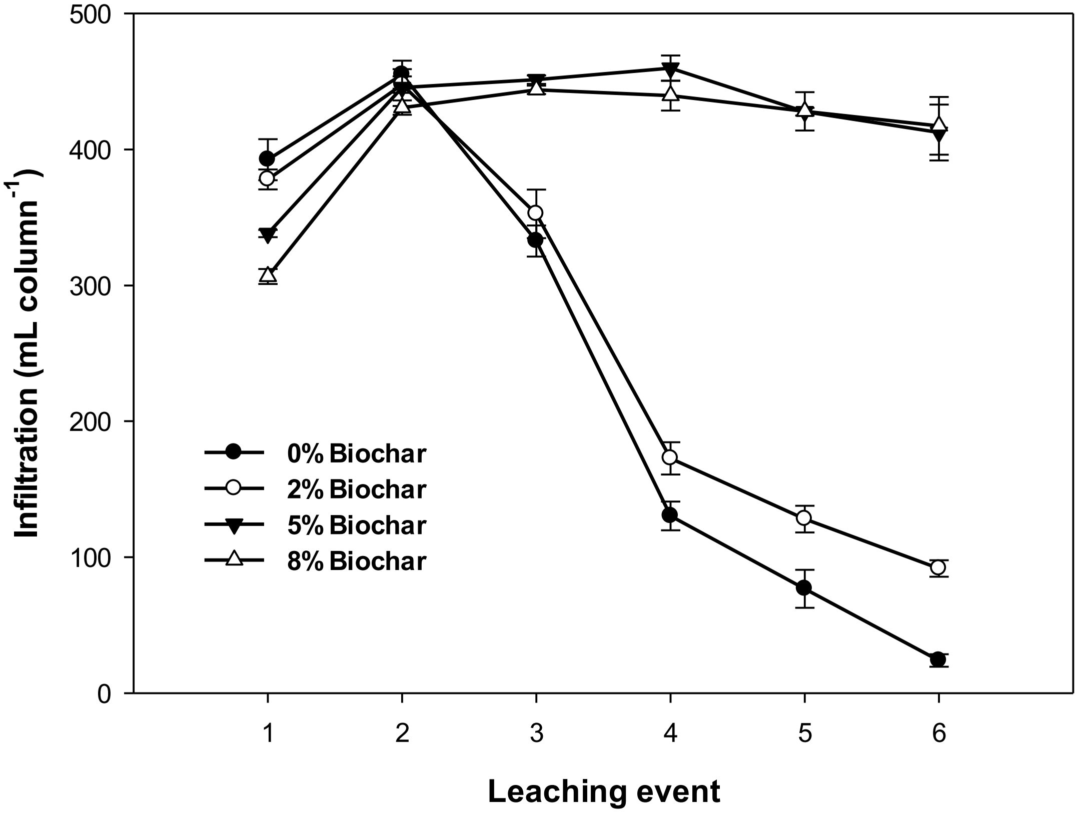

**Figure 4-1**: Effects of biochar application rate on volume of infiltration from saline-sodic soil during six events. Each line illustrates the mean (n=3).Vertical bars are SE of the means (SEM).

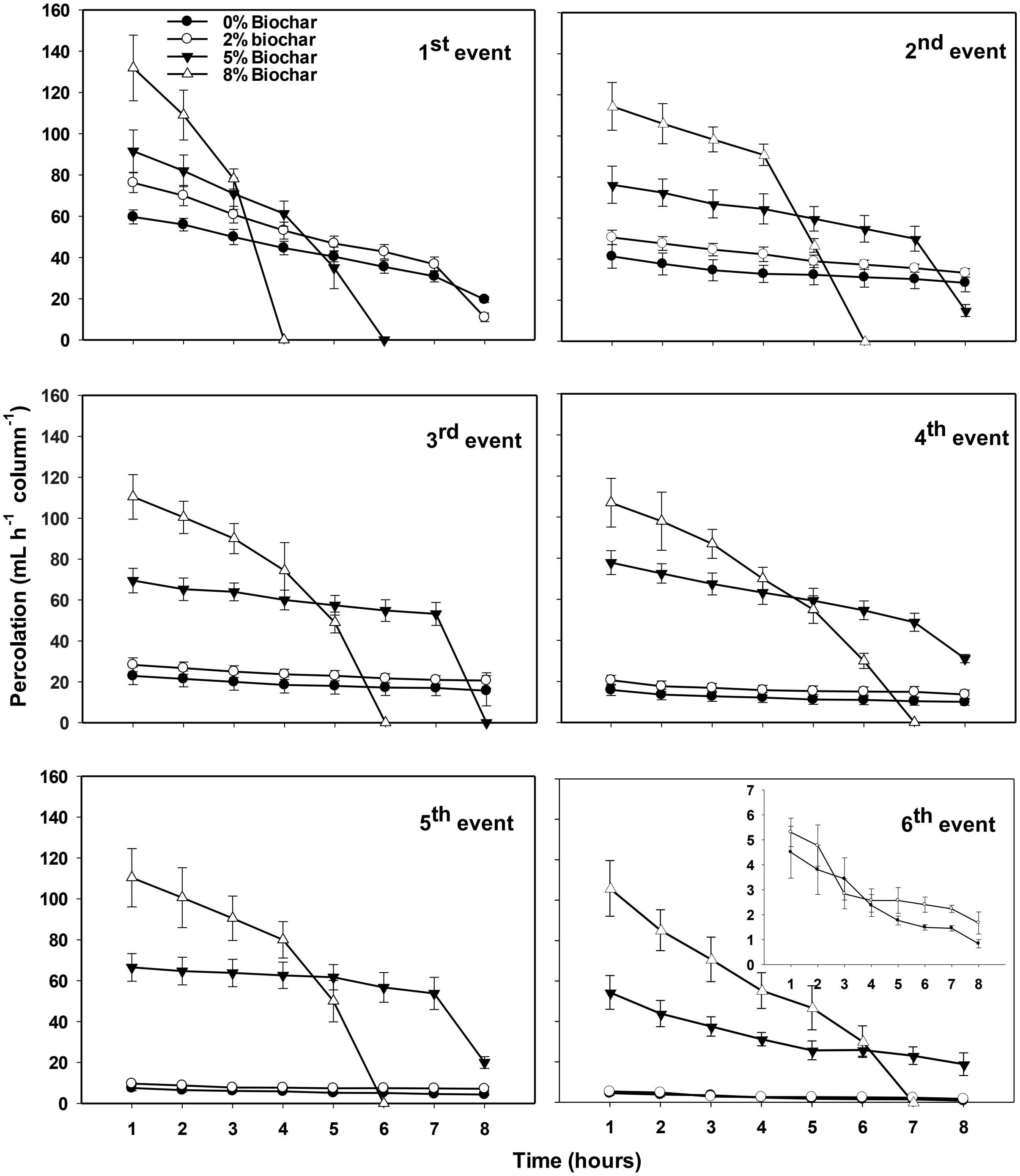

**Figure 4-2**: Effects of biochar application rate on changes of percolation with time during six leaching events of saline-sodic soil. Vertical bars are SE of the means (n=3).

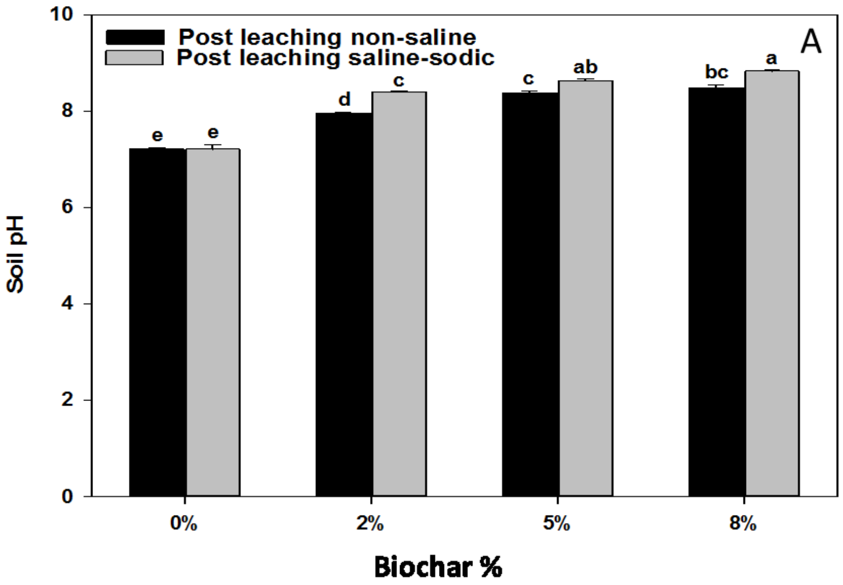

**Figure 4-3**: Soil pH of post leaching of non-saline and saline-sodic soils with different biochar treatments after leaching. Mean (± SE, n=3) followed by same letters indicate no significant differences among treatments ($p<0.05$).

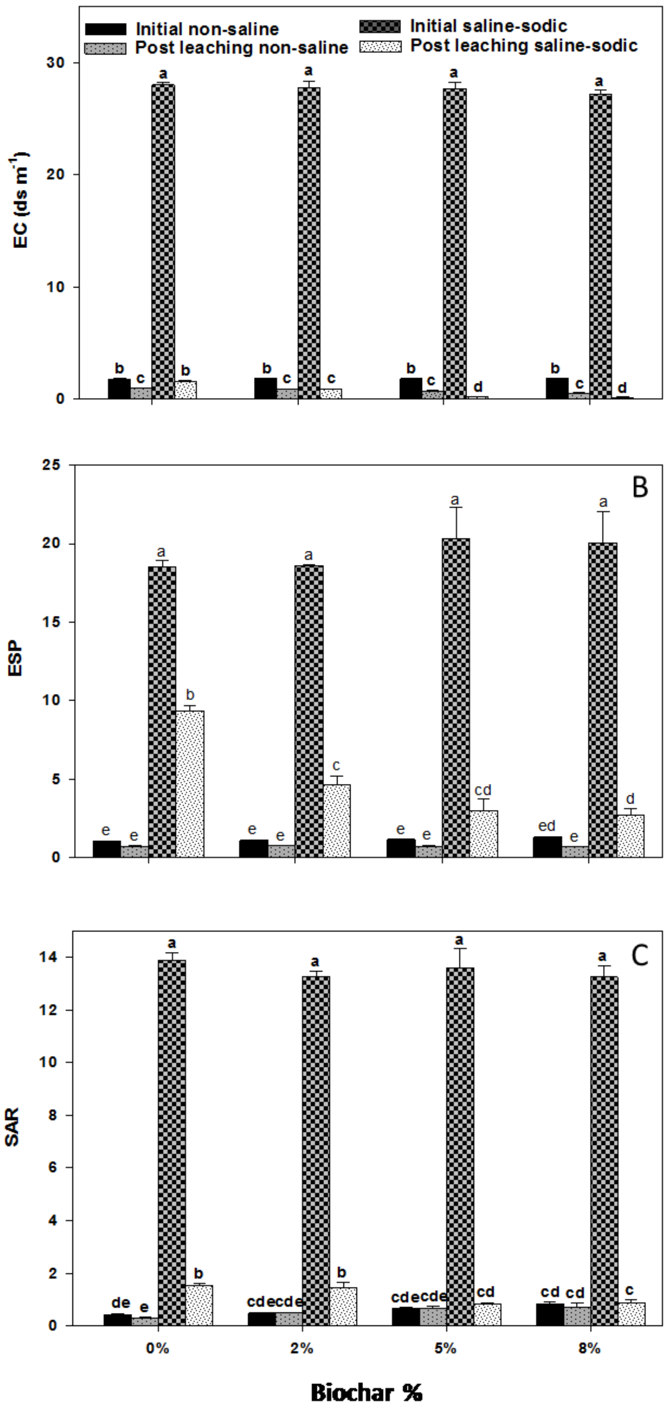

**Figure 4-4:** a) Electrical conductivity of saturated paste soil; b) Exchangeable sodium percentage; c) Sodium adsorption ratio of two soil types with different biochar treatment after leaching. Mean (± SE, n=3) followed by same letters indicate no significant differences among treatments ($p<0.05$).

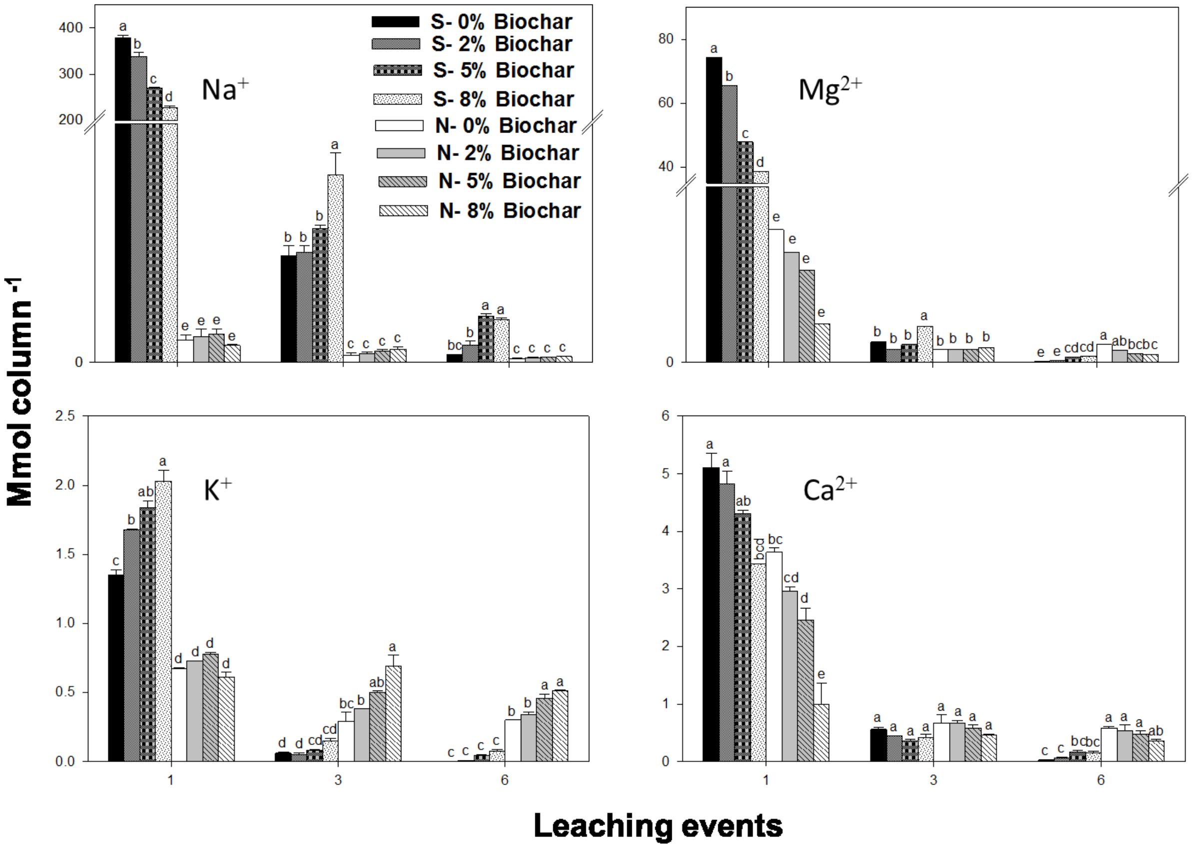

**Figure 4-5:** Leachate losses of cations from two soil types with different treatments during selected three events. Mean (± SE, n=3) followed by same letters indicate no significant differences among treatments ($p<0.05$). Codes: N = Non-saline soil; S= Saline-sodic soil.

# CHAPTER 5. BIOCHAR APPLICATION IMPROVED SOIL QUALITY AND SPRING WHEAT GROWTH IN MANURE AMENDED SALINE-SODIC SOIL UNDER GREENHOUSE CONDITIONS.

## 1. Introduction

Soil salinity is the major factor influencing crop production in many agricultural lands (Rengasamy, 2010; Tavakkoli et al., 2011). However, levels of tolerance of crops to salinity vary. Wheat species, for example, are classified as moderately tolerant to salinity when compared to other crops, and can grow normally in lands with salinity ranging from 3 to 7 deciSiemens per meter (dS $m^{-1}$) (Wilson et al., 2002).

“Salt-affected lands” are defined as groups of soils in which concentration of soluble salt is high enough to restrict the growth of most crops (Paul, 2013) and to degrade the physicochemical properties of soils (Shrivastava and Kumae, 2015). These lands occupy around 23% of the earth’s surface, and have a major negative impact on the productivity of agricultural crops and pastures (NLWRA, 2001; Szabolcs, 1994). The majority of these lands are classified as saline-sodic soils, which occupy around 10% of all salt-affected lands worldwide (NLWRA, 2001). In the Canadian prairies (Alberta, Saskatchewan, and Manitoba), more than 80,000 and 2.5 million hectares of irrigated and non-irrigated lands respectively, are classified as saline or saline-sodic soils. Sulfates of sodium ($Na^+$), magnesium ($Mg^{2+}$), calcium ($Ca^{2+}$), and potassium ($K^+$) are found to be the dominant salts on these areas. Small portions of these mineral salts are combined with bicarbonate, carbonates, and chloride (Sommerfeldt et al., 1988).

The dominant presence of $Na^+$ in saline-sodic soil increases soil compaction and baulk density and reduces the pore size distribution (Troeh and Thomson, 2005). This in turn minimizes salt leaching, root penetration, and seed germination (Lashari et al., 2013). Moreover, salinization poses direct and severe problems for crop production and food quality (Kammann et al., 2011). It restricts crop production by affecting seed germination and water and nutrient uptake (Singh and Chatrath, 2001; Akbarimoghaddam et al., 2011). For example, excess salt in the soil solution increases osmotic pressure (Sperry and Hacke, 2002; Munns et al., 2006), resulting in the limitation of water uptake in which decreas crop yield. However, high concentrations of specific ions (particularly $Na^+$ and $Cl^-$), which are more common in sodic and saline-sodic soils, can be toxic for plant growth (Smith et al., 2010a) and cause unbalanced uptake of essential nutrients (Maas and Hoffman, 1977; Blaylock et al., 1994; Ashraf, 2004).

Animal manure has long been used as an alternative for inorganic fertilizers globally and it is considered as a substantial resource that is capable of providing essential nutrients for maintaining sustainable crop production (Chambers et al., 2000). Under saline condition, the interaction between the effects of fertility and salinity on plant nutrition and productivity is complex (Zeng and Shannon, 2000). Yet studies focusing on this interaction are limited, and results from earlier studies are inconsistent. The degree of plant tolerance to salinity depends on either salinity or fertility based on which of these factors is more limiting for plant growth (Maas and Hoffman, 1977). For example, when nutrient deficiency limits plant growth, the plant becomes more tolerant to salinity than if it was provided with sufficient nutrients. However, Bernstein et al. (1974) suggested that salinity and nutrition have independent effects on plant growth, which becomes additive in soils with moderate salinity combined with nutrient deficiency. This means that when one of these factors imposes a severe limitation on plant growth the other factor will have little additional effect on plant growth. Grattan and Grieve (1998) reported that the effect of salinity on P uptake and accumulation in plants depends on the severity of soil salinity and the nutrient content in soils. They reported both negative and positive effects, as well as no effect, of salinity on P uptake depending on salinity and P concentration in soils. Khoshgoftarmanesh and Nourbakhsh (2009) found that the availability of P is higher in saline soils than in non-saline soils due to the effect of reduced pH in the former. But logically, the benefits of the available nutrients for plant uptake could be impaired by salinity as a result of increasing osmotic pressure of the soil solution. The interaction between salinity and fertility could also be applicable when nutrient toxicity is limiting plant growth instead of nutrient deficiency. The potential for the existence of salt-affected soil, combined with high or excessive nutrient contents is high in agricultural lands. This is because salt-affected soil mostly develops in imperfectly- to poorly-drained discharge areas (lowland areas), due to water movement from well-drained recharge areas (upland areas) (Manitoba Agriculture, Food and Rural Initiatives, 2008). Concurrently, nutrients translocate through erosion, along with surface runoff (Kleinman et al., 2006; Blanco and Lal, 2010), and may eventually accumulate in salt-affected soil in lowland areas. Nutrients may also exist in excessive levels in saline areas, due to the common practice in some regions of using these unproductive lands for animal production and or manure storage.

The reclamation of existing salt-affected land is also urgently required due to the increased demand for food and agricultural products (Ilyas et al., 1997). Amendments such as gypsum as well as other organic material have long been used to ameliorate the harmful effects of saline-sodic soil on the growth and production of many crops (Lakhdar et al., 2009; Mahmoodabadi et al., 2013). Recently, the application of biochar to soils has been widely recognized as a useful management intervention, one that promotes plant productivity and yield through many different mechanisms. These include changes in physical and chemical properties of soils. Its dark color facilitates seed germination by altering thermal dynamics of the soils (Genesio et al., 2012) while, its high surface areas (200–300 $m^2$ $g^{-1}$) (Chun et al., 2004) and cation exchange capacity (CEC) (27.7–222.4 mmolc/kg) (Liang et al., 2006) could improve the water holding capacity and hydraulic conductivity of soils (Jien and Wang, 2013; Hardie et al., 2014). The properties of biochar are also found to be effective for nutrient retention (DeLuca et al., 2015; Major et al., 2009), including P (Chintala et al., 2014), which increased nutrition uptake by crops (Major et al., 2010). Application of biochar, in conjunction with inorganic fertilizers or manure, is likewise found to be an important strategy to increase the efficiency of fertilizers (Chan et al., 2008a; Steiner et al., 2008). Generally, plant growth and productivity respond differently to biochar as both positive and negative responses have been reported depending on biochar type, application rates, fertilization condition and crop variety (Chan et al., 2008a; Tagoe et al., 2008; Gaskin et al., 2010; Solaiman et al., 2010; Dempster et al., 2012; Farrell et al., 2014).

