Effect of Biochar on Soil Fertility, Nitrate Losses, Dissolved Organic Carbon, Forage Crop Production and Greenhouse Gas (GHG) Emissions

by

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in

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Dedicated to:

my parents….

, my wife….

, and my kids….

Riad.

Abstract

The growing need to improve soil fertility and enhance crop production has led to increase in the nitrogenous (N) fertilizer use, which could result in detrimental effects due to the possible increase in greenhouse gas (GHG) emissions and nitrate leaching losses. Therefore, there is a pressing need to address the negative environmental effects of nitrogen fertilizer use through better management practices. Biochar applications to the agricultural soils have been recognized as a unique strategy for improving soil fertility, mitigating GHG emission, enhancing carbon sequestration, and plant nutrient use efficiencies by increasing nutrients uptake while reducing the leachate losses. Considering multidimensional benefits of biochar, the current study investigated the effects of different biochar application rates on podzolic soil fertility, GHGs mitigation potential, soil nitrogen dynamics, crop productivity and forage quality in eastern Newfoundland podzolic soils. The first experiment was conducted to assess the nitrate adsorption potential of four different biochar feedstocks including, spruce-bark biochar at 550°C (SB550), hardwood biochar at 500°C (HW500), fir/spruce biochar at 427°C (FS427), and softwood biochar at 500°C (SW500). The results showed that SB550 has the highest nitrate adsorption capacity (184 mg g^{-1}) among others. The second experiment was conducted in a greenhouse with five rates of SB550 and two N application levels to (i) investigate the capability of biochar application for improving the soil fertility, forage production, forage quality, and nutrient uptake, (ii) assess their effects on soil total nitrogen (TN), nitrate (NO_3^-), ammonium (NH_4^+) dynamics and dissolved organic carbon (DOC). Results indicated that biochar application significantly improved soil pH, Soil Organic Matter (SOM), Cation Exchange Capacity (CEC), and available nutrients in the soil. Moreover, SB550 biochar has significantly reduced NO_3^-, NH_4^+, TN, and DOC in the leachate compared to the control treatment. The third experiment was conducted under field conditions. Four rates of

HW500 biochar applications, with three levels of nitrogen fertilizer applications (Urea 46-0-0) that were applied at the rates of 0, 65 and 130 N kg/ha to the *Festulolium* forage crop field. Biochar application has significantly reduced GHG emissions and increased the *Festulolium* productions. Thus, biochar application has shown to be a promising technique for sustainable agricultural management practices in the eastern Newfoundland Podzolic soil.

Keywords: nitrogenous fertilizer, agriculture, biochar, nitrate leaching losses, greenhouse gas emissions, forage production.

Co-authorship statement

Four manuscripts were based on chapter 2, entitled "***Influence of biochar feedstocks on nitrate adsorption capacity***", chapter 3 " ***Effects of spruce bark biochar on soil fertility, forage crop production, forage quality, and nutrient uptake in the eastern Newfoundland podzolic soil***", chapter 4 " ***Spruce bark biochar application minimizes nitrogen and carbon leaching losses from the eastern Newfoundland podzolic soil***", and chapter 5 " ***Effect of hardwood biochar and nitrogen applications on greenhouse gas emission from the agricultural forage crop system in the eastern Newfoundland podzolic soil***". Manuscript chapters from 2 to 5 were being prepared to be submitted for publication by Riad Eissa, Jianghua Wu, David B. McKenzie, and Lordwin Jeyakumar. Riad Eissa, the thesis author, was responsible for data collection, data analysis and manuscript writing. Dr. Jianghua Wu (supervisor), Dr. David McKenzie (co-supervisor) and Dr. Lordwin Jeyakumar (committee member) were the supervisory authors, and they were involved in the thesis formulation and manuscripts editing.

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List of Abbreviations

ADF: Acid Detergent Fibre

AEC: anion exchange capacity

B: Biochar

C_0: nitrate initial concentration

Ce: nitrate equilibrium concentration

CEC: cation exchange capacity

CH_4: Methane

CO_2: Carbon dioxide

Dig. Energy: Digestible Energy

DOC: Dissolved organic carbon

ECD: Electron Capture Detector

F.C: Field capacity

FID: Flame Ionization Detector

FT-IR: Fourier Transfer Infrared

k_f: Freundlich affinity coefficient

k_L: Langmuir sorption binding strength coefficient n: Freundlich linearity constant

N: Nitrogen

NDF: Neutral Detergent Fibre

NH_4^+: ammonium

NO_3^-: nitrate

N_2O: Nitrous oxide

qe: amount of the absorbed nitrate

qm: Langmuir maximum adsorption capacity

Øs: soil porosity

SEM: Scanning electron microscopy

SM: Soil moisture

SOC: Soil organic carbon

SOM: Soil organic matter

TCD: Thermal Conductivity Detector

TDN: Total Digestible Nutrients

TN: total nitrogen

W.P: Wilting point

Chapter 1

1. Introduction

1.1. Overview

1.1.1. Food security and sustainable agriculture

The Newfoundland and Labrador government is striving to increase food self-sufficiency at least by 20 per cent in 2022. To make this happen, the provincial government is taking efforts to convert forestland into farmland. However, soil acidity is one of the key issues in the province and soil amendments are therefore required to enhance soil productivity and to improve the efficiency of fertilizers required to promote plant growth. Nitrogen (N) fertilizers is the most common nutrient that needs to be added for improving soil fertility, forage crop production and yield. It may cause a serious threat to the quality of surface and groundwater (Gai et al., 2014), and it can also, increase greenhouse gas (GHG) emissions from agricultural ecosystems (Gregorich et al., 2005). Therefore, in order to improve soil quality, boost crop production, reduce nitrate (NO_3^-) losses and mitigate global warming at the same time, it is necessary to find out beneficial strategies to accomplish all these issues together through biochar application, which has been found to have significant potential to boost the biomass production via increasing soil quality and reducing nitrate leaching and GHG emissions (Gai et al., 2014; Zhai et al., 2015; Zhang et al., 2013). This research introduces biochar as a soil amendment to improve soil fertility and reduce GHG. Application of biochar to acidic soils may provide a new solution for Newfoundland and Labrador soils and enhance long-term carbon sequestration.

1.1.2. Biochar production and properties

Biochar is a carbon-rich organic material produced from forest and agricultural waste such as wood, manure, and leaves by pyrolysis of these organic materials under high-temperature and low-oxygen conditions (Singh and Singh, 2020). In general, biochar has low bulk density, lower than 0.6 g cm^{-3} (Blanco-Canqui, 2017), high porosity, which increases with increasing temperature during the pyrolysis (Brewer et al., 2014; Somerville and Jahanshahi, 2015). The biochar surface area ranges from 100 to 800 m^2 g^{-1} (Weber and Quicker, 2018), and biochar pore diameters are from 1000 to 0.0001 µm (Brewer et al., 2014), and biochar pH ranges from 5.9 to 12.3 with an average of 8.9 (Ahmad et al., 2014), which increases with increase pyrolysis temperatures as well as cation exchange capacity (CEC) (Wang et al., 2015). Biochar has broad application, it is used for soil quality improvement, soil remediation, carbon sequestration, climate change mitigation, remediation of organic and inorganic pollutants (Ahmad et al., 2014; Lehmann et al., 2006; Novak et al., 2009). The positive effects of biochar on soil fertility have been demonstrated fundamentally by increased soil pH in the acidic soils (Van Zwieten et al., 2010) or improving nutrient retention through cation adsorption (Liang et al., 2006). Biochar can also change soil microbial community composition (Grossman et al., 2010; Lehmann et al., 2011; Liang et al., 2010). Such changes as a result of biochar amendment can affect the nutrient cycles (Steiner et al., 2008), soil structure (Rillig and Mummey, 2006) and hence, affect plant growth (Warnock et al., 2007).

1.1.3. Effect of feedstock and pyrolysis temperature on Biochar quality

The sources of wood feedstock material may influence the resulting biochar's chemical and physical characteristics due to the variation in chemical nature of these sources. Atkinson et al., 2010) reported that the initial number of mineral elements in the feedstock before burning could positively affect the quality of produced biochar. Gaskin et al., (2008) found the chemical composition of the biochar generated from three different sources (Poultry litter, Peanut hulls, and Pine chips) was influenced strongly by the total element concentration on the feedstock sources. Biochar generated from feedstocks with a low nutrient content may affect soil quality leading to insignificant improvement in crop growth, which may be attributed to the limitation of available nutrients in the generated biochar. Thus, the positive effects of biochar on plant growth and crop yields are associated with higher nutrient availability in the generated biochar (Alburquerque et al., 2014). The meta-analysis by Jeffery et al., (2011) showed that biochar produced from different feedstocks under the same pyrolysis conditions were different in their impact on soil and crop properties. These results have been attributed to the variations in the feedstock chemical composition, such as cellulose and lignin contents (Streubel and Kruger, 2011). Also, the variations in species wood structure can change the properties of produced biochar, such as porosity and adsorptive capacity (Voorde et al., 2014). Feedstock can also affect biochar molecular structure and pores size distribution (Ahmad et al., 2012; Keiluweit et al., 2010), surface area, and functional groups (Sohi et al., 2010) in biochar, and consequently affect the adsorption properties of generated biochar (Gai et al., 2014). Sun et al., (2011) found that biochar produced from poultry-litter has larger porosity and surface area than wheat-straw biochar, despite the fact that both biochar were generated under the same temperature (400^{o}C) during pyrolysis.

The feedstock types and pyrolysis conditions are important factors that can influence biochar structural, morphological, and physicochemical properties. In general, the feedstock consists of three types of natural polymers: lignin (20-40% in woods and 10-40% in grass materials, cellulose (50% of dry matter), and hemicellulose (10-30% in woods and 20-40% in grass materials) (Jindo et al., 2014). Biochar also contains different active adsorption sites which includes aromatic carbon skeleton, mineral crystal, C–C, C=C, OH–, CHO–, –COOH, and oxygen-containing functional groups which can be influenced by feedstock and pyrolysis temperature (Liu et al., 2018; Tomczyk et al., 2020; Wang et al., 2019). In addition to feedstock nature, pyrolysis temperature is another factor that can affect biochar properties. Increase pyrolysis temperature may lead to increase surface area and develop aromatic compounds of biochar (Jia et al., 2018; Jindo et al., 2014). The higher pyrolysis temperature increase biochar pH and EC values. Hadi and Norazlina, (2021) reported that increase pyrolysis temperature from 350 to 750 ^{o}C has increased the biochar pH and EC values. This was attributed to minerals separation from the organic matrix, volatile matter losses, and formation alkaline metal salts (ash) (Claoston et al., 2014).

The value of biochar as a nutrient source can also be varied by feedstock; Gaskin et al. (2010) reported that the addition of biochar made from peanut hull increased K, Ca, and Mg in the applied surface soil, while the pine chip biochar had no effect on the other nutrients except Ca, and the two biochar additions had a little different impact on nutrient concentration in corn tissue. 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. Atkinson et al. (2010) reported that the feedstock's chemical composition influences the generated biochar's chemical and structural composition and, therefore, it is reflected in its behaviour, and function in soils. Sources of biochar are expected to have a different influence not only on the generated biochar but also on the biochar amended soils. Furthermore, as biochar may serve as nutrient sources when they are incorporated into the soils, it is critical to study the effects of different biochar generated from different feedstocks on the benefits of soil amendments. However, the rate of biochar added to the soil can affect plant growth. Atkinson et al. (2010) found a significant improvement in plant productivity depending on the amount of biochar addition to the soil in the tropical regions. This result indicates that the value of biochar addition to each soil in different areas must be explored for saving time, costs, labour, and for reducing harmful impacts of nitrate leaching on the health, land, and the surrounding environment.

1.1.4. Potential of biochar application to reduce nitrate leaching and increase nutrient retention

Nitrogen (N) fertilizer applications have an important influence on soil carbon pools as well as on plant biomass production (Al-Kaisi et al., 2008), and it is responsible for about 30-50% of crop yield increases (Zhou et al., 2016). The N fertilizer application could have a negative impact on the environment through NO_3^- leaching to surface and groundwater. Thus, NO_3^- is considered the most common contaminant of groundwater in the world (Goodwin et al., 2015; Gurdak and Qi, 2012). Studies have found that biochar application can have the potential of lowering NO_3^- leaching. Steiner et al. (2010) found that mixed poultry litter with 20% of biochar reduced total N leaching losses by up to 52%. Also, Yao et al. (2012) concluded that the Brazilian pepperwood biochar and peanut hull biochar reduced the total amount of NO_3^- in the leachates by 34%, and they suggested that the impact of biochar application on the nutrients leaching from agricultural soils is different, depending on the biochar and nutrient types. According to Kumar et al. (2016), biochar application at the rate of 20 g kg^{-1} soil reduced the NO_3^- leaching up to 29% in the low carbon soils. Likewise, the amount of NO_3^- leaching significantly decreased with biochar application on Chinese upland red soil, and the water holding, and cation exchange capacities increased dramatically by increased biochar application rates (Jin et al., 2016). The positive impact of biochar application on the NO_3^- leaching in biochar- amended soil could be attributed to the increase of soil cation exchange capacity (CEC) and soil anion exchange capacity (AEC) by the biochar application (Kim, 2014; Sika and Hardie, 2014). Increasing the water holding capacity of biochar-amended soil can reduce dissolved N concentration in the leached water, which can be attributed to the decrease in the solute movement with the leachate (Jin et al., 2016). Likewise, changing the soil physicochemical properties due to the biochar applications can alter soil microbial community and activity, shifting microbial N transformation and minimizing NO_3^- leaching under the biochar soil amended (Kim, 2014; Xu et al., 2016).

1.1.4.1. Mechanisms involved in nitrate retention in biochar and biochar-amended soils

Different mechanisms that can explain the nitrate retention by biochar have been proposed by previous literature, including (i) bridge bonding between nitrate and the negatively charged functional groups of biochar surfaces through bridge bonds of polyvalent cations, such as Ca^{2+} or Mg^{2+}, or through nitrate and H-bonding (Libutti et al., 2016; Mukherjee et al., 2011). (ii) direct nitrate adsorption through the electrostatic attraction mechanisms in acidic conditions (Lawrinenko and Laird, 2015). (iii) nitrate adsorption through capillary forces of biochar pores, in which the biochar porosity can contribute to nitrate adsorption by imprisoning nitrate containing water within its pores. (Libutti et al., 2016; Major et al., 2009).

The pore-filling is another important mechanism that can allow nutrient adsorption into the micropores and narrow mesopores of biochar. The micropores (< 2 nm) and mesopores (2– 50 nm) of the biochar surface determine the ability of the pore-filling mechanism in the nutrient adsorption (Abbas et al., 2018; Hao et al., 2013). Thus, the pore size of biochar are major factors for adsorbate diffusion (Wang et al., 2018), as the pore-filling mechanism perform when the biochar pore and the adsorbate molecular structure are close in size (Binh and Kajitvichyanukul, 2019; Lian et al., 2016). Mathurasa and Damrongsiri, (2018) reported that decrease in the average pore diameter of the modified rice husk biochar after ammonium and nitrate adsorption was referred to the pore-filling mechanism.

1.1.4.2. Biochar surface functional groups and pH

It has been reported that the pH of the aqueous solution influences the biochar adsorption capacities, which is found to be directly related to the biochar surface oxygen-containing functional groups (Ambaye et al., 2020). The surface charge of biochar depends on the aqueous solution's pH, which characterizes the biochar adsorption capacity (Zhang et al., 2013). Mukherjee et al., (2011) found that the biochar surface has a positive charge at a low pH value, whereas it has a negative charge at a higher pH value. Thus, the anions adsorption by the biochar surface positive charge was increased at low pH values and decreased at higher pH values due to the electrostatic attraction between biochar surface and negatively charged anions (Chintala et al., 2013; Ganesan et al., 2013; Olgun et al., 2013).

Biochar surface is usually negatively charged, which can assist the electrostatic attraction/repulsion of positively and negatively charged ionic organic compounds with biochar (Qiu et al., 2009; Xu et al., 2011). Biochar contains changeable charge surfaces (pH-dependent charge). An increase in the pH on these surfaces leads to an increase in the negative charge (Xu et al., 2011). Thus, the relative impact of ionic strength on the adsorption onto the biochar surface is depending on pH, in which the effect of ionic strength on adsorption onto biochar can be positive or negative based on the pH value (Bolan et al., 1999).

The surface functional groups of biochar could receive or donate a proton (H^+) depending on the pH value of the aqueous solution. At a higher pH, the carboxylic acids (-COOH) and some of the hydroxyls (-OH) give up protons and become negatively charged. Whereas, at the low pH value of the aqueous solution, these same groups can accept a proton and become positively charged (Abbas et al., 2018). This means that the biochar could carry a negative charge at the higher pH solution (≥ 8.0) and a positive charge at the lower pH solution (< 7.0). Thus, the electrostatic attraction could exist between the positively charged biochar and the negatively charged anions and between the negatively charged biochar and the positively charged cations. This mechanism is considered as one of the most reasonable mechanisms that explain the adsorption of positively and negatively charged compounds to the surfaces of the biochar (Li et al., 2018)

1.1.5. Potential of biochar application to reduce greenhouse emissions.

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the primary GHG emitted from agricultural soil (Ali et al., 2017). Agriculture contributes about 10-12% of the global anthropogenic emissions (Serrano-Silva et al., 2014; Van Zandvoort, 2016), which is expected to increase due to the intense agricultural practices worldwide (S. Chen et al., 2016; Smith et al., 2007). CO_2 is produced in the soil through heterotrophic microbial respiration and autotrophic root respiration, which are considered the main carbon emissions from terrestrial ecosystems to the atmosphere (Dalal and Allen, 2008; Han et al., 2007). CH_4 is released by methanogenesis under anaerobic conditions; therefore, animal manure ((liquid or semi-liquid), rice paddies and wetlands are CH_4 sources resulting from organic matter bacterial decomposition. Whereas, under aerobic conditions, soils are CH_4 sink (methanotrophs) by methane assimilating bacteria and autotrophic ammonium-oxidizing bacteria (Dalal and Allen, 2008). N_2O is produced in the soil primarily by microbial nitrification and denitrification (Dalal and Allen, 2008). Denitrifying bacteria produce N_2O during the NO_3^- and/or NO_2 reduction under anaerobic conditions. While in aerobic conditions, nitrifying bacteria oxidize NH_4^+ to NO_3^- and release N_2O as a transitional product (Dalal et al., 2003). Denitrification is considered the primary microbial process responsible for N_2O consumption by converting N_2O to N_2 (Chapuis-lardy et al., 2007; Liu and Greaver, 2009). Lower inorganic nitrogen (N) and lower oxygen content are assumed to support N_2O consumption. However, the N_2O combustion mechanism is still not completely understood (Chapuis-lardy et al., 2007).

The application of biochar in the agricultural soil has been proposed as means of establishing a long-term sink for atmospheric CO_2 (Fowles, 2007; Lehmann et al., 2006; Steiner et al., 2007). Likewise, biochar can impact the other GHG emissions from soil, such as nitrous oxide (N_2O) or methane (CH_4) (Clough et al., 2010; Singh et al., 2010; Taghizadeh-toosi et al., 2011; Zhang et al., 2010). Applying biochar to the soil can change soil physical characteristics, such as soil bulk density (Lim et al., 2016; Major et al., 2010) and soil-water holding capacity; thus, such changes can affect the production and emission of CO_2, CH_4, and N_2O (Hawthorne et al., 2017; Major et al., 2009). Therefore, the application of biochar in agricultural soil has the potential to reduce GHG emissions and mitigate climate change (Cayuelaa et al., 2014; Lehmann et al., 2011).

Yang et al., (2018) found that biochar application at rates 20 t ha^{-1} decreased CO_2 emission by 1.64 - 8.83 % in rice paddy fields under water-saving irrigation, relative to the control. Likewise, Shen et al., (2017) reported that over two years of field biochar application at 20 and 30 t ha^{-1} significantly reduced the cumulative CO_2 emissions from biochar-soil amended treatment compared to the non-biochar amendment soil. Biochar as a soil amendment can also reduce CH_4 and N_2O from agricultural fields, which was attributed to the high organic carbon content in the biochar and changing soil properties and soil microbial activity (Liu et al., 2010; Zhang et al., 2010). Karhu et al., (2011) reported that biochar has reduced CH_4 emissions from water-logged rice paddies and increased CH_4 uptake in aerobic soils. Similarly, the wood biochar application at a rate of 20 t ha^{-1} has shown a significant reduction of CH_4 in non-fertile tropical soil (Rondon et al., 2006). Another study by Rondon et al., (2005) reported that applying biochar at 15 g kg^{-1} and 30 g kg^{-1} completely suppressed the CH_4 from the agricultural field of Brachiaria humidicola grass and soybean cropland, respectively. Similarly, biochar application was found to reduce the N_2O emissions. Yanai et al., (2007) found a significant decrease of N_2O emissions followed by the application of biochar in a wetted Typic Hapludand. Also, Rondon et al. (2006), observed a significant reduction in the N_2O emissions from acid savanna soil reached 15 mg m^{-2} in the eastern Colombian Plains. These reductions of N_2O emissions were attributed to the enhancement of ammonium adsorption and retention under the biochar-soil amended (Yanai et al., 2007; Zhang et al., 2010).

1.1.5.1. Mechanisms involved in reducing soil GHG emissions from biochar-amended soils

Soil biochar application has a direct and indirect impact on soil physical and chemical properties and soil microbial activities, which in turn affect soil GHG production and emission (Singh and Singh, 2020). However, the potential effect of biochar to reduce GHG emissions is still controversial. Sun et al., (2014) reported that the application of biochar at the rate of 30 t ha^{-1} had reduced CO_2 emission by 31.5% from pine forest soil. Whereas, in a field experiment, wheat straw biochar had significantly increased CO_2 emissions by 12% while reducing N_2O emissions by 41.8% (Zhang et al., 2012). However, Hawthorne et al., (2017) found that CO_2 emission from Douglas-fir Forest soil was higher under biochar application at the rate of 10% compared to the rate of 1%. The underlying mechanisms of biochar effects on soil CO_2 emissions can be generally summarized by the following processes: (i) biochar contains labile organic carbon pool in the soil, which may promote soil CO_2 emissions (Mukherjee and Lal, 2013; Spokas, 2013; Yoo and Kang, 2012); (ii) biochar has a large adsorption capacity that can absorb soil CO_2 molecules and decrease microbes' enzymatic activities (Horák and Šimanský, 2017; Kasozi et al., 2010; Liang et al., 2010) ; (iii) biochar application can affect physical and chemical properties such as aggregation, porosity, water content, CEC, and pH (Jones et al., 2011; Liang et al., 2010), which in turn indirectly affect

CO_2 emissions; and (iv) biochar application can influence the diversity and activities of CO_2 microbial producers (Mitchell et al., 2015; J. Wang et al., 2016; Zhang et al., 2012).

Using synthetic nitrogen (N) fertilizer is considered the main source of agricultural soil emission of N_2O (W. N. Smith et al., 2008). However, reduction of soil N_2O emission by biochar was first reported by Rondon et al. (2005); they found that soil N_2O emission was reduced by up to 50% for soybean and by up to 80% for grass growing in a low-fertility oxisol Colombian savanna. In a meta-analysis of short and long-term studies for the effect of biochar on N_2O emissions, Cayuela et al. (2015) recorded that soil N_2O emission was decreased by 54 % under lab conditions and 28 % under field conditions. Also, Fidel et al. (2019) noticed a significant reduction of N_2O emission by biochar from a corn cropping system, and they were attributed that to the impacts of soil moisture and soil temperature on N_2O after biochar amendment in the soil. In the meta-analysis of the role of biochar in mitigating soil N_2O emissions, Cayuela et al., (2014) found that biochar decreased soil N_2O emissions by 54 % in laboratory and field studies. The meta-analysis suggested that biochar feedstock, pyrolysis conditions and biochar chemical properties were the main factors affecting the N_2O emissions, while the reduction of N_2O emissions directly correlated to the biochar application rates (Cayuela et al., 2014). Likewise, the meta-analysis proposed that the interactions between biochar, soil texture, and nitrogen fertilizer form have a significant effect on the soil N_2O emissions (Cayuela et al., 2014).

Biochar application has been reported to reduce the soil N_2O emissions through its impact on soil physical properties, by reducing soil bulk density (Rogovska et al., 2011), or by improving soil moisture (Yanai et al., 2007), and increasing soil porosity and aeration (Heincke and Kaupenjohann, 1999). Different hypotheses have been proposed to explain the underlying mechanisms for reducing the soil N_2O emissions by biochar. The primary mechanism of reducing soil N_2O emissions is increasing oxygen in the soil due to soil aeration (Singh and Singh, 2020). Soil moisture and aeration can control the oxygen availability for microorganisms in the soil through water-filled pore space (WFPS), which in turn affect the nitrifiers and denitrifiers activities, as nitrification was the main dominant process for N_2O generation at 35–60% WFPS, whereas denitrification was the dominant process at 70% WFPS and above (Bateman and Baggs, 2005). Under the oxygen (O_2) deficit conditions, NO_3^- reduce to di-nitrogen (N_2) without emitting a considerable amount of N_2O. However, by increasing O_2 availability in the soil, the amount of emitted N_2O can be significantly increased. In this situation, nitrifier denitrification is the main process of N_2O emission (Toyoda et al., 2011). The denitrification process is shown in Equations (1.1) as described by (Muñoz et al., 2010).