Biochar could on the other hand, be an important source of divalent cations, such as $Ca^{2+}$ and $Mg^{2+}$ (Major et al., 2010; Laird et al., 2010a; Tsai et al., 2012), which help increase soil aggregation (George et al., 2012; Mukherjee and Lal, 2013). Both of these elements are highly important for saline-sodic soil reclamation to offset $Na^+$ at the exchange sites of soils and to facilitate leaching. Despite benefits of biochar for non-saline soils, not much attention has been paid to its benefits for saline-sodic soils. There is also knowledge gap about the possible combined benefits of biochar, such as reducing salinity stress, increasing water holding capacity and improving nutrient retention, for crop production.

The benefits of biochar as a soil amendment require careful assessments for each targeted soil management in order to fully capture the economic benefits and costs while minimize unacceptable risk to the environment. Economic feasibility must be included in the cost of transportation, feedstock availability, the used and supplied energy, production and application balanced with profitability. For instance, transportation distances reported as one of the limitation to any feedstock use from an economic point of view (Caputo et al, 2005). Few studies linked the quantitative assessments of biochar based on soil management goal with regard to economic perspectives (Fowles, 2007; Gaunt et al., 2008). Generally, biochar is considered as being economically viable due the reduction in the cost spent on commercial mineral fertilizers (Steiner et al. 2008). Also, the economic peak with biochar application could be increased through a gain in crop yield. Furthermore, better utilization of the co-products of pyrolysis might improve the economic prospects of biochar production. Biochar addition to soil was found to have a continuous effect on soil physical and chemical properties, which in turn contribute to long-lasting effects of soil fertility (Gavin et al., 2003; Gouveia et al., 2002; Pessenda et al., 2010). For instance, Terra Preta soils are still fertile since 800 years after charcoal application (Glaser et al., 2002; Lehmann et al., 2003). That means single applications of biochar can provide positive effects over several growing seasons (Steiner et al., 2007; Major et al., 2010). Therefore, biochar application is not required with each crop, as is commonly the case for other soil amendments such as manures, compost, and synthetic fertilizers (Major, 2010). In conclusion, the recalcitrant nature of biochar for long time reduces the frequency of biochar application which in turn increases the profitability over the costs.

The objective of this study therefore is to evaluate the growth and yield of spring wheat in response to biochar application as a reclamation material in manured and un-manured non-saline and saline-sodice soils. We hypothesize that plant growth will increase as more nutrients are retained and large quantities of salts and exchangeable $Na^+$ are eliminated from soils due to improvement of the soils' physical and chemical properties (particularly water holding capacity (WHC), water infiltration rate as well as soil pH).

## 2. Materials and Methods

### 2.1 Soil and amendments

The top saline-sodic and non-saline soils (0-10 cm) used in this study were collected from an agricultural field located in Holden, Beavder County in Alberta, which is 100 km east of Edmonton, Canada.

Prior to use, the soils were air-dried and sieved (<2 mm) to remove stones and plant debris. The particle size distribution was determined using the hydrometer method (Gavlak et al., 2003). The sand content was 22% and the clay content was 34% (equivalent to a clay loam). The used saline-affected soil belongs to saline-sodic category with electrical conductivity ($EC_e$) >4 ds $m^{-1}$, exchangeable sodium percentage (ESP)>15, sodium adsorption ratio (SAR)> 13%, and pH> 8.5. Detailed descriptions of the soil sampling methodology, soil classification, and soil analyses used to determine different physical and chemical properties, are discussed in chapter 4. Important soil physical and chemical characteristics are presented in Table 5-1.

The mixed hard wood biochar used in this trial was provided by Alberta Innovates Technology Futures (now InnoTech Alberta), Vegreville, Alberta, Canada. The biochar was produced in a batch-type carboniser, Prototype 1.0) at 500–550 °C from a mixture of Spruce, Pine and Fir chips. The same dry cattle manure that used in earlier study (chapter 3) was used as a source of nutrients to generate two levels of soil nutrient content for evaluating the interaction between biochar and soil nutrient level on plant growth in the two soils. Sources, production techniques, and characteristics of biochar and manure are described in chapter 1 and 3, respectively. Some properties of these materials are given in table 5-2.

## 2.2 Experimental design and sampling

The experimental treatments consisted of two soil type (saline-sodic (S) and non-saline soils (N)), two rates of biochar application (0% and 5% (w/w)) and two levels of manure application (0 t ha$^{-1}$ and 5.17 t ha$^{-1}$). The 5% of biochar application is corresponded to an application of 60 t biochar ha$^{-1}$ (for the used soil with 1.12 g cm$^{-3}$ density and 0.1 m depth). The treatment combinations were set up in a completely randomized block design with four replicates. Thus, four treatments were set up for each soil: control, no biochar and no manure application (0% -), no biochar and 5.17 t ha$^{-1}$ manure application (0% +), 5% biochar and no manure application (5 % -), and 5% biochar and 5.17 t ha$^{-1}$ manure application (5 % +). Based on the treatment combinations, the soil, manure and biochar were thoroughly mixed and ~2.7 kg of the mixture was used to fill the experimental pots (height: 11 cm; diameter at base: 16 cm; diameter at top: 18 cm).

The seeds of Coleman hard red spring wheat (*Triticum aestivum* L.), used in this study, were developed by the University of Alberta, Edmonton AB, Canada. The wheat was grown in a greenhouse from February to May 2016. Prior to seeding, the water content of the soil mixtures was adjusted to 60% WHC and incubated for two weeks in greenhouse. The condition of the greenhouse was day temperature of 22$^{o}$C and night temperature of 18$^{o}$C, and 65% relative humidity. The photoperiod in the greenhouse was from 6 am to 10 pm using LED artificial lamps to supplement natural light.

Fifteen seeds were sown per pot to compensate for the possibility of a low germination and seedling survival rate, particularly in the saline-sodic soil. One week after germination, the plants were thinned to 8 plants pot$^{-1}$ for the rest of the growing period. All pots were watered daily to field capacity (F.C) to prevent water stress and soil cracking of the saline-sodic soil. The volume of irrigation water for each treatment was determined using a TDR 300 soil moisture meter (Spectrum Technologies, INC., 6430FS). The survival rate (SR) and germination are expected to be the best indicator for the plants response to the treatments particularly in the saline-sodic soil. Therefore, these two parameters were monitored daily until plants were fully established. The grain and straw were harvested 90 days after seeding (at grain maturity) and dried in a forced-air oven at 70 °C for 72 h. The roots were carefully extracted and washed once with tap water and then twice with deionized water to remove any adhering soil particles prior to drying in a forced-air oven at 70 °C for 72 h. The agronomic parameters of root and shoot dry matter weight, and also root to shoot ratio, were measured. These parameters evaluated the influence of the treatments on the growth and production of plants in the experimental unit (pot) bases. Therefore, three additional plant parameters were measured on the individual plant bases in order to gain a better understanding of the plants' response to the examined treatments. These parameters include spikelet weight; grain weight; and the number of grains per spikelet, per plant. Plant straw samples were ground using a ball mill (MM200, REtsch GmbH, Haan, Germany) and digested (nitric-perchloric acid) at 125 °C for 24 h for total nutrient and element contents. The concentrations of N, P, K, S Ca, Mg, Mn, Zn, Cu, and Na were determined by an inductively coupled plasma molecular absorption spectrophotometry (ICP-MS) (ELAN 6000, PerkinElmer, Inc., MA).

Immediately after crop harvesting, the soil in each pot was mixed thoroughly, air-dried, sieved using a 2-mm sieve and used for the analysis of soil physicochemical properties. The electrical conductivity (EC) of the original soil samples were measured on saturated paste extracts following the method described by Richards (1954), using an AP75 portable waterproof conductivity/TDS meter (Thermo Fisher Scientific Inc., Waltham, MA, US). Air dried sub sample of original soil sample was ground into fine powder using a ball mill (MM200, REtsch GmbH, Haan, Germany) and used for total C and total N analyses. Soil pH was measured in a 1:1 (m:v) ratio using an Orion pH meter (Thermo Fisher Scientific Inc., Beverly, MA, US). Soluble cations were analyzed by extraction of samples with deionized water in a 1:1 (m:v) ratio using an inductively coupled plasma molecular absorption spectrophotometry (ICP-MS) (ELAN 6000, PerkinElmer, Inc., MA). Total P (TP) in soil was extracted by the digestion of 2 g finely ground soil using $HClO_4^+$ $HNO_3$. Soil samples were also analyzed for available phosphorus (AP) using the modified Kelowna extraction method (0.015 *M* NH4F, 1.0 *M*

HOAc, 0.5 *M* NH4OAc) proposed by Ashworth and Mrazek (1995). All P analyses were conducted using the ascorbic acid molybdate blue method (Murphy and Riley, 1962).

### 2.3 Statistical analysis

All collected data were subjected to analysis of variance using PROC MIXED in the Statistical Analysis Systems software (SAS) package (SAS 9.4). A three-way ANOVA was used to test the degree of significance of the biochar rates effect; the soil type effect; nutrients concentration (manure) effect; and the interaction between these factors ($\alpha<0.05$). Significant differences between the treatment means were analyzed using Tukey's test at 95% significance level. Residual and influential plots were evaluated to make sure ANOVA assumptions of normality and equal variance were fulfilled. Only data on plant concentration of N, Na, S, and Mn were skewed to the right therefore, log-transformation were applied to these data before further analysis, however original untransformed data are presented.

## 3. Results and Discussion

### 3.1 Plant survival and production

As wheat is known to be highly affected by salinity during germination and seedling growth, seedling survival rate (SR) is a good indicator of the ameliorating effects of biochar and manure application. There was significant interaction among the three factors for the SR ($p=0.026$). For the non-saline soil, the percentage of SR of the control treatment (N0% -) was 86%. The SR increased to 96% in non-saline soil amended with biochar, which was not significant compared with the controls. On the other hand, the application of manure alone caused a significant reduction of the SR, relative to that of the control treatment (N0 % -), the SR was about 28% in this case (Figure 5-1A). Compared to the control treatment, there was a minor insignificant increase in the SR when manure was added in combination with biochar (Figure 5-1A). These results suggest that manure application to the non-saline soil likely raised the soil nutrients to a toxicity level that affected seed germination and SR. The results also suggest that biochar can mitigate the observed harmful effects, particularly nutrient toxicity through reduction of metal nutrients (particularly Zn and Cu) availability and accumulation into plant tissue (Puga et al., 2015). The observed trends were different in the saline-sodic soil with initial SR of 20% in the control (S0% -), which increased significantly to 88% in the biochar amended treatments

(Figure 5-1A). Manure application significantly increased SR only when it was combined with biochar (Figure 5-1A). The average SR of the manure alone and of the combined biochar with manure treatments were 16% and 96%, respectively (Figure 5-1A). It is not surprising that low survival and growth of plants are obtained particularly during the early growth stage when exposed to either high salinity (Zhou et al., 2010; and Chen and Jiang, 2010) or excessive metal nutrients that are introduced with manure such as Zn, Cu, Fe, and Mn (Yadav, 2010; Nagajyoti et al., 2010) or both. In the saline-sodic soil, nutrient toxicity effect due to manure application seemed to be negligible. This is because in such soils with a very high EC, salinity would be the more limiting factor for plant growth, rather than fertility or nutrient conditions (Maas and Grattan, 1999). The other possible reason for this phenomena is that the ranges for nutrient deficiency, sufficiency, and toxicity for plant growth could be widened or narrowed under conditions of salinity (Grieve and Grattan, 1999). Therefore, in the soils used for the present study, the nutrients added along with manure may have led to excess conditions that were toxic for plant growth in the non-saline soil, but not in the saline-sodic soil.

Crop yield is also an important parameter for evaluating the response of plant to biochar and manure application. The significant interaction (p=0.032) between the three factors revealed that biochar application did not affect the yield of plants grown in the non-saline soil (Figure 5-1B). However corresponding with the reduction of SR and due to the toxicity effect discussed earlier, manure application without biochar was the only treatment that caused a minor reduction (~18%) of yield, relative to the control treatment (N0% -). In the saline-sodic soil, the application of manure alone did not affect the yield. Biochar application however resulted in significant increases in the yield relative to that of the control treatment (S0 % -). However the increase was more significant when the biochar application was combined with manure, which resulted in an increase of 57% and 100% for biochar and manure-and-biochar combined treatments, respectively. The high initial nutrient contents of the saline-sodic soil may have partially contributed to the high plant performance when biochar was incorporated. However, as all soil treatments initially started with adequate levels of nutrients for plant growth (Table 5-1), biochar in this case seemed to be more important for soil reclamation than for soil nutrition. Thus, the application of biochar resulted in a significant increase in yield only in the saline-sodic soil. This could be due to the expected benefits of biochar in terms of reducing salt stress for the plant roots by salt sorption (Thomas et al., 2013) and facilitating salt movement away from the root zone. Biochar may also increase crop growth and yield by reducing water stress and improving plant water use efficiency due to its role in increasing soil-water holding capacity, as shown in figure 5-2A.

Our results are similar to those of Vaccari et al. (2011) and Wang et al. (2012) who reported that wheat yield and grain quality responded positively to biochar application.

Root and shoot dry matter (RDM and SDM, respectively) were influenced by soil type and biochar application, as shown in table B-1. The root dry matter was significantly higher in the saline-sodic soil than in the non-saline soil ($p < 0.001$), with a difference of about 3-fold (Table B-1). Application of biochar also significantly increased RDM ($p = 0.043$), with a 2-fold difference. However, for the SDM, there was significant interaction between the three factors of soil type, manure, and biochar application ($p < 0.001$) (Table 5-3). Regardless of manure treatment, the application of biochar caused a significant increase in SDM, relative to that of the control treatments for both soils; the average increases were 40% and 26% for non-saline and saline-sodic soils, respectively. Furthermore, the application of biochar in combination with manure caused a significant increase in the SDM over biochar alone in the saline-sodic soil. The difference between the two cases was around 1.3-fold. The increased RDM and SDM in the saline-sodic soil over that in the non-saline soil in this study agrees with previous results reported by Qados (2011) and Andriolo et al. (2005). The increase in RDM and SDM is attributed to the influence of salt-stress on increasing the size of plants' sap vacuoles in order to collect a lot of water to dissolve the accumulated salt ions (Munns, 2002).

In our study, the applied manure provided and maintained sufficient and in some cases excess nutrients for plant growth. In addition, Biochar may also increase the accessibility of nutrients by plant roots, which combined resulted in good plant growth and dry matter production in the manure-and-biochar combined treatments. Lehmann and Joseph (2015) suggested that the application of biochar with the aim of increasing soil fertility must be accompanied by the application of fertilizers. Chan et al. (2008a) reported significant increase of radish dry matter when N fertilizer was applied together with biochar.

The average spikelet weight per plant grown in saline-sodic soil was significantly higher than that of plants grown in non-saline soil ($p < 0.001$), with a difference of about 2-fold. The significant interaction ($p < 0.001$) among the three factors showed that for the non-saline soil the average spikelet weight per plant for the treatment that received manure only (N0 % +) was at least 70% higher than that of all other treatments (Table 5-3). The low SR in the N0 % + resulted in fewer plants per pot which in turn led to higher spikelet weight possibly through compensatory growth. However, for the saline-sodic soil, plants grown in the manure or biochar amended soils produced smaller spikelets compared with the controls, which may be due to the higher SR in these treatments. The reductions in spikelets weight were 40% and 36%, for manure and biochar treatments, respectively. Surprisingly, combined biochar and manure treatments did not show any significant reduction of spikelet weight (Table 5-3). The low SR in the control saline-sodic soil (S0 % -) and also in the NO% + (due to nutrient toxicity), may have resulted in low competition among plants for nutrient uptake, especially at the later growth stages. This in turn may have resulted in higher spikelet weight relative to the other treatments with high survival rates (where there was high competition) and with the exception of the combined biochar and manure treatment of the saline-sodic soil (SH5%). In that combined treatment, soil condition seemed to be appropriate for maintaining high SR (highest number of plant) with high spikelet weight. Very similar results were obtained for the average grain weight and number of grain per spikelet/plant, particularly for the plants grown in the saline-sodic soil (Table 5-3). These results confirmed the common recommendation for the importance of adding biochar in combination with fertilizers in order to increase plant growth and yield (Steiner et al., 2008; Gaskin et al., 2008; Ding et al., 2010; Nelson et al., 2011). Our results also agreed with the general concept in the literature about the influence of plant density on growth. For instance, Valério et al. (2009) found that yield and grain weight of different wheat genotypes were highly dependent on seeding density of each genotype. Wood et al. (2003); and Valério et al. (2013) also reported higher wheat grain yields at reduced plant densities.

### 3.2 Nutrient concentrations in plants

The nutritional status of the plants may be another useful indicator for assessing plant response to the treatments evaluated in this study. The reference values for wheat crop nutrition, which were prepared by Reuter and Robinson (1986) as critical levels, were used in assessing the nutrients level in the present study. Although all soil treatments began with high and in some cases more than sufficient nutrients for optimal crop yield (Table 5-1), the N concentration in the shoot samples of all treatments was found to be within the deficient level. The reason for this is not clear, but possibly the easily mobile N form ($NO_3^-$), which is considered a primary form for crop assimilation was leached away from the root zone by the daily irrigation that was applied in this study. Despite the observed shoot N deficiency, the studied factors varied in their effects on N uptake by plants. Nitrogen concentrations in plant shoots were influenced by soil salinity and biochar, but not by manure application; there was also no interaction effect (Table 5-4). Thus nitrogen concentration was significantly higher in the shoots of the plants grown in the saline-sodic soil than in those grown in the non-saline soil (p=0.029). Also, the

N concentration in the shoots significantly increased due to biochar application ($p=0.04$). The difference in N concentration was about 0.43 g $kg^{-1}$ between the two cases of biochar treatment (Table B-2). A similar result was observed by Chan et al. (2008a) who found a significant increase in N uptake at a higher level of biochar. On the other hand, biochar was also found to improve the efficiency of mineral N fertilizer (Chan et al., 2008a; Steiner et al., 2008; Gaskin et al., 2008; Ding et al., 2010). However, in our study, there was no interaction between manure and biochar on the uptake of N. This disagreement may be due to the nature of the fertilizer type, and/or to the initial adequate N status of the control soils. Generally, the observed variances of N concentrations in plant shoots positively reflected the differences of the available N in the final soil treatments used as growth media (Table 5-5).

Phosphorus concentrations in plant shoots were also influenced only by biochar and salinity. The concentrations of P were significantly higher in the plant shoots grown in the non-saline soil than in those grown in the saline-sodic soil ($p<0.001$). These were at sufficient (2.47 g $kg^{-1}$) and deficient (1.22 g $kg^{-1}$) levels in the plants grown in non-saline and saline-sodic soils, respectively. Phosphorus concentrations in the plant shoots grown in the soils without biochar were at the sufficient level (2.17 g $kg^{-1}$). However, biochar application significantly reduced the P concentration to a deficient level (1.52 g $kg^{-1}$) ($p=0.001$, Table B-2). Madiba et al. (2016) found that P uptake by wheat crops depended on the biochar type. The P uptake increased and was not changed relative to control, when wheat and chicken manure biochar were used, respectively. Chan et al. (2008a) found an increase in P uptake in the biochar treatment, but they attributed this to the appreciable amount of available P (AP) that was present in the biochar material since it was produced from fertile green waste feedstock. In our study, the manure factor that represented two levels of P showed no effect on the P concentration in plant shoots. Furthermore, there was no interaction among all factors on the P uptake. This might be due to the adequate level of initial P among all treatments. Generally, this result agreed with the conclusion of Zribi et al.’s (2012), where the effects of salinity and P level on plant nutrient uptake were reported not to be additive.

Potassium concentrations in plant shoots ranged between marginal deficiency to high levels, through the influences of salinity, biochar, and manure applications. Similar to the case of P concentration in the plants, K concentrations were also significantly higher in the shoots of the plants grown in non-saline soil (29.5 g $kg^{-1}$) than from those grown in saline-sodic soil (20.9 g $kg^{-1}$, $p<0.001$). However, unlike in the P case, biochar increased the concentration of K in the plant shoots ($p<0.001$)

with a difference of about 5 g $kg^{-1}$ between the two cases of biochar treatment. Furthermore, manure application also significantly increased the K of plant shoots ($p=0.03$) (Table B-2). Biochar has been found to be an important source for K when applied to soils (Laird et al., 2010a; Buecker et al., 2016) and has also been found to increase K uptake (Lehmann et al., 2003). Moreover, the specific biochar used was found to provide soils with a high concentration of K, which was about 8-fold compared to the control treatment (chapter 4). In a greenhouse study, Chan et al. (2008a) also reported an increase in K concentration in radish plants grown in soil amended with biochar. This finding held true even when no fertilizers were combined in the treatments. This could explain the higher K uptake obtained in the biochar-amended soils relative to those with no biochar treatments. The higher content of K in plants from the non-saline soil compared to those grown in the saline-sodic soil may reflect the significant difference of K availability in the final soil of each type (this is discussed below). But generally, under salinity stress, K uptake was found to be influenced by the concentration of other nutrients in soil. For example, K uptake in saline soil is influenced by Ca concentration in the soil. The presence of Ca in such soil at high concentrations increases K uptake to maintain its content at an adequate level in the plants (Ben-Hayyim et al., 1987). Also, the significantly higher Na uptake by plants in the saline-sodic soil, compared to that in the non-saline soil (Table B-2) is expected because it is needed for halophyte plants to adjust their osmotic pressure gradient for water uptake (Flowers and Yeo, 1995; Wetson and Flowers, 2010; Chen and Jiang, 2010). However, the accumulation of Na at high concentrations is expected to decrease K uptake in the saline-sodic soil (Shabala et al., 2003; Chen et al., 2007; Slabu et al., 2009), resulting in a significant low K content in plants from the saline-sodic soil. Similar results were reported by Amirjani (2010) who found Na content in plant tissue to be significantly increased, but K content decreased, with increased soil salinity.

The concentrations of some selected micronutrients (Cu, Mn, and Zn) in the plant shoots were higher than the levels required for optimal crop yield, yet all were below toxic levels. Even with this high nutrient concentration in plant shoots among the treatments, the soil type was found to significantly influence the plants' uptake of these nutrients. The uptake was significantly higher in the saline-sodic soil than in the non-saline soil, except for Cu, which showed an opposite trend, as indicated by the concentration of the nutrients in the plant shoots ($p<0.001$ for Mn and Zn, and $p=0.004$ for Cu) (Table B-2). Furthermore, the studied factors showed significant interaction only for the Mn ($p=0.038$), which suggests that the biochar and manure influenced Mn concentration in plant shoots in the saline-sodic soil alone. Thus, relative to the control treatment (S0 %-), manure application significantly reduced Mn concentration in plant shoots by about 2-fold. Similarly, biochar application significantly reduced the Mn in plant shoots regardless of manure treatment, with a reduction, in this case, of at least 6-fold (Table 5-4). Biochar application may indirectly influence plant availability of micronutrients (particularly Mn) in soils. The increase of soil pH due to biochar application (Figure 5-2B), which were also in agreement with many other studies (Laird et al., 2010b; Yao et al., 2011a; Chintala et al., 2014) are expected to be responsible for the reduction of micronutrients content in the plant shoots. It has long been known that micronutrient availability in soils decreases with increases in soil pH (Islam et al., 1980; Alam et al., 1981; Jariel et al., 1991). In another study, substantial increases in soil pH due to biochar application were reported to cause micronutrient deficiencies and yield reduction (Mikan and Abrams, 1995).

### 3.3 Nutrient availability in soils

The analysis of pre-experimental soils (non-saline and saline-sodic soil) showed that both soils were fertile and have sufficient amounts of the nutrients required for optimal wheat crop yield (Table 5-1). Therefore, excess nutrient and plant toxicity was expected in the manured treatments. The soil analysis at the end of experiment showed the saline-sodic soil to contain significantly higher AP than the non-saline soil ($p<0.001$) with P contents of 38 and 105, respectively. The application of manure or biochar caused significant increase in the soil AP ($p<0.001$for both manure and biochar) (Table B-3); however there was no interaction between these factors ($p=0.08$) (Table 5-5). Our results agree with those of Khoshgoftarmanesh and Nourbakhsh (2009) who found the availability of P to be higher in saline soils than in non-saline soils. They attributed this to the effect of reduced pH in the saline soils. Lashari et al. (2013) also reported a significant increase of the AP in salt-affected land due to biochar application. An opposite result was found by Bano and Fatima (2009) and by Grattan and Grieve (1998) who found that salt-stressed soil caused an appreciable reduction in the availability of soil P and in turn on the P uptake by the plants. They attributed this to the precipitation of P with Ca ions in salt-stressed soil. In our study the initial AP in the saline-sodic soil was about 3-fold higher than that of the non-saline soil. This might overcome the possible reduction in the availability of P due to precipitation with Ca. Expectedly the AP was high in the manure treatments however the significant increase in its availability due to biochar application indicates that biochar has a high capacity for providing P in an available form for plant uptake. Our result agrees with that of Chan et al. (2008a), who found significant increase in AP in a biochar-amended soil, relative to the control soil.

The initial available N in the control non-saline soil was found to be at the marginal border below the sufficient level for optimal crop yield. Therefore, the plant parameters discussed earlier could be strongly influenced by the availability of N, rather than by the other nutrients. There was significant interaction among the three factors on the availability of N in soil (p=0.013 for $NO_3$ and p= 0.009 for $NH_4$). Similar to P, the availability of N was significantly higher in the saline-sodic soil than in the non-saline soil regardless of the added treatments (p<0.001) (Table B-3). In the non-saline soil, the concentrations of available N ($NO_3^-$ and $NH_4^+$) were controlled only by manure treatment. Relative to the control treatment (N0% -) the application of manure caused significant increase of the available N in the soils, regardless of the biochar treatment. And no significant changes occurred due to the application of biochar alone (Table 5-5). In other words, biochar caused significant increases in the available N only when it was added in a combination with manure. Similar results were found by Nelson et al. (2011) who suggested that the addition of N is required after biochar application to maximize N availability and in turn increase crop production. On the other hand, saline-sodic soil that received biochar showed significantly higher concentrations of available N than did soil that had not received biochar, regardless of manure application. The highest available N in the biochar-amended saline-sodic soil may have resulted in the observed plant performance as previously discussed (Table 5-2).

The significant interaction (p<0.001) among the three factors for the available S showed that the non-saline soil contained significantly less available S than did the saline-sodic with values of 68 and 542 g $kg^{-1}$, respectively. Furthermore, there were no significant differences between the control (N0 % -) and other treatments on the available S of the non-saline soil (Table 5-5). However, for the saline-sodic soil, the separate application of either manure or biochar caused significant increase in the available S, relative to that of the control treatment (S0 %-); these increases were 175 and 273 mg $kg^{-1}$, respectively. The observed increase was higher and more significant when both manure and biochar were added in combination with an increase of 1181 mg $kg^{-1}$ (Table 5-5). Unlike the other nutrients, the availability of $K^+$ in the non-saline soil was significantly higher than that of the saline-sodic soil (p<0.001), its availability was 470 and 272 mg $kg^{-1}$, respectively. Application of manure and biochar caused a significant increase in the available K (p<0.001 for both) (Table B-3) and the net increases were 90 and 192 mg $kg^{-1}$, respectively; however, no significant interaction was found between these factors (p=0.069). Gaskin et al. (2010) also found increases in available K due to biochar application, which also positively correlated with the concentration of K in corn tissue. Many other studies have considered biochar as a source of K in soils (Chan et al., 2008a; Laird et al., 2010a; Buecker et al., 2016). The significantly higher K in non-saline soil than in saline-sodic soil may reflect the initial high K in the non-saline soil. The initial concentration of $K^+$ in that soil was about 2-fold higher than that in the saline-sodic soil (Table 5-1).

In addition to the already discussed benefits of biochar for improving availability of soil nutrients and nutrient uptake, the application of the biochar used in this study on same soils was found to decrease soil $EC_e$ and other salinity parameters including ESP and SAR (Chapter 4). Furthermore, significant increase was found in soil water movement and infiltration rate in the biochar amended soil relative to that of the control treatment. These improvements in soil chemical and physical properties due to biochar application may also have contributed to the enhanced plant growth and yield that was obtained in the biochar amended saline-sodic soil.

## 4. Conclusions

The response of crops to hardwood biochar and cattle manure application (as a nutrient source) varied based on the soil type. With the presence of biochar, the initial higher nutrient content of the saline-sodic soil compared to that of the non-saline soil corresponded with the observed enhanced wheat performance in the saline-sodic soil. In the non-saline soil, addition of manure (in the absence of biochar) likely raised soil nutrients to excess level that may have become toxic for plant growth as indicated by significant reduction in seedling survival rate and yield. This study validated the potential of hardwood biochar as a reclamation material to increase the productivity of saline-sodic soil, particularly when combined with manure as a source of nutrients. Combined application of manure and biochar may enhance nutrient use efficiency by maintaining adequate level of nutrients in available form for plant uptake while preventing any possible toxicity effects on plant growth due to associated excess nutrients. Furthermore, biochar may ameliorate salinity by adsorption of salts (particularly $Na^+$), and/or by replacing the exchangeable $Na^+$ with $Ca^{2+}$ and $Mg^{2+}$ and facilitating the movement of the soluble $Na^+$ and other saline ions away from the root zone.

**Table 5-1**: Physical and chemical properties of soils with and without manure addition

| Characteristic | Normal soil | Saline-sodic soil | Normal soil | Saline-sodic soil |
|---|---|---|---|---|
| | **Without manure addition** | | **With manure addition** | |
| Sand (%) | 22±0.1 | 23±0.4 | nm | nm |
| Silt (%) | 44±0.3 | 39±0.1 | nm | nm |
| Clay (%) | 34±0.1 | 38±0.2 | nm | nm |
| Texture | Clay loam | Clay loam | nm | nm |
| Bulk density (g $cm^{-3}$) | 1.13±0.1 | 1.15±0.07 | 1.0±0.1 | 1.0±0.1 |
| TC (%) | 2.94±0.09 | 2.56±0.03 | 3.56±0.06 | 3.21±0.21 |
| TN (%) | 0.31±0.06 | 0.26±0.01 | 0.32±0.02 | 0.32±0.02 |
| CEC (cmol $kg^{-1}$) | 34±2.5 | 30±2.0 | 36±1.3 | 31±1.5 |
| pH (w:v) (1:1) | 7.07±0.5 | 7.18 ±0.01 | 7.37±0.3 | 7.51±0.03 |
| $EC_e$ (ds $m^{-1}$) | 1.8±0.05 | 28±0.2 | 2.4± 0.02 | 28.7±0.3 |
| Soluble cations (mg $g^{-1}$) | | | | |
| $Na^+$ | 0.02±0.001 | 4.5±0.201 | 0.05±0.001 | 4.6±0.160 |
| $Ca^{2+}$ | 1.8±0.03 | 1.57±0.11 | 2.1±0.01 | 1.9±0.67 |
| $Mg^{2+}$ | 0.28±0.005 | 1.4±0.13 | 0.33±0.01 | 1.5±0.05 |
| $K^+$ | 0.40±0.01 | 0.19±0.02 | 0.68±0.01 | 0.49±0.03 |
| Available nutrients (mg $kg^{-1}$) | | | | |
| $NO_3^-$-N | 105±0.49 | 334±44.2 | 163±15.9 | 341±46 |
| $NH_4^+$-N | 11.2±0.27 | 22.1±0.21 | 12.5±0.42 | 23.1±0.15 |
| S | 400±10 | 4741±39 | 450±30 | 4832±52 |
| Available P | 32±1.91 | 97.4±14.2 | 80±1.95 | 147±3.40 |
| Total P (g $kg^{-1}$) | 0.51±0.09 | 0.68±0.07 | 0.67±0.04 | 0.74±0.03 |

Mean of parameters expressed with standard error (n = 3); nm= not measured.

**Table 5-2**: Selected properties of biochar and manure

| Biochar | | | | | | | Manure | | |
|---|---|---|---|---|---|---|---|---|---|
| CEC | Surface area | pH | Ca | Mg | Na | K | Total P | DRP | pH |
| cmol kg$^{-1}$ | m$^{2}$ g$^{-1}$ | | mg g$^{-1}$ | | | | g kg$^{-1}$ | mg L$^{-1}$ | |
| 18 | 324.6 | 9.96<br>(0.01) | 1.7<br>(0.23) | 0.18<br>(0.01) | 0.38<br>(0.06) | 2.7<br>(0.24) | 5.89<br>(0.08) | 3.94<br>(0.02) | 8.5<br>(0.05) |

Mean of parameters expressed with standard error (n = 3); DRP = Dissolved reactive phosphorus (in 200:1 extract).

**Table 5-3**: Means of root dry matter production (RDM), shoot dry matter (SDM), total dry matter (TDM), ratio of root to shoot (R/S), and other plant parameters in response to soil type, manure and biochar treatments used in the experiment.

| **Treatment**$^{z}$ | **Number of plants** | **RDM** | **SDM** | **TDM** | **Yield** | **R/S** | **Spikelet weight** | **Grain weight** | **Grain/ Spikelet** |
|---|---|---|---|---|---|---|---|---|---|
| | | g / pot | | | | | g/plant | | |
| N 0% - | 8 | 0.53 | **2.48 e**$^{y}$ | **5.30 d** | **2.82 cd** | 0.21 | **0.47 e** | **0.35 c** | **13 d** |
| N 0% + | 4 | 0.53 | **2.59 de** | **4.74 d** | **2.14 d** | 0.21 | **1.15 bc** | **0.76 b** | **22 bc** |
| N 5% - | 8 | 0.7 | **3.43 dc** | **6.57 cd** | **3.13 cd** | 0.20 | **0.56 e** | **0.41 c** | **15 d** |
| N 5% + | 8 | 0.87 | **3.55 c** | **7.47 c** | **3.92 c** | 0.24 | **0.67 de** | **0.50 bc** | **16 cd** |
| S 0% - | 3 | 2.06 | **4.16 bc** | **8.14 c** | **3.97 c** | 0.49 | **1.63 a** | **1.22 a** | **33 a** |
| S 0% + | 4 | 1.20 | **3.26 cde** | **6.20 cd** | **2.94 cd** | 0.37 | **0.97 cd** | **0.71 b** | **25 b** |
| S 5% - | 8 | 2.23 | **4.63 b** | **10.92** | **6.29 b** | 0.48 | **1.03 cd** | **0.77 b** | **24 b** |
| S 5% + | 8 | 1.75 | **5.92 a** | **14.43 a** | **8.51 a** | 0.3 | **1.45 ab** | **1.10 a** | **33 a** |

$^{y}$Mean values followed by the same letter within a column are not significantly different ($p<0.05$), the bolded values indicate the statically significant data, Codes$^{z}$: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

**Table 5-4**: Means of nutrients concentrations of wheat shoot in response to soil type, biochar and manure treatments used in the experiment.

| Treatment[z] | Nitrogen | Phosphorus | Potassium | Sodium | Zinc | Manganese | Copper |
|---|---|---|---|---|---|---|---|
| | | | | | g kg$^{-1}$ | | |
| N 0% - | 4.50 | 2.80 | 28.2 | **0.46 c**[y] | 0.16 | **0.06 c** | 0.54 |
| N 0% + | 4.92 | 2.69 | 26.2 | **0.79 c** | 0.26 | **0.06 c** | 0.78 |
| N 5% - | 4.34 | 1.66 | 30.2 | **0.33 c** | 0.21 | **0.03 c** | 0.43 |
| N 5% + | 4.78 | 2.73 | 33.6 | **0.43 c** | 0.20 | **0.04 c** | 0.59 |
| S 0% - | 4.46 | 1.66 | 16.7 | **6.60 a** | 0.34 | **0.24 a** | 0.27 |
| S 0% + | 4.70 | 1.53 | 20.1 | **3.21 b** | 0.33 | **0.13 b** | 0.45 |
| S 5% - | 5.65 | 0.66 | 21.6 | **8.01 a** | 0.48 | **0.04 c** | 0.46 |
| S 5% + | 5.45 | 1.02 | 25.2 | **8.41 a** | 0.20 | **0.03 c** | 0.26 |

[y] Mean values followed by the same letter within a column are not significantly different ($p<0.05$), the bolded values indicate the statically significant data, Codes[z]: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

**Table 5-5**: Means of available nutrients concentration of post soil in response to soil type, biochar and manure treatments used in the experiment.

| Treatment[z] | Available P | $NO_3^-$-N | $NH_4^+$-N | Sulfur | Potassium |
|---|---|---|---|---|---|
| | | | mg $kg^{-1}$ | | |
| N 0% - | 28.7 | **69.1 e**[y] | **6.57 e** | **61 c** | 314 |
| N 0% + | 44.1 | **74.7 cd** | **7.42 de** | **45 c** | 517 |
| N 5% - | 31.5 | **69.9 de** | **6.85 e** | **86 c** | 435 |
| N 5% + | 49.0 | **78.5 c** | **8.90 cd** | **79 c** | 615 |
| S 0% - | 97.6 | **93.1 b** | **10.70 bc** | **45 c** | 152 |
| S 0% + | 107.0 | **97.2 b** | **12.32 b** | **220 b** | 324 |
| S 5% - | 105.6 | **106.8 a** | **16.07 a** | **318 b** | 201 |
| S 5% + | 111.5 | **105.4 a** | **15.50 a** | **1226 a** | 412 |

[y] Mean values followed by the same letter within a column are not significantly different ($p<0.05$), the bolded values indicate the statically significant data, Codes[z]: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

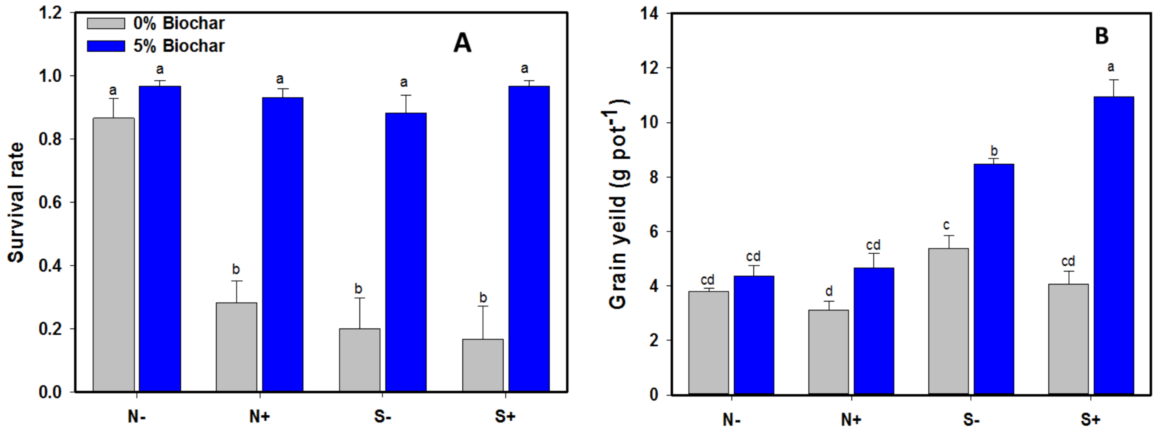

**Figure 5-1**: Changes in survival rate (A) and grain yield (B) of wheat crop as affected by soil type, biochar and manure treatments used in the experiment. Each bar illustrates the mean (n=4). Vertical error bars are standard error of the mean (SEM), Codes: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

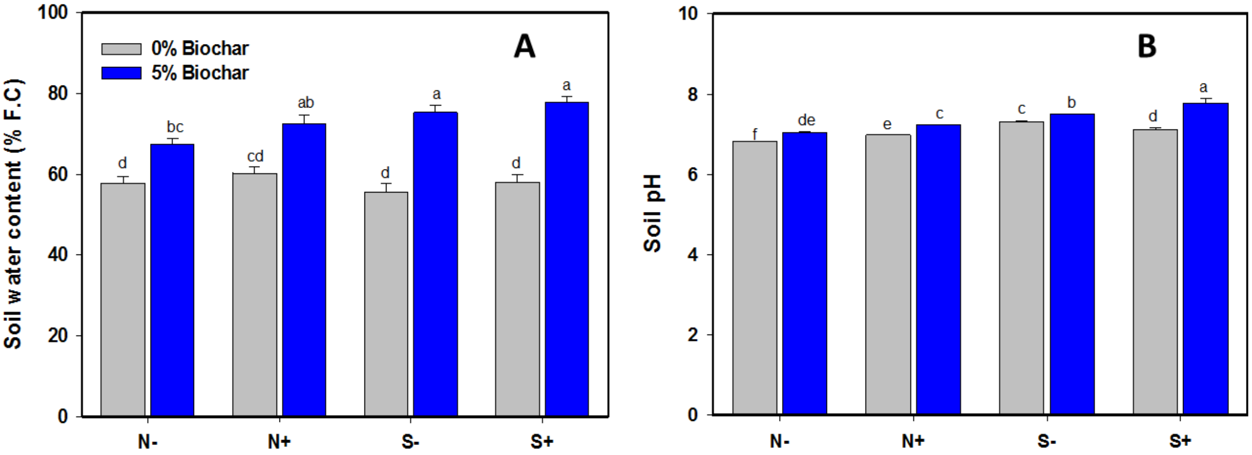

**Figure 5-2**: Changes in soil water content (% F.C) (A) and soil pH (B) and as affected by soil type, biochar and manure treatments used in the experiment. Each bar illustrates the mean (n=4). Vertical error bars are standard error of the mean (SEM), Codes: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

# CHAPTER 6. SYNTHESIS, CONCLUSIONS AND FUTURE RESEARCH

## 1. Overview of Study Objectives

The research reported in this thesis will help in developing effective reclamation practices for saline-sodic soils with high availability of nutrients, particularly phosphorus, by assessing the potential to use biochar as a reclamation material. Improved management of such soils will be possible once we better understand the mechanisms by which biochar affects the soil's physical and chemical properties. Biochar may facilitate leaching of salt away from the root zone while improving retention of available phosphorus for plant uptake and preventing leaching losses. Four studies, including three laboratory experiments and a greenhouse experiment, have been conducted as a part of this thesis research. The influences of biochar type and salinity level on the P sorption capacity of biochar were evaluated by conducting a P sorption isotherm experiment, using biochars derived from different feedstock types (wheat straw, hardwood, and willow wood) under non-saline and saline conditions (0, 4 and 8 ds $m^{-1}$) (Chapter 2). Hardwood biochar showed the highest sorption capacity under both saline and non-saline conditions; therefore, it was selected for use when conducting the other three experiments. An evaluation was made of the effect of biochar application at four rates (0, 2, 5, and 8% [w/w]) on reducing the soil salinity of a saline-sodic soil and reducing the leaching losses of P from non-saline soils. This was done in the laboratory via a soil column leaching experiment (dried cattle manure was used as a source of P in the treatments). The treatment columns were wetted at 60% of water holding capacity (WHC), and incubated at room temperature for two weeks. The columns were then leached by adding deionized water at one pour volume (500 mL for the 0 and 2% treatments, and 650 ml for the 5 and 8% treatments), for 6 leaching events that ran every other day (Chapters 3 and 4). The biochar application rate of 5% was shown to be the optimal application rate. It was thus selected, along with the control treatment (0% biochar), to evaluate the plant responses to the reclamation of a manured saline-sodic soil, using the selected hardwood biochar. For the plant response trials, seeds of spring wheat (*Triticum aestivum* L.) were grown in a greenhouse pot experiment from February to May 2016. The wheat plant's response to the soil treatments was measured by nutrient contents, survival rates, root to shoot ratio, biomass yield, and grain and spike weight per individual plant (Chapter 5).