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \qquad (1.1)$$

When the WFPS is decreased, gas transport and diffusion in the soil is increased, allowing the N_2O to be emitted (Chapuis-Lardy et al., 2007). Decreasing the WFPS increases O_2 availability, which inhibits denitrifiers' activities in the soil (Cayuela et al., 2014; Singh and Singh, 2020).

Another underlying mechanism for N_2O emissions by biochar is adsorption of the inorganic nitrogen pool such as NH_4^+ and NO_3^- (Cornelissen et al., 2013), which in turn leads to decreases in nitrogen availability for nitrifiers and denitrifiers, and thereby reducing N_2O emission (Clough et al., 2013; Singh et al., 2010). Soil pH is also another essential factor that can be affected by biochar application. Nitrifiers and denitrifiers can be encouraged to grow under a specific range of soil pH. The optimum range of pH for nitrifiers is slightly acidic to slightly alkaline, whereas the optimum range for denitrifies is pH 4-8 (Liu et al., 2010; Mørkved et al., 2007). Furthermore, the reduction of N_2O emission is also dependent on biochar type, biochar application rate, soil type, and soil moisture content (Singh et al., 2010; Van Zwieten et al., 2010; Waters et al., 2011).

Biochar was also used to reduce methane (CH_4) emissions. Yu et al., (2013) reported that using 10% w/w of chicken manure biochar has significantly decreased the CH_4 emissions from forest soils. Also, Xiao et al., (2016) found that biochar has significantly increased CH_4 uptake in a chestnut plantation in China, regardless of the application rate. Increasing the CH_4 uptake in the soil may be attributed to increases in soil pH by biochar application, which in turn help the methanotrophs growth (Anders et al., 2013; Jeffery et al., 2016), along with decreases in soil bulk density and increases in soil porosity which encourages CH_4 oxidation and uptake by soil microbes (Brassard et al., 2016; Feng et al., 2012; Karhu et al., 2011). Biochar CH_4 reduction may be ascribed to the biochar chemical's inhibitory effect on soil methanotrophs (Spokas, 2013). The porous structure of biochar may allow new habitats for soil microbes to form and increase CH_4 uptake by methanotrophs more than the CH_4 production due to soil aeration improvement. Karhu et al., (2011) reported that CH_4 uptake increased in the biochar amended soil due to improved soil aeration and increased CH_4 diffusion through the soil profile.

Overall, the primary underlying mechanisms for increases in soil CH_4 uptake are; (i) generally, biochar application increases soil pH, which favours the methanotrophy growth (Jeffery et al., 2016; Li et al., 2018); (ii) biochar application decreases soil bulk density and increases soil porosity, which favours CH_4 oxidation and uptake activities by soil bacteria (Brassard et al., 2016). Increased soil porosity and aeration by biochar application can encourage and promote oxic conditions in the soil and decrease CH_4 production, as CH_4 oxidation is an aerobic metabolic process that is dependent on oxygen availability (Brassard et al., 2016).

1.1.6. Effects of biochar on soil fertility and crop production

Applying biochar to low quality soils can increase soil carbon stocks and improve soil fertility (Lehmann et al., 2006; Sohi et al., 2010; Woolf et al., 2010). Biochar application can also increase crop production (Biederman and Harpole, 2013; Jeffery et al., 2011) through increased soil pH (Raboin et al., 2016; Sun et al., 2017), soil cation exchange capacity (CEC) (Liang et al., 2006), soil water holding capacity, nutrient retention (Biederman and Harpole, 2013; Chen et al., 2015; Fischer et al., 2019; Wei et al., 2020), microbial activity, decreases in nutrient leaching (Liu et al., 2013; Major et al., 2010; Ventura et al., 2012) and reduced Al toxicity in the rhizosphere (Hussain et al., 2017; Karer et al., 2013; Kuka et al., 2013; Yang et al., 2013). Furthermore, biochar application can improve the essential macro-and micronutrients supplements for plant growth, particularly in acidic soils (Hussain et al., 2017; Major et al., 2009). Since biochars are generated from different feedstocks, they are carbon-rich materials, containing groups of macro- and micronutrients such as nitrogen (N), phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K), sulfur (S), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) (Gunarathne et al., 2017; Hossain et al., 2011). The amounts of these nutrients in the biochars are mainly dependent on feedstock types, Chan et al., (2007) found that the total N and P were lower in biochars derived from plant feedstocks (e.g., green and wood waste) than biochars derived from animal feedstocks (e.g., broiler liter and sewage sludge).

It was reported by Jeffery et al., (2011) in a meta-analysis that biochar application has significantly increased crop productivity by 10 % on average, whereas Raboin et al., (2016), reported that biochar application has increased the legume and vegetable crop yields in acidic soil (pH < 5) by 30.3% and 28.6%, respectively. Likewise, Biederman and Harpole, (2013) found a significant increment in the yield and aboveground biomass because of biochar application. Moreover, Thomas and Gale, (2015) found that tree biomass increased by 41% under biochar amended soil. The different responses of crop yields to biochar may represent the variations of biochar feedstocks, production methods, application rates, crops, environments, soil texture and pH (Raboin et al., 2016). The effects of biochar application on soil fertility and crop yields are dependent also on inorganic fertilizers and soil organic matter (SOM) (Karer et al., 2013).

1.2. Problem statement

The Newfoundland and Labrador government is striving to enhance food self-sufficiency by at least 20 per cent in the coming years. Therefore, researchers are playing their part to evaluate and apply research to enhance food and animal feed production. However, the department of Fisheries, Forestry and Agriculture states that the soil in Newfoundland and Labrador (NL) has low fertility, high acidity, low soil organic matter (SOM), low CEC which are affecting forage crop production. Thus, soil amendments are required to enhance soil productivity and to improve the efficiency of fertilizers to promote plant growth. The application of organic materials such as mulches, manure, and compost in combination with lime are a common restoration technique that can improve the physical conditions of the soil and alter its nutrient content. However, the benefits of organic materials amendments may lead to quality issues and rapid decomposition. This research introduces biochar as a soil amendment to improve soil fertility, reduce GHG emissions, and increase C storage in the environment. Application of biochar may provide a new enhancement approach for Newfoundland soils and long-term carbon sequestration. Hence, applying biochar as a soil amendment to such soil could be a potential strategy to mitigate nitrate leaching (Steiner et al., 2010), and to increase forage crop productivity by increasing nutrient retention capacity, CEC and organic matter content of the soils (Mao et al., 2013; Wan et al., 2014), and also, reduce the GHG emissions (Ashiq et al., 2020), by enhancing the soil organic carbon (SOC) storage (Mosier et al., 2006; P. Smith et al., 2008). Abedin, (2017) conducted a study on biochar application to reduce leachate toxicity and GHG emissions in municipal solid waste at Labrador. Still, to date, there were no studies focused on the potential benefits of biochar on improve soil fertility and forage crop productivity and minimize nitrate losses and GHG emissions in the eastern podzolic soil of NL. This study investigates biochar's effect on soil fertility, crop productivity, nitrate losses, and GHG emissions in NL's eastern podzolic soil. Therefore, the research questions that this thesis attempted to answer are:

I. What is the best nitrate adsorption capacity among the four different biochar feedstocks?

II. What is the effect of biochar to reduce nitrogen and carbon leaching losses from the eastern Newfoundland podzolic soil?

III. What is the effect of biochar and nitrogen applications on greenhouse gas emission from the agricultural forage crop system in the eastern Newfoundland podzolic soil?

1.3. Objectives of the study

The specific objectives of this thesis were to determine the effectiveness of biochar on: (i) nitrate removal from aqueous solutions, identify the highest nitrate adsorption capacity among four types of biochar, and determine the associated mechanism of nitrate adsorption onto biochar, (ii) to investigate the capability of biochar application for improving the soil fertility, forage production and quality, and nutrient uptake in the podzolic soil of Newfoundland, (iii) to examine the impact of biochar application on reducing leaching losses of N and C from the eastern Newfoundland podzolic soil, (iv) to investigate the capability of biochar application to improve soil fertility, crop productivity and reduce GHG emissions from podzolic soil. Thus, four biochar experiments were conducted, including laboratory, greenhouse, and field experiments, to test the following hypotheses.

- The nitrate adsorption capacity of biochar produced from various feedstocks increase with increasing nitrate concentration in the solution, The nitrate adsorption capacity of biochar produced from various feedstocks is directly related to the pH solution. (Chapter 2).

- Biochar application to the eastern Newfoundland podzolic soil can improve soil properties, nutrient uptake, forage crop production and quality. (Chapter 3).

- Biochar application to soil can minimize N and C leaching losses from the eastern Newfoundland podzolic soil. (Chapter 4).

- Biochar application to the eastern Newfoundland podzolic soil could improve soil fertility and carbon sequestration, reduce GHG emissions, and increase forage crop production. (Chapter 5).

1.4. Thesis Structure

The structure of this thesis consists of six chapters, as shown in Figure 1-1. Each of the chapters from 2 to 5 constitutes a manuscript that will be submitted for publication.

Chapter 1 provides background information, overall objectives, research questions, hypothesis, and an overview of the thesis.

Chapter 2 focuses on the effects of biochar derived from different feedstock types on nitrate adsorption capacity.

Chapter 3 demonstrate the effects of biochar on soil fertility, forage crop production and quality, and nutrient uptake in the shallow podzolic soil of Newfoundland.

Chapter 4 describes the effects of biochar application rates for minimizing nitrogen and carbon leaching losses from the eastern Newfoundland podzolic soil.

Chapter 5 focuses on the effect of biochar and nitrogen applications on GHG emissions from the agricultural forage crop system in the eastern Newfoundland podzolic soil.

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

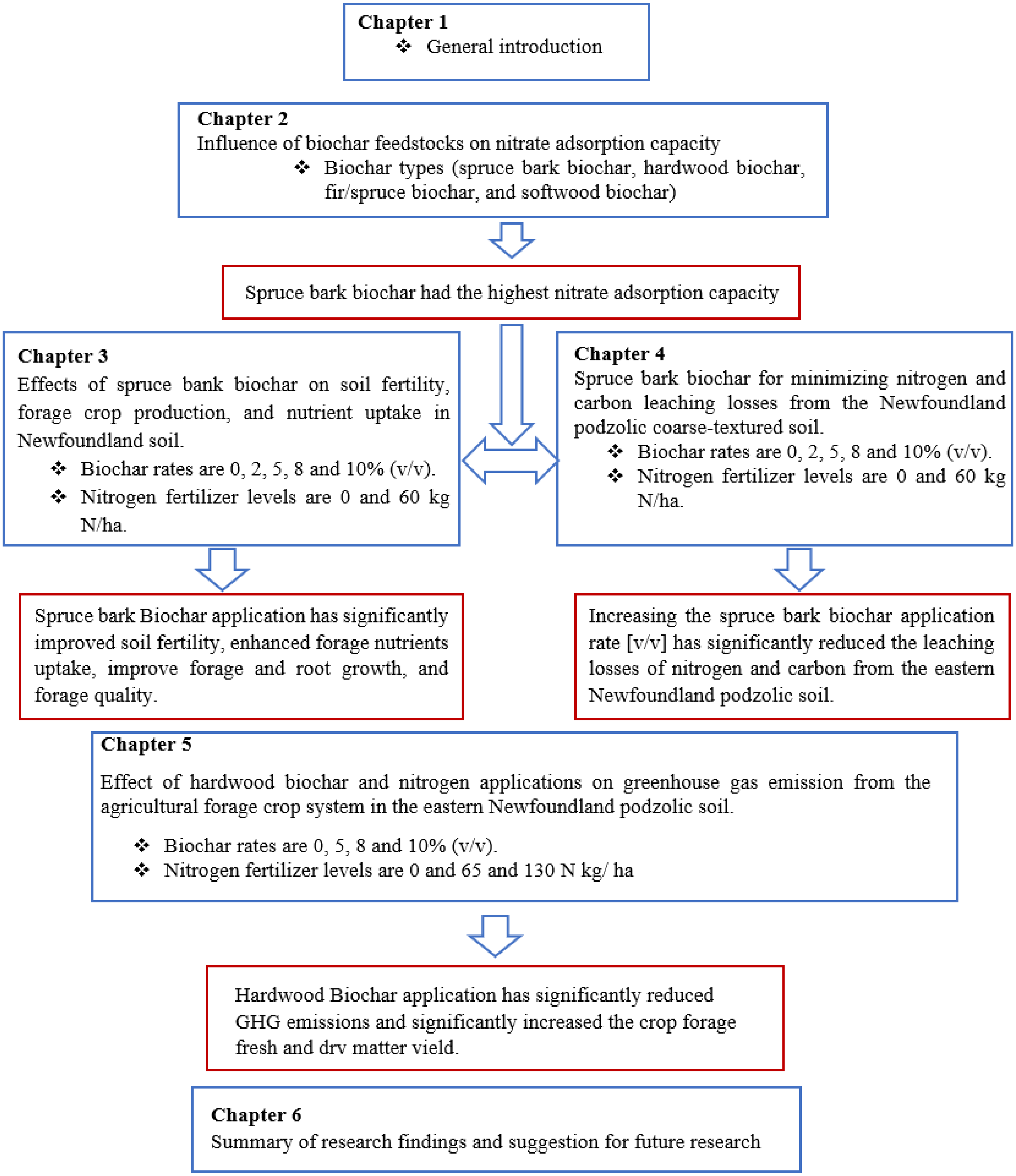

Figure 1-1: Flow chart showing the thesis chapters, blue boxes are indicating the numbers and chapter titles, and the main treatments of the experiments. Red boxes are indicating the main findings of the chapters.

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Chapter 2

Influence of Biochar Feedstocks on Nitrate Adsorption Capacity

Abstract

The demand for intensive agricultural practices to increase food and crop production has risen. Meeting such demand is associated with the usage of high rates of nitrogen (N) as fertilizer. However, serious threats to the quality of the surface and ground waters because of the nitrate losses have been experienced in many areas. The biochar application was used to control and minimize the losses of nitrate. An incubation study of four different biochar feedstocks, including (a) biochar produced from a spruce bark at 550°C (SB550), (b) Neroval biochar produced from hardwood (75% sugar maple) at 500°C (HW500), (c) Airex biochar produced from sawdust of fir/spruce at 427°C (FS427), and (d) mixture biochar produced from softwood at 500°C (SW500), was conducted to assess the nitrate adsorption potential of four different biochar feedstocks. Scanning electron microscopy (SEM) and Fourier transfer infrared (FT-IR) techniques were used to describe the biochars' morphologies and the presence of surface functional groups of biochar. The application of these techniques showed a high surface area with the presence of the surface functional groups such as aromatic C=C stretching and bending, an aromatic C–H bending, and a phenolic O–H bending, which are important for increasing the electrostatic attraction and, subsequently, the nitrate adsorption capacity by the biochar. The Langmuir and Freundlich models were also used to simulate the adsorption isotherms. The equilibrium adsorption data of this study was found to fit well the Langmuir and Freundlich models. The Langmuir model determined that the four biochar types have high nitrate adsorption capacity. Thus, among the four-biochar produced from every feedstock, the SB550 biochar had the highest nitrate adsorption capacity of 184 mg/g.

Keywords: *biochar, feedstock, nitrate, adsorption capacity, Langmuir and Freundlich models*

2. Introduction

2.1. Background

Nitrogen (N) fertilizer is the most common nutrient that needs to be added for improving soil fertility, forage crop production and yield. The global total N fertilizer demand increased by 1.5 % per year from 2015 to 2020, in the amount of 174.78 million tonnes in 2015 to 188.31 million tonnes in 2020 (FAO, 2017). Excessive N fertilizer application can potentially increase the nitrogen losses through leaching, as Zhao et al. (2019), in a meta-analysis study found that the total nitrogen leaching was 217% when nitrogen fertilizer application rate exceeds 570 kg N/ha. Also in a review study, Yu et al., (2019) reported that 50-75% of the applied nitrogen fertilizers were leached through the soils. The nitrogen leaching may cause a serious threat to the quality of surface and groundwater (Gai et al., 2014; Laird et al., 2010; Xu et al., 2016), and other environmental issues, such as cancers and infant methemoglobinemia, nervous tissues and cognition damage (Zhao et al., 2018; Zhou et al., 2019). Therefore, different biological and physicochemical methods have been used to remove nitrate from aqueous solutions (Fan et al., 2012; Schipper and Vojvodic-Vukovic, 2001).

Biochar is a carbon-rich product derived from biomass pyrolysis in an oxygen-limited condition, which is a great candidate as a physicochemical method for decreasing nitrate leaching from aqueous solutions due to its nutrient retention capacity (Lichtfouse, 2018). The high adsorption capacity of biochar is because of its large surface area and pore volume (Mukherjee et al., 2014; Zhao et al., 2018), porous structure, and the variety of functional groups (Ding et al., 2016; Gao et al., 2019; Lehmann et al., 2011; Leng et al., 2019; Lentz and Ippolito, 2012). Feedstock type is one of the critical factors that can identify the physical and chemical properties of the biochar and its uses as well (Ding et al., 2016). Atkinson et al., (2010) and Gai et al., (2014) reported that the feedstock's chemical composition influences the resulting Biochar's chemical and physical characteristics. Likewise, the feedstock of biochar plays an essential role in defining the nitrate adsorption capacity of the resulting biochar (Wang et al., 2015; Shen et al., 2018; Zhao et al., 2018). Zhou et al., (2019), described that the maximum nitrate adsorption capacity of biochar produced from eggshell at pyrolysis temperature of 700^{o}C was 1.426 mg/g. In contrast, the plant waste biochar was varied with limited adsorption capacity of nitrate, whereas the maximum nitrate adsorption capacity of biochar produced from oak sawdust at 300–600^{o}C was100 mg/g (Wang et al., 2015). Thus, different feedstocks can result in biochar that differs in terms of porosity, surface area and functional groups, which lead to other adsorption behaviours of the resulting biochar (Sohi et al., 2010). Zhou et al. (2019) reported that the adsorption capacity of nitrate was affected by the physical characteristics of biochar, such as the high surface area and porosity. The chemical characteristics of the biochar, including total carbon, total nitrogen, phosphorus, pH, Cation Exchange Capacity (CEC), and conductivity, have been shown to depend on the biochar feedstock (Agegnehu et al., 2017).

Sources of biochar are expected to have different influences not only on the generated biochar but also on the biochar amended soils, and consequently, crop yields (Abedin, 2018; Oladele et al., 2019). Various biochar feedstocks have shown different results regarding the nitrate leaching reduction. For instance, Yao et al., (2012) have reported that the Brazilian pepperwood biochar at the rate of 2% of soil weight reduced the total nitrate leaching by 34 %. Xu et al., (2016) found that up to 20 % of leached nitrate was minimized by using 8 % per weight of corn-straw biochar, while the used hardwood biochar at rate of 20 g kg^{-1} of the soil has decreased the total nitrate leaching to 11 % (Laird et al., 2010). Therefore, conducting such a study is another approach to confirm the biochar ability to remove nitrate from aqueous solutions and enhancing the aqueous nitrate removal knowledge through different biochar feedstocks. Furthermore, biochar may serve as nutrient sources when they are incorporated into the soils; therefore, it is critical to study the effects of different biochar generated from different feedstocks on the benefits of biochar nitrate adsorption. The overall aim of this study was to estimate the capacity of biochar as an adsorbent for nitrate removal from aqueous solutions. Laboratory batch adsorption and mathematical models such as Langmuir and Freundlich were used to predict and compare the adsorption performance (Chen, 2015). The specific objectives of the study were (i) to identify the highest nitrate adsorption capacity based on the four-biochar Langmuir and Freundlich models; (ii) to determine the associated mechanism of nitrate adsorption onto biochar.

2.2. Materials and methods

2.2.1. Biochar

The biochar adsorption experiment was conducted at the St. John's Research and Development Centre, NL, Canada, using four biochar types (Figure 2-1). Three types of biochar were collected from GECA Environnement, Quebec, Canada. They were: (a) biochar produced from a spruce bark at 550°C (SB550) using the Abri-Tech technology, in Canada; (b) Neroval biochar constructed from hardwood (75% sugar maple) at 500°C (HW500) using the Proton Power Inc technology, in the USA, certified by the International Biochar Initiative (IBI); (c) Airex biochar produced from sawdust of fir/spruce at 427°C (FS427), using Airex Energy-CarbonFX technology, in Canada, certified by the Canadian Food Inspection Agency (CFIA) (Lange and Allaire, 2018); and the fourth (d) biochar type was collected from the process engineering department, the Memorial University of Newfoundland and Labrador, produced from a different mixture of softwood sawdust at 500°C (SW500) using the Abri-Tech technology, Canada. Biochars were dried at 60°C for 48h, and moisture content (%) was determined before they were used in the experiment. Other physicochemical properties of the biochars (Table 2-1) were obtained using different methods and instruments. Total nitrogen and total carbon analyses were done through Association of Official Agricultural Chemists (AOAC) method 990.03 (Horwitz and Latimer, 2005), using a LECO instrument, model CNS 928, USA, whereas all other minerals, including total phosphorous, total calcium, and total magnesium analyses were obtained using a dry ash method AOAC method 985.01 (Horwitz and Latimer, 2005), analyzed by a Teledyne Instruments Leeman Labs Inc - Prodigy High Dispersion ICP, USA.

Scanning electron microscopy (SEM), FEI MLA 650F equipped with Bruker XFlash X-ray detectors for the compositional analysis Energy-Dispersive X-ray Spectroscopy (EDS), and backscattered electron detector (BSE) were used for taking images of the four biochar, to examine the porous structures of the biochar. Fourier transform infrared (FT-IR) spectra of the biochar were taken using a Bruker Tensor 27 FT-IR spectrometer at 4 cm^{-1} resolutions for 32 scans on the sample material versus wavelength spectral range from 4000 to 400 cm^{-1} to characterize the biochar's surface functional groups (Liu et al., 2015; Zolfi Bavariani et al., 2019).

2.2.2. Adsorption Kinetics Experiments

About 0.2 g of the collected biochar were mixed with 50 mL potassium nitrate (KNO_3) solutions at concentrations of 0, 10, 50, 100, 150 and 300 mg/L, as shown in (Figure 2-2). The mixtures were then shaken in the mechanical shaker (180 oscillations min^{-1}) for 24 h at room temperature to achieve equilibrium (predetermined equilibrium time), and the mixtures were filtered through 0.20 μm nylon membrane filters (Cole-Parmer, Canada), and nitrate concentrations were checked in the mixtures. Nitrate concentrations were determined by Lachat QuikChem®, 8500 Flow Injection

Analysis (FIA), HACH, Canada, using Nitrate/Nitrite 10-107-04-1-A method. Adsorbed nitrate concentrations onto the biochar were calculated based on the difference between the initial and final aqueous concentrations. The initial and equilibrium pH values were measured in the nitrate solutions using the Hach HQ40d portable meter. Nitrate adsorption amount of q (mg/g) was calculated by the equation (2), and removal rate by adsorption, R (%) was calculated by the equation (3). The adsorption experiment was performed for the four biochar with four replications of each of the six concentrations, ending up with 96 samples in total.

$$q = (C_0 - C_e)\mathrm{V}/m \qquad (2)$$

$$q = (C_0 - C_e)/C_0 \text{ X } 100 \qquad (3)$$

Where *V* is the volume of solution (mL) and *m* is the weight of biochar adsorbent (mg), and C_0 and Ce are the initial concentration and equilibrium concentration of nitrate solution (mg/L), respectively.

2.2.3. Langmuir and Freundlich models

Langmuir and Freundlich models (Chen, 2015; Subramanyam and Das, 2014) were used for fitting the experimental data to derive the maximum adsorption capacity of nitrate for each biochar feedstock. The model parameters were estimated using the Origin program , Origin OriginPro 2020 software (OriginLab Corporation, Northampton, MA, USA).

The maximum nitrate adsorption capacity of each biochar was obtained from the Langmuir model (Subramanyam and Das, 2014; Chen, 2015). The Langmuir model is the most commonly used for estimating nitrate adsorption capacity (Afjeh et al., 2020; Chintala et al., 2013; Fidel et al., 2018; Ganesan et al., 2013; Zhao et al., 2018). The governing equations can be written as (4) and (5) respectively (Chen, 2015; Subramanyam and Das, 2014):

Langmuir: $qe = K_l qmax\ C_e/(1 + K_l\ C_e)$ (4)

Freundlich: $qe = K_f\ C_e^{1/n}$ (5)

Where K_l is the Langmuir adsorption binding strength coefficient (L/mg), and K_f is the Freundlich affinity coefficient ((mg/g) $(1/mg)^{1/n}$). *qmax* is the Langmuir maximum adsorption capacity (mg/g), and *Ce* is the equilibrium solution concentration (mg/L) of the sorbate.

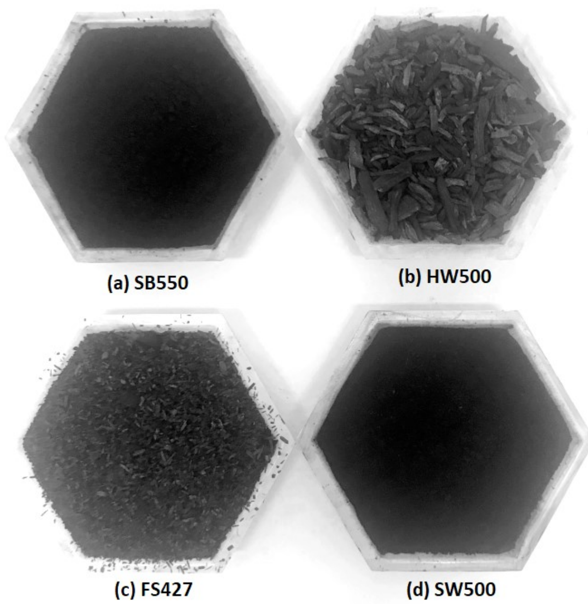

Figure 2-1: Biochar types of samples including (a) SB550, (b) HW500, (c) FS427, and (d) SW500.