## 2. Synthesis of Research Results

## 2.1 Phosphorus sorption capacity of biochar varies with biochar type and salinity level

The biochar properties, which are dependent on the biochar type, together with the salinity level of the aqueous solution, had an important influence on the P sorption capacity of biochar. Willow wood biochar showed the highest P sorption capacity relative to that of wheat straw and hardwood biochars due to the highest CEC, surface area and elemental concentration in the former biochar. However, willow wood biochar had an opposite P sorption trend relative to that sorption of other biochars. Unwashed and both acid- and water-washed hardwood and wheat straw biochars showed the same trend of P sorption, but the P sorption capacity of both biochars was reduced upon washing. However the P sorption trend of willow wood biochar became similar to that of the other used biochars upon washing. The phosphorus sorption capacity of the wheat straw and hardwood biochars increased along with an increase P in solution. However the sorption of willow wood biochar was not greatly affected by the solution pH. The biochar type and initial P concentration of the solution significantly affected the P sorption of the biochar. The phosphorus sorption capacity of washed biochars increased as the initial P in the solution increased. At high initial P concentrations (12.5 to 25 mg P $L^{-1}$), however, hardwood biochar sorbed a higher amount of P than did the other biochars. Phosphorus sorption capacity of the studied biochars was higher under saline than under non-saline conditions; however, P sorption under electrical conductivity of 4 was higher than was that under 8.

The surface area and elemental content (Ca and Mg) were highest in the willow wood biochar relative to that of the other biochars. These properties were considered the main factors responsible for making the P sorption capacity of this biochar the highest, achieved by facilitating the precipitation of P with Ca and Mg from the biochar material. Removing ash by washing the willow biochar may have created more sorption sites on the willow wood biochar's surface and facilitated a greater sorption of P, which resulted in the change obtained in the P sorption trend. Also, releases of elements from the biochar material due to washing could be responsible for the reduction in the P sorption capacity of the washed biochar. Generally, the P sorption of the studied biochars was mainly controlled by the surface area and surface precipitation of P with $Ca^{2+}$ and $Mg^{2+}$. However, the participation of a pH-dependent charge on the P sorption of the biochars was negligible, as indicated by the pH at zero point of charge (ZPC) value of the biochar, which ranged between 2.0 and 3.5. Based on the ZPC value the biochar surface will be negatively charged when the solution pH is greater than the ZPC, which interferes with the P sorption. However, high solution pH indirectly enhanced the P sorption capacity of the biochar by facilitating precipitation of P with Ca and Mg. The increases in ionic strength and ionic double layer thickness, with the increase of the solution electrical conductivity (EC), reduced the diffusion rate of P toward the biochar surface as a sorbent, which explained the significant reduction of P under a solution with high EC.

## 2.2 Hardwood derived biochar reduced leaching loss of phosphorus from a manured soil

The biochar application rates (0, 2, 5, and 8%) and soil salinity conditions (saline-sodic and non-saline soils) had significant interactions, which affected leachate EC, leachate volume, and soil pH. Significant interactions were also obtained when biochar rate and soil salinity levels were tested together with leaching factors (initial and post leaching soils) on the soil parameters, including sodium adsorption ratio( SAR), exchangeable sodium percentage ( ESP), and EC. Even with the significant interaction, the biochar application rate influenced the leachate volume and EC from most leaching events in the saline-sodic soil, but not in the non-saline soil. Water retention time was also influenced by the biochar treatments: it was > 24 and ~8 hours for the control and the biochar treatments, respectively. The measurement of the leachate EC indicated that most of the salt leached in the first event, and was higher from the control treatment (0% biochar) than from the other biochar treatments. However, the leaching of salt was more in the high biochar treatment (8%) for the follow up two leaching events (the second and third events). The trends of salt leaching, among these three events corresponded with the volume of leachate. However, after the third event, the biochar treatments of 0 and 2% reached the point of waterlog. The leaching volume from the other biochar treatments meanwhile remained at a near-constant level during all events. In the comparison amongst the biochar treatments of the post-leaching soils, the 8% biochar treatment caused a more significant reduction of EC, ESP and SAR than did the other biochar treatments; in some cases, the values of these parameters dropped even lower than those of the comparable treatments of the non-saline soil. Leachate losses of some cations including $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$, which were measured during the first, third, and sixth events for the two soils followed a similar trend as for leachate EC. They showed the highest losses in the first event, and reduced sharply during the third and sixth events. The losses were also the highest from the control, in the first event. However, for the remaining selected events, the losses became either equal with the other treatments, or the highest (in the case of the 8% biochar treatment).

In the first and second events, the leachate EC values positively corresponding to the volume of infiltrated water through soil treatments. The more percolated water, the more salt was washed out from the soil treatments. The high retention time that was observed in the control treatment also allowed more salt to be dissolved and eventually moved with water. Moreover, the better soil aggregation in the biochar-amended soil, compared to that of control treatment, could have caused the water to move quickly without penetrating and removing the salt from the small soil pores. After the third event, the clay particles' expansion by $Na^+$ caused waterlogging in both the control and the 2% biochar treatment. On the other hand, a better soil aggregation in the 5 and 8% biochar treatments facilitated constant leaching during all leaching events. Intensive leaching, during all events, caused a significant reduction of the ECe, SAR, and ESP of all saline-sodic soil with the different biochar treatments. However, the effectiveness of biochar application at a high rate, for reducing salinity and the associated salinity parameters, was clear. This was attributed to the high content of divalent cations (such as Ca and Mg) in the biochar material. These cations are important to offset the $Na^+$ in the exchange sites of saline-sodic soil, which eventually leach out with percolated water. Another possible mechanism of biochar, for reducing soil salinity, is through the sorption of $Na^+$, which reduces its content in the soil solution.

## 2.3 Reclamation of a saline-sodic soil with biochar: effects of biochar application rate

The biochar application rate (0, 2, 5, and 8%) and the level of soil test phosphorus (STP) that were obtained through manure treatment had significant interactions, which affected the leaching losses of P. The cumulative leaching loss of P during six leaching events, in the form of total phosphorus (TP) and dissolved reactive phosphorus (DRP) from manure-amended soils, was significantly reduced with increasing biochar application rate. For the soil to which manure had not been added, on the other hand, biochar addition in general caused a significant reduction, but the specific rate of biochar addition seemed not to make a difference on those losses. The leachate loss trends of TP and DRP for each individual leaching event were similar to the accumulative trend, except for the last event (event six), where the leaching losses increased along with increasing biochar addition. The leachate composition revealed that leachate losses of multivalent cations ($Ca^{2+}$ and $Mg^{2+}$) were reduced; however, monovalent cations (particularly $K^+$) increased along with increasing biochar application rate. The biochar application rate also had a significant influence on the soil-water infiltration rate; the infiltration rate increased along with increasing biochar application rate. The trends of the soil-water infiltration rate, based on the rate of biochar application and the associated leaching losses of P were compared.

It is well known that biochar's properties such as its high surface area and CEC, relative to that of soils increase the P sorption capacity of biochar-amended soil. That occurs due to the associated increase of cations that accumulate on the biochar surface and eventually co-precipitate with P. In accordance with this, leaching losses were reduced along with increasing biochar application rate during all leaching events, except in the last event (where the losses increased along with increasing biochar rate). The change to the P leachate trend, in the last event, is attributed to the overall variation between the biochar treatments for P sorption and desorption capacities. The control treatment had the lowest sorption capacity; therefore, it released the highest levels of P during the first leaching events. However, the P sorption capacity increased in the biochar-amended soil, resulting in slow and gradual losses of P. This eventually caused the losses from these treatments to be greater than the losses from the control treatment, at the last leaching event. The high capacity of biochar to retain multivalent cations, together with its ability to increase soil pH, contributed indirectly to the highest P sorption capacity of the biochar-amended soil by facilitating P to precipitate with $Ca^{2+}$ and $Mg^{2+}$. Soil aggregation was expected to improve with increased biochar application rate; this was most likely responsible for the associated increases in soil-water infiltration rate that were observed. On the other hand, the leaching losses of P were reduced with increasing biochar rates, regardless of the associated increase in water infiltration rates. This result indicated that the leaching losses of P were not corresponding to the soil-water infiltration rate meaning that biochar has a great capacity to reduce P losses, even with increased soil-water infiltration.

## 2.4 Biochar and manure application improved saline-sodic soil quality and spring wheat growth under greenhouse conditions

The biochar application rates (0, and 5%), levels of STP, and soil salinity conditions (saline-sodic and non-saline soils) had significant interaction that affected wheat growth and yield, as well as soil quality and fertilization. In the non-saline soil, the addition of manure alone caused a significant reduction in the seedling survival rate. The cause of that reduction is not clear but it possibly occurred due to nutrient toxicity as a result of the additional nutrients that were introduced with manure to that soil with initial fertile status. However, no such reduction occurred when manure addition was combined with biochar. The initial low survival rate in the control saline-sodic soil was increased only when a combination of manure and biochar was added. No significant changes occurred in yield amongst all treatments of the non-saline soil. Biochar addition did cause a significant increase in the yield of wheat plants in the saline-sodic soil, but this increase was more pronounced when biochar was added in combination with manure. Relative to the control treatments for both soils, the addition of biochar or manure alone did not increase either shoot dry matter or total dry matter. Yet both parameters increased significantly when biochar and manure were added in a combination. For both soils, spikelet weight, grain weight, and numbers of grain per plant showed the highest values in the treatments with low survival rate of control saline-sodic soil and non-saline soil that received manure only (S0%- and N0% +, respectively), as well as in the treatments that received a combination of manure and biochar. Generally, for each individual soil, all plant parameters were highest in the combined biochar and manure treatments. Furthermore, the plant parameters in the combined biochar and manure treatment were higher in the saline-sodic soil than in the non-saline soil. The factors studied showed no significant interaction effects on the concentration of most macronutrients in plant shoots but biochar application did generally increase the concentration of some macronutrients in plant shoots, including N, Mg, and K. However, biochar decreased the concentration of P and S, while none of the studied factors caused significant effect on Ca concentration in plant shoots. On the other hand, the concentrations of micronutrients in plant shoots were above the adequate level for optimal crop yield; no pronounced effects of biochar were found on these nutrients, except for Mn, the concentration of which was reduced in the plant shoots due to biochar application. The available N ($NO_3^-$ and $NH_4^+$) and S were highest in the soils that received the biochar and manure combined treatment. The availability of P and K was highest in the saline-sodic soil, and it increased significantly with biochar addition.

Plant growth and yield, as well as other plant parameters, were positively enhanced due to biochar addition. However, the advantages of using biochar are highest when it is combined with manure addition, particularly in saline-sodic soil. Plant competition was low in the treatment with low SR; therefore, plants in these treatments produced spikelets with the highest weight, and with the highest number of grains per spikelet. However, these parameters in the low SR were not significantly different from those in the biochar and manure combined treatments. Furthermore, the manure and biochar combined treatment produced the highest plant growth and yield. The advantages of biochar, for saline-sodic soil reclamation, are attributed to 1) its ability to increase water leaching, which facilitates salt movement away from the root zone; 2) its ability to increase soil-water holding capacity, which in turn reduces the water stress that is common in such saline conditions; and 3) its unique ability to hold nutrients in available form is important, as reflected in the increased nutrient uptake by the plants that was obtained. Yet, because biochar is not a source of nutrients, its application had to be combined with that of a fertilizer source, such as manure or inorganic fertilizer.

## 3. Suggestions for Future Research

### 3.1 Effects of salinity source on P sorption capacity of biochar

In this study, only NaCl was used to produce solutions with different salinity levels, to evaluate the influence of salinity on P sorption. The influence of each single ion on P sorption could be different than that of the others. For instance, P sorption decreased in solutions with either $K^+$ or $NH_4^+$, in comparison to the case of a solution with $Ca_2^+$. The sorption also decreased more significantly, in solutions with either $SO_4^{2-}$ or $NO_3^-$, than in those with $HCO_3^-$ (Shaheen et al. 2009). Naturally, saline solutions consist of various quantities of multivalent ions. The influence of such natural saline solutions on P sorption may also be different than in the case where simple ions of NaCl are present. Therefore, evaluating the effects of salinity source on the P sorption capacity of biochar, by comparing varies saline solutions containing different combinations of ions, would be valuable to better understand these effects. We expected that P sorption capacity of biochar would increase with increasing multivalent ions in saline solution due to the well known important influence of such ions on increasing P precipitation depending on solution pH.

### 3.2 Effects of manure on evaluating crop responses to biochar treatments

The soils used in the study were initially fertile, and no fertilization was required. However, manure was added to keep the soil treatments the same as those used in a previous, connected soil column leaching study in which the optimal biochar application rate (5%) had been selected. Manure addition caused significant increases in crop growth and yield when combined with biochar application, yet manure reduced crop yield and growth when it was added alone. The reasons for this were not clear, but such a reduction could be due to excessive addition of nutrients along with the manure. A study should thus be conducted to determine the specific effects of manure on crop growth and yield, either by using infertile soil or by establishing nutrient toxicity. Another option would be the use of inorganic fertilizers, instead of manure, to create the required levels of soil nutrients without the need to consider possible confounding effects due to manure addition.

### 3.3 Effects of biochar on soil microbes and in turn on plant production could vary based on salinity condition

In this study, enhanced crop growth and production were attributed to the role of biochar in improving soil properties. These improvements included increased soil pH, which is essential for nutrient retention and availability (particularly that of P); increasing soil-water holding capacity, which in turn reduces water stresses; and increasing infiltration rate, which facilitates salt leaching. In addition, plant growth and production are known to be influenced by many soil microorganisms, such as fungi and bacteria. It is well known that biochar has strong influence on soil microorganisms under non-saline conditions. However, not much attention has been paid to its influence under saline conditions. Further research is thus needed, to investigate the effects of biochar on soil microorganisms, as well as to link the plants' responses, which are obtained under the use of such treatments, with the influence of biochar. We expected that the great roles of biochar for reducing salinity, and increasing soil moisture content and nutrient availability would in turn increase the growth of microorganisms and the biological activity of the biochar amended saline-sodic soil. The increases of soil microbes particularly that form symbiotic relationship with plant roots such as Mycorrhizae would definitely participate in the increased plant growth and yield.

## REFERENCES

**Ahmad, M., Moon, D. H., Vithanage, M., Koutsospyros, A., Lee, S. S., Yang, J. E., Lee, S. E., Jeon, C. and Ok, Y. S. 2014.** Production and use of biochar from buffalo-weed (Ambrosia trifida L.) for trichloroethylene removal from water. J Chem Technol Biotechnol 89:150-157.

**Akbarimoghaddam, H., Galavi, M., Ghanbari, A. and Panjehkeh, N. 2011**. Salinity effects on seed germination and seedling growth of bread wheat cultivars. Trakia Journal of Sciences 9(1):43-50.

**Akhtar, S., Andersen, M. N. and Liu, F. 2015a**. Biochar mitigates salinity stress in potato. Journal of Agronomy and Crop Science 201(5):368-378.

**Akhtar, S. S., Andersen, M. N. and Liu, F. 2015b**. Residual effects of biochar on improving growth, physiology and yield of wheat under salt stress. Agricultural Water Management 158:61-68.

**Alam, S. 1981**. Effects of solution pH on the growth and chemical composition of rice plants. Journal of Plant Nutrition 4(3):247-260.

**America, S. S. S. o. 2008**. Glossary of soil science terms 2008. ASA-CSSA-SSSA.

**Amirjani, M. 2010**. Effect of salinity stress on growth, mineral composition, proline content, antioxidant enzymes of soybean. American Journal of Plant Physiology 5(6):350-360.

**Amonette, J. E. and Joseph, S. 2009**. Characteristics of biochar: microchemical properties. Pages 33-52 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: Science and Technology, London: Earthscan.

**Andersson, H., Bergström, L., Djodjic, F., Ulén, B. and Kirchmann, H. 2013**. Topsoil and subsoil properties influence phosphorus leaching from four agricultural soils. Journal of Environmental Quality 42(2):455-463.

**Andriolo, J. L., Luz, G. L. d., Witter, M. H., Godoi, R. d. S., Barros, G. T. and Bortolotto, O. C. 2005**. Growth and yield of lettuce plants under salinity. Horticultura Brasileira 23(4):931-934.

**Antal, M. J. and Grønli, M. 2003**. The art, science, and technology of charcoal production. Industrial & Engineering Chemistry Research 42(8):1619-1640.

**Arai, Y. and Sparks, D. 2007**. Phosphate reaction dynamics in soils and soil components: A multiscale approach. Advances in Agronomy 94:135-179.

**Arnold, P. 1978**. Surface-electrolyte interactions. Pages 135-179 in D. J. and Hayes, M. H. B, eds. The chemistry of soil constituents. Wiley-Interscience, New York.

**Asai, H., Samson, B. K., Stephan, H. M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T. and Horie, T. 2009**. Biochar amendment techniques for upland rice production in Northern Laos: 1. Soil physical properties, leaf SPAD and grain yield. Field Crops Research 111(1):81-84.

**Ashraf, M. 2004**. Some important physiological selection criteria for salt tolerance in plants. Flora-Morphology, Distribution, Functional Ecology of Plants 199(5):361-376.

**Ashworth, J. and Mrazek, K. 1995**. "Modified Kelowna" test for available phosphorus and potassium in soil. Communications in Soil Science and Plant Analysis 26(5-6):731-739.

**Atkinson, C. J., Fitzgerald, J. D. and Hipps, N. A. 2010**. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337(1-2):1-18.

**Aygün, A., Yenisoy-Karakaş, S. and Duman, I. 2003**. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials 66(2):189-195.

**Ayodele, A., Oguntunde, P., Joseph, A., Junior, D. and de Souza, M. 2009**. Numerical analysis of the impact of charcoal production on soil hydrological behavior, runoff response and erosion susceptibility. Revista Brasileira de Ciência do Solo 33(1):137-146.

**Bagreev, A., Bandosz, T. J. and Locke, D. C. 2001**. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. Carbon 39(13):1971-1979.

**Bai, Z., Li, H., Yang, X., Zhou, B., Shi, X., Wang, B., Li, D., Shen, J., Chen, Q. and Qin, W. 2013**. The critical soil P levels for crop yield, soil fertility and environmental safety in different soil types. Plant and Soil 372(1-2):27-37.

**Bano, A. and Fatima, M. 2009**. Salt tolerance in Zea mays (L). following inoculation with Rhizobium and Pseudomonas. Biology and Fertility of Soils 45(4):405-413.

**Bar-Yosef, B., Rosenberg, R., Kafkafi, U. and Sposito, G. 1988**. Phosphorus adsorption by kaolinite and montmorillonite: I. Effect of time, ionic strength, and pH. Soil Science Society of America Journal 52(6):1580-1585.

**Barrow, N. 1974**.The slow reactions between soil and anions:1. Effects of time, temperture, and water content of a soil on the decrease in effectiveness of phosphate for plant growth. Soil Science. Soil Science 118(6):380-386.

**Barrow, N. and Carter, E. 1978**. A modified model for evaluating residual phosphate in soil. Crop and Pasture Science 29(5):1011-1021.

**Barzegar, A. R., Nelson, P. N., Oades, J. M. and Rengasamy, P. 1997**. Organic matter, sodicity, and clay type: Influence on soil aggregation. Soil Science Society of America Journal 61(4):1131-1137.

**Beck, D. A., Johnson, G. R. and Spolek, G. A. 2011**. Amending greenroof soil with biochar to affect runoff water quantity and quality. Environmental Pollution 159(8):2111-2118.

**Beaton, J., Peterson, H. and Bauer, N. 1960**. Some aspects of phosphate adsorption by charcoal. Soil Science Society of America Journal 24(5):340-346.

**Ben-Hayyim, G., Kafkafi, U. and Ganmore-Neumann, R. 1987**. Role of internal potassium in maintaining growth of cultured citrus cells on increasing NaCl and $CaCl_2$ concentrations. Plant Physiology 85(2):434-439.

**Berg, A. and Joern, B. 2006**. Sorption dynamics of organic and inorganic phosphorus compounds in soil. Journal of Environmental Quality 35(5):1855-1862.

**Bergström, L., Bowman, B. and Sims, J. 2005**. Definition of sustainable and unsustainable issues in nutrient management of modern agriculture. Soil Use and Management 21(1):76-81.

**Bernstein, L., Francois, L. and Clark, R. 1974**. Interactive effects of salinity and fertility on yields of grains and vegetables. Agronomy Journal 66(3):412-421.

**Blanco, H. and Lal, R. 2010**. Soil and water conservation. Blanco, H and R Lal:1-19.

**Blaylock, A. D. 1994**. Soil salinity, salt tolerance, and growth potential of horticultural and landscape plants. University of Wyoming, Cooperative Extension Service, Department of Plant, Soil, and Insect Sciences, College of Agriculture.

**Borda, T., Celi, L., Zavattaro, L., Sacco, D. and Barberis, E. 2011**. Effect of agronomic management on risk of suspended solids and phosphorus losses from soil to waters. Journal of Soils and Sediments 11(3):440-451.

**Brennan, J. K., Bandosz, T. J., Thomson, K. T. and Gubbins, K. E. 2001**. Water in porous carbons. Colloids and surfaces A: Physicochemical and Engineering Aspects 187:539-568.

**Brockhoff, S. R., Christians, N. E., Killorn, R. J., Horton, R. and Davis, D. D. 2010**. Physical and mineral-nutrition properties of sand-based turfgrass root zones amended with biochar. Agronomy Journal 102(6):1627-1631.

**Brown, R. 2009**. Biochar production technology. Biochar for environmental management: Science and Technology:127-146.

**Bromfield, S. 1965**. Studies of the relative importance of iron and aluminium in the sorption of phosphate by some australian soils. Soil Research 3(1):31-44.

**Brookes, P., Heckrath, G., Smet, J. d., Hofman, G., Vanderdeelen, J., Tunney, H., Carton, O. and Johnston, A. 1997**. Losses of phosphorus in drainage water. Proc. Phosphorus loss from soil to water. Proceedings of a workshop, Wexford, Irish Republic, 29-31 September 1995.

**Buecker, J., Kloss, S., Wimmer, B., Rempt, F., Zehetner, F. and Soja, G. 2016**. Leachate composition of temperate agricultural soils in response to biochar application. Water, Air, & Soil Pollution 227(2):49.

**Campbell, K. L. and Edwards, D. R. 2001**. Phosphorus and water quality impacts, Phosphorus and water quality impacts, Agricultural nonpoint source pollution -Watershed management and hydrology, Lewis Publishers 91-109.

**Canadian Council of Ministers of the Environment. 2004.** Canadian water quaility guidelines for the protection of aquatic life: Phosphorus: Canadian Guidance Framework for the Management of Freshwater System. In: Canadian Environmental Quality Guidelines, 2004, Canadian Council of Ministers of the environment, Winnipeg. Excerpt from Publication No. 1299;ISBN 1-896997-34-1

**Caputo, A. C., Palumbo, M., Pelagagge, P. M. and Scacchia, F. 2005.** ‘Economics of biomass energy utilization in combustion and gasification plants: Effects of logistic variables’, Biomass and Bioenergy 28: 35–51.

**Cao, X., Ma, L., Gao, B. and Harris, W. 2009**. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environmental Science & Technology 43(9):3285-3291.

**Chaganti, V. N., Crohn, D. M. and Šimůnek, J. 2015**. Leaching and reclamation of a biochar and compost amended saline–sodic soil with moderate SAR reclaimed water. Agricultural Water Management 158:255-265.

**Chambers, B., Smith, K. and Pain, B. 2000**. Strategies to encourage better use of nitrogen in animal manures. Soil Use and Management 16(s1):157-166.

**Chan, K., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. 2008a**. Agronomic values of greenwaste biochar as a soil amendment. Soil Research 45(8):629-634.

**Chan, K., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. 2008b**. Using poultry litter biochars as soil amendments. Soil Research 46(5):437-444.

**Chan, K. Y. and Xu, Z. 2009**. Biochar: nutrient properties and their enhancement. Biochar for environmental management: Science and Technology 1:67-84.

**Chardon, W., Aalderink, G. and Van der Salm, C. 2007**. Phosphorus leaching from cow manure patches on soil columns. Journal of Environmental Quality 36(1):17-22.

**Chen, B., Chen, Z. and Lv, S. 2011**. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresource Technology 102(2):716-723.

**Chen, B., Zhou, D. and Zhu, L. 2008a**. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environmental Science & Technology 42(14):5137-5143.

**Chen, H. and Jiang, J.-G. 2010**. Osmotic adjustment and plant adaptation to environmental changes related to drought and salinity. Environmental Reviews 18(NA):309-319.

**Chen, M., Chen, J. and Sun, F. 2008b**. Agricultural phosphorus flow and its environmental impacts in China. Science of the Total Environment 405(1):140-152.

**Chen, Z., Pottosin, I. I., Cuin, T. A., Fuglsang, A. T., Tester, M., Jha, D., Zepeda-Jazo, I., Zhou, M., Palmgren, M. G. and Newman, I. A. 2007**. Root plasma membrane transporters controlling $K^+/Na^+$ homeostasis in salt-stressed barley. Plant Physiology 145(4):1714-1725.

**Cheng, C.-H., Lehmann, J. and Engelhard, M. H. 2008**. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72(6):1598-1610.

**Cheng, C.-H., Lehmann, J., Thies, J. E., Burton, S. D. and Engelhard, M. H. 2006**. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37(11):1477-1488.

**Chinnusamy, V., Jagendorf, A. and Zhu, J. K. 2005.** Understanding and improving salt tolerance in plants. Crop Science 45:437- 448.

**Chintala, R., Schumacher, T. E., McDonald, L. M., Clay, D. E., Malo, D. D., Papiernik, S. K., Clay, S. A. and Julson, J. L. 2014.** Phosphorus sorption and availability from biochars and soil/biochar mixtures. Clean Soil Air Water 42:626- 634.

**Chien, S. and Clayton, W. 1980**. Application of elovich equation to the kinetics of phosphate release and sorption in soils. Soil Science Society of America Journal 44(2):265-268.

**Chintala, R., Schumacher, T. E., McDonald, L. M., Clay, D. E., Malo, D. D., Papiernik, S. K., Clay, S. A. and Julson, J. L. 2014**. Phosphorus sorption and availability from biochars and soil/biochar mixtures. Clean Soil, Air, Water 42(5):626-634.

**Chun, Y., Sheng, G., Chiou, C. T. and Xing, B. 2004**. Compositions and sorptive properties of crop residue-derived chars. Environmental Science and Technology 38(17):4649-4655.

**Clavero, V., Fernandez, J. and Niell, F. 1990**. Influence of salinity on the concentration and rate of interchange of dissolved phosphate between water and sediment in Fuente Piedra lagoon (S. Spain). Hydrobiologia 197(1):91-97.

**Coelho, B. B., Murray, R., Lapen, D., Topp, E. and Bruin, A. 2012**. Phosphorus and sediment loading to surface waters from liquid swine manure application under different drainage and tillage practices. Agricultural Water Management 104:51-61.

**Collison, M., Collison, L., Sakrabani, R., Tofield, B. and Wallage, Z. 2009**. Biochar and carbon sequestration: a regional perspective. Norwich, UK: The Low Carbon Innovation Centre, University of East Anglia.(A report prepared for East of England Development Agency (EEDA), DA1 Carbon Reduction Ref. No: 7049).

**Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A. and van Noort, P. C. 2005**. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environmental Science and Technology 39(18):6881-6895.

**Correll, D. 1999**. Phosphorus: a rate limiting nutrient in surface waters. Poultry Science 78(5):674-682.

**Csathó, P., Sisák, I., Radimszky, L., Lushaj, S., Spiegel, H., Nikolova, M., Nikolov, N., Čermák, P., Klir, J. and Astover, A. 2007**. Agriculture as a source of phosphorus causing eutrophication in Central and Eastern Europe. Soil Use and Management 23(s1):36-56.

**Day, D., Evans, R. J., Lee, J. W. and Reicosky, D. 2005**. Economical $CO_2$, $SO_x$, and $NO_x$ capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration. Energy 30(14):2558-2579.

**DeLuca, T. H., Gundale, M. J., MacKenzie, M. D. and Jones, D. L. 2015**. Biochar effects on soil nutrient transformations. Biochar for environmental management: Science, Technology and Implementation 2:421-454.

**Demirbas, A. 2004**. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. Journal of Analytical and Applied Pyrolysis 72(2):243-248.

**Dempster, D., Gleeson, D., Solaiman, Z. I., Jones, D. and Murphy, D. 2012**. Decreased soil microbial biomass and nitrogen mineralisation with eucalyptus biochar addition to a coarse textured soil. Plant and Soil 354(1-2):311-324.

**Ding, Y., Liu, Y. X., Wu, W. X., Shi, D. Z., Yang, M. and Zhong, Z.-K. 2010**. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, and Soil Pollution 213(1-4):47-55.

**Downie, A., Crosky, A. and Munroe, P. 2009**. Physical properties of biochar. pages 13-32 in  in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: Science and Technology, London: Earthscan.

**Dume, B., Mosissa, T. and Nebiyu, A. 2016. Effect of biochar on soil properties and lead (Pb) availability in a military camp in South West Ethiopia. African Journal of Environmental Science and Technology 10:77- 85.Eberhardt, T. L., Min, S. H. and Han, J. S. 2006**. Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride. Bioresource Technology 97(18):2371-2376.

**Edwards, A. and Withers, P. 1998**. Soil phosphorus management and water quality: a UK perspective. Soil Use and Management 14(s4):124-130.

**Edwards, D. and Daniel, T. 1994**. Quality of runoff from fescuegrass plots treated with poultry litter and inorganic fertilizer. Journal of Environmental Quality 23(3):579-584.

**Farrell, M., Macdonald, L. M., Butler, G., Chirino-Valle, I. and Condron, L. M. 2014**. Biochar and fertiliser applications influence phosphorus fractionation and wheat yield. Biology and Fertility of Soils 50(1):169-178.

**Flowers, T. and Yeo, A. 1995**. Breeding for salinity resistance in crop plants: where next? Functional Plant Biology 22(6):875-884.

**Fowles, M., 2007**. Black carbon sequestration as an alternative to bioenergy. Biomass and Bioenergy 31(6): 426-432.

**Fukuyama, K., Kasahara, Y., Kasahara, N., Oya, A. and Nishikawa, K. 2001**. Small-angle X-ray scattering study of the pore structure of carbon fibers prepared from a polymer blend of phenolic resin and polystyrene. Carbon 39(2):287-290.

**Gavin, D. G., Brubaker, L. B. and Lertzman, K. P. 2003**. Holocene fire history of a coastal temperate rain forest based on soil charcoal radiocarbon dates. Ecology 84(1):186-201.

**Gadallah, M. 1996**. Abscisic acid, temperature and salinity interactions on growth and some mineral elements in Carthamus plants. Plant Growth Regulation 20(3):225-236.

**Gartley, K. and Sims, J. 1994**. Phosphorus soil testing: Environmental uses and implications. Communications in Soil Science and Plant Analysis 25(9-10):1565-1582.

**Gaskin, J., Steiner, C., Harris, K., Das, K. and Bibens, B. 2008**. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Transactions of the Asabe 51(6):2061-2069.

**Gaskin, J. W., Speir, R. A., Harris, K., Das, K., Lee, R. D., Morris, L. A. and Fisher, D. S. 2010**. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agronomy Journal 102(2):623-633.

**Gaunt, J. L. and Lehmann, J. 2008**. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. Environmental Science and Technology 42(11):4152-4158.

**Gavin, D. G., Brubaker, L. B. and Lertzman, K. P. 2003**. Holocene fire history of a coastal temperate rain forest based on soil charcoal radiocarbon dates. Ecology 84(1):186-201.

**Gavlak, R., Horneck, D., Miller, R. O. and Kotuby-Amacher, J. 2003**. Soil, plant and water reference methods for the western region. WCC-103 Publication, WREP-125:17-36.

**Genesio, L., Miglietta, F., Lugato, E., Baronti, S., Pieri, M. and Vaccari, F. 2012**. Surface albedo following biochar application in durum wheat. Environmental Research Letters 7(1):014025.

**George, C., Wagner, M., Kücke, M. and Rillig, M. C. 2012**. Divergent consequences of hydrochar in the plant–soil system: arbuscular mycorrhiza, nodulation, plant growth and soil aggregation effects. Applied Soil Ecology 59:68-72.

**Gerente, C., Lee, V. K. C., Cloirec, P. L. and McKay, G. 2007.** Application of chitosan for the removal of metals from wastewaters by adsorption-mechanisms and models review. Critical Reviews in Environmental Science and Technology 37:41-127.

**Ghafoor, A., Gill, M., Hassan, A., Murtaza, G. and Qadir, M. 2001**. Gypsum: an economical amendment for amelioration of saline-sodic waters and soils and for improving crop yields. International Journal of Agriculture and Biology 3:266-275.

**Gharaibeh, M., Eltaif, N. and Albalasmeh, A. 2011**. Reclamation of highly calcareous saline sodic soil using Atriplex halimus and by-product gypsum. International Journal of Phytoremediation 13(9):873-883.

**Glaser, B., Lehmann, J. and Zech, W. 2002**. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal-a review. Biology and Fertility of Soils 35(4):219-230.

**Glozier, N., Elliott, J., Holliday, B., Yarotski, J. and Harker, B. 2006**. Water quality characteristics and trends in a small agricultural watershed: South Tobacco Creek, Manitoba, 1992–2001. Environment Canada, Ottawa, ON.

**Gouveia, S., Pessenda, L., Aravena, R., Boulet, R., Scheel-Ybert, R., Bendassoli, J., Ribeiro, A. and Freitas, H. 2002**. Carbon isotopes in charcoal and soils in studies of paleovegetation and climate changes during the late Pleistocene and the Holocene in the southeast and centerwest regions of Brazil. Global and Planetary Change 33(1):95-106.

**Grattan, S. and Grieve, C. 1998**. Salinity–mineral nutrient relations in horticultural crops. Scientia Horticulturae 78(1):127-157.

**Green, D. B., Logan, T. J. and Smeck, N. E. 1978**. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio. Journal of Environmental Quality 7(2):208-212.

**Grieve, C. and Grattan, S. 1999.** "Mineral nutrient acquisition and response by plants grown in saline environments". Pages 203-229 in Handbook of Plant and Crop Stress, Second Edition. CRC Press.

**Guo, Y. and Rockstraw, D. A. 2007**. Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. Bioresource Technology 98(8):1513-1521.

**Gupta, R. K. and Abrol, I. 1990.** Salt-affected soils: their reclamation and management for crop production. Advances in soil science. Springer. New York 223-288.

**Hale, S., Alling, V., Martinsen, V., Mulder, J., Breedveld, G. and Cornelissen, G. 2013**. The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere 91(11):1612-1619.

**Herath, H., Camps-Arbestain, M. and Hedley, M. 2013**. Effect of biochar on soil physical properties in two contrasting soils: an Alfisol and an Andisol. Geoderma 209:188-197.

**Hardie, M., Clothier, B., Bound, S., Oliver, G. and Close, D. 2014**. Does biochar influence soil physical properties and soil water availability? Plant and Soil 376(1-2):347-361.

**Huang, W., Lu, Y., Li, J., Zheng, Z., Zhang, J. and Jiang, X. 2015**. Effect of ionic strength on phosphorus sorption in different sediments from a eutrophic plateau lake. RSC Advances 5(97):79607-79615.

**Ilyas, M., Qureshi, R. and Qadir, M. 1997**. Chemical changes in a saline-sodic soil after gypsum application and cropping. Soil Technology 10(3):247-260.

**Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R. and Cao, X. 2011**. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. Separation Science and Technology 46(12):1950-1956.

**Inyang, M., Gao, B., Pullammanappallil, P., Ding, W. and Zimmerman, A. R. 2010**. Biochar from anaerobically digested sugarcane bagasse. Bioresource Technology 101(22):8868-8872.

**Islam, A. K., Edwards, D. and Asher, C. 1980**. pH optima for crop growth. Plant and Soil 54(3):339-357.

**Jalali, M. and Ranjbar, F. 2009**. Effects of sodic water on soil sodicity and nutrient leaching in poultry and sheep manure amended soils. Geoderma 153(1):194-204.

**James, D. W., Hanks, R. J. and Jurinak, J. J. 1982**. Modern irrigated soils. Wiley. New York.

**Jariel, D., Wallace, S., Jones, U. and Samonte, H. 1991**. Growth and nutrient composition of maize genotypes in acid nutrient solutions. Agronomy Journal 83(3):612-617.

**Jeffery, S., Verheijen, F. G., Van Der Velde, M. and Bastos, A. C. 2011**. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agriculture, Ecosystems and Environment 144(1):175-187.

**Ji, L., Wan, Y., Zheng, S. and Zhu, D. 2011**. Adsorption of tetracycline and sulfamethoxazole on crop residue-derived ashes: implication for the relative importance of black carbon to soil sorption. Environmental Science and Technology 45(13):5580-5586.

**Jien, S.-H. and Wang, C.-S. 2013**. Effects of biochar on soil properties and erosion potential in a highly weathered soil. Catena 110:225-233.

**Jones, D., Rousk, J., Edwards-Jones, G., DeLuca, T. and Murphy, D. 2012**. Biochar-mediated changes in soil quality and plant growth in a three year field trial. Soil Biology and Biochemistry 45:113-124.

**Joseph, S., Peacocke, C., Lehmann, J. and Munroe, P. 2009**. Developing a biochar classification and test methods. Pages 107-126 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: London, England: Earthscan.

**Jun, M., Altor, A. E. and Craft, C. B. 2013**. Effects of increased salinity and inundation on inorganic nitrogen exchange and phosphorus sorption by tidal freshwater floodplain forest soils, Georgia (USA). Estuaries and Coasts 36(3):508-518.

**Jung, K.-W., Hwang, M.-J., Ahn, K.-H. and Ok, Y.-S. 2015**. Kinetic study on phosphate removal from aqueous solution by biochar derived from peanut shell as renewable adsorptive media. International Journal of Environmental Science and Technology 12(10):3363-3372.

**Kammann, C. I., Linsel, S., Gößling, J. W. and Koyro, H.-W. 2011**. Influence of biochar on drought tolerance of Chenopodium quinoa Willd and on soil–plant relations. Plant and Soil 345(1-2):195-210.

**Kang, J., Amoozegar, A., Hesterberg, D. and Osmond, D. L. 2011**. Phosphorus leaching in a sandy soil as affected by organic and inorganic fertilizer sources. Geoderma 161(3):194-201.

**Karunanithi, R., Szogi, A. A., Bolan, N., Naidu, R., Loganathan, P., Hunt, P. G., Vanotti, M. B., Saint, C. P., Ok, Y. S. and Krishnamoorthy, S. 2015**. Chapter Three-Phosphorus Recovery and Reuse from Waste Streams. Advances in Agronomy 131:173-250.

**Keiluweit, M., Nico, P. S., Johnson, M. G. and Kleber, M. 2010**. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environmental Science and Technology 44(4):1247-1253.

**Khoshgoftarmanesh, A. H. and Nourbakhsh, F. 2009**. Salinity and plant residue effects on soil available phosphorus. Journal of Plant Nutrition 32(6):954-966.

**Kim, S.-S., Agblevor, F. A. and Lim, J. 2009**. Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. Journal of Industrial and Engineering Chemistry 15(2):247-252.

**Kinniburgh, D. G. 1986**. General purpose adsorption isotherms. Environmental Science and Technology 20(9):895-904.

**Kirkham, M. B. 2014**. Principles of soil and plant water relations. Academic Press.

**Kjearsgaard, A. 1983**. Soil survey of the county of Newell, Alberta. Research Branch, Agriculture Canada.

**Kleinman, P., Sullivan, D., Wolf, A., Brandt, R., Dou, Z., Elliott, H., Kovar, J., Leytem, A., Maguire, R. and Moore, P. 2007**. Selection of a water-extractable phosphorus test for manures and biosolids as an indicator of runoff loss potential. Journal of Environmental Quality 36(5):1357-1367.

**Kleinman, P. J., Sharpley, A. N., Saporito, L. S., Buda, A. R. and Bryant, R. B. 2009**. Application of manure to no-till soils: phosphorus losses by sub-surface and surface pathways. Nutrient Cycling in Agroecosystems 84(3):215-227.

**Kleinman, P. J., Srinivasan, M., Dell, C. J., Schmidt, J. P., Sharpley, A. N. and Bryant, R. B. 2006**. Role of rainfall intensity and hydrology in nutrient transport via surface runoff. Journal of Environmental Quality 35(4):1248-1259.

**Kleinman, P. J., Srinivasan, M., Sharpley, A. N. and Gburek, W. J. 2005**. Phosphorus leaching through intact soil columns before and after poultry manure application. Soil Science 170(3):153-166.

**Knowles, O., Robinson, B., Contangelo, A. and Clucas, L. 2011**. Biochar for the mitigation of nitrate leaching from soil amended with biosolids. Science of The Total Environment 409(17):3206-3210.

**Koopmans, G., Chardon, W. and McDowell, R. 2007**. Phosphorus movement and speciation in a sandy soil profile after long-term animal manure applications. Journal of Environmental Quality 36(1):305-315.

**Koopmans, G., Chardon, W. and Van der Salm, C. 2005**. Disturbance of water-extractable phosphorus determination by colloidal particles in a heavy clay soil from the Netherlands. Journal of Environmental Quality 34(4):1446-1450.

**Koutcheiko, S., Monreal, C., Kodama, H., McCracken, T. and Kotlyar, L. 2007**. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. Bioresource Technology 98(13):2459-2464.

**Kronvang, B., Bechmann, M., Lundekvam, H., Behrendt, H., Rubæk, G. H., Schoumans, O., Syversen, N., Andersen, H. E. and Hoffmann, C. C. 2005**. Phosphorus losses from agricultural areas in river basins. Journal of Environmental Quality 34(6):2129-2144.

**Kumar, P., Sudha, S., Chand, S. and Srivastava, V. C. 2010**. Phosphate removal from aqueous solution using coir-pith activated carbon. Separation Science and Technology 45(10):1463-1470.

**Lai, D. Y. and Lam, K. C. 2009**. Phosphorus sorption by sediments in a subtropical constructed wetland receiving stormwater runoff. Ecological Engineering 35(5):735-743.

**Laird, D., Fleming, P., Wang, B., Horton, R. and Karlen, D. 2010a**. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158(3):436-442.

**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 Journal 100(1):178-181.

**Laird, D. A., Fleming, P., Davis, D. D., Horton, R., Wang, B. and Karlen, D. L. 2010b**. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158(3):443-449.

**Lakhdar, A., Rabhi, M., Ghnaya, T., Montemurro, F., Jedidi, N. and Abdelly, C. 2009**. Effectiveness of compost use in salt-affected soil. Journal of Hazardous Materials 171(1):29-37.

**Lashari, M. S., Liu, Y., Li, L., Pan, W., Fu, J., Pan, G., Zheng, J., Zheng, J., Zhang, X. and Yu, X. 2013**. Effects of amendment of biochar-manure compost in conjunction with pyroligneous solution on soil quality and wheat yield of a salt-stressed cropland from Central China Great Plain. Field Crops Research 144:113-118.

**Lawrinenko, M. and Laird, D. A. 2015**. Anion exchange capacity of biochar. Green Chemistry 17(9):4628-4636.

**Lee, J. W., Kidder, M., Evans, B. R., Paik, S., Buchanan Iii, A., Garten, C. T. and Brown, R. C. 2010**. Characterization of biochars produced from cornstovers for soil amendment. Environmental Science and Technology 44(20):7970-7974.

**Lehmann, J. 2007**. Bio-energy in the black. Frontiers in Ecology and the Environment 5(7):381-387.

**Lehmann, J. and Joseph, S. 2009.** Biochar for environmental management: An introduction. Pages 1-12 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: London, England: Earthscan.