Table 2-1: Moisture Content, pH, CEC, Total Nitrogen, Total Carbon, Total Phosphorus, Total Calcium, and Total Magnesium of the biochar

Analysis	SB550	HW500	FS427	SW500
Moisture Content (%)	<1	2.6	3.6	2.2
pH	9.9	11	8.8	8.2
Total Nitrogen, N (%)	0.95	0.54	0.29	0.17
Total Carbon, C (%)	77.2	92.8	87	83
Total Phosphorus, P (%)	0.29	0.052	0.032	0.025
Total Calcium, Ca (%)	1.75	1.93	0.65	0.6
Total Magnesium, Mg (%)	0.24	0.17	0.11	0.088
CEC cmol/kg	28.5	22.3	23.6	25.4

Basic properties of the biochar SB550, HW500, FS427, and SW500

Figure 2-2: Adsorption kinetics experiments showing the mixtures of biochar and potassium nitrate (KNO_3) solutions at different concentrations.

2.3. Statistical analysis

The experimental adsorption data were fitted to the Langmuir and Freundlich isotherms models for describing and predicting the best fits using R^2 values, and the data fittings and figures were plotted using Origin OriginPro 2020 software (OriginLab Corporation, Northampton, MA, USA).The results were expressed as means and standard deviations.

2.4. Results and discussion

2.4.1. Biochar characterization by SEM and FT-IR

The technique of SEM is often used to characterize the biochar's physical structure and the architecture and morphology of cellulosic plant material retained, whereas the FT-IR technique is used to detect the surface functional groups of biochar (Gai et al., 2014). The SEM images of the four studied biochar in the current study depicted in (Figure 2-3), which described the morphologies and porous structures of biochar materials. From the SEM images, there were uniform micropores that appeared within the biochar structures, which beneficially increase the surface areas and the number of surface-active sites, in turn, nutrient retention and adsorption processes (Chintala et al., 2014). The SEM images of the biochar materials were taken in a wide range of magnifications between 40-100 μm scales to show the structural development of each biochar as they have different particle sizes (Figure 2-3).

FT-IR spectra of the biochar before and after nitrate adsorption (Figure 2-4) shown that the biochar SB550, FS427 and SW500 have five different peaks at different wavenumbers. The associated wavenumber peaks of these three biochar are at the ranges of 1575, 1430, 1375, 875, 815 and 750 cm^{-1}. These wavenumber peaks of the three biochar are referred to as aromatic C=C stretching, aromatic C=C bending, aromatic C–H bending, and phenolic O–H bending (Keiluweit et al., 2010; Zhengtao et al., 2018), which appears at high and lower wavenumbers peaks. Whereas, the FT-IR spectra of the biochar HW550 have only two wavenumber peaks at 1430 and 875 cm^{-1}. These two wavenumber peaks of the HW500 biochar are also an indication of aromatic C=C and aromatic C–H bending (Keiluweit et al., 2010; Zhengtao et al., 2018). The wavenumber peaks indicate lots of aromatic rings associated with fewer functional groups in the biochar structures. Therefore, due to the presence of these functional groups within the biochar, the electrostatic attraction increased and improved the nitrate adsorption capacity (J. Yang et al., 2017; Yin et al., 2018). The FT-IR analyses of the biochar showed the same trends of having similar functional groups. However, the HW500 biochar had slightly less functional groups than the other biochar, which may be the reason for it being the least effective biochar in terms of nitrate adsorption capacity compared to the other three biochar. Biochar functional groups' details are shown in (Table 2-2), in which the range of the biochar wavenumbers peaks are between 1575-750 cm^{-1}.

Table 2-2: Biochar FT-IR spectroscopy wavenumber (cm^{-1})

Biochar	Wavenumbers (cm^{-1})	Assignments
SB550	1575	Aromatic C=C stretching
	1430	Aromatic C=C bending
	1375	Phenolic O–H bending
	875,815, and 750	Aromatic C–H bending
HW500	1430	Aromatic C=C bending
	875	Aromatic C–H bending
FS427	1575	Aromatic C=C stretching
	1375	Phenolic O–H bending
	875,815, and 750	Aromatic C–H bending
SW500	1575	Aromatic C=C stretching
	1375	Phenolic O–H bending
	875,815, and 750	Aromatic C–H bending

Biochar: spruce bark biochar (SB550), hardwood biochar (HW500), fir/spruce biochar (FS427), and softwood biochar (SW500).

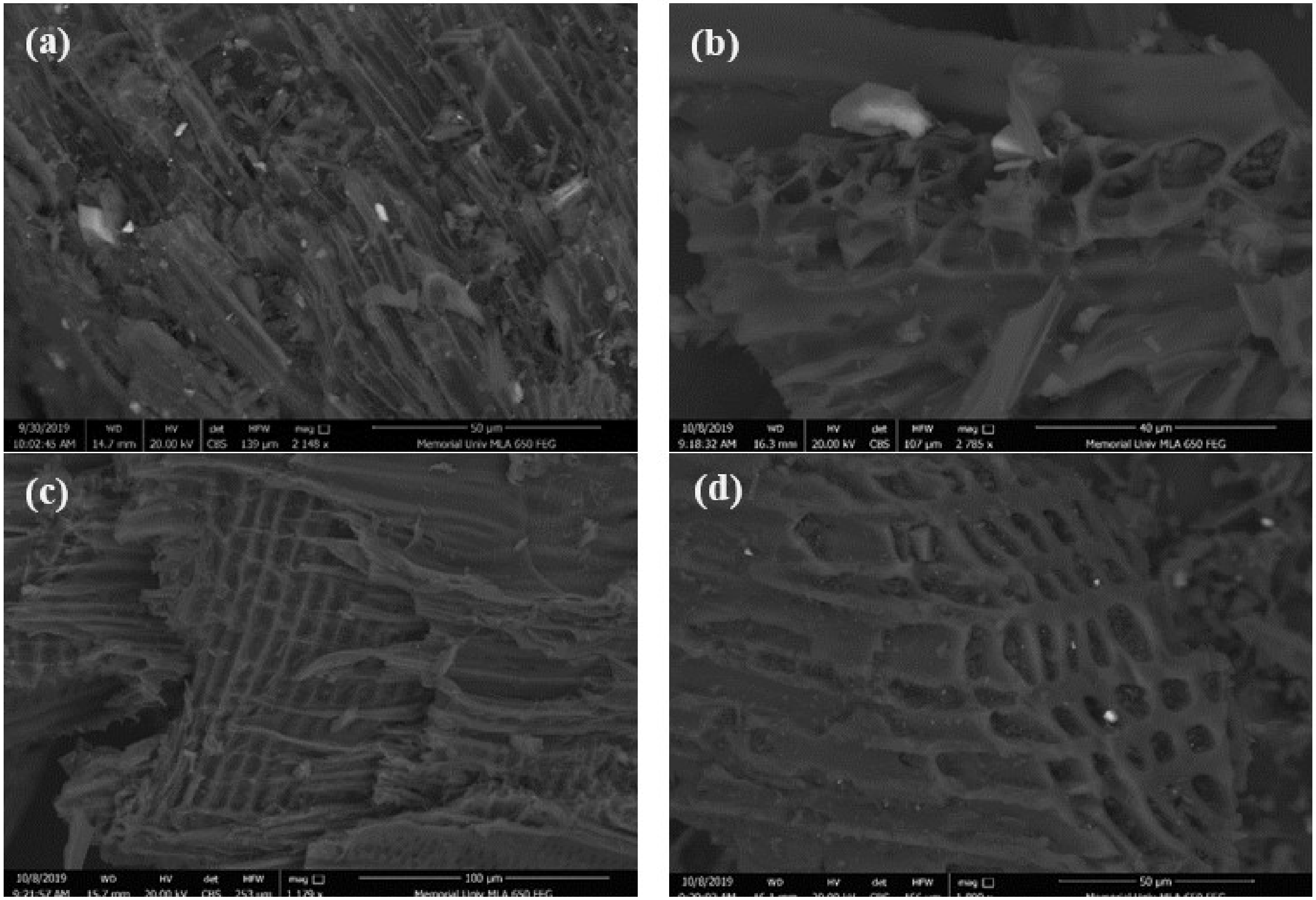

Figure 2-3: SEM images of the biochars, including (a) SB550, (b) HW500, (c) FS427, and (d) SW500

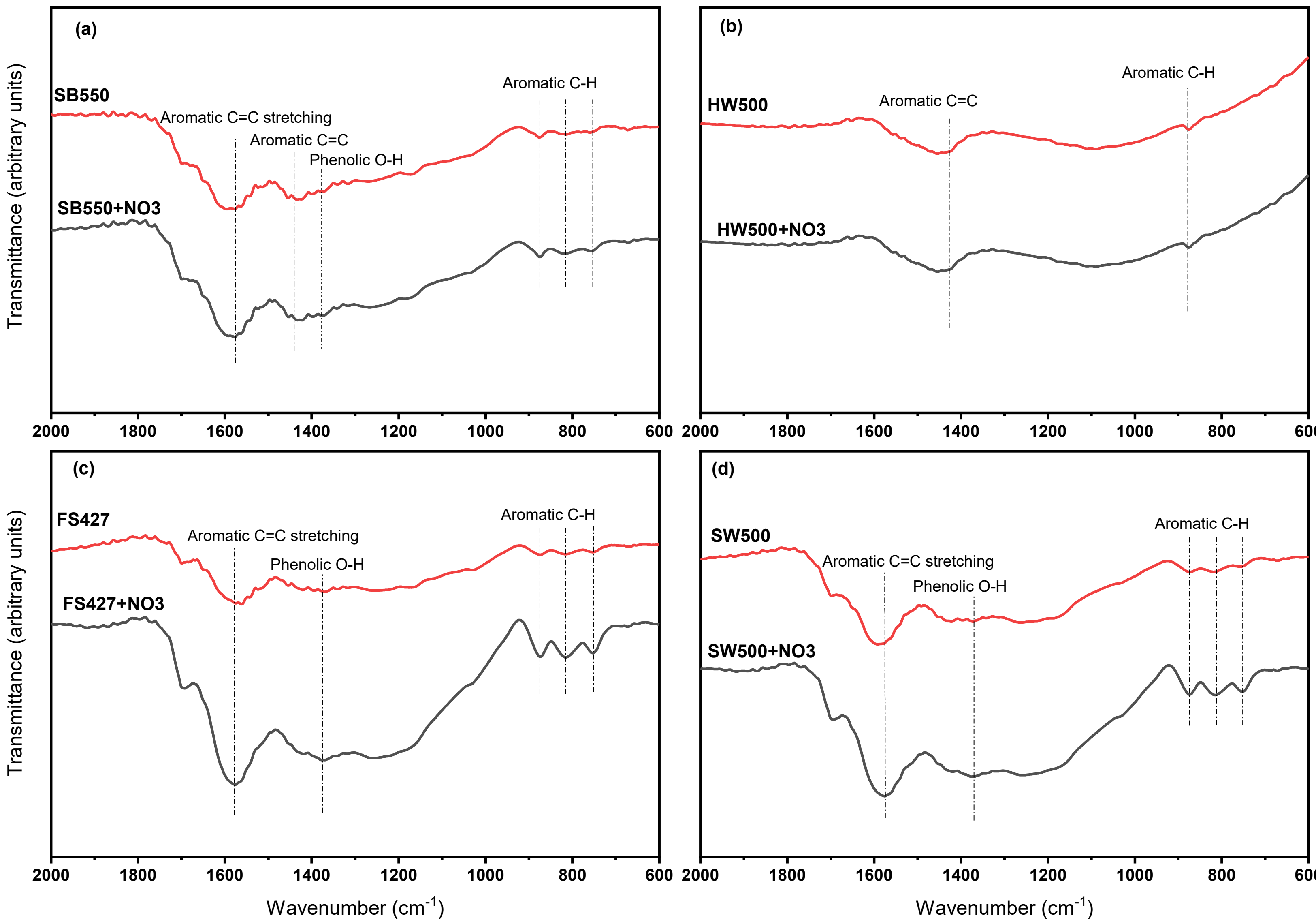

Figure 2-4: FT-IR spectra of biochar before and after nitrate adsorption, including (a) SB550, (b) HW500, (c) FS427, and (d) SW500

2.4.2. Adsorption kinetics and isotherms

Langmuir and Freundlich models were used as the most common isotherm models (Chen, 2015; Khayyun and Mseer, 2019) to help with the comprehensive understanding of the interaction between nitrate and biochar and to estimate the maximum adsorption capacities of nitrate onto selected biochar. The nitrate equilibrium adsorption data onto biochar were well-fitted in both models. The correlation coefficient (R^2) of the Langmuir models was 0.998, 0.998, 0.999 and 0.987, and R^2 of the Freundlich models were 0.997, 0.997, 0.998 and 0.995, for the biochar SB550, HW500, FS427 and SW500, respectively. The models' fitting parameters and identical statistical standards are summarized in Table 2-3. The Langmuir and Freundlich models identified that the most fitting estimations of the statistical standards of the experimental data belonged to both models, for the four biochar, as depicted in Figure 2-5. The results were consistent with other studies (Wang et al., 2015; Yin et al., 2018; Zhou et al., 2019), who reported that the equilibrium adsorption data fitted better by Langmuir models. The maximum adsorption capacity (qmax) values calculated by Langmuir isotherm models increased in the order of 184 ,174, 165, 152 mg/g for SB550, SW500, FS427, and HW500, respectively.

The Langmuir model results demonstrated that the calculated values of qmax for biochar nitrate adsorption are highly acceptable (Table 2-3 & Figure 2-5), as these values are close to the experimental data. Wang et al. (2021) reported that the nitrate adsorption capacity (qmax) of biochar derived from wood waste was156.8 mg/g, while Zhanghong et al., (2015), determined that qmax of nitrate adsorption reached 100 mg/g. The result was attributed to multilayers adsorption (Lu et al., 2014), hydrogen bonding, phenolic hydroxyl and carboxyl acidic functional groups (Yin et al., 2018). However, lower qmax between 0.443 to 1.426 mg/g for an eggshell biochar was obtained by Zhou et al., (2019), which was attributed to the low surface area and low pH of the eggshell biochar.

The results of this study confirmed that the nitrate adsorption capacity is relatively high for the four-biochar types. They demonstrated the promising potential of the biochar to be used as adsorbents for the removal of nitrate from aqueous solutions and keeping nitrate from being lost from the soil system.

Table 2-3: Langmuir and Freundlich isotherm models parameters for nitrate adsorption onto biochars

Biochar	Langmuir isotherm			Freundlich isotherm		
	K_l	qmax	R^2	K_f	n	R^2
SB550	0.0049	184	0.998	1.07	1.09	0.997
HW500	0.0057	152	0.998	1.06	1.12	0.997
FS427	0.0053	165	0.999	1.07	1.11	0.998
SW500	0.0052	174	0.987	1.05	1.09	0.995

K_l is the Langmuir adsorption binding strength coefficient (L/mg), K_f is the Freundlich affinity coefficient ((mg/g) $(1/\text{mg})^{1/n}$), respectively. qmax is the Langmuir maximum capacity (mg/g), and n is the Freundlich linearity constant.

2.4.3. Effect of initial nitrate concentration

The initial nitrate concentration effect was studied with different initial nitrate concentrations ranging from 0 to 300 mg/L. High nitrate removal rates were adsorbed by all four biochars, with an average of 75.24%, which confirmed the high nitrate adsorption capacity for all of them (Figure 2-6). The nitrate adsorption capacity of the biochar was increased up to 77% as the initial nitrate concentration rose, following a linear regression, as shown in (Figure 2-7). In the same trend, the nitrate removal rate increased from 65 % to 77 % at 100 mg/L of the initial nitrate concentrations. With further increase of the initial nitrate concentrations up to 300 mg/L, the nitrate percentage removal reached 78%. The changes in the nitrate percentage removal from 77% at 100 mg/L to

78% at 300 mg/L of the initial nitrate showing that only 1% of the nitrate was removed after the initial nitrate concentration increased from 100 and 300 mg/L. These results suggested that nitrate adsorption by biochar was at the saturated status when the initial nitrate concentration was high enough at 100 mg/L, led to a decrease in nitrate removal rate (Tong et al., 2017). This also is an indication of the limited active sites at a constant amount of biochar (Afjeh et al., 2020). In other words, the adsorption behaviour can be illustrated that the higher nitrate concentration increased the collisions between nitrate ions and biochars' active sites. However, with the adsorption process advances, the biochars' active sites reached adsorption saturation, which led to reduce biochar nitrate removal efficiency (Publishing and Supply, 2019; Zhao et al., 2017). Similar results were also reported in which nitrate adsorption increased with increasing the initial nitrate concentration (Milmile et al., 2011; Olgun et al., 2013).

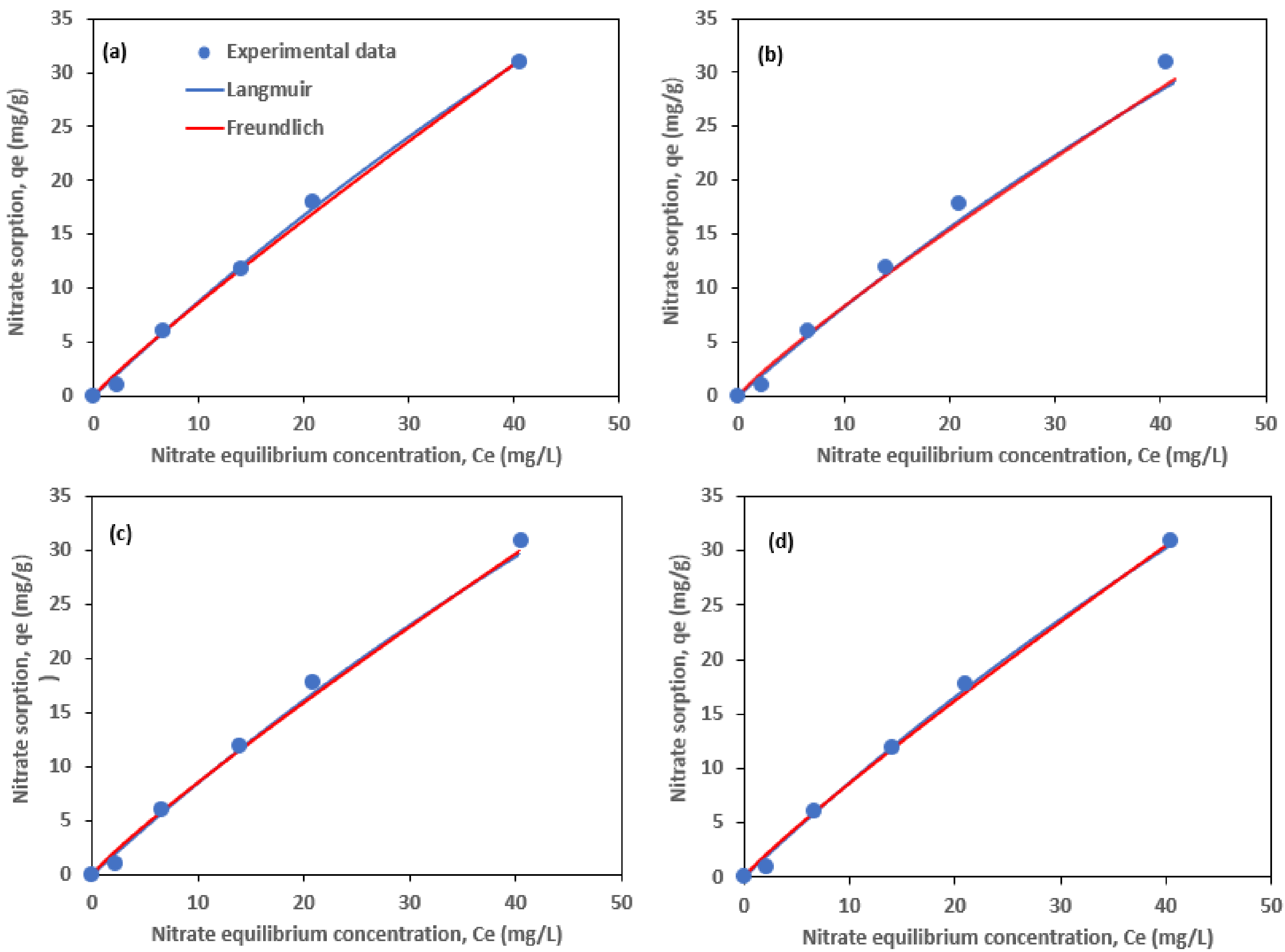

Figure 2-5: Langmuir and Freundlich Isotherms models for nitrate adsorption onto biochar, including (a) SB550, (b) HW500, (c) S427, and (d) SW500

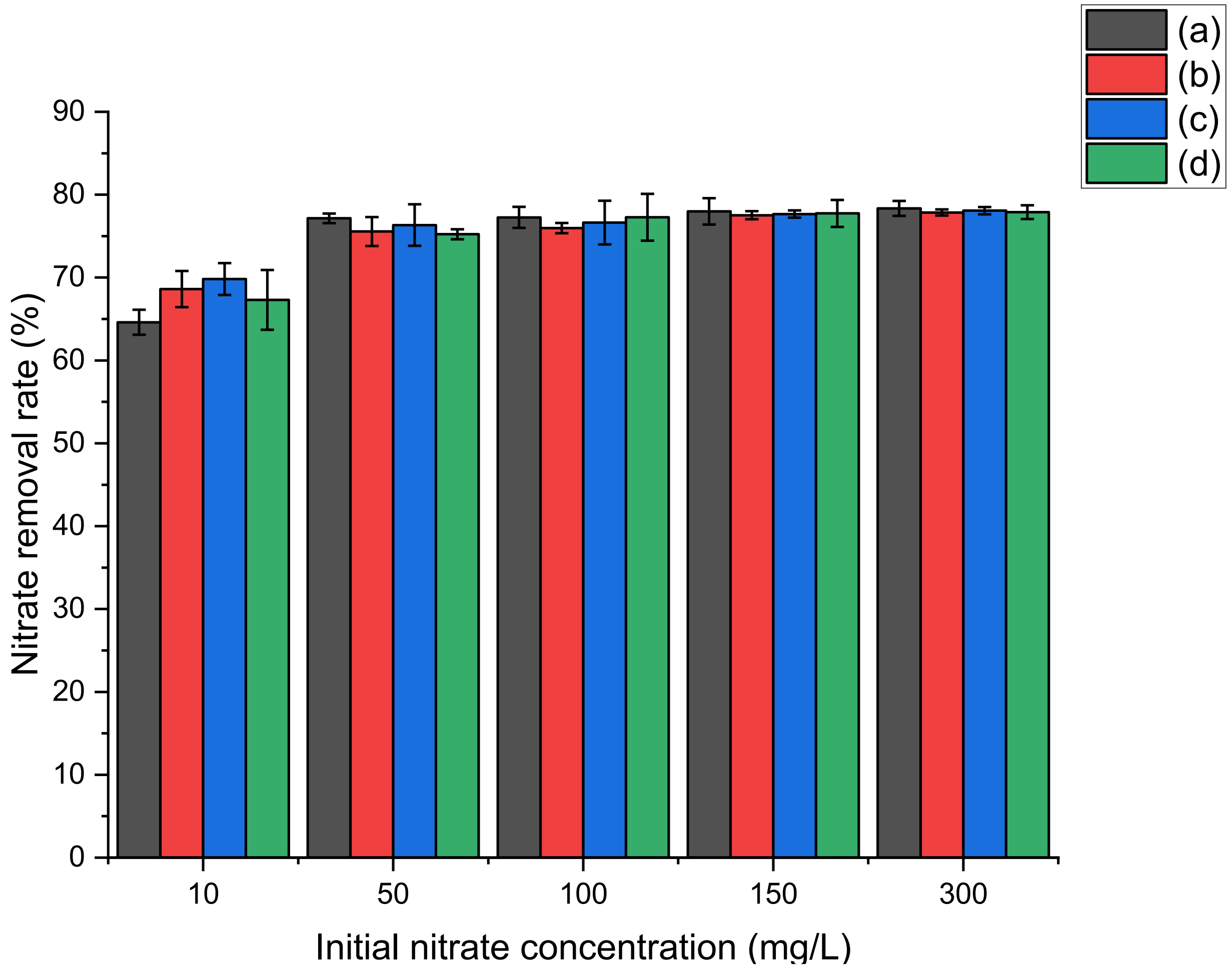

Figure 2-6: Nitrate removal rates from aqueous solutions by different biochar types including (a) SB550, (b) HW500, (c) FS427, and (d) SW500.

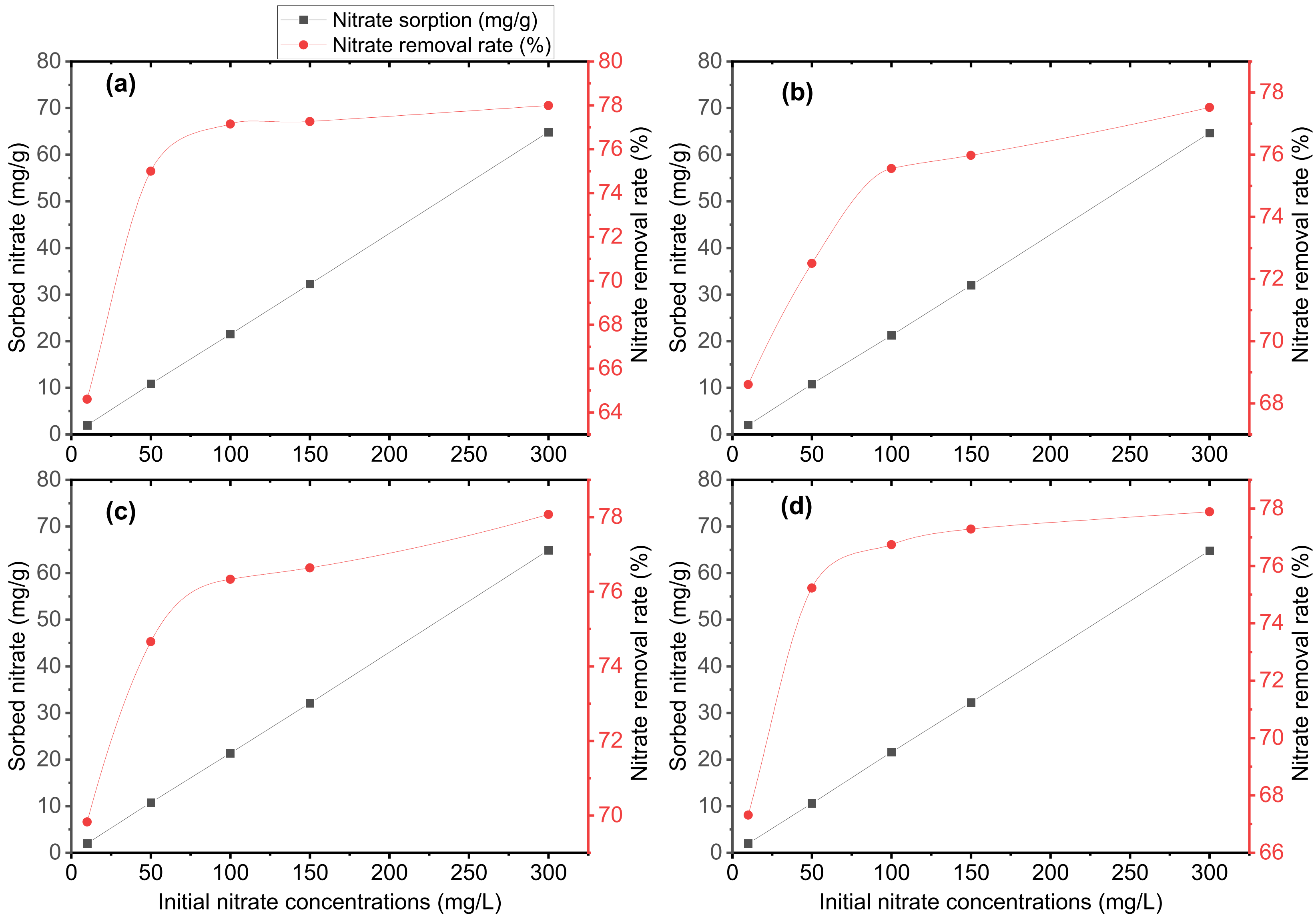

Figure 2-7: Effect of initial nitrate concentration on nitrate adsorption (mg/g) and nitrate removal rate (%) by biochar (a) SB550, (b) HW500, (c) FS427, and (d) SW500.

2.4.4. Effects of solution pH

Nitrate adsorption onto biochar was considerably affected by initial solution pH. The results indicated that the nitrate adsorption capacity of the biochar was higher at low pH values (Figure 2-8). The maximum nitrate adsorption capacities for the four biochar were obtained at pH 7.24, 8.72, 7.38, and 7.21 as the lowest initial solution pH values. In contrast, the highest pH values of 7.75, 8.97, 8.80, and 7.48 correspond to the lowest nitrate concentrations of SB550, HW500, FS427, and SW500, respectively. A considerable nitrate removal rate for the four biochar types, as an average of 75%, was observed. Increase in the initial solution pH affected the nitrate removal rate, the highest percentage of 77.99, 77.87, 78.07 and 77.89 % nitrate removal were obtained at the lowest initial solution pH values of 7.24, 8.72, 7.38, and 7.21 for SB550, HW500, FS427, and SW500 respectively. At the lower initial solution pH, there are more H ions on the biochar functional groups, which probably resulted in attracting the nitrate ions by biochars and enhancing nitrate adsorption due to increased electrostatic interactions between the negatively charged nitrate and the positively charged functional groups (Ahmadvand et al., 2018; Chatterjee and Woo, 2009). At the same time, increase in the pH solution results in negative zeta potential (electrical potential) that increases the electrostatic repulsion between biochar surface negative charge and the nitrate ions negative charge, which reduced the nitrate adsorption capacity by biochar (Olgun et al., 2013). Increasing the solution pH to 7.71, 8.95, 8.64, and 8.49 led to decrease in the nitrate removal rates to 64.6, 68.6, 69.8, and 67.3% for SB550, HW500, FS427, and SW500 respectively. With the nitrate adsorption processes continued, the solution pH values were increased compared to the initial solution pH (Figure 2-8), which led to a decrease in the nitrate removal rates of the four biochar. That can be explained by the competition between OH ions and nitrate ions to be adsorbed onto the biochar at higher pH (Iida et al., 2013; Zhao et al., 2018; Zhou et al., 2019). At low pH values, there are more H ions on the biochar, which probably attracted the nitrate ions (Ahmadvand et al., 2018).

The initial pH of nitrate solutions was not adjusted in this study; nevertheless, the results showed the same trend as Hu et al., (2018), and Zhao et al., (2018), who adjusted the initial solution pH values from 3 to11. These results are consistent with Chatterjee and Woo, (2009); Hu et al., (2018); Tong et al., (2017); Wang et al., (2017); Yang et al., (2017), who concluded that the nitrate removal rate increased along with increase in the initial solution pH from 3 up to 7, and decreased when the initial solution pH was higher than 9.

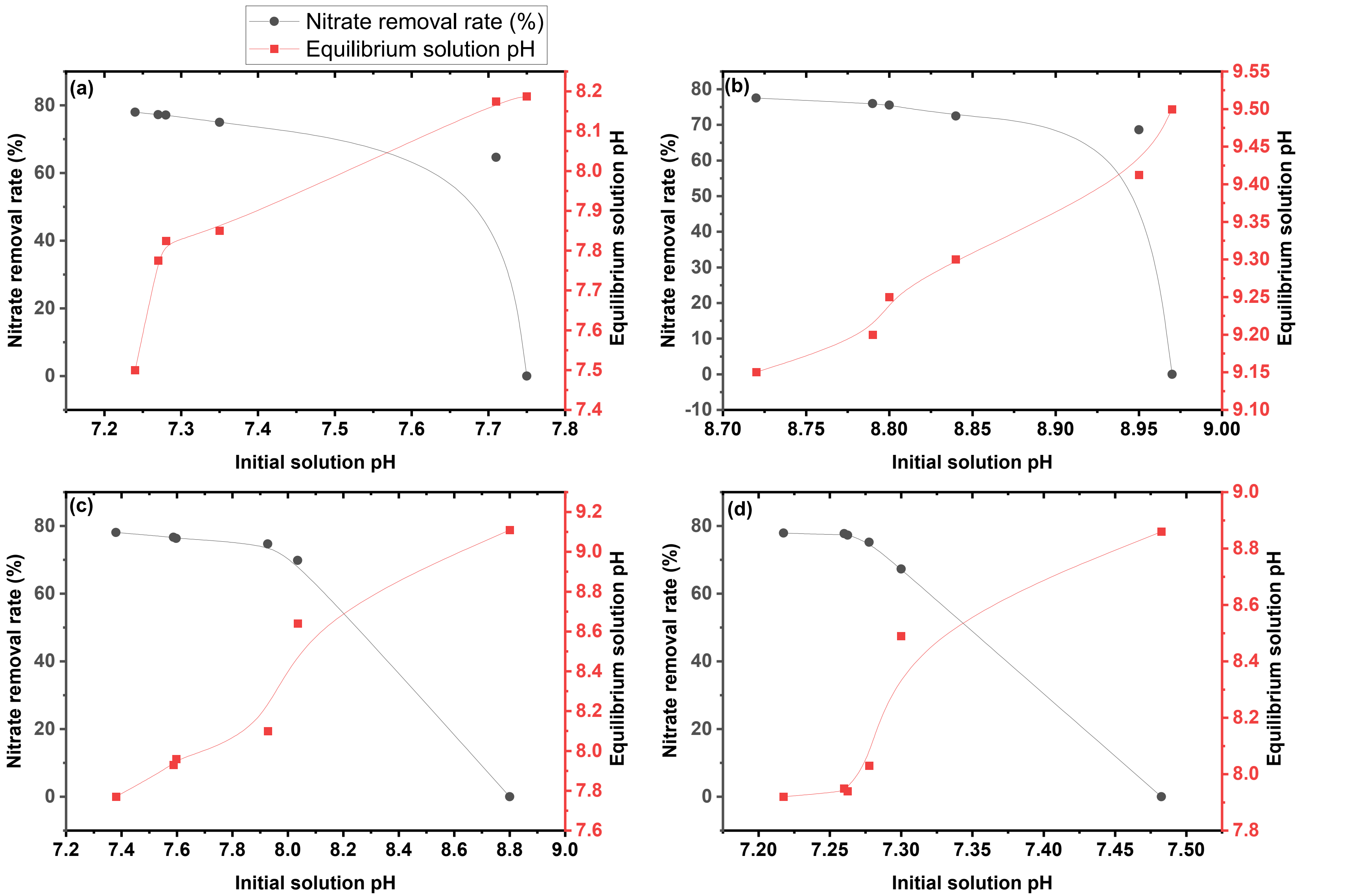

Figure 2-8: Effect of initial solution pH and the equilibrium solution pH on nitrate removal rate, (a) SB550, (b) HW500, (c) FS427, and (d) SW500.

2.5. Conclusions

This study investigated the adsorption characteristics of nitrate onto four different biochar, including spruce bark biochar (SB550), hardwood biochar (HW500), softwood biochar (SW500), and fir/spruce biochar (FS427). They were produced from different feedstocks as a potential adsorbent for nitrate. The results of the description of the biochar through the SEM and FT-IR techniques confirmed; (i) the porous structures of biochar which beneficially increase the surface areas and the number of surface-active sites and (ii) the presence of the surface functional groups such as aromatic C=C stretching and bending, aromatic C–H bending, and phenolic O–H bending. These high surface area and surface functional groups are important for increased electrostatic attraction and the nitrate adsorption capacity of the biochar, which were also confirmed by Langmuir and Freundlich models in simulating the adsorption isotherms. Although the four-biochar feedstock had resulted in influencing the nitrate adsorption capacity, the SB550 biochar was the highest among all. The maximum adsorption capacity (qmax) of SB550 for nitrate was found to be 184 mg/g. The results also demonstrated that the nitrate removal rate was (i) directly proportional to the initial nitrate concentration and (ii) inversely proportional to the initial solution pH. While this study assured the relatively high nitrate adsorption capacities of the four-biochar feedstocks, it also highlighted the effect of feedstock as a critical factor on nitrate adsorption by biochar.

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Chapter 3

Effects of Spruce Bark Biochar on Soil Fertility, Forage Crop Production, Forage Quality, and Nutrient Uptake in the Eastern Newfoundland Podzolic Soil

Abstract

Biochar has broad application in agriculture and has been used in agriculture for soil quality improvement, soil remediation, carbon sequestration, and climate change mitigation. Hence, applying biochar as a soil amendment along with nitrogen application could be an alternative strategy to improve soil quality, forage nutrients uptake, fresh and dry matter yields, and forage quality. Thus, the study objective is to investigate the capability of biochar application to improve soil fertility, and forage productivity in the podzolic soil of Newfoundland. Five biochar rates were added as percentages based on the soil volume 0, 2, 5, 8 and 10 %, with two nitrogen fertilizer applications, 0 and 60 kg N/ha. The study results indicated that biochar application significantly improved soil pH, Soil Organic Matter (SOM), Cation Exchange Capacity (CEC), and available nutrients in the soil, including Ca, Mg, K, P, S, Zn, Mn, and B. The improvement of soil fertility by biochar application has enhanced the *Festulolium* nutrients uptake, which was reflected in improving the soil fertility, forage production, forage quality, and nutrient uptake in the eastern Newfoundland podzolic soil along with increasing both biochar and nitrogen applications.

Keywords: *Newfoundland soil, spruce bark biochar, nitrogen application, nutrients uptake, forage, fresh and dry matter yield.*

3. Introduction

3.1. Background

Soil of Newfoundland and Labrador (NL), Canada has low fertility, very acidic soil, low cation exchange capacity (CEC), low soil organic matter (SOM), very coarse soil texture, and very stony soils, which could affect food and forage crop production. In general, the acidic soil has low fertility because of the high availability of Al and Mn and low P, Ca, and Mg availability, which result in low crop production (Yu et al., 2019). Hence, applying biochar as a soil amendment to such soil could be an alternative strategy to increase forage crop productivity by increasing CEC and SOM content of the soil, which in turn increases nutrient retention capacity (Mao et al., 2013; Wan et al., 2014). Abedin, (2018), found that biochar application in the top 0-15 cm of a very acidic soil had increased soil pH and nutrient availability of Ca, K, S, and Mn, likewise, K, Ca and Mg were raised in the top biochar amendment soil (Gaskin et al., 2010). Kim et al., (2016), and Solaiman et al., (2010), reported that biochar application had increased soil CEC, SOM, P, K availability, and crop growth and yield.

Biochar is referring to a carbon-rich product produced by pyrolysis of any agricultural biomass such as crop residues, wood, and waste, under a controlled pyrolyzing condition such as high temperature and limited supply of oxygen. Biochar soil application is a modern development matter related to soil management (Gunarathne et al., 2017; Kookana et al., 2011). Thus, biochar has broad application, and its use-value for soil quality improvement, soil remediation, carbon sequestration, climate change mitigation, remediation of organic and inorganic pollutants; therefore, carbon farming has been carefully reviewed (Ahmad et al., 2013; Laird, 2009; Lehmann et al., 2006). It has been reported that soil biochar application increased agricultural crop production and it is highly dependent on biochar feedstock and the application rates (Atkinson et al., 2010). The feedstock sources are reported to highly influence the chemical and physical characteristics of the produced biochar due to the initial variation of feedstock and its chemical material contents. For example, Atkinson et al., (2010) reported that the initial number of mineral elements in the feedstock could profoundly affect their outcome level within the produced biochar. Also, Gaskin et al., (2008) found that the chemical composition of the biochar, which were generated from three different sources (poultry litter, peanut hulls, and pine chips) are influenced strongly by the total element concentration on the feedstock sources. The improvement of the agricultural crop production by biochar application potentially because of the release of essential nutrients such as K, Ca, Mg, Mn, Cu, and Zn to the soil; and also, due to the roles that biochar play in the salt-affected soils by reducing crops Na adsorption and increasing the K content, which in turn helps in reducing the salt stress and improve crop growth (Yu et al., 2019). Furthermore, biochar application can immobilize the heavy metal in contaminated soils. Lu et al., (2017) found that applying rice straw biochar at 5 % had decreased the metal concentrations of Cd < Cu < Pb < Zn by 11, 17, 34 and 6%, compared to the control, respectively. Also Yu et al., (2019), reported that green-waste biochar application at 1 % had decreased the extractable concentrations of Cd, Cu, and Pb, while chicken manure biochar increased Indian mustard's shoot and dry root weights by 353 and 572%, respectively, that was due to the reduction of the metal toxicity and increased nutrients availability of P and K.

In the recent decade, studies were also conducted to investigate biochar's value as a source of nutrients. Gaskin et al., (2010) reported that the addition of biochar made from Peanut Hull increased K, Ca, and Mg when applied to surface soil, while the Pine chip biochar had no effect on the other nutrients except Ca. The two biochar additions had a little different impact on the nutrient concentration in corn tissue; however, the rate of the biochar application plays an essential role in soil amendment and agricultural crop production. Atkinson et al., (2010) found a significant improvement in plant productivity, depending on the amount of biochar addition to the soil in the tropical regions. Koyama et al., (2016), reported that rice husk biochar application at a rate of 40 g pot^{-1} had increased the rice yield about 100% higher than the usual average of the rice in the Japanese paddy fields. In another study, the 5 % [w/w] willow biochar application had increased the spinach growth by 102% and 353% in spring and autumn, respectively (Zemanová et al., 2017).

These results of these mentioned studies indicate that the ideal value of biochar addition to each soil in different areas must be explored for the purpose of saving time, costs, labours, and for reducing its possible harmful impact on the health, land, and the surrounding environment. Thus, the objective of this study was to investigate the capability of biochar application as an amendment material for improving the soil fertility, forage production, forage quality, and nutrient uptake in the eastern Newfoundland podzolic soil, which could enhance the requirement for expanded local agricultural production and the province's food security.

3.2. Materials and methods

3.2.1. Biochar production and characterization

The type of used biochar was selected based on the highest nitrate adsorption capacity of 184 mg/g for the SB550 biochar in the first experiment. It was collected from GECA Environnement, Quebec, Canada. The biochar was produced from a spruce bark at 550°C (SB550) using the Abri-Tech technology, in Canada (Lange and Allaire, 2018). Biochar were dried at 60°C for 48h, and moisture content (%) was determined before it was used in the experiment. Nitrogen and carbon analyses were done through AOAC method 990.03 (Horwitz and Latimer, 2005), using a LECO instrument, model CNS 928, USA, whereas all other minerals analyses obtained using a dry ash method AOAC method 985.01 (Horwitz and Latimer, 2005), analyzed by a Teledyne Instruments Leeman Labs Inc - Prodigy High Dispersion ICP, USA (Table 3-1). Scanning electron microscopy (SEM), FEI MLA 650F equipped with Bruker XFlash X-ray detectors for the compositional analysis (EDS), and backscattered electron detector (BSE) were used for taking images of the four biochar, in order to examine the porous structures of the Biochar (Figure 3-1). The Fourier Transfer Infrared (FT-IR) spectra displayed the presence of functional groups on SB550 biochar at different wavenumber peaks at the ranges of 1575, 1430, 1375, 875, 815 and 750 cm^{-1}. These wavenumber peaks are referred to aromatic C=C stretching, aromatic C=C bending, aromatic C–H bending, and phenolic O–H bending (Figure 3-2).

Table 3-1: Moisture Content, pH, CEC, Total Nitrogen, Total Carbon, Total Phosphorus, Total Potassium, Total Calcium, Total Magnesium, Total Iron, Total Copper, Total Manganese, Total Zinc, Total Boron, Total Sodium, Total Sodium, and Soluble Salts of the SB550 biochar

Analysis	**SB550**
Moisture Content (%)	<1
pH	9.9
Total Nitrogen, N (%)	0.95
Total Carbon, C (%)	77.2
Total Phosphorus, P (%)	0.29
Total Potassium, K (%)	1.33
Total Calcium, Ca (%)	1.75
Total Magnesium, Mg (%)	0.24
Total Iron, Fe (mg/L)	7690
Total Copper, Cu (mg/L)	26
Total Manganese, Mn (mg/L)	330
Total Zinc, Zn (mg/L)	400
Total Boron, B (mg/L)	64
Total Sodium, Na (mg/L)	352
Soluble Salts (dS/m)	0.7
CEC cmol/kg	28.5

Basic properties of SB550 biochar

3.2.2. Experimental set-up and design

The experiment was conducted in a greenhouse at Memorial University Botanical Garden between December 2018 to April 2019. The forage crop *Festulolium* was grown in plastic pots 30.48 cm diameter and 27.5 cm height (Figure 3-3), contained 15 kg silt loam soil under 8-16 h day-night photoperiod and temperature 18–20 °C. *Festulolium* was developed by crop scientists crossing Meadow or Tall Fescue with Perennial or Italian Ryegrass; this promotes a combination of the best properties of the two types of grasses. The Fescues support high dry matter yield, cold resistance, and drought tolerance and persistence. In contrast, Ryegrass is represented by good spring growth, good digestibility, sugar content and palatability. The individual *Festulolium* varieties have numerous combinations of these qualities, but all yield substantially higher than their parent lines. (Boller et al., 2010). The experimental design consisted of one soil type collected from the St. John's Research and Development Centre. Five rates of biochar applications including, control 0% biochar, 2, 5, 8 and 10% biochar rates [v/v], were applied in the top 10 cm of the soil (Figure 3-4), and two nitrogen fertilizers, Urea (46-0-0) were applied in the rates of 0 and 60 N kg/ha. Two levels of *Festulolium* (with and without crops) were included, all variations ended up with a total of 20 treatments (Figure 3-4). This experiment was set up in a Completely Randomized Design (CRD), with three replicates resulting in a total of 60 pots, as shown in the experimental layout (Figure 3-5). Biochar was thoroughly mixed with the soil, and then the mixture was placed in the top 10 cm of the soil, followed by the nitrogen fertilizer applications of Urea (46-0-0) in the top of 2.5-3.0 cm of the soil. The *Festulolium* seeds were uniformly seeded in the top 0.5 cm of soil at the recommended field seeding rate of 35 lbs per acre adjusted to the pot surface area. The *Festulolium* was grown in the experimental pots from December 2018, when the seeds were seeded, to April 2019, when the forage crop was harvested.

A preliminary experiment was done to estimate the amount of water needed to be added to each pot of soil to avoid excess leaching and to measure soil field capacity (F.C.). Soil F.C. was determined to be 35% (g water/g oven-dry soil) using a gravimetric oven drying method. The wet soil was sampled 24 h after water addition, and soil moisture content was calculated based on a standard drying method: 5 g of soil samples were dried for 48 h at 105°C. To maintain suitable soil water content for crop growth, the soil moisture content of the pots was determined every 3-4 days using GS3 VWC, temperature, ECw and ProCheck Sensor Read-Out and Storage System (METER Group, Inc. USA), and all pots were watered up to the F.C. to ensure the soil is getting at least 20% of the total available water.