**Lehmann, J. and Joseph, S. 2015**. Biochar for environmental management: An Introduction. Pages 1-9 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: Science and Technology.

**Lehmann, J., Kuzyakov, Y., Pan, G. and Ok, Y. S. 2015.** Biochars and the plant-soil interface. Springer 395:1-5.

**Lehmann, J., Lan, Z., Hyland, C., Sato, S., Solomon, D. and Ketterings, Q. M. 2005**. Long-term dynamics of phosphorus forms and retention in manure-amended soils. Environmental Science and Technology 39(17):6672-6680.

**Lehmann, J., Pereira da Silva, J., Steiner, C., Nehls, T., Zech, W. and Glaser, B. 2003**. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant and Soil 249(2):343-357.

**Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'neill, B., Skjemstad, J., Thies, J., Luizao, F. and Petersen, J. 2006**. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70(5):1719-1730.

**Lima, I. M. and Marshall, W. E. 2005**. Granular activated carbons from broiler manure: physical, chemical and adsorptive properties. Bioresource Technology 96(6):699-706.

**Liu, T., Liu, B. and Zhang, W. 2014**. Nutrients and heavy metals in biochar produced by sewage sludge pyrolysis: its application in soil amendment. Polish Journal of Environmental Studies 23(1):271-275.

**Li, X., Shen, Q., Zhang, D., Mei, X., Ran, W., Xu, Y. and Yu, G. 2013.** Functional groups determine biochar properties (pH and EC) as studied by two-dimensional 13C NMR correlation spectroscopy. PLoS One 8:65949.

**Lou, K., Rajapaksha, A. U., Ok, Y. S. and Chang, S. X. 2016.** Pyrolysis temperature and steam activation effects on sorption of phosphate on pine sawdust biochars in aqueous solutions. Chemical Speciation & Bioavailability 28:42-50.

**Lobell, D. B., Ortiz-Monasterio, J. I., Gurrola, F. C. and Valenzuela, L. 2007**. Identification of saline soils with multiyear remote sensing of crop yields. Soil Science Society of America Journal 71(3):777-783.

**Maas, E. V. and Grattan, S. 1999**. Crop yields as affected by salinity. Agronomy 38:55-110.

**Maas, E. V. and Hoffman, G. J. 1977**. Crop salt tolerance\-current assessment. Journal of The Irrigation and Drainage Division 103(2):115-134.

**Mace, J. and Amrhein, C. 2001**. Leaching and reclamation of a soil irrigated with moderate SAR waters. Soil Science Society of America Journal 65(1):199-204.

**Madiba, O. F., Solaiman, Z. M., Carson, J. K. and Murphy, D. V. 2016**. Biochar increases availability and uptake of phosphorus to wheat under leaching conditions. Biology and Fertility of Soils 52(4):439-446.

**Mahmoodabadi, M., Yazdanpanah, N., Sinobas, L. R., Pazira, E. and Neshat, A. 2013**. Reclamation of calcareous saline sodic soil with different amendments (I): Redistribution of soluble cations within the soil profile. Agricultural Water Management 120:30-38.

**Major, J., Rondon, M., Molina, D., Riha, S. J. and Lehmann, J. 2010**. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant and Soil 333(1-2):117-128.

**Major, J., Steiner, C., Downie, A. and Lehmann, J. 2009**. Biochar effects on nutrient leaching. pages 271-287 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: London, England: Earthscan.

**Major, J., 2010**. Guidelines on practical aspects of biochar application to field soil in various soil management systems. International Biochar Initiative, 8.

**Manchanda, G. and Garg, N. 2008**. Salinity and its effects on the functional biology of legumes. Acta Physiologiae Plantarum 30(5):595-618.

**Mao, J.-D., Johnson, R., Lehmann, J., Olk, D., Neves, E. G., Thompson, M. and Schmidt-Rohr, K. 2012**. Abundant and stable char residues in soils: implications for soil fertility and carbon sequestration. Environmental Science and Technology 46(17):9571-9576.

**Martinez-Beltran, J. and Manzur, C. L. 2005**. Overview of salinity problems in the world and FAO strategies to address the problem. Proceedings of The International Salinity Forum, Riverside, California 311-313.

**Masoud, A. and Koike, K. 2006**. Arid land salinization detected by remotely-sensed landcover changes: A case study in the Siwa region, NW Egypt. Journal of Arid Environments 66(1):151-167.

**McLaughlin, H., Anderson, P. S., Shields, F. E. and Reed, T. B. 2009**. All biochars are not created equal, and how to tell them apart. Proceedings, North American Biochar Conference, Boulder, Colorado.

**Mia, S., Dijkstra, F.A. and Singh, B. 2017**. Aging induced changes in biochar's functionality and adsorption behavior for phosphate and ammonium. Environmental Science & Technology, 51(15): 8359-8367.

**Mikan, C. J. and Abrams, M. D. 1995**. Altered forest composition and soil properties of historic charcoal hearths in southeastern Pennsylvania. Canadian Journal of Forest Research 25(5):687-696.

**Mikan, C. J. and Abrams, M. D. 1996**. Mechanisms inhibiting the forest development of historic charcoal hearths in southeastern Pennsylvania. Canadian Journal of Forest Research 26(11):1893-1898.

**Morse, G., Brett, S., Guy, J. and Lester, J. 1998**. Review: phosphorus removal and recovery technologies. Science of The Total Environment 212(1):69-81.

**Motts, C. J. B. 1981.** Anion and ligand exchange. Pages 179-220 in D. J. Greenland, and M. H. B. Hayes, eds. The chemistry of soil processes. Wiley Interscience, New York.

**Mueller, D., Wendt, R. and Daniel, T. 1984**. Phosphorus losses as affected by tillage and manure application. Soil Science Society of America Journal 48(4):901-905.

**Mukherjee, A., Zimmerman, A. and Harris, W. 2011**. Surface chemistry variations among a series of laboratory produced biochars. Geoderma 163(3):247-255.

**Mukherjee, A. and Lal, R. 2013**. Biochar impacts on soil physical properties and greenhouse gas emissions. Agronomy 3(2):313-339.

**Mukherjee, A. and Zimmerman, A. R. 2013**. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures. Geoderma 193:122-130.

**Munns, R. 2002**. Comparative physiology of salt and water stress. Plant, Cell and Environment 25(2):239-250.

**Munns, R., James, R. A. and Läuchli, A. 2006**. Approaches to increasing the salt tolerance of wheat and other cereals. Journal of Experimental Botany 57(5):1025-1043.

**Murphy, J. and Riley, J. P. 1962**. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27:31-36.

**Nagajyoti, P., Lee, K. and Sreekanth, T. 2010**. Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters 8(3):199-216.

**Nair, P., Logan, T., Sharpley, A., Sommers, L., Tabatabai, M. and Yuan, T. 1984**. Interlaboratory comparison of a standardized phosphorus adsorption procedure. Journal of Environmental Quality 13(4):591-595.

**Navarro, A., Cegarra, J., Roig, A. and Garcia, D. 1993**. Relationships between organic matter and carbon contents of organic wastes. Bioresource Technology 44(3):203-207.

**Nelson, N. O., Agudelo, S. C., Yuan, W. and Gan, J. 2011**. Nitrogen and phosphorus availability in biochar-amended soils. Soil Science 176(5):218-226.

**Nelson, P., Baldock, J. and Oades, J. 1998**. Changes in dispersible clay content, organic carbon content, and electrolyte composition following incubation of sodic soil. Soil Research 36(6):883-898.

**Ngatia, L. W., Reddy, K. R., Nair, P. R., Pringle, R. M., Palmer, T. M. and Turner, B. L. 2014**. Seasonal patterns in decomposition and nutrient release from East African savanna grasses grown under contrasting nutrient conditions. Agriculture, Ecosystems and Environment 188:12-19.

**NLWRA** (National Land and Water Resources Audit)**. 2001.** Australian Dryland Salinity Assessment 2000: extent, impacts, processes, monitoring and management options. National Land and Water Resource Audit, Canberra.

**Normandin, V., Kotuby-Amacher, J. and Miller, R. O. 1998**. Modification of the ammonium acetate extractant for the determination of exchangeable cations in calcareous soils. Communications in Soil Science and Plant Analysis 29(11-14):1785-1791.

**Novak, J., Ro, K., Ok, Y. S., Sigua, G., Spokas, K., Uchimiya, S. and Bolan, N. 2016a**. Biochars multifunctional role as a novel technology in the agricultural, environmental, and industrial sectors. Chemosphere 142:1-3.

**Novak, J., Sigua, G., Watts, D., Cantrell, K., Shumaker, P., Szogi, A., Johnson, M. G. and Spokas, K. 2016b**. Biochars impact on water infiltration and water quality through a compacted subsoil layer. Chemosphere 142:160-167.

**Novak, J. M., Busscher, W. J., Laird, D. L., Ahmedna, M., Watts, D. W. and Niandou, M. A. 2009a**. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Science 174(2):105-112.

**Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D. W. and Busscher, W. J. 2009b**. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Annals of Environmental Science 3(2).

**Olsen, S. R., Sommers, L. E. and Page, A. L. 1982.** Methods of soil analysis. Part 2. Chemical and microbiological properties of Phosphorus. ASA Monograph, (9):403-430.

**Oster, J., Shainberg, I. and Abrol, I. 1996**. Reclamation of salt-affected soil. Soil erosion, Conservation and Rehabilitation:315-352.

**Park, M. and Komarneni, S. 1998**. Ammonium nitrate occlusion vs. nitrate ion exchange in natural zeolites. Soil Science Society of America Journal 62(5):1455-1459.

**Parvage, M. M., Ulén, B., Eriksson, J., Strock, J. and Kirchmann, H. 2013**. Phosphorus availability in soils amended with wheat residue char. Biology and Fertility of Soils 49(2):245-250.

**Pathak, H. and Rao, D. 1998**. Carbon and nitrogen mineralization from added organic matter in saline and alkali soils. Soil Biology and Biochemistry 30(6):695-702.

**Paul, D. 2013**. Osmotic stress adaptations in rhizobacteria. Journal of Basic Microbiology 53(2):101-110.

**Peng, X., Ye, L., Wang, C., Zhou, H. and Sun, B. 2011**. Temperature-and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. Soil and Tillage Research 112(2):159-166.

**Pessenda, L. C. R., Gouveia, S. E. M., de Souza Ribeiro, A., De Oliveira, P. E. and Aravena, R. 2010**. Late Pleistocene and Holocene vegetation changes in northeastern Brazil determined from carbon isotopes and charcoal records in soils. Palaeogeography, Palaeoclimatology, Palaeoecology 297(3):597-608.

**Philip, N. 1988**. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buifer mechanism1. Oceanography 33(4 -Part 2).

**Phongikaroon, S. and Simpson, M. F. 2006**. Equilibrium model for ion exchange between multivalent cations and zeolite-A in a molten salt. Aiche Journal 52(5):1736-1743.

**Ping, Z., Guangyao, S. and Yucheng, F. 2006**. Predominance of char sorption over substrate concentration and soil pH in influencing biodegradation of benzonitrile. Biodegradation 17(1):1-8.

**Pluchon, N., Gundale, M. J., Nilsson, M. C., Kardol, P. and Wardle, D. A. 2014**. Stimulation of boreal tree seedling growth by wood-derived charcoal: effects of charcoal properties, seedling species and soil fertility. Functional Ecology 28(3):766-775.

**Polemio, M. and Rhoades, J. 1977**. Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils. Soil Science Society of America Journal 41(3):524-528.

**Puga, A., Abreu, C., Melo, L. and Beesley, L. 2015**. Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. Journal of Environmental Management 159:86-93.

**Qadir, M., Ghafoor, A. and Murtaza, G. 2000**. Amelioration strategies for saline soils: a review. Land Degradation and Development 11(6):501-521.

**Qadir, M. and Oster, J. 2004**. Crop and irrigation management strategies for saline-sodic soils and waters aimed at environmentally sustainable agriculture. Science of The Total Environment 323(1):1-19.

**Qadir, M., Oster, J., Schubert, S., Noble, A. and Sahrawat, K. 2007**. Phytoremediation of sodic and saline-sodic soils. Advances in Agronomy 96:197-247.

**Qadir, M., Qureshi, R. and Ahmad, N. 2002**. Amelioration of calcareous saline sodic soils through phytoremediation and chemical strategies. Soil Use and Management 18(4):381-385.

**Qadir, M. and Schubert, S. 2002**. Degradation processes and nutrient constraints in sodic soils. Land Degradation and Development 13(4):275-294.

**Qados, A. M. A. 2011**. Effect of salt stress on plant growth and metabolism of bean plant Vicia faba (L.). Journal of the Saudi Society of Agricultural Sciences 10(1):7-15.

**Qian, T., Zhang, X., Hu, J. and Jiang, H. 2013**. Effects of environmental conditions on the release of phosphorus from biochar. Chemosphere 93(9):2069-2075.

**Quirk, J. 1994**. Interparticle forces: a basis for the interpretation of soil physical behavior. Advances in agronomy 53. 121 - 183.

**Rajapaksha, A. U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S. X. and Ok, Y. S 2014.** Pyrolysis condition affected sulfamethazine sorption by tea waste biochars. Bioresource Technology 166:303- 308.

**Rahaman, M., Ellis, N. and Mavinic, D. 2008**. Effects of various process parameters on struvite precipitation kinetics and subsequent determination of rate constants. Water Science and Technology 57(5):647-654.

**Reddy, K., Kadlec, R., Flaig, E. and Gale, P. 1999**. Phosphorus retention in streams and wetlands: a review. Critical reviews in environmental Science and Technology 29(1):83-146.

**Reddy, K., Overcash, M., Khaleel, R. and Westerman, P. 1980**. Phosphorus adsorption-desorption characteristics of two soils utilized for disposal of animal wastes. Journal of Environmental Quality 9(1):86-92.

**Regan, J. T., Fenton, O., Daly, K., Grant, J., Wall, D. P. and Healy, M. G. 2014**. Effects of overland flow on critical soil test phosphorus thresholds in tillage soils. Water, Air, and Soil Pollution 225:1-13.

**Rengasamy, P. 2006**. World salinization with emphasis on Australia. Journal of Experimental Botany 57(5):1017-1023.

**Rengasamy, P. 2010**. Soil processes affecting crop production in salt-affected soils. Functional Plant Biology 37(7):613-620.

**Rengasamy, P. and Olsson, K. 1991**. Sodicity and soil structure. Soil Research 29(6):935-952.

**Rengasamy, P. and Sumner, M. 1998.** Processes involved in sodic behavior. Pages 35-50 in M.E. Sumner and R. Naidu, eds. Sodic soils: distribution, properties, management and environmental consequences. Oxford University Press, New York.

**Reuter, D. and Robinson, J. 1986**. Plant analysis (An interpretation manual) inkata Press. Melbourne Sydney:27-30.

**Richards, L. 1954**. Diagnosis and improving of saline and alkaline soils. US, Salinity Laboratory Staff. Agric. Handbook(60).

**Roy, S. J., Negrão, S. and Tester, M. 2014.** Salt resistant crop plants. Current Opinion in Biotechnology 26:115-124.

**Roberts, K. G., Gloy, B. A., Joseph, S., Scott, N. R. and Lehmann, J. 2009**. Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. Environmental Science and Technology 44(2):827-833.

**Rodriguez-Mirasol, J., Cordero, T. and Rodriguez, J. 1993**. Preparation and characterization of activated carbons from eucalyptus kraft lignin. Carbon 31(1):87-95.

**Rondon, M. A., Lehmann, J., Ramírez, J. and Hurtado, M. 2007**. Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. Biology and Fertility of Soils 43(6):699-708.

**Sanghi, R. and Singh, V. 2012**. Green chemistry for environmental remediation. John Wiley and Sons.

**Sarkhot, D., Ghezzehei, T. and Berhe, A. 2013**. Effectiveness of biochar for sorption of ammonium and phosphate from dairy effluent. Journal of Environmental Quality 42(5):1545-1554.

**SAS Institute Inc. 2015**. The SAS system for Windows, release 9.4. Inst. Inc., Cary, NC, US.

**Schnitzer, M. I., Monreal, C. M., Facey, G. A. and Fransham, P. B. 2007**. The conversion of chicken manure to biooil by fast pyrolysis I. Analyses of chicken manure, biooils and char by $^{13}C$ and 1H NMR and FTIR spectrophotometry. Journal of Environmental Science and Health Part B 42(1):71-77.

**Schoumans, O. and Groenendijk, P. 2000**. Modeling soil phosphorus levels and phosphorus leaching from agricultural land in the Netherlands. Journal of Environmental Quality 29(1):111-116.

**Shaaban, M., Abid, M. and Abou-Shanab, R. 2013**. Amelioration of salt affected soils in rice paddy system by application of organic and inorganic amendments. Plant, Soil and Environment 59(5):227-233.

**Shabala, S., Shabala, L. and Van Volkenburgh, E. 2003**. Effect of calcium on root development and root ion fluxes in salinised barley seedlings. Functional Plant Biology 30(5):507-514.

**Sharpley, A. N., Chapra, S., Wedepohl, R., Sims, J., Daniel, T. C. and Reddy, K. 1994**. Managing agricultural phosphorus for protection of surface waters: Issues and options. Journal of Environmental Quality 23(3):437-451.

**Sharpley, A. N., McDowell, R. W., Weld, J. L. and Kleinman, P. J. 2001**. Assessing site vulnerability to phosphorus loss in an agricultural watershed. Journal of Environmental Quality 30(6):2026-2036.

**Shepherd, J. G., Sohi, S. P. and Heal, K.V. 2016.** Optimising the recovery and re-use of phosphorus from wastewater effluent for sustainable fertiliser development. Water Research 94:155-165.

**Shepherd, J. G., Joseph, S., Sohi, S. P. and Heal, K. V. 2017.** Biochar and enhanced phosphate capture: Mapping mechanisms to functional properties. Chemosphere 179:57-74.

**Shrivastava, P. and Kumar, R. 2015**. Soil salinity: A serious environmental issue and plant growth promoting bacteria as one of the tools for its alleviation. Saudi Journal of Biological Sciences 22(2):123-131.

**Sika, M. and Hardie, A. 2014**. Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil. European Journal of Soil Science 65(1):113-119.

**Silber, A., Levkovitch, I. and Graber, E. 2010**. pH-dependent mineral release and surface properties of cornstraw biochar: agronomic implications. Environmental Science and Technology 44(24):9318-9323.

**Simard, R., Beauchemin, S. and Haygarth, P. 2000**. Potential for preferential pathways of phosphorus transport. Journal of Environmental Quality 29(1):97-105.

**Sims, J., Edwards, A., Schoumans, O. and Simard, R. 2000**. Integrating soil phosphorus testing into environmentally based agricultural management practices. Journal of Environmental Quality 29(1):60-71.

**Sims, J. T., Maguire, R. O., Leytem, A., Gartley, K. and Pautler, M. 2002**. Evaluation of Mehlich 3 as an agri-environmental soil phosphorus test for the Mid-Atlantic United States of America. Soil Science Society of America Journal 66(6):2016-2032.

**Singh, K. N and Chatrath, R. 2001**. Salinity tolerance. Pages 101-110 in M. P. Reynolds, J. I. O. Monasterio, and A. McNab, eds. Application of physiology in wheat breeding. Cimmyt, Mexico.

**Singh, B., Singh, B. P. and Cowie, A. L. 2010a**. Characterisation and evaluation of biochars for their application as a soil amendment. Soil Research 48(7):516-525.

**Singh, B. P., Hatton, B. J., Singh, B., Cowie, A. L. and Kathuria, A. 2010b**. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. Journal of Environmental Quality 39(4):1224-1235.

**Singh, B. P., Menchavez, R., Fuji, M. and Takahashi, M. 2006**. Characterization of concentrated colloidal ceramics suspension: A new approach. Journal of Colloid and Interface Science 300(1):163-168.

**Slabu, C., Zörb, C., Steffens, D. and Schubert, S. 2009**. Is salt stress of faba bean (Vicia faba) caused by $Na^+$ or $Cl^-$toxicity? Journal of Plant Nutrition and Soil Science 172(5):644-651.

**Slavich, P., Sinclair, K., Morris, S., Kimber, S., Downie, A. and Van Zwieten, L. 2013**. Contrasting effects of manure and green waste biochars on the properties of an acidic ferralsol and productivity of a subtropical pasture. Plant and Soil 366(1-2):213-227.

**Smernik, R. J. 2005**. A new way to use solid-state carbon-13 nuclear magnetic resonance spectroscopy to study the sorption of organic compounds to soil organic matter. Journal of Environmental Quality 34(4):1194-1204.

**Smith, T., Grattan, S., Grieve, C., Poss, J. A. and Suarez, D. L. 2010a**. Salinity's influence on boron toxicity in broccoli: I. Impacts on yield, biomass distribution, and water use. Agricultural Water Management 97(6):777-782.

**Smith, T., Grattan, S., Grieve, C., Poss, J. A. and Suarez, D. L. 2010b**. Salinity's influence on boron toxicity in broccoli: II. Impacts on boron uptake, uptake mechanisms and tissue ion relations. Agricultural Water Management 97(6):783-791.

**Sohi, S., Krull, E., Lopez-Capel, E. and Bol, R. 2010**. A review of biochar and its use and function in soil. Advances in Agronomy 105:47-82.

**Solaiman, Z. M., Blackwell, P., Abbott, L. K. and Storer, P. 2010**. Direct and residual effect of biochar application on mycorrhizal root colonisation, growth and nutrition of wheat. Soil Research 48(7):546-554.

**Sommerfeldt, T. G. 1988.** Management of saline soils under irrigation. Agriculture Canada, Ottawa.

**Sperry, J. S. and Hacke, U. 2002**. Desert shrub water relations with respect to soil characteristics and plant functional type. Functional Ecology 16(3):367-378.

**Spokas, K., Koskinen, W., Baker, J. and Reicosky, D. 2009**. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77(4):574-581.