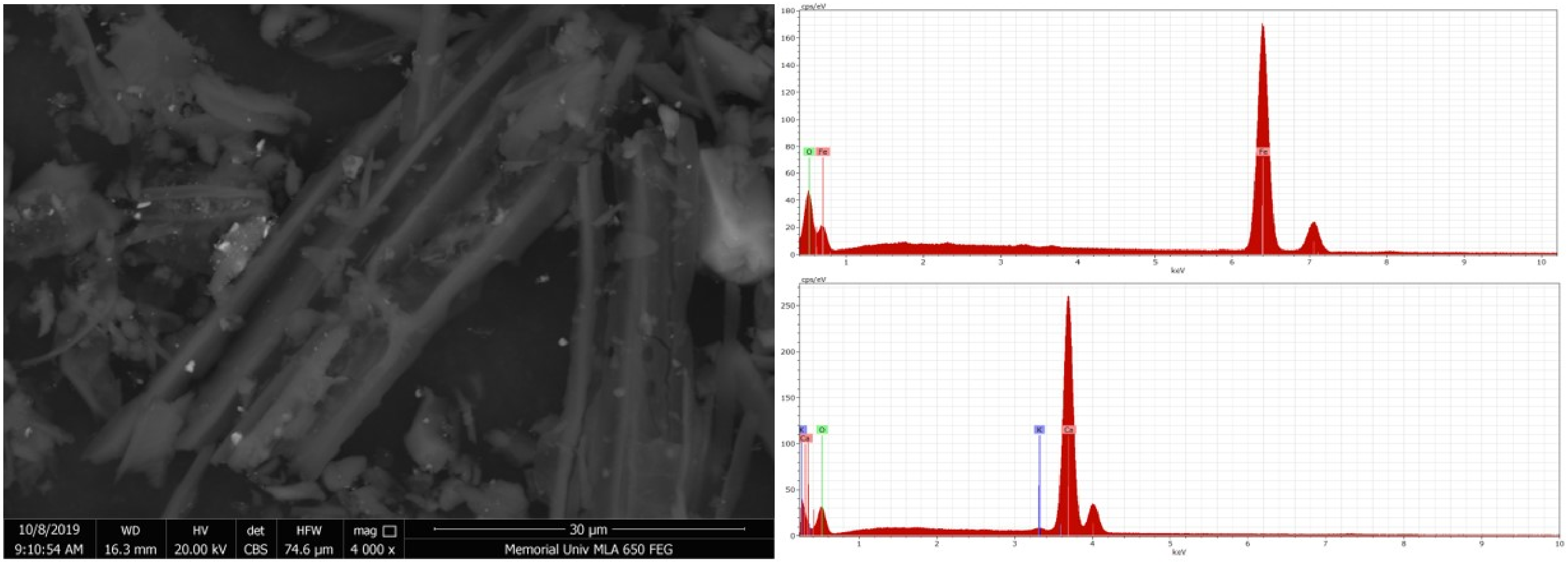


Figure 3-1: Scanning electron microscopy (SEM) images of the used biochar, and different minerals compounds such as Fe, K and Ca on the biochar surface

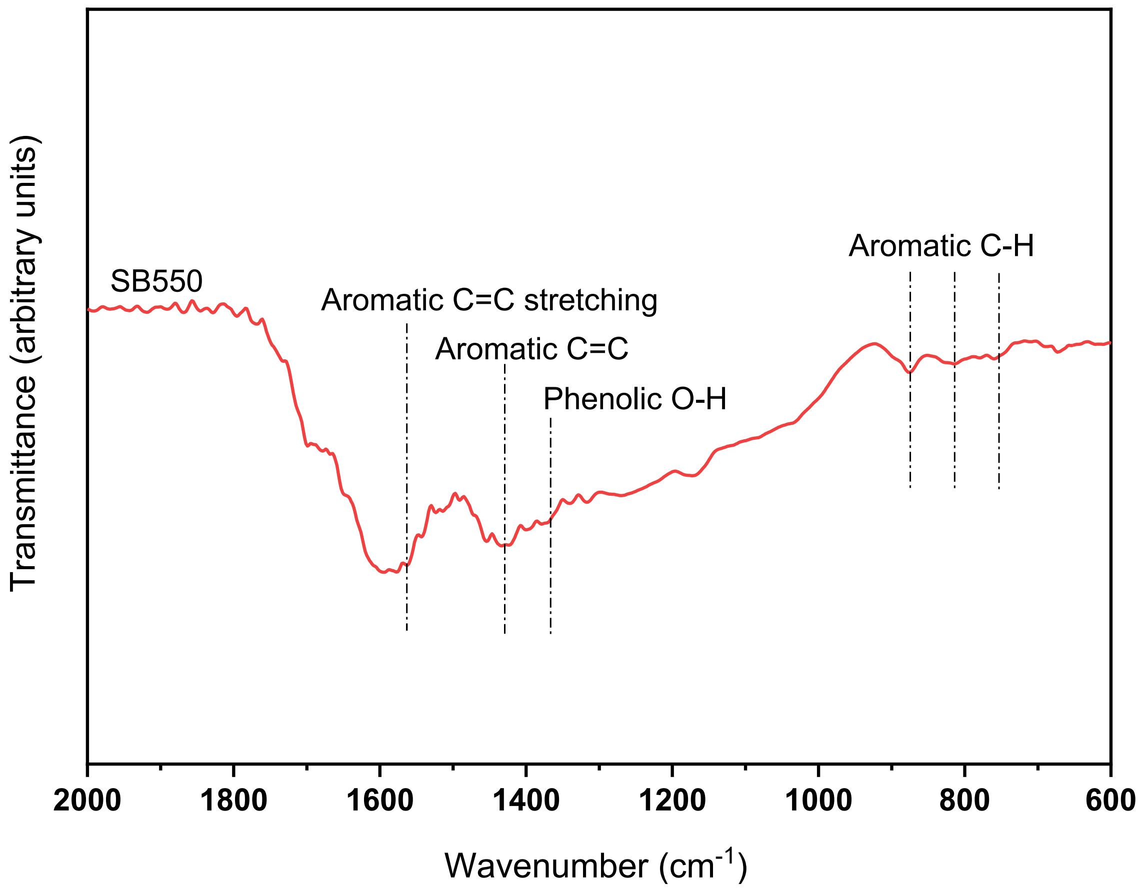


Figure 3-2: FT-IR spectra showed the presence of functional groups on SB550 biochar

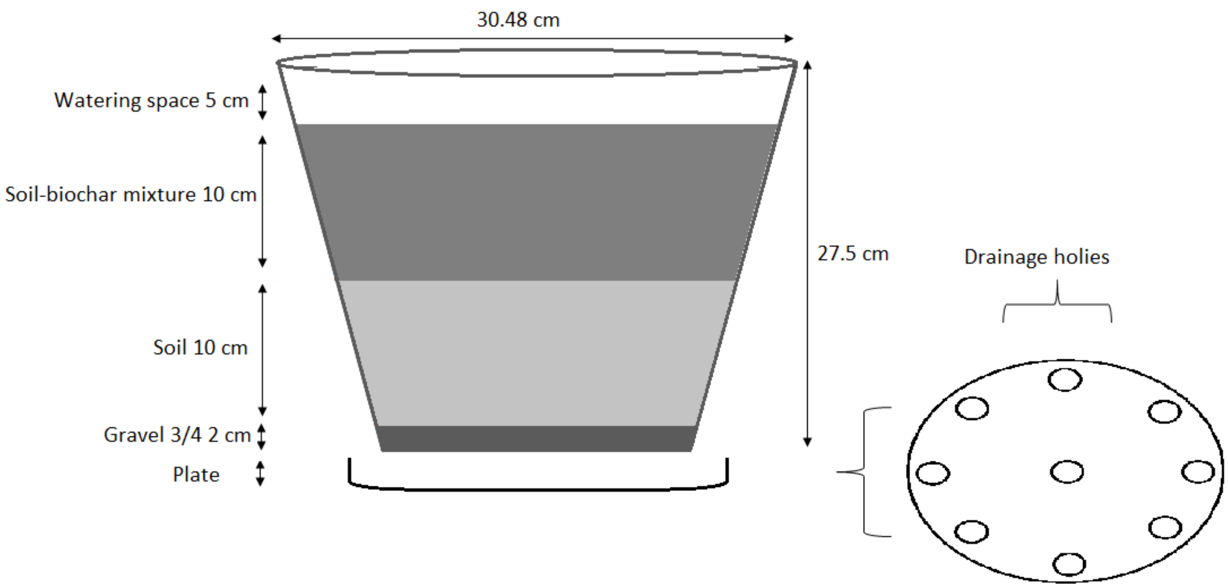


Figure 3-3: Soil column in the experiment pots used for soil leachate collection

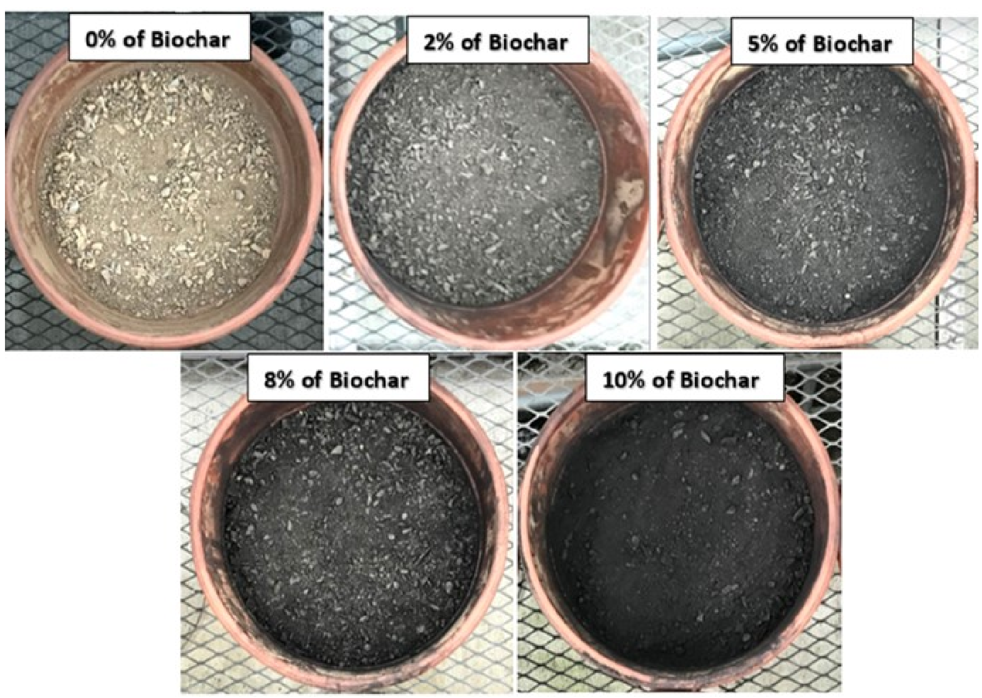
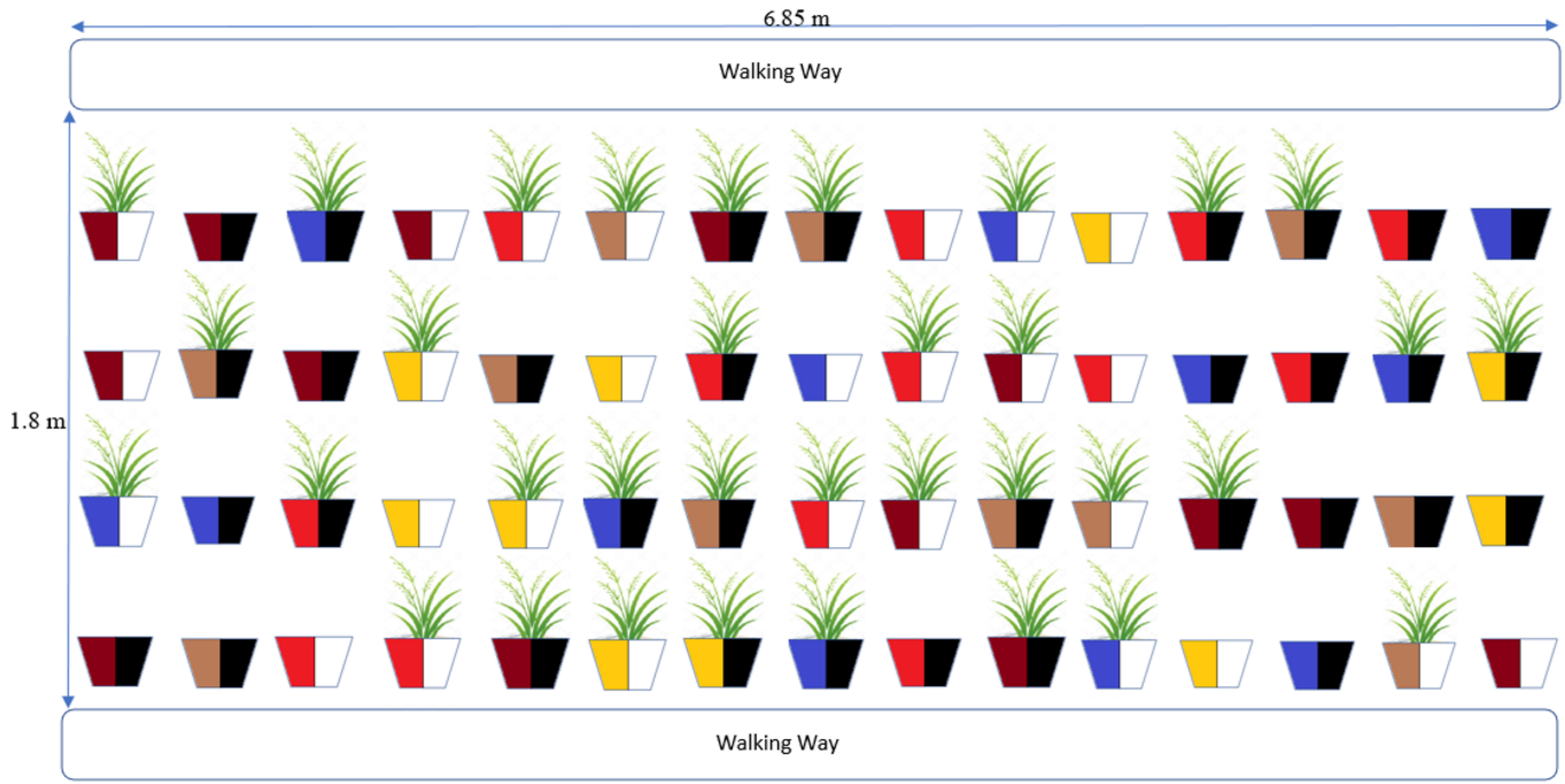


Figure 3-4: Biochar and mixtures prepared at five application rates added as percentages based on the soil volume [v/v] (0, 2, 5, 8 and 10%) in the top 10 cm of the soil.



Biochar application rates	0 %	2 %	5 %	8 %	10 %
Nitrogen application levels	0 kg N/ha		60 kg N/ha		
Crops treatments	crop		no crop		

Treatments codes	*Treatment Description*	*Treatments codes*	*Treatment Description*	*Treatments codes*	*Treatment Description*	*Treatments codes*	*Treatment Description*
T_1	B_0%-N_0-crop	T_6	B_0%-N_{60}-crop	T_{11}	B_0%-N_0-no crop	T_{16}	B_0%-N_{60}-no crop
T_2	B_2%-N_0-crop	T_7	B_2%-N_{60}-crop	T_{12}	B_2%-N_0-no crop	T_{17}	B_2%-N_{60}-no crop
T_3	B_5%-N_0-crop	T_8	B_5%-N_{60}-crop	T_{13}	B_5%-N_0-no crop	T_{18}	B_5%-N_{60}-no crop
T_4	B_8%-N_0-crop	T_9	B_8%-N_{60}-crop	T_{14}	B_8%-N_0-no crop	T_{19}	B_8%-N_{60}-no crop
T_5	B_{10}%-N_0-crop	T_{10}	B_{10}%-N_{60}-crop	T_{15}	B_{10}%-N_0-no crop	T_{20}	B_{10}%-N_{60}-no crop

Figure 3-5: Experimental layout, shown biochar, nitrogen, and crop levels and the treatment descriptions within a completely randomized design (CRD).

3.2.3 Soil, biochar, and nitrogen fertilizer

The soil was collected from Agriculture and Agri-Food Canada, St. John's Research and Development Centre (47°31'N; 52°47'W; 115 m above sea level). The soil was taken from the top 20 cm, dried in the drying room for 72 h at 35°C, and sieved using 9.5 mm sieve to remove big stones from the soil. Five levels of biochar applications were added as percentages based on the soil [v/v], and two nitrogen fertilizer applications Urea (46-0-0) in the rates of 0 and 60 N kg/ha as recommended by Newfoundland and Labrador Provincial Agriculture Soil & Plant Laboratory in the soil analysis report, based on soil nitrogen test, and crop requirements. Two levels (with and without crops) of *Festulolium* were planted uniformly in the top 0.5 cm of the soil at the recommended field seeding rate of 35 lbs/acre adjusted to the pot surface area.

3.2.4. Soil sample preparation for analysis

A composite soil sample of the original soil was collected from 20 soil samples at 0-20 cm depth from the field number 3 at the St. John's Research and Development, using a stainless-steel soil sampling auger (76 mm) diameter and (305) mm length (AMS. USA). The composite samples were air-dried at 35°C, sieved by 2-mm mesh and analyzed for texture, pH, SOM, CEC, total N, total C, and available nutrients of P, K, Ca, Mg, S, Zn, Cu, Na, Fe, B, Mn, and Al prior to adding any soil amendments. After harvesting the crop, the final soil samples were collected at 0-10 cm depths from all experimental pots. Soil samples were air-dried at 35°C, sieved with 2-mm mesh before analysis, and then the samples were analyzed for texture, pH, SOM, CEC, total N, total C, and available nutrients of P, K, Ca, Mg, S, Zn, Cu, Na, Fe, B, Mn, and Al.

3.2.5. Soil characterization

The soil of the study had a silt loam texture (29.31% sand, 17.9% clay, and 52.8 % silt), slightly acidic soil pH (6.1), moderate levels of SOM, and low CEC (Table 3-2). Whereas, the extractable concentrations of P, K, Ca, Mg, S, Zn, Cu, Na, B, and Mn have significantly increased; however, Fe and Al concentrations have decreased along with the study treatments as shown in (Table 3-3) and (Table 3-4).

Table 3-2: Mean of original soil texture of pH, CEC, % N, and % C before any soil mendments.

Treatments	% Sand	% Clay	% Silt	Soil pH	% N	% C	% SOM	CEC (cmol/Kg
Original Soil	29.3	17.9	52.8	6.1	0.5	6.8	7.94	9.5

Table 3-3: Mean of original soil extractable nutrient concentrations before any soil amendments

Parameters	P	K	Ca	Mg	S	Zn	Cu	Na	Fe	B	Mn	Al
	mg/L											
Original soil	77	153	1305	300	23	3.1	3.7	38	140	1	16	1204

3.3. Experiment evaluations

3.3.1. Soil analysis

Chemical analyses were conducted after sieving sub-samples of soil using a 2-mm sieve. Soil pH was measured for the original and final soils, and the measurements were done on 1:1, soil: water ratio (w:v), using a pH meter (Thermo Fisher Scientific accumet™ XL250 pH, Canada). CEC was calculated using a buffer pH (Adams and Evans, 1962). Other extractable elements P, K, Ca, Mg, S, Zn, Cu, Na, Fe, B, Mn, and Al, were extracted by the Mehlich 3 extraction solution method (Carter and Gregorich, 2008) using a Teledyne Prodigy ICP instrument. Nitrogen and Carbon analyses were done through AOAC method 990.03 (Horwitz and Latimer, 2005), using a LECO instrument, model CNS 928, USA. Electrical conductivity (EC), moisture, and temperature at 5 cm were checked regularly in the pots using GS3 VWC, temperature, ECw and ProCheck Sensor

Read-Out and Storage System (METER Group, Inc. USA). Soil temperature at 20 cm was checked regularly using Traceable Digital Pocket High-Accuracy, 11.5" Long-StemThermometer (Cole-Parmer Scientific, Canada). The particle size distribution of either the original or final soils was determined using the hydrometer method (Carter and Gregorich, 2008). Soil bulk density (Core segment method) (Carter and Gregorich, 2008), and soil organic matter (loss on ignition method) (Ball, 1964) were also checked.

3.3.2. Forage and root sampling and Analysis

A SPAD meter was used to estimate the leaf chlorophyll concentration due to the strong correlation between leaf chlorophyll and soil nitrogen application (Chang and Robison, 2003). For each pot, SPAD values were recorded from three different leaves and at three different times (right away after the harvest, after two hours of the harvest, and after four hours of the harvest), using a SPAD 502 Plus Chlorophyll Meter (Spectrum Technologies Inc, USA). After that, the forage crop samples were weighed (Fresh yield), dried at 60^{o}C for 72 h, dry weights were recorded (Dry matter yield), and the moisture contents of the samples were calculated. The root biomass was also measured after washing them with running tap water, rinsing three times with distilled water, and drying them at 60^{o}C for 72 h. The forage and root samples were then ground using a Wiley Mill with 1-mm screen and kept cool in sealed glass containers until analyzed for total elemental analysis.

All forage and root samples' physicochemical properties were obtained using different methods and instruments. Nitrogen and Carbon analyses were done through AOAC method 990.03 (Horwitz and Latimer, 2005), using a LECO instrument, model CNS 928, USA, whereas all other mineral analyses were obtained using a dry ash method AOAC method 985.01 (Horwitz and

Latimer, 2005), and analyzed by a Teledyne Instruments Leeman Labs Inc - Prodigy High Dispersion ICP, USA.

Crude Protein was calculated from the total nitrogen present in the feed material, using the combustion (AOAC 990.03) method (Horwitz and Latimer, 2005) by LECO Instrument model CNS 928, USA. The Crude Protein was calculated by converting the nitrogen percentage to protein by multiplying by 6.25. Acid Detergent Fibre (ADF) accounts for lignin, cellulose, silica and insoluble forms of nitrogen and was measured using the Reflux (AOAC 973.18) method (Horwitz and Latimer, 2005). Neutral Detergent Fibre (NDF) refers to fibre constituents of feedstuffs as it measures cellulose, hemicellulose, lignin, silica, tannins and cutins using the Reflux (AOAC 2002.04) method. Both ADF and NDF were determined using the ANKOM 200 Fiber Analyzer Instrument, USA.

3.4. Statistical analysis

Statistical analysis of variances (ANOVA) was performed using a general linear model in the Minitab 19 software (Minitab, 2019). To test the degree of the significance of biochar effect, nitrogen effect, crop effect, and the interaction between these three factors at $\alpha \leq 0.05$ were looked at, taking the experimental design (RCD) into consideration. The normality of distribution and homogeneity of variance were tested before ANOVA analysis was conducted, and all assumptions were met. Significant differences between the treatment means were analyzed using Tukey's test at a 95% significance level ($P < 0.05$). A two- and three-way analysis of variances (ANOVA) were performed according to a linear models (1) and (2), respectively,(Dunn and Smyth, 2018).

$$Yijk=\mu+Ai+ Bj+ (AB)ij+ \varepsilon ijk \quad (1)$$

$$Yijk=\mu+Ai+ Bj+C_k+ (AB)_{ij}+(AC)_{ik}+(BC)_{jk}+(ABC)_{ijk}+ \varepsilon_{ijkl} \quad (2)$$

Where $Yijk$ is the dependent variable, μ is the overall mean, Ai, Bj, and Ck are the effects of *ith* (biochar levels), *jth* (nitrogen levels), and *kth* (crop levels), respectively, and $\varepsilon ijkl$ is the random error terms within the experiment.

3.5. Results

3.5.1. Status of soil nutrient

As expected, the biochar application had a significant effect on nutrients concentrations, soil pH, SOM, and CEC by the end of the experiment (Tables 3-4 & 3-5). In general, biochar application has affected soil nutrient in different ways. Most of the nutrient's concentrations such as C, P, K, Ca, Mg, S, Zn, Cu, Na, B, and Mn were all significantly increased by increasing the biochar rates (Tables 3-4 & 3-5). The trend of Fe and Al concentrations were decreased by increasing of the biochar rates, but only the Fe showed significant results (Tables 3-6 & 3-7). Soil pH, CEC followed the same trend as for most of the nutrients that were significantly increased with the increase of biochar rates, while soil N concentrations were not significantly different within the treatments (Tables 3-4 & 3-5). Whereas the SOM was different and varied within the treatments (Tables 3-4 & 3-5).

The soil pH values were affected by the biochar application ($p\text{-value} < 0.001$), where the Tukey's test at 95% confidence results showed that the rates of 8 % and 10 % [v/v] were significantly higher than the rates of 2 % and 5 % [v/v]. They were all different than the control treatment at 0 %. In the same way, soil pH values were significantly affected by the nitrogen levels ($p\text{-value} = 0.05$), and Tukey's test results showed that 0 kg N/ha was different than 60 kg N/ha. Also, crop levels have affected the soil pH values ($p\text{-value} < 0.001$) in which no crop treatments had significantly higher soil pH values compared to the crop treatments. In contrast, nitrogen levels and the interaction between biochar, nitrogen and crop were not significantly different in terms of soil pH (p-value = 0.2) (Tables 3-4 & 3-5).

Soil N values were not affected by any of the three factors, biochar, nitrogen, and crop (p-values > 0.05, for all of them) (Tables 3-4 & 3-5). Alternatively, soil C values were affected by the three factors (p-values < 0.001), for all biochar, nitrogen, and crop effects and even for the effect of the interaction. The Tukey's test results showed a significant linear response to biochar application rates, in which the C concentrations were the highest percentage of 10 % [v/v] of biochar. The biochar applications of 5, 8 and 10 % [v/v] were different than the biochar applications of 0 and 2 % [v/v] in term of C concentration (%). Furthermore, SOM and CEC showed the same trend as the C concentrations, and they were affected by the three factors and their interactions (p-values < 0.001) (Tables 3-4 & 3-5).

Soil elements of Ca, Mg, K, P, S, Zn, Mn, and B were also influenced by the three factors and their interactions (p-values < 0.001, for all factors and interactions). The Tukey test results indicated significant linear responses to biochar, as they significantly increased along with increasing the biochar rates. Whereas most of the soil elements, including Ca, Mg, K, Zn, Cu, Fe, Al, and B, were higher within the no crop treatments than in the crop treatments. Other soil elements such as P, Na, S, and Mn were significantly higher within the crop treatments than in the no crop treatments. In terms of nitrogen application, the elements of Ca, Mg, K, Fe, and Zn significantly increased in the 0 kg N/ha level more than the 60 kg N/ha level. In contrast, only Na, Al, and Cu increased more in the 60 kg N/ha level than in the 0 kg N/ha level (Tables 3-6 &3-7).

Table 3-4: Mean values of Final soil pH, % N, % C, % SOM, and CEC in response to biochar, nitrogen fertilizer and crops treatments used in the experiment.

Treatments	Soil pH	% N	% C	% SOM	CEC (cmol/Kg
B0%-N0-C	6.1 d	0.5	6.70 r	6.19 m	17.4 ef
B2%-N0-C	6.3 cd	0.6	11.0 n	8.58 a	17.9 cd
B5%-N0-C	6.3 cd	0.6	16.9 i	6.96 j	17.1 fg
B8%-N0-C	6.4 bcd	0.6	16.0 j	8.47 b	17.4 ef
B10%-N0-C	6.4 bcd	0.6	18.5 f	6.97 j	18.3 ab
B0%-N60-C	6.1 d	0.5	7.10 q	6.62 l	17.6 de
B2%-N60-C	6.2 d	0.6	10.7 o	7.49 g	16.5 h
B5%-N60-C	6.3 cd	0.6	17.1 h	7.95 e	14.6 k
B8%-N60-C	6.3 cd	0.6	13.8 k	6.87 k	16.0 i
B10%-N60-C	6.3 cd	0.6	19.0 e	8.03 d	17.7 cde
B0%-N0-NC	6.3 cd	0.6	7.80 p	7.66 f	17.1 fg
B2%-N0-NC	6.6 abc	0.6	11.8 l	8.47 b	15.6 j
B5%-N0-NC	6.7 ab	0.6	18.2 g	7.36 h	18.0 bc
B8%-N0-NC	6.9 a	0.7	19.7 d	7.23 i	17.5 e
B10%-N0-NC	6.8 a	0.6	21.3 a	6.97 j	17.4 ef
B0%-N60-NC	6.3 d	0.6	7.80 p	7.63 f	17.9 cd
B2%-N60-NC	6.6 abc	0.6	11.3 m	7.61 f	18.6 a
B5%-N60-NC	6.6 abc	0.6	18.4 f	8.36 c	17.0 g
B8%-N60-NC	6.8 a	0.6	20.0 c	6.95 j	16.4 h
B10%-N60-NC	6.8 a	0.6	20.7 b	6.67 l	17.6 de

Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test). Treatments including five biochar application (B0%, B2%, B5%, B8%, and B10%), nitrogen levels are (N0 and N60), and crop levels are: crop (C) and no crop (NC).

Table 3-5: Analysis of variance (ANOVA) of estimated final soil pH, % N, % C, % SOM, and CEC in response to the main effects of biochar, nitrogen fertilizer, crop, and interactions.

Source of Variance	*P-Values*				
	Soil pH	Total N %	Total C %	SOM %	CEC
B % (v/v)	< 0.001	0.556	< 0.001	< 0.001	< 0.001
Crop	< 0.001	0.221	< 0.001	< 0.001	< 0.001
N (kg/ha)	0.05	0.36	< 0.001	< 0.001	< 0.001
B % (v/v)*Crops	< 0.001	0.294	< 0.001	< 0.001	< 0.001
B % (v/v)*N (kg/ha)	0.358	0.377	< 0.001	< 0.001	< 0.001
N (kg/ha)*Crop	0.506	0.337	< 0.001	< 0.001	< 0.001
B % (v/v)*N (kg/ha)*Crop	0.200	0.387	< 0.001	< 0.001	< 0.001

Statistically significant difference (P < 0.05). Source of variance codes including biochar (B), Crop, and nitrogen (N).

Table 3-6: Mean values of Final soil available nutrients concentrations in response to biochar, nitrogen fertilizer, crop, and interactions among them

Treatments	P	K	Ca	Mg	S	Zn	Cu	Na	Fe	B	Mn	Al
	mg/L											
B0%-N0-C	73.6 h	18 o	1426 t	257 p	22 cd	2 kl	3.5 k	45 e	171 b	0.2 g	54 i	1258 d
B2%-N0-C	104.6 a	21 n	1745 n	313 k	25 b	2.6 j	4 hi	47 d	161 f	0.3 fg	84 a	1047 o
B5%-N0-C	104.6 a	54 k	1879 i	316 ij	26 ab	4 f	3.9 i	45 e	160 fg	0.5 de	60 f	1170 j
B8%-N0-C	101.6 b	65 i	1827 j	304 l	25 b	4 f	3.7 j	42 f	154 i	0.5 de	57 g	1172 i
B10%-N0-C	100.6 b	92 f	1953 f	318 i	27 a	4.6 d	3.9 i	41 f	161 f	0.6 cd	47 j	1165 k
B0%-N60-C	88.6 f	20 n	1594 s	275 o	23 c	2.7 j	4.1 gh	49 c	166 cd	0.2 g	67 e	1287 c
B2%-N60-C	101.6 b	21 n	1772 l	312 k	25 abc	2.6 j	4.5 cd	51 ab	160 fg	0.3 fg	80 b	1115 q
B5%-N60-C	104.6 a	29 m	1760 m	286 m	23 c	3.6 h	4 hi	50 bc	159 g	0.4 ef	67 e	1124 p
B8%-N60-C	94 e	30 m	1738 o	281 n	25 b	3.5 h	3.7 j	52 a	155 i	0.4 ef	67 e	1190 g
B10%-N60-C	104.6 a	43 l	1759 n	281 n	22 cd	3.9 g	3.6 jk	45 e	157 h	0.4 ef	71 d	1048 o
B0%-N0-NC	98.6 c	62 j	1669 r	353 g	16 h	2.1 k	4.2 fg	36 h	174 a	0.6 cd	59 f	1289 b
B2%-N0-NC	93.6 e	76 h	1797 k	386 c	21 de	2.9 i	4.3 ef	34 i	165 de	0.4 ef	41 k	1105 n
B5%-N0-NC	93.6 e	176 d	2019 d	405 b	20 ef	4.3 e	4.6 bc	36 h	159 g	0.7 bc	33 n	1163 l
B8%-N0-NC	97.6 c	251 a	2050 c	387 c	21 cd	5.4 a	4.7 b	39 g	167 c	0.8 b	56 gh	1135 o
B10%-N0-NC	89.6 f	233 b	2057 b	386 c	18 g	5.1 b	4.7 b	38 g	174 a	0.8 b	73 c	1193 f
B0%-N60-NC	98.6 c	64 i	1690 p	338 h	20 ef	1.9 l	4.1 gh	34 i	173 a	0.3 fg	37 m	1336 a
B2%-N60-NC	86.6 g	84 g	2117 a	450 a	20 ef	3.0 i	5.1 a	38 g	166 cd	0.6 cd	39 l	1217 e
B5%-N60-NC	93.6 e	145 e	1892 h	380 d	19 fg	3.8 g	4.4 de	34 i	164 e	0.6 cd	32 n	1140 n
B8%-N60-NC	95.6 d	205 c	1916 g	360 f	22 cd	4.9 c	4.3 ef	35 hi	167 c	0.8 b	42 k	1157 m
B10%-N60-NC	88.6 f	206 c	1979 e	371 e	20 ef	4.8 c	4.3 ef	39 g	173 a	1.5 a	55 hi	1184 h

Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test). Treatments codes including five biochar application (B0%, B2%, B5%, B8%, and B10%), nitrogen levels are: (N0 and N60), and crop levels are: crop (C) and no crop (NC)

Table 3-7: Analysis of variance (ANOVA) of estimated soil available nutrients in response to the main effects of biochar, nitrogen fertilizer, crop, and interactions among them

Source of Variance	*P-Values*											
	P	*K*	*Ca*	*Mg*	*S*	*Zn*	*Cu*	*Na*	*Fe*	*B*	*Mn*	*Al*
B % (v/v)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001
Crop	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.049
N (kg/ha)	0.187	< 0.001	< 0.001	< 0.001	0.05	< 0.001	< 0.001	< 0.001	< 0.001	0.506	< 0.001	0.49
B % (v/v) *Crop	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.094
B % (v/v) *N (kg/ha)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.766
N (kg/ha) *Crop	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.011	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.119
B % (v/v) *N (kg/ha) *Crop	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.365

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), Crop, and nitrogen (N).

3.5.2. Treatments effects on forage crop yield

The data from the *Festulolium* forage showed that either the fresh or dry matter yield was significantly affected by both biochar and nitrogen applications (p-values < 0.001). In contrast, there was no significant impact of the biochar and nitrogen interaction on the fresh and dry matter (p-values > 0.05), as shown in Table 3-9. The fresh and dry matter yields were increased by increasing either the biochar or/and nitrogen applications. Tukey pairwise comparisons of biochar showed that the biochar rate of 5 % [v/v] had the highest fresh and dry matter yields; however, this rate (5%) was only different than the biochar rate of 0 % [v/v]. The Tukey's test results also indicated that fresh yield was considerably increased by 8.5 %, 15.3 %, 19.5 % and 27.5 %, at biochar rates of 2 %, 10 %, 8 % and 5 %, respectively, compared to the 0 % biochar rate. While the nitrogen 60 kg N/ha level had increased the yield by 73.6 % compared to the control 0 kg N/ha level (Figure 3-6A). With the same trend, the dry matter yield was significantly increased by 18 %, 19 %, 29 % and 32 %, at biochar rates of 2 %, 10 %, 8 % and 5 % [v/v], respectively, compared to the 0 % biochar rate. Also, the nitrogen 60 kg N/ha level increased the dry matter yield by 70 % compared to the control at 0 kg N/ha level (Figure 3-6B).

3.5.3. Treatment effects on SPAD value

SPAD meter is used to estimate the leaf chlorophyll concentration, and due to the strong correlation between leaf chlorophyll and soil nitrogen application, the SPAD value is used to estimate crops nitrogen content (Pirtle et al., 2019; Singh et al., 2002). Leaf SPAD values of the *Festulolium* forage crop is shown in Figure 3-6C, which explain the main effect of biochar application, nitrogen levels, and the effects of biochar and nitrogen interaction (Table 3-8). The leaf SPAD value was significantly (p-value = 0.042) affected by biochar application and nitrogen levels (p-value $<$ 0.001) (Table 3-8). Whereas there was no interaction effect of the biochar and nitrogen on the leaf

SPAD value. The biochar application increased the leaf SPAD value by 6 %, 7%, 9 % and 14 %, for the biochar application rates of 2 %, 10 %, 8 % and 5 % [v/v], respectively. While the nitrogen 60 kg N/ha level increased the leaf SPAD value by 32 % compared to the 0 kg N/ha level.

3.5.4. Treatment effects on forage quality

The forage quality of *Festulolium* was affected by only the biochar application, as there was no significant difference among treatments in terms of nitrogen and interaction effects (p-values > 0.05) as shown in Tables 3-9 & 3-10, for all the forage quality. The crude protein content of *Festulolium* was significantly increased by biochar addition rates (p-value < 0.001) (Tables 3-9 & 3-10). The crude protein content increased with the increasing of the biochar application rates. Thus, according to the Tukey's test there was a significant difference in crude protein content which followed the order of 0 % < 2 % < 5 % < 8 % < 10 % biochar rates. In the same tendency, Total Digestible Nutrients (TDN) and Digestible Energy had significantly (p-value < 0.001) (Tables 9 & 10) increased by following the order of higher biochar application rates (Table 3-10). Whereas Acid Detergent Fibre (ADF) and Neutral Detergent Fibre (NDF) contents were significantly affected by biochar application in an opposite tendency in the order of 0 % > 2 % > 5 % > 10 % > 8 % biochar rates (p-values < 0.001) (Tables 9 & 10). The ADF content was decreased by 10 %, 9 %, 6 %, and 5 % for the biochar rates 8 %, 10 %, 5 %, and 2 % [v/v] respectively. While the NDF decreased by 10 %, 8.5 %, 8 %, and 7 % for the biochar rates of 8 %, 10 %, 5 %, and 2 % [v/v] respectively.

3.5.5. Treatment effects on forage nutrient uptake

The impact of biochar application, nitrogen levels, and biochar and nitrogen interaction on *Festulolium* forage macro- and micronutrient uptake (N, P, K, Ca, Mg Na, Fe, Cu, Mn, and Zn) was shown in (Tables 3-11 & 3-12). The biochar application significantly increased most of the nutrient's uptake (p-values < 0.05), including N, P, K, Ca, and Mg; however, it significantly decreased Na and Mn uptake, whereas biochar had no effects on Fe, Cu, and Zn (Tables 11 & 12). In contrast, nitrogen levels had significantly increased the nutrients uptake of N, P, K, and Mg (p-values < 0.05). At the same time, it decreased both Na and Mn uptake (p-values < 0.05) and had no significant effects on Ca and Zn (p-values > 0.05). Furthermore, the biochar and nitrogen interaction had significantly increased K, Ca, and Mg uptake (p-values < 0.05), and only decreased Na uptake (p-values = 0.004) (Tables 3-11 & 3-12). There were no interaction effects on most of the nutrients, including N, P, Fe, Cu, Mn, and Zn uptake.

3.5.6. Treatment effects on forage root

The wet weight of the forage roots was significantly increased up to 32 % by the nitrogen application levels (p-value < 0.001) (Table 3-13), as the Tukey's test illustrated that level of 60 kg N/ha had more influence on wet weight than the 0 kg N/ha level (Figure 3-7A). Despite that, there were no significant differences among treatments in terms of biochar effect and the biochar and nitrogen interaction (p-values > 0.05) (Table 3-13). Quite similar results to the wet weight of the forage roots, the root's dry weight of the forage was significantly affected by both the biochar application and nitrogen levels (p- values > 0.05), but there was no biochar and nitrogen interaction effect on the root's dry weight (Table 3-13, & Figure 3-7B).

3.5.7. Treatment effects on root nutrient uptake

The biochar application, nitrogen levels, and biochar and nitrogen interaction effects on *Festulolium* roots' macro- and micronutrient uptake (N, P, K, Ca, Mg Na, Fe, Cu, Mn, and Zn), are shown in (Tables 3-14 & 3-15). Most of the essential macronutrient uptake, including N, P, K, Ca, and Mg were significantly increased through biochar application rates (p-values < 0.001) (Tables 3-14 & 3-15). In contrast, Na and Mn uptake significantly reduced along with increase biochar application rate (p-values > 0.05) (Tables 3-14 & 3-15). However, the nitrogen levels have significantly affected some of the nutrient's uptakes such as N, Ca, Na, Cu, and Mn (p-values < 0.05), whereas there was no effect of the nitrogen levels on the other nutrients' uptakes (p-values > 0.05) (Tables 3-14 & 3-15).

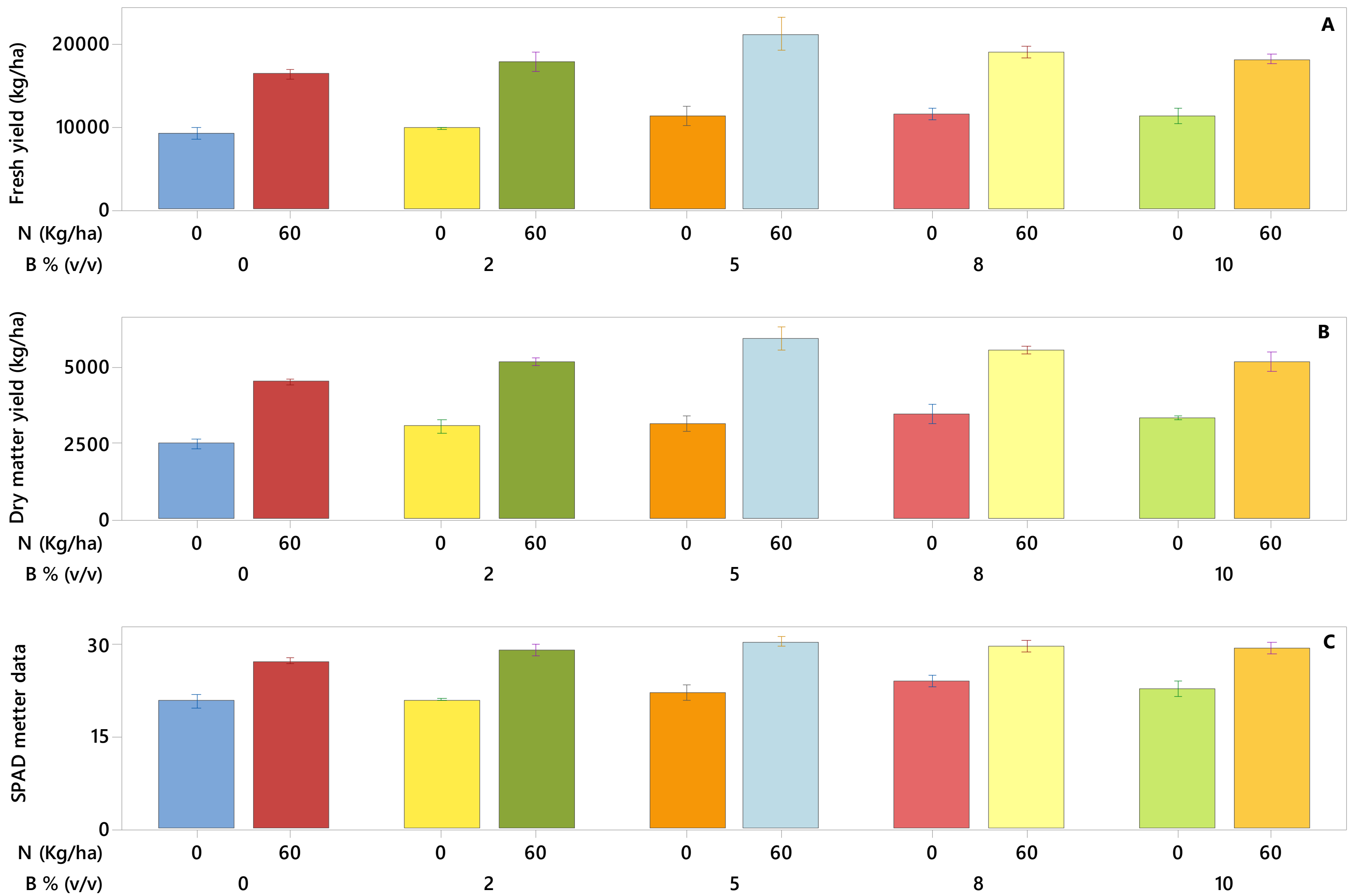


Figure 3-6: Effect of biochar and nitrogen applications on *Festulolium* forage (A) fresh yield, (B) dry matter yield, and (C) SPAD meter value. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 3-8: Analysis of variance (ANOVA) of estimated fresh yield, dry matter yield, and SPAD value in response to the main effects of biochar, nitrogen fertilizer, and interactions.

Source of Variance		Fresh yield		Dry matter yield		SPAD value	
	df	*F-Value*	*P-Value*	*F-Value*	*P-Value*	*F-Value*	*P-Value*
B % (v/v)	4	3.76	0.019	6.84	0.001	3.02	0.042
N (kg/ha)	1	160.98	< 0.001	227.13	< 0.001	144.11	< 0.001
B % (v/v) *N (kg/ha)	4	0.76	0.564	1.14	0.367	0.74	0.578

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B) and nitrogen (N).

Table 3-9: Mean values of Forage quality with different treatments in response to biochar, nitrogen fertilizer, crop, and interactions

Treatments	Crude Protein %	ADF %	NDF %	Est. TDN %	Dig. Energy Mcal/kg
B0%-N0	5.16	21.80	37.20	76.56	3.37
B2%-N0	5.40	20.40	34.76	78.40	3.44
B5%-N0	5.50	20.23	34.76	78.60	3.46
B8%-N0	5.63	19.03	33.33	79.83	3.52
B10%-N0	6.00	19.30	34.06	80.20	3.51
B0%-N60	5.26	20.73	37.50	77.86	3.43
B2%-N60	5.40	20.20	35.00	78.66	3.45
B5%-N60	5.70	19.93	35.13	79.03	3.46
B8%-N60	5.76	19.40	34.36	79.70	3.50
B10%-N60	6.13	19.33	34.26	79.80	3.51

Treatments codes including five biochar application (B0%, B2%, B5%, B8%, and B10%), nitrogen levels are: (N0 and N60). Mean values of forage quality including Crude Protein (%), Acid Detergent Fibre (ADF) (%), Neutral Detergent Fibre (NDF) (%), Total Digestible Nutrients (TDN) (%), and Digestible Energy (Mcal/kg), shown as a % dry matter basis.

among them

Table 3-10: Analysis of variance (ANOVA) of estimated forage quality in response to the main effects of biochar, nitrogen fertilizer,

Source of Variance	*df*	Crude Protein % *p-value*	ADF % *p-value*	NDF % *p-value*	Est. TDN % *p-value*	Dig. Energy *p-value*
B % (v/v)	4	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
N (kg/ha)	1	0.116	0.358	0.260	0.364	0.545
B% (v/v) *N(kg/ha)	4	0.922	0.472	0.948	0.509	0.470
Error	20					
Total	29					

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B) and nitrogen (N).
and interactions

Table 3-11: Mean values of *Festulolium* forage nutrients uptake with different treatments in response to biochar, nitrogen fertilizer, and interactions of them

Treatments	N Kg/ha	P Kg/ha	K Kg/ha	Ca Kg/ha	Mg Kg/ha	Na Kg/ha	Fe mg/kg	Cu mg/kg	Mn mg/kg	Zn mg/kg
B0%-N0	3.50	0.94	7.81 bc	1.79 ef	0.86 de	0.80 bc	110.3	8.76	255.6	12.00
B2%-N0	3.62	0.96	9.82 a	1.88 def	0.98 cd	0.52 bc	147.6	8.23	174.3	11.00
B5%-N0	3.61	0.94	11.17 a	1.92 de	0.91 de	0.20 c	116.0	8.43	149.6	11.66
B8%-N0	3.66	1.04	11.13 a	2.09 cd	0.89 de	0.13 c	85.66	11.33	112.0	13.00
B10%-N0	4.01	1.08	11.08 a	2.43 b	1.26 b	0.14 c	244.3	9.73	127.3	12.00
B0%-N60	3.67	0.75	4.38 d	1.60 f	0.78 e	2.57 a	60.66	6.90	211.3	13.66
B2%-N60	3.63	0.79	6.07 cd	1.72 ef	0.84 de	1.62 ab	44.66	6.60	161.3	10.66
B5%-N60	3.84	0.78	9.81 a	1.88 def	0.94 de	0.39 c	41.00	6.16	85.33	15.00
B8%-N60	3.94	0.88	9.63 ab	2.28 bc	1.14 bc	0.27 c	49.66	6.86	132.6	11.00
B10%-N60	4.27	0.98	10.42 a	2.90 a	1.46 a	0.16 c	60.00	7.16	85.00	10.50

Treatments codes including five biochar application (B0%, B2%, B5%, B8%, and B10%), nitrogen levels are: (N0 and N60). Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test)

Table 3-12: Analysis of variance (ANOVA) of estimated *Festulolium* forage nutrients uptake in response to the main effects of

	p-values									
Source of Variance	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn
B % (v/v)	0.001	0.015	< 0.001	< 0.001	< 0.001	< 0.001	0.454	0.629	< 0.001	0.323
N (kg/ha)	0.018	< 0.001	< 0.001	0.189	0.049	< 0.001	0.008	0.006	0.028	0.784
B% (v/v) *N (kg/ha)	0.763	0.938	0.003	< 0.001	< 0.001	0.004	0.567	0.830	0.242	0.264

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B) and nitrogen (N).

biochar, nitrogen fertilizer, and interactions of them

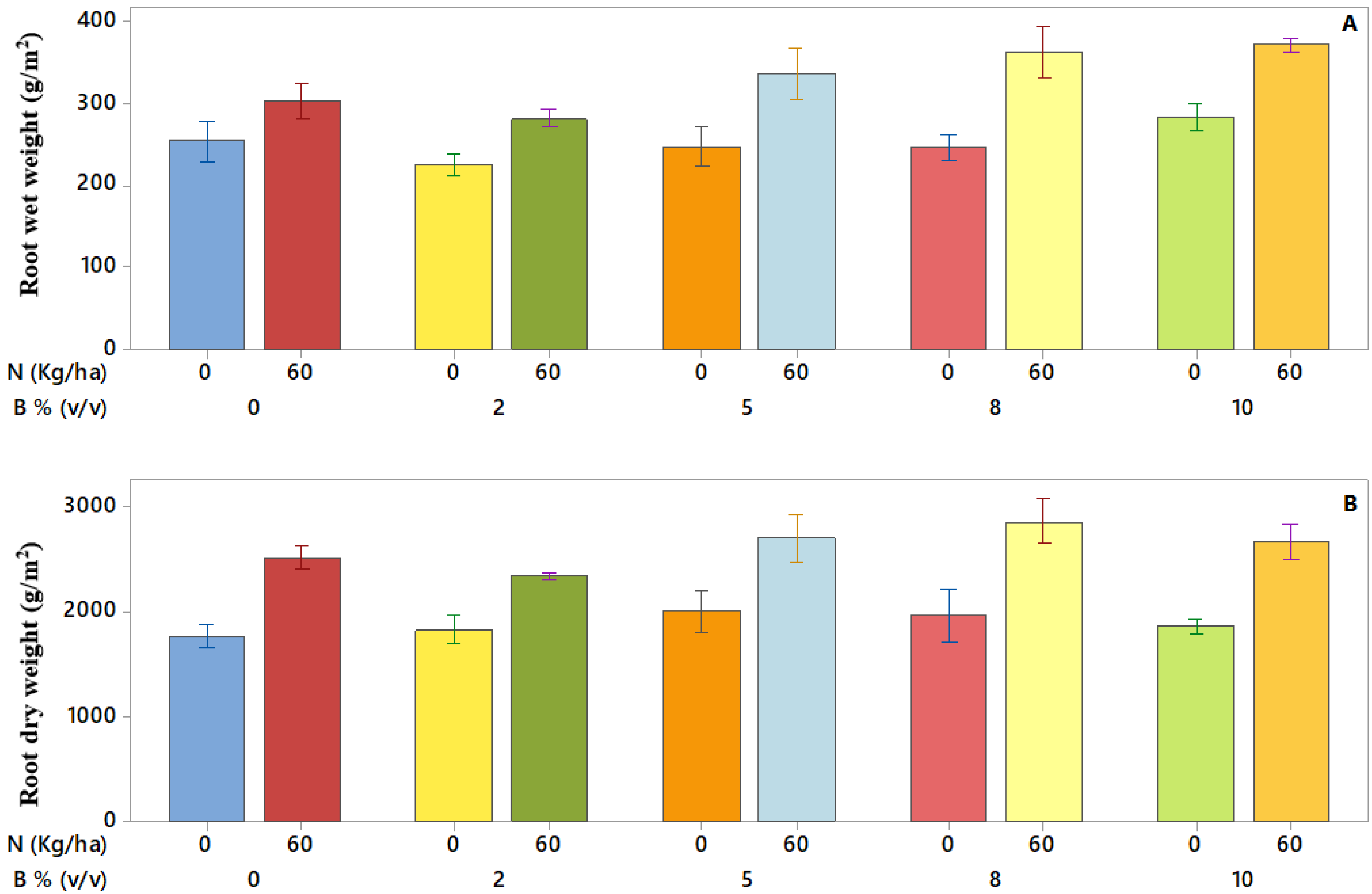


Figure 3-7: Effect of biochar and nitrogen applications on *Festulolium* forage roots wet weight (A), and roots dry weight (B), Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 3-13: Analysis of variance (ANOVA) of the estimated wet and dry weight of *Festulolium* forage roots in response to the main effects of biochar, nitrogen fertilizer, and interactions

	Roots wet weight						Roots dry weight					
Source of Variance	*df*	*Seq SS*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*	*df*	*Seq SS*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B% (v/v)	4	462196	462196	115549	1.39	0.273	4	18308	18308	4577	3.44	0.027
N (kg/ha)	1	3998917	3998917	3998917	48.16	< 0.001	1	47641	47641	47641	35.86	< 0.001
B % (v/v) *N (kg/ha)	4	117105	117105	29276	0.35	0.839	4	4413	4413	1103	0.83	0.522
Error	20	1660790	1660790	83040			20	26573	26573	1329		
Total	29	6239009					29	96936				

Statistically significant difference (P < 0.05). Source of variance codes including biochar (B) and nitrogen (N).