**Sposito, G. 1989**. The chemistry of soils Oxford University Press Oxford Google Scholar.

**Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macedo, J.L.V., Blum, W.E.H., Zech, W., 2007**. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant and Soil 291, 275.

**Steiner, C., Glaser, B., Geraldes Teixeira, W., Lehmann, J., Blum, W. E. and Zech, W. 2008**. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. Journal of Plant Nutrition and Soil Science 171(6):893-899.

**Sumner, M. E. 1993**. Sodic soils-New perspectives. Soil Research 31(6):683-750.

**Sun, K., Jin, J., Kang, M., Zhang, Z., Pan, Z., Wang, Z., Wu, F. and Xing, B. 2013a**. Isolation and characterization of different organic matter fractions from a same soil source and their phenanthrene sorption. Environmental Science and Technology 47(10):5138-5145.

**Sun, K., Kang, M., Zhang, Z., Jin, J., Wang, Z., Pan, Z., Xu, D., Wu, F. and Xing, B. 2013b**. Impact of deashing treatment on biochar structural properties and potential sorption mechanisms of phenanthrene. Environmental Science and Technology 47(20):11473-11481.

**Swiatkowski, A., Pakula, M., Biniak, S. and Walczyk, M. 2004**. Influence of the surface chemistry of modified activated carbon on its electrochemical behaviour in the presence of lead (II) ions. Carbon 42(15):3057-3069.

**Syers, J., Evans, T., Williams, J. and Murdock, J. 1971**. Phosphate sorption parameters of representative soils from rio grande do sul, brazil. Soil Science 112(4):267-275.

**Szabolcs, I. 1994**. Soils and salinisation. Handbook of plant and crop stress:3-11.

**Tagoe, S. O., Horiuchi, T. and Matsui, T. 2008**. Effects of carbonized and dried chicken manures on the growth, yield, and N content of soybean. Plant and Soil 306(1-2):211-220.

**Tavakkoli, E., Fatehi, F., Coventry, S., Rengasamy, P. and McDonald, G. K. 2011**. Additive effects of $Na^+$ and $Cl^-$ions on barley growth under salinity stress. Journal of Experimental Botany 62(6):2189-2203.

**Tazeh, E. S., Pazira, E., Neyshabouri, M. R., Abbasi, F. and Abyaneh, H. Z. 2013**. Effects of two organic amendments on EC, SAR and soluble ions concentration in a saline-sodic soil. International Journal of Biosciences 3(9):55-68.

**Tejada, M., Hernandez, M. and Garcia, C. 2009**. Soil restoration using composted plant residues: Effects on soil properties. Soil and Tillage Research 102(1):109-117.

**Thangarajan, R., Bolan, N., Mandal, S., Kunhikrishnan, A., Choppala, G., Karunanithi, R. and Qi, F. 2015**. Biochar for inorganic contaminant management in soil. Biochar: Production, Characterization, and Applications:100.

**Thies, J. E. and Rillig, M. C. 2009**. Characteristics of biochar: biological properties. Pages 85-105 in J.L. Lehmann and S. Joseph, eds. Biochar for environmental management: London, England: Earthscan.

**Thomas, S. C., Frye, S., Gale, N., Garmon, M., Launchbury, R., Machado, N., Melamed, S., Murray, J., Petroff, A. and Winsborough, C. 2013**. Biochar mitigates negative effects of salt additions on two herbaceous plant species. Journal of Environmental Management 129:62-68.

**Topoliantz, S., Ponge, J.-F. and Ballof, S. 2005**. Manioc peel and charcoal: a potential organic amendment for sustainable soil fertility in the tropics. Biology and Fertility of Soils 41(1):15-21.

**Torrent, J. 1987**. Rapid and slow phosphate sorption by Mediterranean soils: Effect of iron oxides. Soil Science Society of America Journal 51(1):78-82.

**Troeh, F. R. and Thompson, L. M. 2005**. Soils and soil fertility. Ames Blackwell.

**Tryon, E. H. 1948**. Effect of charcoal on certain physical, chemical, and biological properties of forest soils. Ecological Monographs 18(1):81-115.

**Tsai, W.-T., Liu, S.-C., Chen, H.-R., Chang, Y.-M. and Tsai, Y.-L. 2012**. Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. Chemosphere 89(2):198-203.

**Tseng, R.-L. and Tseng, S.-K. 2006**. Characterization and use of high surface area activated carbons prepared from cane pith for liquid-phase adsorption. Journal of Hazardous Materials 136(3):671-680.

**Uchimiya, M., Chang, S. and Klasson, K. T. 2011**. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. Journal of Hazardous Materials 190(1):432-441.

**Ulén, B., Djodjic, F., Etana, A., Johansson, G. and Lindström, J. 2011**. The need for an improved risk index for phosphorus losses to water from tile-drained agricultural land. Journal of Hydrology 400(1):234-243.

**Ulén, B. and Snäll, S. 2007**. Forms and retention of phosphorus in an illite-clay soil profile with a history of fertilisation with pig manure and mineral fertilisers. Geoderma 137(3):455-465.

**Ulén, B., von Brömssen, C., Johansson, G., Torstensson, G. and Forsberg, L. S. 2012**. Trends in nutrient concentrations in drainage water from single fields under ordinary cultivation. Agriculture, Ecosystems and Environment 151:61-69.

**United States Salinity Laboratory Staff. 1954.** Diagnosis and improvement of saline and alkali soils. US Department of Agriculture, Agricultural Handbook

**Vaccari, F., Baronti, S., Lugato, E., Genesio, L., Castaldi, S., Fornasier, F. and Miglietta, F. 2011**. Biochar as a strategy to sequester carbon and increase yield in durum wheat. European Journal of Agronomy 34(4):231-238.

**Valério, I. P., Carvalho, F. I. F. d., Benin, G., Silveira, G. d., Silva, J. A. G. d., Nornberg, R., Hagemann, T., Luche, H. d. S. and Oliveira, A. C. d. 2013**. Seeding density in wheat: the more, the merrier? Scientia Agricola 70(3):176-184.

**Valério, I. P., Carvalho, F. I. F. d., Oliveira, A. C. d., Benin, G., Souza, V. Q. d., Machado, A. d. A., Bertan, I., Busato, C. C., Silveira, G. d. and Fonseca, D. A. R. 2009**. Seeding density in wheat genotypes as a function of tillering potential. Scientia Agricola 66(1):28-39.

**Van de Graaff, R. and Patterson, R. A. 2001**. Explaining the mysteries of salinity, sodicity, SAR and ESP. pages 361-368 in R. A. Patterson and M. J. Jones, eds. On-site Practice in Proceedings of On-site '01 conference: advancing on-site wastewater systems, University of Armidale, New England.

**Van Zwieten, L., Kimber, S., Morris, S., Chan, K., Downie, A., Rust, J., Joseph, S. and Cowie, A. 2010**. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 327(1-2):235-246.

**Verheijen, F., Jeffery, S., Bastos, A., Van der Velde, M. and Diafas, I. 2010**. Biochar application to soils. A critical scientific review of effects on soil properties, processes, and functions. European Communities 24099:162.

**Villapando, R. and Graetz, D. 2001**. Phosphorus sorption and desorption properties of the spodic horizon from selected Florida Spodosols. Soil Science Society of America Journal 65(2):331-339.

**Walker, D. J. and Bernal, M. P. 2008**. The effects of olive mill waste compost and poultry manure on the availability and plant uptake of nutrients in a highly saline soil. Bioresource Technology 99(2):396-403.

**Wan, Q., Yuan, J. H., Xu, R. K. and Li, X. H. 2014**. Pyrolysis temperature influences ameliorating effects of biochars on acidic soil. Environmental Science and Pollution Research 21(4):2486-2495.

**Wang, Y. Y., Lu, H. H., Liu, Y. X., Yang, S. M. 2016.** Removal of phosphate from aqueous solution by SiO 2–biochar nanocomposites prepared by pyrolysis of vermiculite treated algal biomass. Rsc Advances 6:83534-83546.

**Wang, J., Pan, X., Liu, Y., Zhang, X. and Xiong, Z. 2012**. Effects of biochar amendment in two soils on greenhouse gas emissions and crop production. Plant and Soil 360(1-2):287-298.

**Wang, T., Zhu, B., Gao, M., Xu, T. and Kuang, F. 2006**. Nitrate pollution of groundwater in a typical small watershed in the central Sichuan hilly region. Journal of Ecology and Rural Environment 22(3):84-87.

**Wetson, A. M. and Flowers, T. J. 2010**. The effect of saline hypoxia on growth and ion uptake in Suaeda maritima. Functional Plant Biology 37(7):646-655.

**Willenborg, C. J., Gulden, R. H., Johnson, E. N. and Shirtliffe, S. J. 2004**. Germination characteristics of polymer-coated Canola (L.) seeds subjected to moisture stress at different temperatures. Agronomy Journal 96(3):786-791.

**Wilson, C., Read, J. J. and Abo-Kassem, E. 2002**. Effect of mixed-salt salinity on growth and ion relations of a quinoa and a wheat variety. Journal of Plant Nutrition 25(12):2689-2704.

**Wong, V. N., Dalal, R. C. and Greene, R. S. 2009**. Carbon dynamics of sodic and saline soils following gypsum and organic material additions: a laboratory incubation. Applied Soil Ecology 41(1):29-40.

**Wood, G., Welsh, J., Godwin, R., Taylor, J. C., Earl, R. and Knight, S. 2003**. Real-time measures of canopy size as a basis for spatially varying nitrogen applications to winter wheat sown at different seed rates. Biosystems Engineering 84(4):513-531.

**Xiao, Q., Zhang, H., Shen, Y. and Li, S. 2015**. Effects of biochar on water infiltration, evaporation and nitrate leaching in semi-arid loess area. Transactions of the Chinese Society of Agricultural Engineering 31(16):128-134.

**Wu, Y., Xu, G. and Shao, H. 2014**. Furfural and its biochar improve the general properties of a saline soil. Solid Earth 5(2):665.

**Xu, G., Sun, J., Shao, H. and Chang, S. X. 2014**. Biochar had effects on phosphorus sorption and desorption in three soils with differing acidity. Ecological Engineering 62:54-60.

**Xu, R. k., Xiao, S. C., Yuan, J. H. and Zhao, A. Z. 2011**. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresource Technology 102(22):10293-10298.

**Yadav, S. 2010**. Heavy metals toxicity in plants: an overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. South African Journal of Botany 76(2):167-179.

**Yang, Y., Zhao, Y., Babatunde, A., Wang, L., Ren, Y. and Han, Y. 2006**. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Separation and Purification Technology 51(2):193-200.

**Yao, Y., Gao, B., Zhang, M., Inyang, M. and Zimmerman, A. R. 2012.** Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere 89:1467-1471.

**Yao, H., Campbell, C. D. and Qiao, X. 2011a**. Soil pH controls nitrification and carbon substrate utilization more than urea or charcoal in some highly acidic soils. Biology and Fertility of Soils 47(5):515-522.

**Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P. and Yang, L. 2011b**. Biochar derived from anaerobically digested sugar beet tailings: characterization and phosphate removal potential. Bioresource Technology 102(10):6273-6278.

**Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P. and Yang, L. 2011c**. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. Journal of Hazardous Materials 190(1):501-507.

**Yao, Y., Gao, B., Zhang, M., Inyang, M. and Zimmerman, A. R. 2012**. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere 89(11):1467-1471.

**Yoon, J. Y., Hamayun, M., Lee, S. K. and Lee, I. J. 2009**. Methyl jasmonate alleviated salinity stress in soybean. Journal of Crop Science and Biotechnology 12(2):63-68.

**Zeng, L. and Shannon, M. C. 2000**. Effects of salinity on grain yield and yield components of rice at different seeding densities. Agronomy Journal 92(3):418-423.

**Zeng, Z., Li, T. Q., Zhao, F. l., He, Z. l., Zhao, H. P., Yang, X. E., Wang, H. l., Zhao, J. and Rafiq, M. T. 2013**. Sorption of ammonium and phosphate from aqueous solution by biochar derived from phytoremediation plants. Journal of Zhejiang University Science B 14(12):1152-1161.

**Zhang, H., Dong, H., Li, W. and Zhang, D. 2012**. Effects of soil salinity and plant density on yield and leaf senescence of field-grown cotton. Journal of Agronomy and Crop Science 198(1):27-37.

**Zhang, J. Z. and Huang, X. L. 2011**. Effect of temperature and salinity on phosphate sorption on marine sediments. Environmental Science and Technology 45(16):6831-6837.

**Zhang, W., Faulkner, J. W., Giri, S. K., Geohring, L. D. and Steenhuis, T. S. 2010**. Effect of soil reduction on phosphorus sorption of an organic-rich silt loam. Soil Science Society of America Journal 74(1):240-249.

**Zheng, W., Sharma, B. and Rajagopalan, N. 2010**. Using biochar as a soil amendment for sustainable agriculture. A report submitted to the sustainable agriculture grant program of Illinois Department of Agriculture, grant number: SA 09e37

**Zhou, G., Ma, B., Li, J., Feng, C., Lu, J. and Qin, P. 2010**. Determining salinity threshold level for castor bean emergence and stand establishment. Crop Science 50(5):2030-2036.

**Zribi, O. T., Labidi, N., Slama, I., Debez, A., Ksouri, R., Rabhi, M., Smaoui, A. and Abdelly, C. 2012**. Alleviation of phosphorus deficiency stress by moderate salinity in the halophyte Hordeum maritimum L. Plant Growth Regulation 66(1):75-85.

# APPENDICES

## Appendix A

**Table A-1.** Mean leachate $EC_e$ for non-saline and saline-sodic soils with different biochar application rate during six events in soil column leaching experiment.

| Group means | Treatment [z] | | 1st event[*] | 2nd event | 3rd event | 4th event | 5th event | 6th event | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | | | $ds\ m^{-1}$ | | | | | | |
| Salinity | N | | 2.7 | 0.61 | 0.45 | 0.41 | 0.39 | 0.39 | 0.77 |
| | S | | 58 | 6.19 | 0.94 | 0.54 | 0.50 | 0.48 | 11.1 |
| Biochar | 0% | | 33.6a[y] | 3.35bc | 0.58b | 0.49 | 0.57 a | 0.58 a | 6.53a |
| | 2% | | 32.1b | 2.92c | 0.62b | 0.48 | 0.46 b | 0.50 b | 6.11b |
| | 5% | | 29.1c | 3.40b | 0.67b | 0.44 | 0.37 c | 0.34 c | 5.73c |
| | 8% | | 26.6d | 3.92a | 0.90a | 0.48 | 0.38 c | 0.32 c | 5.43d |
| Salinity X Biochar | N | 0% | 3.6e | 0.53d | 0.37c | 0.40 | 0.42 c | 0.42 c | 0.80e |
| | N | 2% | 2.6e | 0.57d | 0.44c | 0.41 | 0.42 c | 0.43 c | 0.80e |
| | N | 5% | 2.6e | 0.64d | 0.46c | 0.39 | 0.37 c | 0.36 cd | 0.81e |
| | N | 8% | 1.9e | 0.68d | 0.52c | 0.42 | 0.37 c | 0.33 d | 0.69e |
| | S | 0% | 63a | 6.17b | 0.80b | 0.58 | 0.73 a | 0.73 a | 12.2a |
| | S | 2% | 61b | 5.28c | 0.81b | 0.55 | 0.51 b | 0.57 b | 11.4b |
| | S | 5% | 55c | 6.16b | 0.87b | 0.49 | 0.37 c | 0.32 d | 10.6c |
| | S | 8% | 51d | 7.17a | 1.28a | 0.54 | 0.39 c | 0.31 d | 10.1d |

| Analysis of variances | P>F | P>F | P>F | P>F | P>F | P>F | P>F |
|---|---|---|---|---|---|---|---|
| Salinity | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Biochar | <0.01 | <0.01 | <0.01 | 0.13 | <0.01 | <0.01 | <0.01 |
| Salinity X Biochar | <0.01 | <0.02 | <0.06 | 0.25 | <0.01 | <0.01 | <0.01 |

[*] A separate analysis was done for each event and also for events mean.

[y] Mean (± SE, n=3) followed by the same letter within a column are not significantly different ($p<0.05$).

Codes[z]: N: Non-saline soil; S: Saline-sodic soil; 0%, 2%, 5% and 8% denote biochar application rate based on weight.

**Table A-2.** Volume of infiltration during six events as affected by soil type and rate of biochar application.

| Group means | Treatment [z] | | 1st event[*] | 2nd event | 3rd event | 4th event | 5th event | 6th event |
|---|---|---|---|---|---|---|---|---|
| | | | mL column$^{-1}$ | | | | | |
| Salinity | N | | 312 | 449 | 449 | 444 | 443 | 429 |
| | S | | 348 | 444 | 395 | 300 | 265 | 236 |
| Biochar | 0% | | **385a** | 451 | **397b** | **289b** | **260b** | **233b** |
| | 2% | | **373a** | 446 | **395b** | **304b** | **282b** | **245b** |
| | 5% | | **308b** | 453 | **451a** | **454a** | **436a** | **421a** |
| | 8% | | **272c** | 437 | **444a** | **442a** | **438a** | **431a** |
| Salinity X Biochar | N | 0% | **378a** | 447 | **461a** | **447a** | **444a** | **443a** |
| | N | 2% | **368ab** | 444 | **439a** | **436a** | **436a** | **400a** |
| | N | 5% | **279d** | 460 | **451a** | **448a** | **444a** | **430a** |
| | N | 8% | **238e** | 444 | **445a** | **445a** | **449a** | **446a** |
| | S | 0% | **392a** | 455 | **332b** | **130c** | **76c** | **23c** |
| | S | 2% | **378a** | 447 | **352b** | **172b** | **128b** | **91b** |
| | S | 5% | **338bc** | 445 | **451a** | **459a** | **427a** | **412a** |
| | S | 8% | **306cd** | 430 | **443a** | **439a** | **428a** | **417a** |

| Analysis of variances | df | P>F | P>F | P>F | P>F | P>F | P>F |
|---|---|---|---|---|---|---|---|
| Salinity | 1 | <0.01 | 0.37 | <0.01 | <0.01 | <0.01 | <0.01 |
| Biochar | 3 | <0.01 | 0.15 | <0.01 | <0.01 | <0.01 | <0.01 |
| Salinity X Biochar | 3 | <0.02 | 0.31 | <0.01 | <0.01 | <0.01 | <0.01 |

[*] A separate analysis was done for each event and also for events mean.

[y] Mean (± SE, n=3)followed by same letters within column for a group of means are not significantly different ($p<0.05$).

Codes[z]: N: Non-saline soil, S: Saline-sodic soil, 0%, 2%, 5% and 8% denote biochar application rate based on weight.

**Table A-3.** Soil exchangeable cations of initial and post leaching non-saline and saline-sodic soils with different biochar application rate.

| Group means | Treatment | | $Ca^{2+}$ | | $Mg^{2+}$ | | $K^{+}$ | | $Na^{+}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | cmol $kg^{-1}$ | | | | | | | |
| | | | Initial | P. Leaching | Initial | P. Leaching | Initial | P. Leaching | Initial | P. Leaching |
| Salinity (Sa.) | N | | **29.0** | **27.2** | **6.0** | **5.8** | **2.6** | **2.6** | **0.4** | **0.2** |
| | S | | **12.5** | **15.3** | **13.0** | **9.5** | **1.8** | **1.3** | **6.8** | **1.2** |
| Biochar(Bio.) | 0% | | **19.4b$^{y}$** | **19.7b** | 8.4 | **6.5b** | **1.5c** | **1.5c** | 2.9 | **1.2a** |
| | 2% | | **21.3a** | **21.5a** | 9.8 | **7.8a** | **2.0bc** | **1.8b** | 3.4 | **0.8b** |
| | 5% | | **21.4a** | **21.8a** | 10.1 | **8.2a** | **2.4ab** | **2.1ab** | 3.9 | **0.5b** |
| | 8% | | **20.9a** | **22.1a** | 9.7 | **8.1a** | **2.8a** | **2.3a** | 4.3 | **0.5b** |
| Sa. X Bio. | N | 0% | 27.7 | 26.4 | 27.7 | **5.6b** | 1.8 | 2.1 | 0.4 | **0.25d** |
| | N | 2% | 29.7 | 27.1 | 29.7 | **5.9b** | 2.4 | 2.5 | 0.4 | **0.30 d** |
| | N | 5% | 29.9 | 27.5 | 29.9 | **6.0b** | 2.8 | 2.8 | 0.5 | **0.25d** |
| | N | 8% | 28.7 | 27.7 | 28.7 | **5.9b** | 3.5 | 3.0 | 0.5 | **0.25d** |
| | S | 0% | 11.1 | 12.9 | 11.1 | **7.4b** | 1.2 | 0.9 | 5.5 | **2.2 a** |
| | S | 2% | 12.9 | 15.8 | 12.9 | **9.8a** | 1.6 | 1.2 | 6.4 | **1.3b** |
| | S | 5% | 13.1 | 16.1 | 13.1 | **10.4a** | 2.1 | 1.4 | 7.3 | **0.85bc** |
| | S | 8% | 13.2 | 16.5 | 13.2 | **10.4a** | 2.2 | 1.7 | 8.2 | **0.8c** |
| Analysis of variances | | | P>F | P>F | P>F | P>F | P>F | P>F | P>F | P>F |
| Salinity | | | <0.01 | <0.01 | 0.01 | <0.01 | <0.03 | <0.01 | <0.01 | <0.01 |
| Biochar | | | <0.01 | 0.01 | 0.66 | <0.06 | <0.08 | <0.01 | 0.13 | <0.01 |
| Sa. X Bio. | | | 0.61 | 0.17 | 0.98 | 0.02 | 0.28 | 0.56 | 0.17 | <0.01 |

$^{y}$Mean (± SE, n=3)followed by same letters within column indicate no significant differences among treatments ($p<0.05$). Codes$^{z}$: N: Non-saline soil, S: Saline-sodic soil, P. leaching= Post leaching. 0%, 2%, 5% and 8% denote biochar application rate based on weight.