Table 3-14: Mean values of *Festulolium* forage roots nutrients uptake with different treatments in response to biochar, nitrogen fertilizer, and interactions of them

Treatments	N Kg/ha	P Kg/ha	K Kg/ha	Ca Kg/ha	Mg Kg/ha	Na Kg/ha	Fe mg/kg	Cu mg/kg	Mn mg/kg	Zn mg/kg
B0%-N0	13.02	4.23	14.80	8.99	1.79	2.35	1340.0	46.66	195.6	26.66
B2%-N0	13.02	4.20	16.83	10.37	1.83	2.13	1303.3	35.33	124.0	19.66
B5%-N0	14.08	4.95	25.02	10.11	2.11	1.90	1273.3	36.66	102.0	23.33
B8%-N0	15.16	5.26	26.76	11.43	2.24	1.65	1486.6	41.66	134.3	27.66
B10%-N0	16.41	6.13	30.78	12.65	2.36	1.77	1450.0	36.00	103.3	23.00
B0%-N60	15.35	5.04	17.73	14.01	1.52	2.75	1406.6	51.66	122.3	23.00
B2%-N60	16.13	4.75	20.24	14.41	1.81	3.25	1433.3	47.66	106.6	21.00
B5%-N60	17.15	4.78	26.15	14.62	2.42	2.71	1366.6	59.33	89.33	25.33
B8%-N60	19.68	5.67	29.60	16.53	3.09	2.04	1168.0	63.33	91.33	26.33
B10%-N60	20.75	5.92	31.74	16.67	3.26	10.47	1049.6	55.66	62.33	24.00

Treatments codes including five biochar application (B0%, B2%, B5%, B8%, and B10%), nitrogen levels are: (N0 and N60).

Table 3-15: Analysis of variance (ANOVA) of estimated *Festulolium* forage roots nutrients uptake in response to the main effects of biochar, nitrogen fertilizer, and interactions of them

Source of Variance	*p-values*									
	N	P	K	Ca	Mg	Na	Fe	Cu	Mn	Zn
B% (v/v)	0.005	0.014	< 0.001	0.027	0.001	0.001	0.664	0.108	0.013	0.131
N(kg/ha)	< 0.001	0.339	0.134	< 0.001	0.059	0.003	0.149	< 0.001	0.008	0.931
B% (v/v) *N (kg/ha)	0.864	0.730	0.973	0.967	0.189	0.058	0.017	0.163	0.583	0.757

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B) and nitrogen (N).

3.6. Discussion

Biochar application affected the fresh and dry matter yields. Increase in the yields was associated with increase in the biochar application rates. Sarfraz et al., (2017) reported similar observations that biochar application and nitrogen rates had increased the fresh and dry matter yields of the maize crop. Koyama et al. (2016), also reported that the biochar application significantly increased both the grain and the straw yields of the rice. Besides, Tian et al., (2018) found that the biochar application increased the seed cotton yields in three years of study, and they attributed the improvement of the yields to the increase of the nutrients addition, soil structure and moisture conditions, and soil water holding capacity along with the biochar application. The benefits of biochar application on crop biomass production were positively reported either in pot and field experiments (Jeffery et al., 2011; Pirtle et al., 2019). The increase in crop production by biochar is more within the acidic and low CEC of the soils; the biochar balance the soil acidity to more optimum status for crop growth, increase soil CEC, and releasing soluble nutrients such as P, K, Ca, and Mg to the soil (Liu et al., 2019). Oram et al., (2014) confirmed that the biochar application had increased the available K concentration 3 to 4 times more than the treatment with K fertilizer, which significantly led to increasing the red clover biomass.

It can be seen in (Figure 3-6C), that the biochar application rates and the nitrogen levels increased the leaf SPAD values. Elli et al., (2015) who used different levels of nitrogen (0, 40, 80, 120, and 160 Kg/ha) found an increase of the leaf SPAD value of three types of the wheat crop as a response to increasing the nitrogen levels. Likewise, Chang and Robison, (2003), reported that SPAD values were increased for four hardwood species (sweetgum, sycamore, swamp, and green ash) by increasing the nitrogen level to 336 kg/ha. Conversely, Asai et al., (2009) and Pirtle et al., (2019), demonstrated that biochar application decreased rice leaf SPAD value due to increased N immobilization by biochar as a result of the high C: N ratio of the biochar.

An improvement of the crude protein content was observed by increasing biochar application rates either with or without nitrogen application. That was confirmed when the crude protein content was increased even when the nitrogen application was reduced to 0 kg N/ha. These findings are consistent with Muni et al., (2016), who concluded that fly ash amended soil had increased the crude protein in the rice crop even when nitrogen application was reduced. Similar to the crude protein contents, the TDN and Digestible Energy were more significant in the treatments with higher biochar application rates. While the ADF and NDF contents are inversely related to foraging quality, their lower content improve the forage quality (Revell et al., 2012). The observation reported by Revell et al., (2012) was consistent with the results in which ADF and NDF contents decreased by increasing the biochar application rates. These results are in agreement with Chhay et al., (2013), and Husk and Major, (2011), who found that crude protein content significantly increased; in contrast, ADF and NDF contents were decreased along with increasing the biochar application rates. Consequently, the results suggested that the *Festulolium* forage quality increased by increasing the crude protein, TDN and Digestible Energy while decreasing the ADF and NDF contents within the higher biochar application rates.

Biochar application to the soil can affect the plant nutrients uptakes. The increase of the exchangeable elements such as K, Ca, Mg, Mn, and Na in the biochar can increase the availability of these elements in the soil and turn into plants' nutrients uptake. On the other hand, the shortage of these elements in biochar can decrease the concentration of these elements in plant tissues such as leaves and roots (Rees et al., 2016). The results of this study revealed that the biochar application had increased *Festulolium* forage nutrient uptake of C, N, P, K, Ca, Mg, and Cu. It was in agreement with Yang et al. (2020), who found that N, P, and K uptake increased in potato plants grown in biochar amendment soil by increasing the biochar application rate. Similarly, Coumaravel et al. (2015) concluded that biochar application of 10 t/ha with NPK supplement had increased the total NPK uptake by maize crop. The results are also consistent with Maftu and Nursyamsi (2019) and Xiao et al., (2019), who found that maize NPK uptake was linearly increased by increasing biochar application rates. Likewise, biochar application had increased phragmites karka plant's K, Ca, and Mg uptake, which are attributed to the biochar function of improving soil water retention and ions exchange (Zainul et al., 2017), as well as to the high CEC of produced biochar (Sarfraz et al., 2017). Besides, the results presented in (Tables 13 & 14) showed that *Festulolium* Na and Mn uptake were reduced either with biochar application or nitrogen levels. These findings are consistent with Zemanová et al., (2017), who reported that maize Na uptake was decreased as a result of high K, Ca, and Mg contents within the applied biochar (Kim et al., 2016; Schimmelpfennig et al., 2015). A similar tendency was observed with plants Mn uptake was reduced by biochar application (Win et al., 2019), that was due to the high pH value of the applied biochar, which decreases the micronutrient availability in the soil, especially Mn availability (Kloss et al., 2014). However, the *Festulolium* Fe, Cu, and Zn uptake were not affected by biochar application. This is consistent with Win et al., (2019), who demonstrated that plant Fe and Zn uptake are negatively affected by biochar application through lowering the availability of the micronutrients. This is due to the high pH related function causing micronutrient deficiencies in the soil (Kloss et al., 2014). While the result regarding Cu uptake is in agreement with Novak et al., (2009), who reported no significant effect of the biochar on Cu uptake; in contrast, Lentz and Ippolito, (2012), observed a reduction in the Cu uptake through the biochar application. This may be attributed to immobilize availability of Cu by the formation of an inorganic metal complexation (Hee et al., 2011). At the same time, Fe and Cu uptake were decreased by nitrogen levels, whereas Zn uptake was also not affected by the nitrogen levels. The macro-and micronutrient accumulation of *Festulolium* leaves has the same tendency as the nutrient's uptakes by roots. An increase in most of the macronutrient such as N, P, K, Ca, and Mg, and a decrease in the micronutrient (Na, Fe, Cu, Mn, and Zn) in *Festulolium* forage crop can be attributed to the the influences of the biochar on the concentration of the element in the crop.

The soil pH value was significantly affected by biochar application rates, nitrogen fertilizer, and crop treatments. The soil pH values increased by increasing the biochar application rates due to the enhancing cations (e.g., Ca^{2+}, Mg^{2+}, and K^{+}) retention within the soil (Yang et al., 2017). While the increment of soil pH by the nitrogen fertilizer can be assigned to the enhancement of OH^{-} and NH_4^{+} concentrations as a function of urea hydrolysis (Wang et al., 2020; Zhou et al., 2014). Also, it has been found in this study that the soil pH value was affected by crop treatments, in which the soil pH in no crop treatments was higher than that in crop treatments. It has been reported that soil pH can be varied by up to two units based on plant and soil factors, as the soil pH near the plant roots can be different than that of the bulk soil (Custos et al., 2020). The main reason behind that can be explained by "cation-anion ex-change between root and soil, root excretion of organic anions, root respiration (CO_2 production) and root-induced redox processes"(Custos et al., 2020). Thus, the plants nutrient uptake can be an important reason to reduce the soil pH in the root's zones, when the root adsorb more cations than anions, protons (H^{+}) will be released by the roots to balance the positive charges in the root cells, leading to a decrease in the soil pH in the roots zones (Custos et al., 2020).

Most soils in Newfoundland are podzolic, and they are recognized with low pH values (Kedir et al., 2021; Sanborn et al., 2011) . Thus, lime is used to increase its pH, and the amount of limestone that needs to be added depends on the soil pH, and the selected fertilizers (Heringa, 1981). The soil pH values of this study have risen from 6.1 to 6.9 at different levels of biochar, nitrogen, and crop treatments (Table 3 16). Increased soil pH was followed by improvement in soil fertility and subsequently increment in the *Festulolium* forage crop yields (Figure 3 4), and improvement in the

Festulolium forage quality (Table 3 17). Although lime was not added to the soil in this study, the soil pH was raised with biochar. Therefore, biochar application can be considered an alternative agent for increasing soil pH, improving soil fertility, and reducing the required amount of limes to be added to the soil.

3.7.Conclusion

The results of this study suggest that the combination of biochar and nitrogen applications has a positive impact on forage growth, root growth, forage quality, and forage nutrients uptake by the *Festulolium* forage crop. This may occur because of the improvement of soil properties and soil nutrients concentrations under the greenhouse condition. Biochar application to the soil has improved soil pH, SOM, CEC, and nutrients availability in the soil, including Ca, Mg, K, P, S, Zn, Mn, and B. Improvement of the soil fertility by biochar and nitrogen applications has enhanced the *Festulolium* nutrients uptake, which was reflected in the improvement of the forage leaves, roots growth, and forage quality. Thus, based on these results, the combination of biochar and nitrogen applications can improve soil properties, forage nutrient uptake, and forage quality in the eastern Newfoundland podzolic soil.

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Chapter 4

Spruce Bark Biochar Application Minimizes Nitrogen and Carbon Leaching Losses from the Eastern Newfoundland Podzolic Soil

Abstract

Biochar has a broad use in the agriculture sector; its application to the soils has been recognized as a unique strategy for soil quality improvement, soil remediation, carbon sequestration, and climate change mitigation. Furthermore, the application of biochar in combination with Nitrogen (N) fertilizer would improve their use efficiency by plants by increasing their availability. The application of biochar as a soil amendment to the eastern agricultural Newfoundland soil could be an alternative strategy to mitigate the leaching of N and C species. Nevertheless, the biochar application for enhancing N and C retention in the soil is not clearly defined for the eastern Newfoundland podzolic soil. Therefore, this study investigated the effect of spruce bark biochar (SB550) application for minimizing the leaching losses of total nitrogen (TN), nitrate (NO_3^-), (NH_4^+), and dissolved organic carbon (DOC) from soil. In this experiment, the *Festulolium* forage crop was grown in a greenhouse on a soil-biochar mixture that was prepared at five rates of 0, 2, 5, 8 and 10% (v/v), with and without N fertilizer (0 and 60 kg N/ha). The results indicated that SB550 biochar has significantly reduced NO_3^-, NH_4^+, TN, and DOC in the leachate. The SB500 biochar reduced NO_3^- leaching by 11.61 %, 38.93 %, 42.50 %, and 47.75 %, NH_4^+ leaching by 34.65 %, 59.65 %, 69.55 %, and 70.04 %, TN by 11.31 %, 33.18 %, 48.95, and 52.95 %, and DOC by 13.43 %, 27.70 %, 40.33 %, and 74.26 %, at the biochar rates of 2 %, 5 %, 8 %, and 10 % [v/v], respectively, in comparison to that of the control treatment (0 % [v/v]). The results indicated that biochar application was an excellent method for reducing the leaching loss of N and C in the eastern Newfoundland podzolic soil.

Keywords: *agriculture, biochar, nitrate, ammonium, dissolved organic carbon*

4. Introduction

4.1. Background

The world's, as well as Canada's demand for food, is rising to increase the food self-sufficiency; the Newfoundland and Labrador (NL) government has committed to improving the province's food self-sufficiency to at least 20 percent by executing strategies that support the development of farmlands and local livestock operations (Government of Newfoundland and Labrador, 2017). The biggest challenge facing the local agricultural sector is improving soil quality. The NL's soils are classified as podzolic, which is characterized by most as being naturally acidic, which is caused by parent material formation under extremely high precipitation (approximately 1000 mm/ annually). (Sanborn et al., 2011; Walker, 2012). The combination of these circumstances, such as the very coarse soil texture and the existence of a significant proportion of stones and gravels in the NL's soil, resulted in extreme elements leaching losses from the surface soil, leaving the soil to be strongly acid. Therefore, the soil in the NL province has low fertility, high acidity, low cation exchange capacity (CEC), and low soil organic matter (SOM). Accordingly, while preparing these lands for crop production, the appropriate types and amounts of commercial fertilizers and/or manures must be applied to enhance and maintain the essential plant supplements in such soils.

N fertilizer as an essential nutrient is required by most crops, and thus, it needs to be added for improving soil fertility, forages crop protein and yield (Drury and Tan, 1995). However, the amount of N leaching significantly increases with an inorganic N application (Gu et al., 2016; Mack et al., 2005; Yang et al., 2014; Zhang et al., 2015). It has been reported that more than 30 % of the applied inorganic N move down, resulting in a significant amount of N leaching losses to the environment (Cai et al., 2002; Ju et al., 2009), and in turn, causing a severe threat to the quality of surface and groundwater (Gai et al., 2014). With such circumstances of the extreme high precipitation and specific soil conditions of strong acidity that are combined with such stony coarse soil texture in the NL soil, there is a need for an urgent intervention that would improve soil fertility and crop production while reducing N losses through leaching to prevent the negative impact of the N losses to the environment.

Dissolved organic carbon (DOC) is an essential part of soil organic carbon stock (Xiao et al., 2012), and it is one of the most mobile and active components of the soil organic carbon cycle (Lei et al., 2018; Lorenz and Lal, 2012). DOC was defined as the continuum of organic molecules of different sizes and structures that pass through a filter pore size of 0.45 μm (Kalbitz et al., 2000; Royer et al., 2007). The losses of DOC by leaching can lower soil fertility and, in turn, its crop productivity. Furthermore, the leached DOC has significant environmental and ecological consequences for both terrestrial and aquatic ecosystems (Dhillon and Inamdar, 2013; Mukherjee and Zimmerman, 2013). The amount of leached DOC can be affected by soil properties (e.g., texture, microbes, pH), crops, and environmental factors such as temperature and precipitation as well (Xiao et al., 2012). Increasing the DOC concentration in the leachate from agricultural soil can affect metabolism, plant nutrient uptake, microorganisms growth, and water quality (Stanley et al., 2011).

Biochar is a carbon-rich organic material produced from forest and agricultural waste such as wood, manure, and leaves by pyrolysis of these organic materials under high-temperature and low-oxygen conditions. Biochar application to soil has been considered as a promising and effective strategy to reduce N and carbon (C) leaching losses from soils (Ahmad et al., 2016; Hussain et al., 2017; Igalavithana et al., 2016; Smith, 2016). Recently, biochar attracted more attention as a soil amendment material due to its positive effect on improving soil physical and chemical properties, soil fertility, and, thus, crop production. In addition to the benefits of biochar application for improving soil fertility and crop production (Agegnehu et al., 2017; Mao et al., 2013; Stavi and Lal, 2013; Yu et al., 2019), it is also reported to mitigate nutrient leaching (Taghizadeh-toosi et al., 2012; Wan et al., 2014; Yuan et al., 2016), and to increase soil organic C (Ippolito et al., 2016; Tian et al., 2016; Yu et al., 2019), soil CEC and soil pH of the acidic soil (El-naggar et al., 2018; Ippolito et al., 2016; Mao et al., 2013; Yu et al., 2019), as well as improve soil structure (Burrell et al., 2016), resulting in an increase in soil microbial biomass and microbial activity (Domene et al., 2014; Ge et al., 2019; Lehmann et al., 2011a; Xu et al., 2018). Many other benefits of biochar application were reported, such as a decreasing soil bulk density (Abrol et al., 2016; Oduor et al., 2016; Xiao et al., 2016), increasing soil moisture content (Haider et al., 2017) and water holding capacity (Farkas, 2019; Oduor et al., 2016; Zheng et al., 2013), mitigating nitrate and ammonium leaching (Fidel et al., 2018; Prima et al., 2016; Steiner et al., 2010; Yao et al., 2012). Biochar was also found to be a useful material for carbon sequestration and greenhouse gas emissions mitigation (Atkinson et al., 2010; Borchard et al., 2019a; Cayuelaa et al., 2014; Laghari et al., 2016; Mosier et al., 2006; P. Smith et al., 2008; Stavi and Lal, 2013).

In the literature, many studies used biochar was generated from different feedstock sources, which was then applied at different rates with or without a combination of other organic materials to examine its potential for lowering the N leaching. For example, Steiner et al. (2010) found that mixed poultry litter with 20% of biochar reduced total N losses by up to 52%. According to Kumar et al. (2016), the application rate of 20 g of corn biochar kg^{-1} soil reduced the leachate nitrate up to 29% in the low carbon soils. Likewise, the amount of nitrate leaching significantly decreased with biochar application on Chinese upland red soil. Prima et al., (2016) found that the rice husk biochar application at a rate of 4 % (w/w) into loamy soils reduced total leached ammonium by 11% and total leached nitrate by 23%. They concluded that adding the rice husk biochar is a potential strategy for nitrogen leaching mitigation in a loamy soil. In laboratory columns containing sandy soil and biochar at rates of 0.5, 2.5, and 10.0% w/w, the pine wood biochar has significantly reduced the total cumulative amount of nitrate in the leachate by 26, 42 and 96%, respectively, and the total cumulative amount of ammonium in the leachate by 12, 50 and 86%, respectively (Sika and Hardie, 2014). Also, Yao et al. (2012) concluded that the Brazilian peanut hull biochar reduced the total amount of nitrate and ammonium in the leachates by 34 % and 14 %, respectively. However, most of the existing studies only applied the arbitrary rate of specific biochar when studying its benefits in reducing N leaching. Still, very few studies examined the optimum application rate for particular biochar applied in the soil to reduce N leaching and increase soil fertility.

The impacts of biochar application on the nutrients leaching from agricultural soils are depending on many factors such as the biochar characteristics and soil properties (Mukherjee and Zimmerman, 2013; Yao et al., 2012). Globally, a large number of studies have been conducted to check the potential benefits of biochar in different applications. Likewise, several studies were done elsewhere in Canada, such as in Ontario, Quebec, and Alberta. However, no study has been done in the province of Newfoundland and Labrador, Canada, looking at the effect of biochar to reduce the nitrogen and carbon leaching losses from a Newfoundland podzolic soil developed in a cool, high precipitation environment. Consequently, the objective of the study was, to investigate the impact of biochar application on potentially reducing leaching of N and C leaching losses from the eastern Newfoundland Podzolic soil.

4.2. Materials and methods

4.2.1. Biochar production and characterization

The selected biochar was obtained from GECA Environnement, Quebec, Canada. The biochar was produced from a spruce bark feedstock at 550°C (SB550) using the Abri-Tech technology in Canada, and physicochemical properties were determined as shown in (Table 1). Detailed information about the biochar preparation and characteristics are presented elsewhere (Allaire, 2018; Lange and Allaire, 2018). Whereas the Scanning electron microscopy (SEM) images of the biochar (Figure 4-1) showed the morphologies and porous structures, and the Fourier Transfer Infrared (FT-IR) spectra displayed the presence of functional groups on SB550 biochar at different wavenumber peaks at the ranges of 1575, 1430, 1375, 875, 815 and 750 cm^{-1}. These wavenumber peaks are referred to aromatic C=C stretching, aromatic C=C bending, aromatic C–H bending, and phenolic O–H bending (Figure 4-2).

Table 4-1: Moisture Content, pH, CEC, Total Nitrogen, Total Carbon, Total Phosphorus, Total Potassium, Total Calcium, Total Magnesium, Total Iron, Total Copper, Total Manganese, Total Zinc, Total Boron, Total Sodium, Total Sodium, and Soluble Salts of the SB550 biochar

Analysis	SB550
Moisture Content (%)	<1
pH	9.9
Total Nitrogen, N (%)	0.95
Total Carbon, C (%)	77.2
Total Phosphorous, P (%)	0.29
Total Potassium, K (%)	1.33
Total Calcium, Ca (%)	1.75
Total Magnesium, Mg (%)	0.24
Soluble Salts (dS/m)	0.7
CEC cmol/kg	28.5

Basic properties of SB550 biochar

4.2.2. Experimental set-up and design

The experiment was conducted in a greenhouse at Memorial University Botanical Garden (St. John's, Canada) between December 2018 to April 2019. *Festulolium* forage crop was grown in a plastic pot with dimensions of 30.48 cm diameter and 27.5 cm height (Figure 4-3), contained 15 kg soil, under 8-16 h of day-night photoperiod and a temperature of 18–20 °C. The *Festulolium* was developed from Meadow or Tall Fescue with Perennial or Italian Ryegrass grass by crossing Meadow or Tall Fescue with Perennial or Italian Ryegrass (Boller et al., 2010). The used soil was classified as silt loam in the US/ Canadian system, which was collected from St. John's Research and Development Centre's agricultural research site. The experimental design consisted of five rates of biochar applications including, 0% (control), 2, 5, 8 and 10% biochar rates [v/v] (Figure 4-4), and with two levels of nitrogen fertilizer applications (Urea 46-0-0) that were applied at the rates of 0 and 60 N kg/ ha to the plastic pots with and without the planting of *Festulolium* forage crop (crop and no crop treatments). The design ended up with a total of 20 treatments. The experiment was set up in a Completely Randomized Design (CRD), with three replicates resulting in a total of 60 pots, as shown in the experimental layout (Figure 4-5).

4.2.3. Soil, biochar, and nitrogen fertilizer

The soil was collected from the agriculture research site of Agriculture and Agri-Food Canada, St. John's Research and Development Centre (47°31'N; 52°47'W; 115 m above sea level). The soil was taken from the top 20 cm, dried in a forced air-drying room for 72 h at 35°C. Biochar was thoroughly mixed with a portion of the soil to prepare soil-biochar mixtures in percentages of 0, 2, 5, 8 and 10% [v/v], and then the combinations were added to the top 10 cm above the remaining soil. Two nitrogen fertilizer applications of Urea (46-0-0) were applied in the top 2.5-3.0 cm of the soil at the rates of 0 and 60 N kg/ha as recommended by Newfoundland and Labrador

Provincial Agriculture Soil & Plant Laboratory, based on soil nitrogen test, and crop requirements. In the end, the *Festulolium* seeds were uniformly seeded in the top 0.5 cm of topsoil at the recommended field seeding rate of 35 lbs per acre adjusted to the pot surface area.

A preliminary experiment was done to estimate the amount of water to add to each pot of soil to avoid excess leaching and to measure soil field capacity (F.C.). Soil F.C. was determined to be 35% (g water/g oven-dry soil) using a gravimetric oven drying method. The wet soil was sampled 24 h after water addition, and soil moisture content was calculated based on a standard drying method: 5 g of soil samples were dried for 48 h at 105°C. The soil moisture content of the pots was determined every 3-4 days using GS3 VWC, temperature, ECw and ProCheck Sensor Read-Out and Storage System (METER Group, Inc. USA), and all pots were watered up to the F.C. to ensure the soil getting at least 20% of the total available water.

4.2.4. Leachate sampling and analysis

Leachate samples were collected every three weeks during the 24 h after irrigation. The collection was made from the trays that installed underneath the pots (Figure 4-3), using 60 ml syringes, and then stored in a freezer at -20°C before analysis. All leachate samples were subjected to several chemical analyses. The pH and electrical conductivity (EC) of the leachate samples were measured using the Hach HQ40d portable meter, and then the sub-samples of leachate were filtered using 0.45-μm filters for further analysis. Nitrate (NO_3^-) and ammonium (NH_4^+) were measured using AutoAnalyzer (Seal analytical continuous flow analyzer (AA3 HR) (Cao et al., 2017; Heman et al., 2016). TN and DOC concentrations were also analyzed in the leachate with a ShimadzuTOC-LCPH/TN analyzer (Shimadzu Inc., Japan).