**Table A-4.** Leachate losses of monovalent cations from non-saline and saline-sodic soils with different biochar rate during selected three events

| Group means | Treatment [z] | | $Na^+$ | | | $K^+$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1st event* | 3rd event | 6th event | 1st event* | 3rd event | 6th event |
| | | | mmol column$^{-1}$ | | | | | |
| Salinity | N | | 0.59 | 0.25 | 0.12b | 0.70 | 0.46 | 0.40 |
| | S | | 303 | 3.39 | 0.72 | 1.72 | 0.09 | 0.03 |
| Biochar | 0% | | **189a**[y] | **1.43b** | **0.14b** | **1.01b** | **0.18b** | **0.15c** |
| | 2% | | **169b** | **1.50b** | **0.28b** | **1.21a** | **0.22b** | **0.17c** |
| | 5% | | **135c** | **1.83ab** | **0.65a** | **1.31a** | **0.29b** | **0.25b** |
| | 8% | | **114d** | **2.53a** | **0.62a** | **1.32a** | **0.42a** | **0.29a** |
| Salinity X Biochar | N | 0% | **0.56e** | **0.180c** | **0.09c** | **0.67d** | **0.29bc** | **0.30b** |
| | N | 2% | **0.65e** | **0.220c** | **0.118c** | **0.73d** | **0.38b** | **0.34b** |
| | N | 5% | **0.71e** | **0.280c** | **0.142c** | **0.78d** | **0.50ab** | **0.46a** |
| | N | 8% | **0.43e** | **0.342c** | **0.15c** | **0.61d** | **0.69a** | **0.51a** |
| | S | 0% | **378a** | **2.680b** | **0.20b** | **1.35c** | **0.06d** | **0.001c** |
| | S | 2% | **338b** | **2.786b** | **0.44b** | **1.68b** | **0.05d** | **0.007c** |
| | S | 5% | **270c** | **3.382b** | **1.16a** | **1.84ab** | **0.08cd** | **0.043c** |
| | S | 8% | **228d** | **4.735a** | **1.08a** | **2.03a** | **0.15cd** | **0.077c** |
| Analysis of variances | | | P>F | P>F | P>F | P>F | P>F | P>F |
| Salinity | | | <0.01 | <0.04 | <0.01 | <0.01 | <0.01 | <0.01 |
| Biochar | | | <0.01 | <0.01 | <0.01 | <0.02 | <0.01 | <0.01 |
| Salinity X Biochar | | | <0.01 | 0.01 | <0.01 | <0.01 | 0.02 | <0.02 |

*A separate analysis was done for each event.

[y] Mean (± SE, n=3)followed by same letters within column for a group of means are not significantly different ($p<0.05$). Codes[z]: N: Non-saline soil, S: Saline-sodic soil, 0%, 2%, 5% and 8% denote biochar application rate based on weight.

**Table A-5.** Leachate losses of divalent cations from non-saline and saline-sodic soils with different biochar rate during selected three events

| Group means | Treatment $^z$ | | $Ca^{2+}$ | | | $Mg^{2+}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1st event* | 3rd event | 6th event | 1st event* | 3rd event | 6th event |
| | | | mmol column$^{-1}$ | | | | | |
| Salinity | N | | 2.51 | 0.59 | 0.49 | 1.1 | 0.15 | 0.13 |
| | S | | 4.42 | 0.44 | 0.11 | 56.6 | 0.23 | 0.04 |
| Biochar | 0% | | **4.37a**$^y$ | 0.62 | 0.32 | **37.9a** | 0.19 | 0.10 |
| | 2% | | **3.89ab** | 0.56 | 0.30 | **33.4b** | 0.15 | 0.08 |
| | 5% | | **3.39b** | 0.47 | 0.32 | **24.5c** | 0.17 | 0.08 |
| | 8% | | **2.21c** | 0.43 | 0.26 | **19.5d** | 0.26 | 0.08 |
| Salinity X Biochar | N | 0% | 3.64 | 0.67 | **0.58a** | **1.51e** | 0.15 | **0.20a** |
| | N | 2% | 2.96 | 0.67 | **0.54a** | **1.25e** | 0.15 | **0.14ab** |
| | N | 5% | 2.46 | 0.58 | **0.48a** | **1.05e** | 0.15 | **0.10bc** |
| | N | 8% | 0.99 | 0.46 | **0.36a** | **0.44e** | 0.17 | **0.09bc** |
| | S | 0% | 5.11 | 0.56 | **0.02c** | **74.3a** | 0.23 | **0.009e** |
| | S | 2% | 4.83 | 0.44 | **0.06c** | **65.5b** | 0.15 | **0.02de** |
| | S | 5% | 4.31 | 0.36 | **0.17bc** | **47.9c** | 0.20 | **0.06cde** |
| | S | 8% | 3.43 | 0.41 | **0.15bc** | **38.6d** | 0.35 | **0.07cd** |
| Analysis of variances | | | P>F | P>F | P>F | P>F | P>F | P>F |
| Salinity | | | <0.01 | <0.09 | <0.01 | <0.01 | 0.01 | <0.01 |
| Biochar | | | <0.01 | 0.07 | 0.51 | <0.01 | 0.08 | 0.18 |
| Salinity X Biochar | | | 0.18 | 0.48 | 0.01 | <0.01 | 0.16 | <0.02 |

*A separate analysis was done for each event.

$^y$Mean (± SE, n=3) followed by same letters within column for a group of means are not significantly different ($p<0.05$). Codes$^z$: N: Non-saline soil, S: Saline-sodic soil, 0%, 2%, 5% and 8% denote biochar application rate based on weight.

# Appendix B

**Table B-1**. Root dry matter production (RDM), shoot dry matter (SDM), total dry matter (TDM), ratio of root to shoot (R/S), and other plant parameters in response to soil type, manure and biochar treatments used in the experiment.

| Group | Treatment | RDM | SDM | TDM | yield | R/S | Spikelet weight | Grain weight | Grain per Spikelet |
|---|---|---|---|---|---|---|---|---|---|
| | | g / pot | | | | | g/plant | | |
| Soil | N | **0.66 b** | **3.01 b** | **3.67 b** | **3.98 b** | **0.22 b** | **0.71 b** | **0.51 b** | **17 b** |
| | S | **1.81 a** | **4.49 a** | **6.31 a** | **7.22 a** | **0.41 a** | **1.27 a** | **0.95 a** | **29 a** |
| Biochar (Bio.) | 0% | **1.08 b** | **3.12 b** | **4.21 b** | **4.09 b** | 0.32 | **0.93 b** | 0.76 | 23 |
| | 5% | **1.39 a** | **4.38 a** | **5.77 a** | **7.11 a** | 0.31 | **1.06 a** | 0.70 | 22 |
| Manure (Man.) | - | 1.38 | 3.67 | 5.06 | 5.50 | 0.35 | **0.92 b** | 0.69 | **21 b** |
| | + | 1.09 | 3.83 | 4.92 | 5.70 | 0.28 | **1.06 a** | 0.77 | **24 a** |
| Soil X Bio | N 0% | 0.53 | **2.54 c** | 3.07 | **3.46 c** | 0.21 | 0.81 | 0.55 | 18 |
| | N 5% | 0.78 | **3.49 b** | 4.28 | **4.50 bc** | 0.22 | 0.61 | 0.46 | 16 |
| | S 0% | 1.63 | **3.71 b** | 5.35 | **4.72 b** | 0.43 | 1.30 | 0.97 | 29 |
| | S 5% | 1.99 | **5.28 a** | 7.27 | **9.71 a** | 0.39 | 1.24 | 0.94 | 28 |
| Soil X Man. | N - | **0.61 c** | 2.96 | 3.57 | 4.07 | **0.21 b** | **0.51 c** | **0.38 c** | **14 c** |
| | N+ | **0.70 c** | 3.07 | 3.78 | 3.89 | **0.22 b** | **0.91 b** | **0.63 b** | **19 b** |
| | S - | **2.15 a** | 4.39 | 6.55 | 6.93 | **0.48 a** | **1.33 a** | **1.00 a** | **29 a** |
| | S + | **1.47 b** | 4.59 | 6.07 | 7.51 | **0.33 b** | **1.21 a** | **0.91 a** | **29 a** |
| Bio X Man. | 0% - | 1.30 | **3.32 c** | **4.62 b** | **4.52 c** | 0.355 | **1.05 a** | **0.78 a** | **23 ab** |
| | 5% - | 1.46 | **4.03 b** | **5.50 a** | **6.41 b** | 0.345 | **0.80 b** | **0.59 b** | **20 b** |
| | 0% + | 0.87 | **2.93 c** | **3.80 c** | **3.59 c** | 0.290 | **1.06 a** | **0.73 ab** | **23 ab** |
| | 5% + | 1.31 | **4.74 a** | **6.05 a** | **7.8 a** | 0.274 | **1.06 a** | **0.80 a** | **24 a** |
| Soil X Bio. X Man. | N 0% - | 0.53 | **2.48 e** | **3.02 d** | **3.80 cd** | 0.21 | **0.47 e** | **0.35 c** | **13 d** |
| | N 0% + | 0.53 | **2.59 de** | **3.13 d** | **3.12 d** | 0.21 | **1.15 bc** | **0.76 b** | **22 bc** |
| | N 5% - | 0.7 | **3.43 dc** | **4.13 cd** | **4.35 cd** | 0.20 | **0.56 e** | **0.41 c** | **15 d** |
| | N 5% + | 0.87 | **3.55 c** | **4.42 c** | **4.65 cd** | 0.24 | **0.67 de** | **0.50 bc** | **16 cd** |
| | S 0% - | 2.06 | **4.16 bc** | **6.23 b** | **5.38 c** | 0.49 | **1.63 a** | **1.22 a** | **33 a** |
| | S 0% + | 1.20 | **3.26 cde** | **4.47 c** | **4.07 cd** | 0.37 | **0.97 cd** | **0.71 b** | **25 b** |
| | S 5% - | 2.23 | **4.63 b** | **6.87 ab** | **8.47 b** | 0.48 | **1.03 cd** | **0.77 b** | **24 b** |
| | S 5% + | 1.75 | **5.92 a** | **7.6 a** | **10.95 a** | 0.3 | **1.45 ab** | **1.10 a** | **33 a** |
| | | Analysis of variances Prob>F | | | | | | | |
| Soil | | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** |
| Biochar | | 0.04 | **<0.01** | **<0.01** | **<0.01** | 0.70 | **0.04** | 0.15 | 0.26 |
| Manure | | 0.05 | 0.27 | 0.48 | 0.52 | 0.06 | **0.02** | 0.07 | 0.01 |
| Soil X Bio. | | 0.70 | **0.04** | 0.07 | **<0.01** | 0.47 | 0.25 | 0.41 | 0.46 |
| Soil X Man. | | **0.01** | 0.77 | 0.09 | 0.22 | **0.01** | **<0.01** | **<0.01** | **<0.01** |
| Bio. X Man. | | 0.34 | **<0.01** | **<0.01** | **<0.01** | 0.92 | **0.05** | **<0.01** | **0.02** |
| Soil X Bio. X Man. | | 0.71 | **<0.01** | **<0.01** | **0.03** | 0.39 | **<0.01** | **<0.01** | **<0.01** |

$^{y}$Mean values followed by the same letter within a column for a group of means are not significantly different ($p<0.05$, Tukey's test), the bolded values indicate the statically significant data, Codes$^{z}$: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

**Table B-2.** Nutrients concentrations of wheat shoot in response to soil type, biochar and manure treatments used in the experiment.

| Group | Treatment | N | P | K | Na | Ca | Mg | S | Zn | Mn | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | g kg$^{-1}$ | | | | | |
| Soil | N | **4.64 b** | **2.47 a** | **29.5 a** | **0.50 b** | 6.46 | **3.3 b** | **6.52 b** | **0.21 b** | **0.05 b** | **0.58 a** |
| | S | **5.06 a** | **1.22 b** | **20.9 b** | **6.56 a** | 5.91 | **4.4 a** | **18.13 a** | **0.34 a** | **0.11 a** | **0.36 b** |
| Biochar (Bio.) | 0% | **4.64 b** | **2.17 a** | **22.8 b** | **2.76 b** | 6.33 | **3.54 b** | **14.89 a** | 0.27 | **0.12 a** | 0.51 |
| | 5% | **5.05 a** | **1.52 b** | **27.6 a** | **4.30 a** | 6.04 | **4.20 a** | **9.76 b** | 0.27 | **0.03 b** | 0.44 |
| Manure (Man.) | - | 4.74 | 1.70 | **24.2 b** | 3.85 | 6.24 | **4.0 a** | **7.88 b** | 0.30 | **0.09 a** | 0.43 |
| | + | 4.96 | 1.99 | **26.3 a** | 3.21 | 6.13 | **3.7 b** | **16.77 a** | 0.25 | **0.06 b** | 0.52 |
| Soil X Bio | N 0% | **4.71 b** | 2.75 | 27.2 | **0.62 c** | 7.00 | **3.43 b** | 7.68 | 0.21 | **0.06 b** | 0.66 |
| | N 5% | **4.56 b** | 2.20 | 31.9 | **0.38 c** | 5.92 | **3.18 b** | 5.36 | 0.20 | **0.04 bc** | 0.51 |
| | S 0% | **4.58 b** | 1.60 | 18.4 | **4.90 b** | 5.67 | **3.65 b** | 22.1 | 0.33 | **0.18 a** | 0.36 |
| | S 5% | **5.55 a** | 0.84 | 23.4 | **8.21 a** | 6.15 | **5.23 a** | 14.1 | 0.34 | **0.03 c** | 0.36 |
| Soil X Man. | N - | 4.42 | 2.23 | 29.2 | **0.39 c** | 6.56 | 3.32 | **6.36 c** | **0.18 b** | **0.05 c** | 0.48 |
| | N+ | 4.85 | 2.71 | 29.9 | **0.61c** | 6.36 | 3.28 | **6.68bc** | **0.23 b** | **0.05 bc** | 0.69 |
| | S - | 5.06 | 1.16 | 19.2 | **7.30 a** | 5.92 | 4.74 | **9.40 b** | **0.41 a** | **0.14 a** | 0.37 |
| | S + | 5.07 | 1.28 | 22.6 | **5.81 b** | 5.90 | 4.15 | **26.8 a** | **0.27 ab** | **0.08 b** | 0.36 |
| Bio X Man. | 0% - | 4.48 | **2.23 a** | 22.4 | 3.53 | 6.64 | 3.81 | **6.84 b** | **0.25 ab** | **0.15 a** | 0.41 |
| | 5% - | 5.00 | **1.16 b** | 25.9 | 4.17 | 5.84 | 4.25 | **8.91 b** | **0.34 a** | **0.04 c** | 0.44 |
| | 0% + | 4.81 | **2.11 a** | 23.1 | 2.00 | 6.02 | 3.27 | **22.9 a** | **0.30 ab** | **0.09 b** | 0.61 |
| | 5% + | 5.11 | **1.88 a** | 29.4 | 4.42 | 6.23 | 4.16 | **10.6 b** | **0.20 b** | **0.03 c** | 0.43 |
| Soil X Bio. X Man. | N 0% - | 4.50 | 2.80 | 28.2 | **0.46 c** | 7.01 | 3.45 | **7.36 cd** | 0.16 | **0.06 c** | 0.54 |
| | N 0% + | 4.92 | 2.69 | 26.2 | **0.79 c** | 6.99 | 3.41 | **7.99 cd** | 0.26 | **0.06 c** | 0.78 |
| | N 5% - | 4.34 | 1.66 | 30.2 | **0.33 c** | 6.12 | 3.20 | **5.35 d** | 0.21 | **0.03 c** | 0.43 |
| | N 5% + | 4.78 | 2.73 | 33.6 | **0.43 c** | 5.73 | 3.16 | **5.37 d** | 0.20 | **0.04 c** | 0.59 |
| | S 0% - | 4.46 | 1.66 | 16.7 | **6.60 a** | 6.28 | 4.17 | **6.33 d** | 0.34 | **0.24 a** | 0.27 |
| | S 0% + | 4.70 | 1.53 | 20.1 | **3.21 b** | 5.05 | 3.14 | **37.8 a** | 0.33 | **0.13 b** | 0.45 |
| | S 5% - | 5.65 | 0.66 | 21.6 | **8.01 a** | 5.57 | 5.30 | **12.4 bc** | 0.48 | **0.04 c** | 0.46 |
| | S 5% + | 5.45 | 1.02 | 25.2 | **8.41 a** | 6.74 | 5.16 | **15.8 b** | 0.20 | **0.03 c** | 0.26 |
| Analysis of variances Prob>F | | | | | | | | | | | |
| Soil | | **0.02** | **<0.01** | **<0.01** | **<0.01** | 0.16 | **<0.01** | **<0.01** | **0.001** | **<0.01** | **<0.01** |
| Biochar | | **0.04** | **<0.01** | **<0.01** | **0.02** | 0.45 | **<0.01** | **0.01** | 0.972 | **<0.01** | 0.17 |
| Manure | | 0.22 | 0.07 | **0.03** | 0.27 | 0.76 | **0.02** | **<0.01** | 0.20 | **0.01** | 0.08 |
| Soil X Bio. | | **<0.01** | 0.51 | 0.86 | **<0.01** | 0.06 | **<0.01** | 0.18 | 0.83 | **<0.01** | 0.14 |
| Soil X Man. | | 0.25 | 0.25 | 0.15 | **<0.01** | 0.81 | 0.06 | **<0.01** | **0.01** | **0.01** | 0.05 |
| Bio. X Man. | | 0.64 | **0.01** | 0.13 | 0.06 | 0.19 | 0.10 | **<0.01** | **0.01** | **<0.01** | 0.05 |
| Soil X Bio. X Man. | | 0.49 | 0.19 | 0.17 | **<0.01** | 0.08 | 0.11 | **<0.01** | 0.30 | **0.03** | 0.16 |

[y]Mean values followed by the same letter within a column for a group of means are not significantly different ($p<0.05$, Tukey's test), the bolded values indicate the statically significant data, Codes[z]: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.

**Table B-3.** Available nutrients concentration of post soil in response to soil type, biochar and manure treatments used in the experiment.

| Group | Treatment | P | $NO_3^-$-N | $NH_4^+$-N | S | K |
|---|---|---|---|---|---|---|
| | | | | mg kg$^{-1}$ | | |
| Soil | N | **38.3 b** | **73.1 b** | **7.4 b** | **68 b** | **470 a** |
| | S | **105.4a** | **100.6 a** | **13.6 a** | **452 a** | **272 b** |
| Biochar (Bio.) | 0% | **69.3 b** | **83.5 b** | **9.25 b** | **93 b** | **326 b** |
| | 5% | **74.4 a** | **90.1 a** | **11.1 a** | **427a** | **416 a** |
| Manure (Man.) | - | **65.8 b** | **84.7 b** | **10.1 b** | 171 | **275 b** |
| | + | **77.9 a** | **88.9 a** | **3.36 a** | 349 | **467 a** |
| Soil X Bio | N 0% | 36.4 | **71.9 c** | **7.00 c** | **53 c** | **415 b** |
| | N 5% | 40.2 | **74.2 c** | **7.87 c** | **82 b** | **525 a** |
| | S 0% | 102.3 | **95.1 b** | **11.5 b** | **132 b** | **238 d** |
| | S 5% | 108.5 | **106.1 a** | **15.78 a** | **772 a** | **307 c** |
| Soil X Man. | N - | **30.1 d** | **69.5 c** | 6.71 | 73 | 374 |
| | N+ | **46.5 c** | **76.6 b** | 8.16 | 62 | 566 |
| | S - | **101.6 b** | **99.9 a** | 13.3 | 269 | 176 |
| | S + | **109.2 a** | **101.3 a** | 13.9 | 635 | 368 |
| Bio X Man. | 0% - | 63.1 | 81.1 | 8.63 | **140 c** | 233 |
| | 5% - | 68.5 | 88.4 | 11.4 | **202 b** | 318 |
| | 0% + | 75.5 | 86.0 | 9.87 | **45 d** | 420 |
| | 5% + | 80.2 | 91.9 | 12.2 | **652 a** | 513 |
| Soil X Bio. X Man. | N 0% - | 28.7 | **69.1 e** | **6.57 e** | **61 c** | 314 |
| | N 0% + | 44.1 | **74.7 cd** | **7.42 de** | **45 c** | 517 |
| | N 5% - | 31.5 | **69.9 de** | **6.85 e** | **86 c** | 435 |
| | N 5% + | 49.0 | **78.5 c** | **8.90 cd** | **79 c** | 615 |
| | S 0% - | 97.6 | **93.1 b** | **10.70 bc** | **45 c** | 152 |
| | S 0% + | 107.0 | **97.2 b** | **12.32 b** | **220 b** | 324 |
| | S 5% - | 105.6 | **106.8 a** | **16.07 a** | **318 b** | 201 |
| | S 5% + | 111.5 | **105.4 a** | **15.50 a** | **1226 a** | 412 |
| Analysis of variances Prob>F | | | | | | |
| Soil | | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** |
| Biochar | | **<0.01** | **<0.01** | **<0.01** | **<0.01** | **<0.01** |
| Manure | | **<0.01** | **<0.01** | **0.03** | 0.67 | **<0.01** |
| Soil X Bio. | | 0.13 | **<0.01** | **<0.01** | **<0.01** | **0.01** |
| Soil X Man. | | **<0.01** | **0.01** | 0.13 | 0.21 | 0.97 |
| Bio. X Man. | | 0.63 | 0.43 | 0.41 | **<0.01** | 0.65 |
| Soil X Bio. X Man. | | 0.08 | **0.01** | **0.09** | **<0.01** | 0.06 |

[y] Mean values followed by the same letter within a column for a group of means are not significantly different ($p<0.05$, Tukey's test), the bolded values indicate the statically significant data, Codes[z]: N: Non-saline soil, S: Saline-sodic soil, (+) and (-): with and without manure addition, respectively, 0% and 5% denote biochar application rate based on weight.