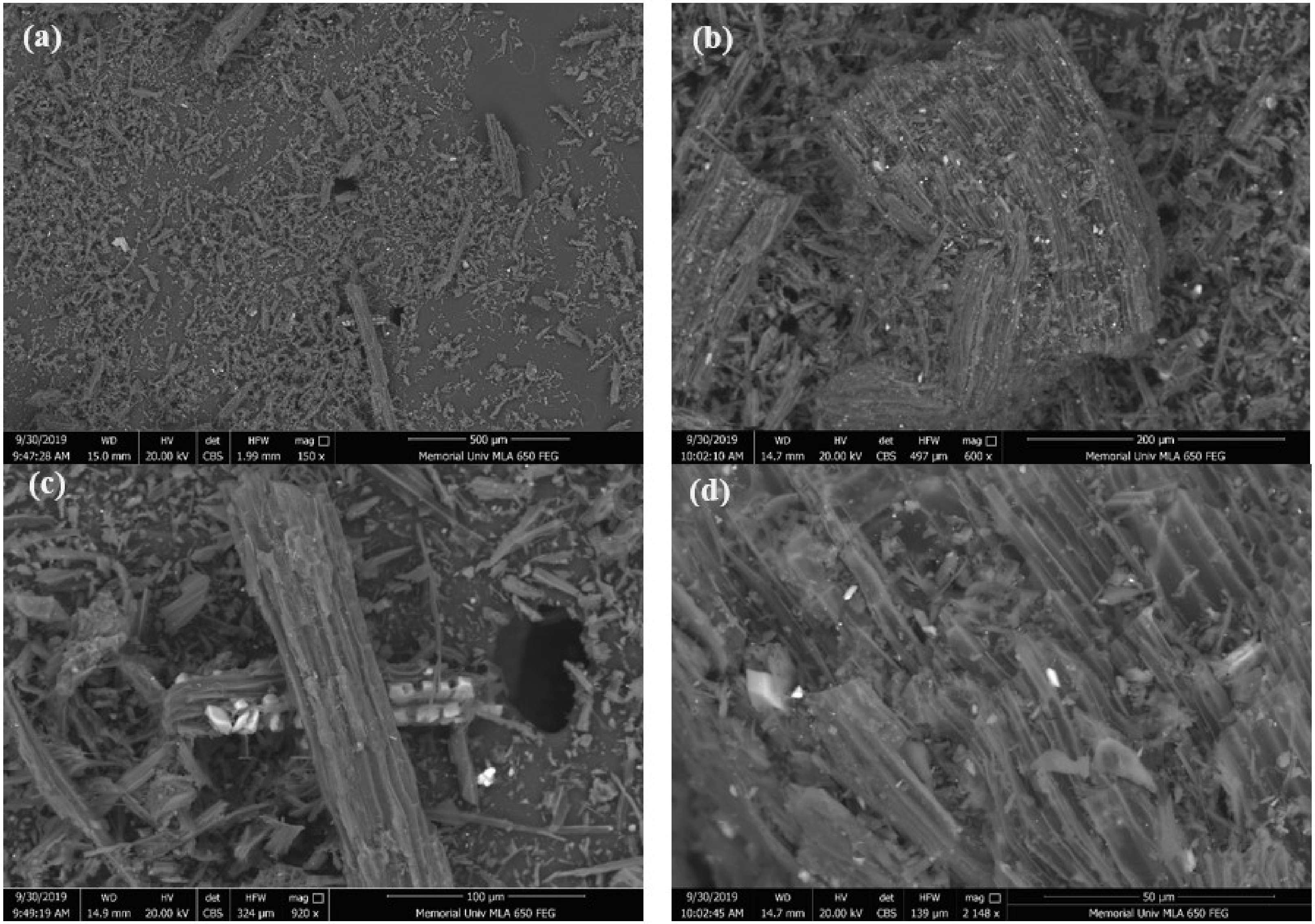


Figure 4-1: SEM images of spruce bark biochar (SB550) at different scales, including (a) 500 µm, (b) 200 µm, (c)100 µm, and (d) 50 µm.

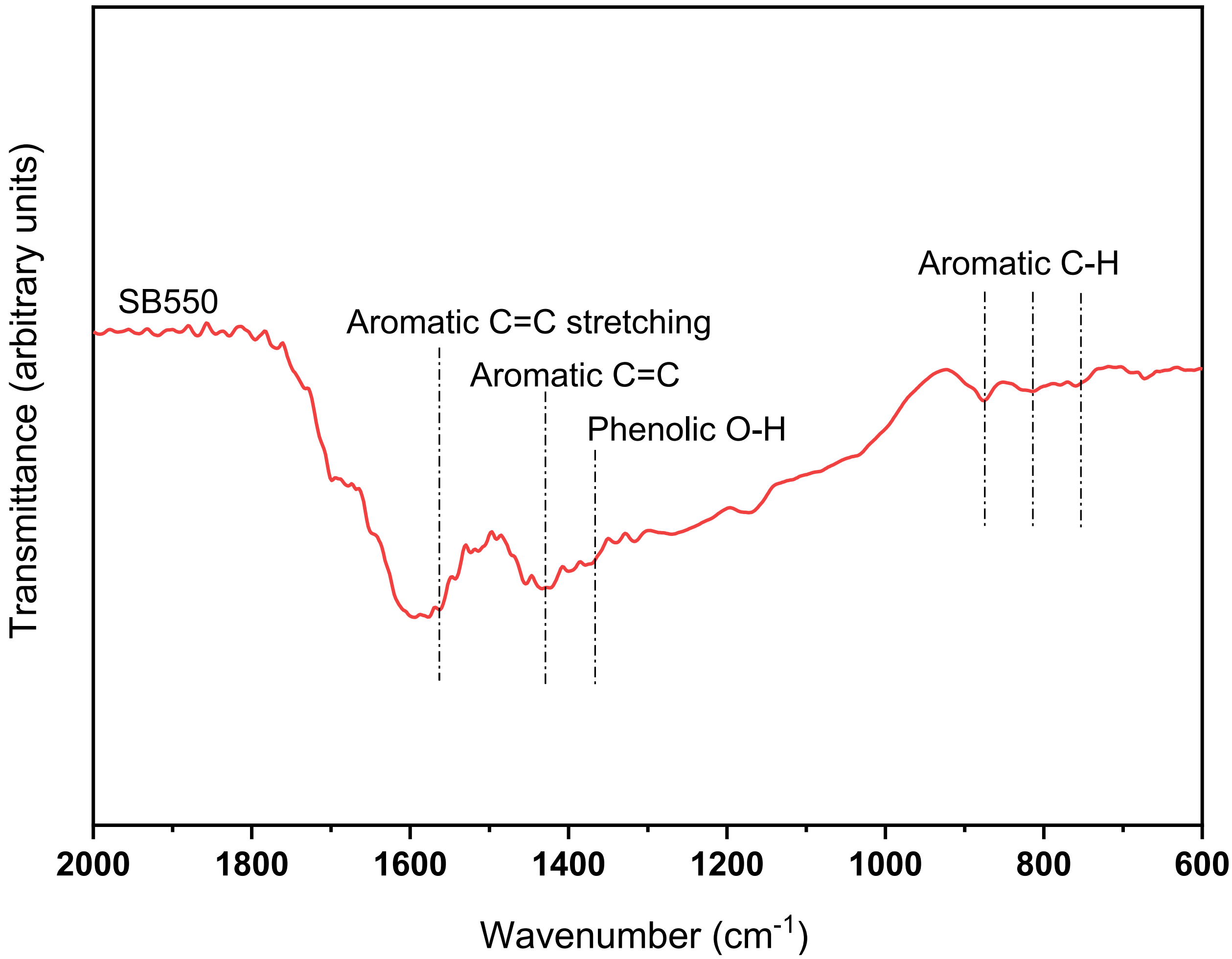


Figure 4-2: FT-IR spectra showed the presence of functional groups on SB550 biochar

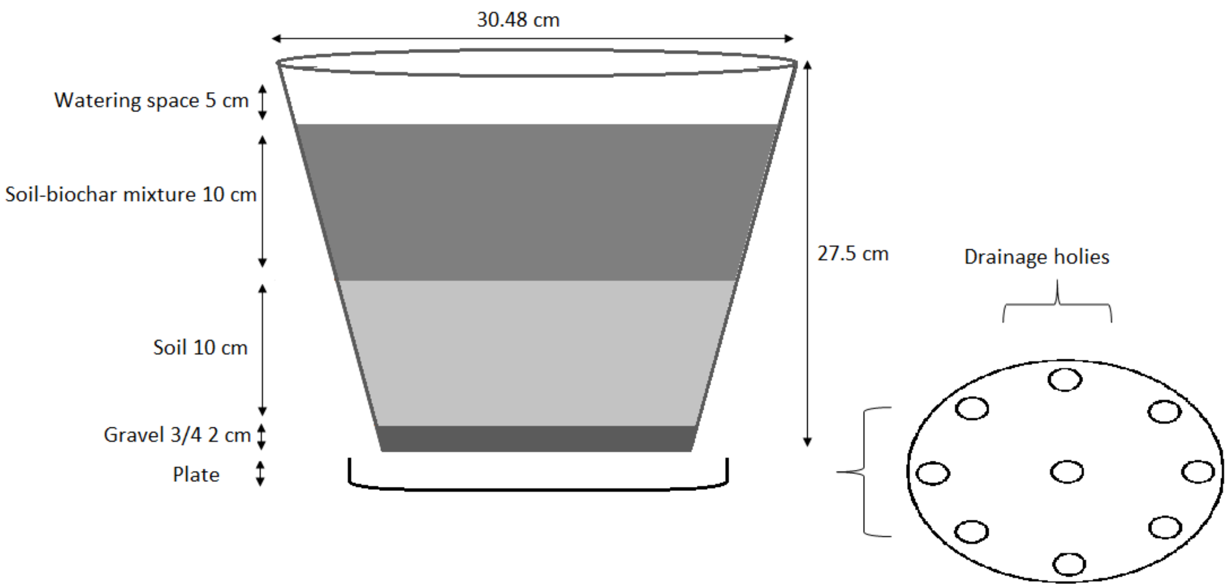


Figure 4-3: Soil column in the experiment pots used for soil leachate collection

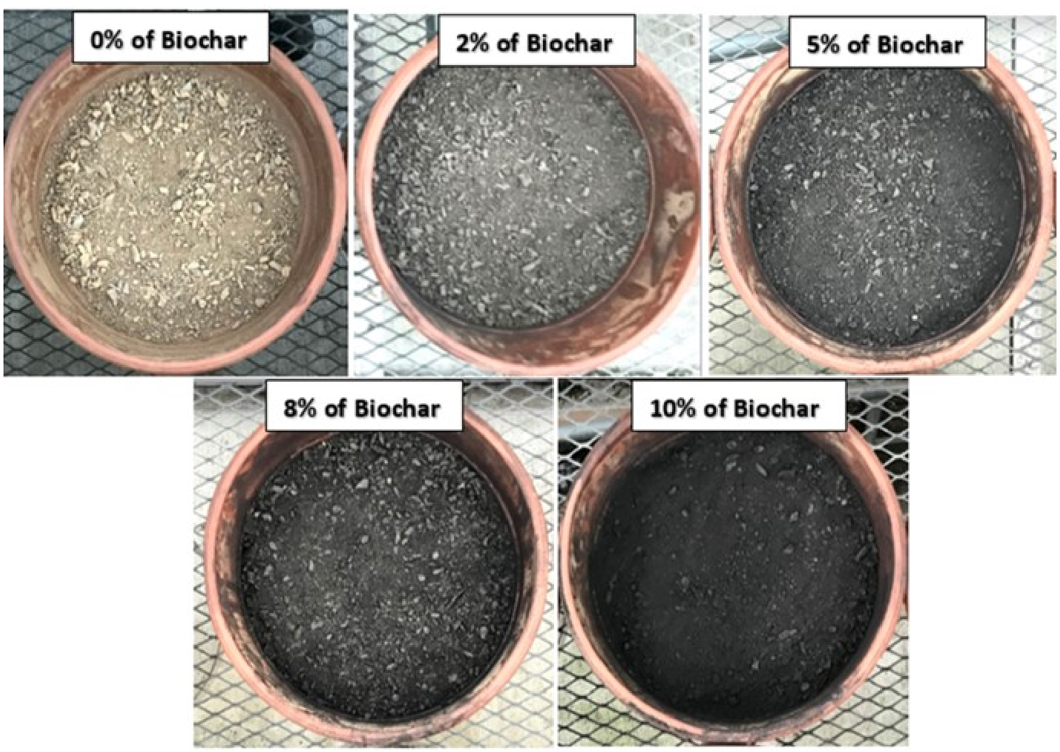
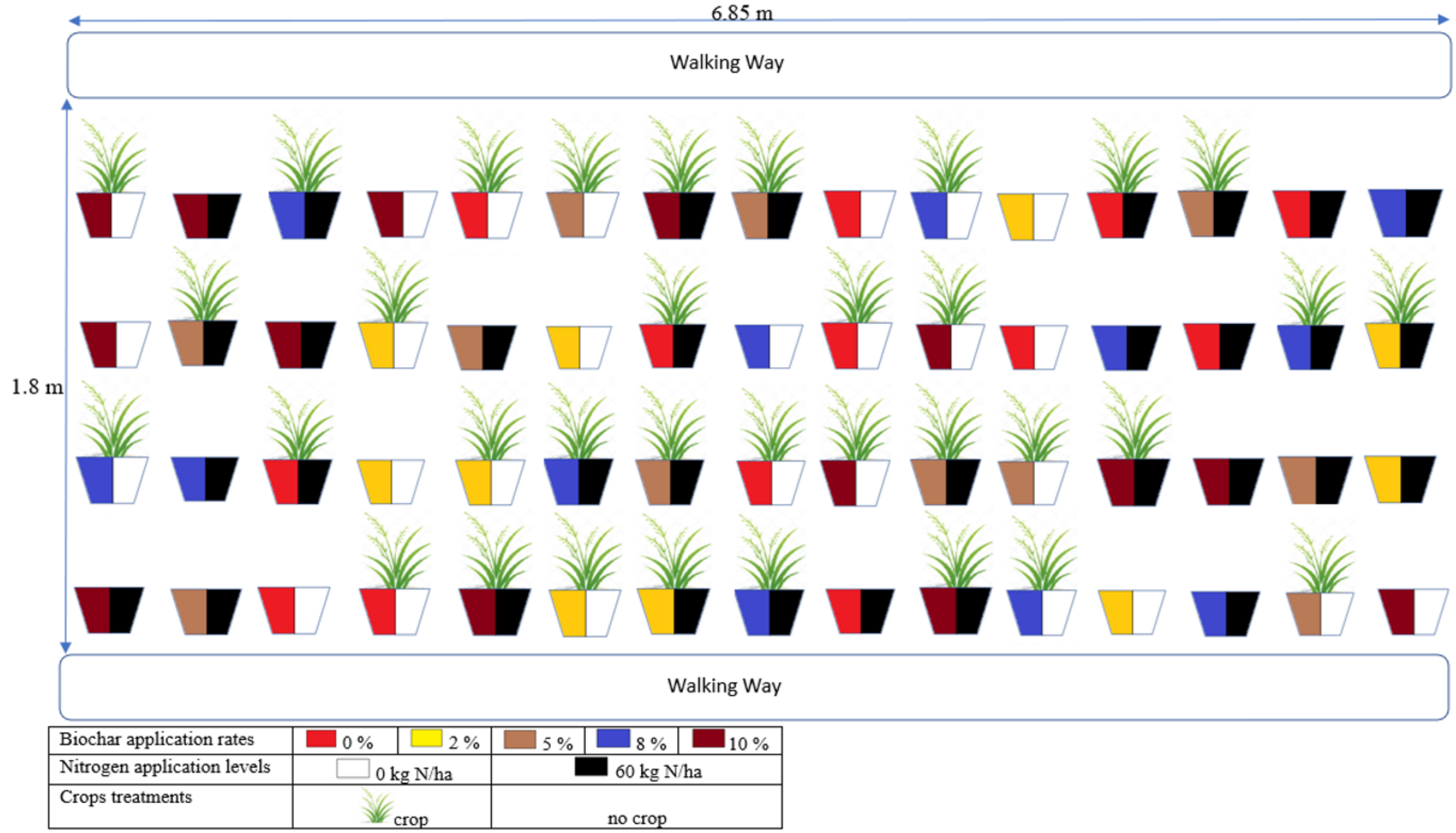


Figure 4-4: Soil-biochar mixtures prepared at five application rates, which were added as percentages based on the soil volume [v/v] (0, 2, 5, 8 and 10%) in the top 10 cm of the soil



Treatments codes	Treatment Description	Treatments codes	Treatment Description	Treatments codes	Treatment Description	Treatments codes	Treatment Description
T_1	B_0%-N_0-crop	T_6	B_0%-N_{60}-crop	T_{11}	B_0%-N_0-no crop	T_{16}	B_0%-N_{60}-no crop
T_2	B_2%-N_0-crop	T_7	B_2%-N_{60}-crop	T_{12}	B_2%-N_0-no crop	T_{17}	B_2%-N_{60}-no crop
T_3	B_5%-N_0-crop	T_8	B_5%-N_{60}-crop	T_{13}	B_5%-N_0-no crop	T_{18}	B_5%-N_{60}-no crop
T_4	B_8%-N_0-crop	T_9	B_8%-N_{60}-crop	T_{14}	B_8%-N_0-no crop	T_{19}	B_8%-N_{60}-no crop
T_5	B_{10}%-N_0-crop	T_{10}	B_{10}%-N_{60}-crop	T_{15}	B_{10}%-N_0-no crop	T_{20}	B_{10}%-N_{60}-no crop

Figure 4-5: Experimental layout, showing biochar, nitrogen, and crop levels and the treatment descriptions within a completely randomized design (CRD)

4.3. Statistical analysis

Statistical analysis of variances (ANOVA) was performed using a general linear model in the Minitab 19 software (Minitab, 2019). To test the degree of the significance of biochar effect, nitrogen effect, and crop effect, and the interaction between these three factors at $\alpha \leq 0.05$, the experimental design (RCD) was taken into consideration. The normality of distribution and homogeneity of variance were tested before ANOVA analysis was conducted, and all assumptions were met. Significant differences between the treatment means were analyzed using Tukey's test at a 95% significance level ($P < 0.05$). A three-way analysis of variances (ANOVA) was performed according to a linear model (1) (Dunn and Smyth, 2018).

$$Yijk=\mu+Ai+Bj+C_k+(AB)_{ij}+(AC)_{ik}+(BC)_{jk}+(ABC)_{ijk}+\varepsilon_{ijkl} \quad (1)$$

Where *Yijk* is the dependent variable, μ is the overall mean, *Ai, Bj,* and *Ck* are the effects of *ith* (biochar rates), *jth* (nitrogen levels), and *kth* (crop treatments), respectively, and *εijkl* is the random error terms within the experiment.

4.4. Results

4.4.1. Leachate pH and EC.

The statistical analysis of the leachate pH showed that the biochar application had a significant effect on the leachate pH (p-value < 0.001) (Table 4-2). Tukey's test results indicated a significant increase in the leachate pH following the increase in the biochar application rate, where all biochar rates, including 2 %, 5 %, 8 %, and 10 % [v/v] were significantly different than the control (0 % [v/v]) (Figure 4-6). Also, the biochar and nitrogen interaction had a significant impact on the leachate pH (p-value = 0.011) (Table 4-2). The leachate pH values were highest in the treatment of higher biochar rates (10 % [v/v]) and with the nitrogen application 60 kg N/ha (Figure 4-6). Moreover, the biochar and crop interaction had significantly affected the leachate pH (p-value =

0.004) (Table 4-2). Increase in the leachate pH were following the higher biochar rates and no crop treatments, as shown in (Figure 4-6). Additionally, the leachate pH was also affected by the biochar, nitrogen, and crop interactions, but regardless of the crop effects, the leachate pH increased along with the increasing of the biochar rates and nitrogen levels (Figure 4-6). Whereas the ANOVA analysis of leachate EC showed different scenarios, where there was a significant reduction in the leachate EC by the biochar application rates, nitrogen levels, and crop levels (p-values < 0.001) (Table 4-3). The leachate EC reduction was following the increase of the biochar rates, nitrogen levels in the no crop treatments (Figure 4-7).

4.4.2. Leachate nitrate and ammonium

The leachate nitrate ANOVA analysis was shown in (Table 4-4), which stated that biochar, nitrogen and crop significantly affected the leachate nitrate. The leachate nitrate was significantly increased by 119 % at the N level of 60 kg/ha in comparison to that for the control treatment (p-value < 0.001) (Table 4-4 & Figure 4-8). Also, crop levels had significantly decreased the nitrate leaching by 86.63 % in comparison to the case of no crop treatments (p-value < 0.001) (Table 4-4 & Figure 4-8), which may demonstrate the forage crops' roles in minimizing the nitrate leaching from the agricultural crop system. The biochar effect comes through the leachate nitrate reduction, in which nitrate was significantly reduced in the leachate (p-value < 0.001) (Table 4-4), by 11.61 %, 38.93 %, 42.50 %, and 47.75 % at the biochar rates of 2 %, 5 %, 8 %, and 10 % [v/v], respectively, in comparison to that of the control treatment (0 % [v/v]). This outcome illustrated the biochar roles in minimizing nitrate leaching from the fertilized crop systems. Furthermore, the leachate ammonium ANOVA analysis (Table 4-5), stated that the biochar and nitrogen have affected the ammonium leaching. A significant and intensive increase by 1029 % was found at the 60 kg N/ha level in comparison to the control level 0 kg N/ha (p-value < 0.001) (Table 4-5 &

Figure 4-9). However, biochar had significantly reduced the ammonium leaching by 34.65 %, 59.65 %, 69.55 %, and 70.04 % at the biochar rates of 2 %, 5 %, 8 %, and 10 % [v/v], respectively in comparison to that of the control treatment (0 % [v/v]) (p-value < 0.001) (Table 4-5 & Figure 4-9), which also reflect the roles of biochar in ammonium leaching reduction from the fertilized crop systems.

4.4.3. Leachate total nitrogen and dissolved organic carbon

The ANOVA analysis of leachate total nitrogen was shown in (Table 4-6), which illustrated the significant effects of biochar, nitrogen, and crop on the total leachate nitrogen. The nitrogen level of 60 kg N/ha had significantly increased the total nitrogen leaching by 375 %, in comparison to the control level of 0 kg N/ha (p-value < 0.001) (Table 4-6 & Figure 4-10). Likewise, the nitrogen level increased the total nitrogen by 106 % within the no crop level (p-value < 0.001) (Table 4-6 & Figure 4-10). Whereas, in a deferent scenario, biochar had significantly decreased the total leached nitrogen by 11.31 %, 33.18 %, 48.95, and 52.95 % at the biochar rates of 2, 5, 8, and 10 % [v/v], respectively, in comparison to that of the control treatment (0 % [v/v]), as a confirmation of the important role of biochar for leachate nitrogen reduction from the fertilized crop systems. Moreover, the statistical analysis of leachate dissolved organic carbon (DOC) in (Table 4-7) showed the significant effects of biochar, nitrogen, and crop on leachate DOC. A significant increase in the DOC leaching by 69.13 % was found within the 60 kg N/ha treatments in relative to the 0 kg N/ha (p-value < 0.001) (Table 4-7 & Figure 4-11). In contrast, a significant reduction of the leached DOC by 34.21 % was found in the no crop treatment compared to crop treatment (p-value < 0.001) (Table 4-7 & Figure 4-11). Also, a significant reduction of the leached DOC by 13.43 %, 27.70 %, 40.33 %, and 74.26 % was found at the biochar rates of 2, 5, 8, and 10 % [v/v], respectively, in comparison to that of the control treatment (0 %) (p-value < 0.001) (Table 4-7).

Table 4-2: Analysis of variance (ANOVA) of estimated soil leachate pH in response to the main effects of biochar, nitrogen levels, crop, and interactions

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	0.57612	0.144030	25.37	0.000
N (kg/ha)	1	0.01896	0.018963	3.34	0.075
Crop	1	0.00600	0.006000	1.06	0.310
B % (v/v)*N (kg/ha)	4	0.08527	0.021319	3.75	0.011
B % (v/v)*Crops	4	0.10307	0.025767	4.54	0.004
N (kg/ha)*Crops	1	0.30057	0.300570	52.93	0.000
B % (v/v)*N (kg/ha)*Crops	4	0.16615	0.041536	7.32	0.000
Error	40	0.22713	0.005678		
Total	59	1.48327			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop.

Table 4-3: Analysis of variance (ANOVA) of estimated soil leachate EC (μs/cm) in response to the main effects of biochar, nitrogen levels, crop, and interactions

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	0.11142	0.027856	6.53	0.000
N (kg/ha)	1	0.37985	0.037985	89.09	0.000
Crop	1	0.33690	0.336900	79.01	0.000
B % (v/v)*N (kg/ha)	4	0.00601	0.001504	0.35	0.841
B % (v/v)*Crops	4	0.00897	0.002243	0.53	0.717
N (kg/ha)*Crops	1	0.09728	0.097284	22.82	0.000
B % (v/v)*N (kg/ha))*Crops	4	0.04048	0.010120	2.37	0.068
Error	40	0.17056	0.004264		
Total	59	1.15148			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop.

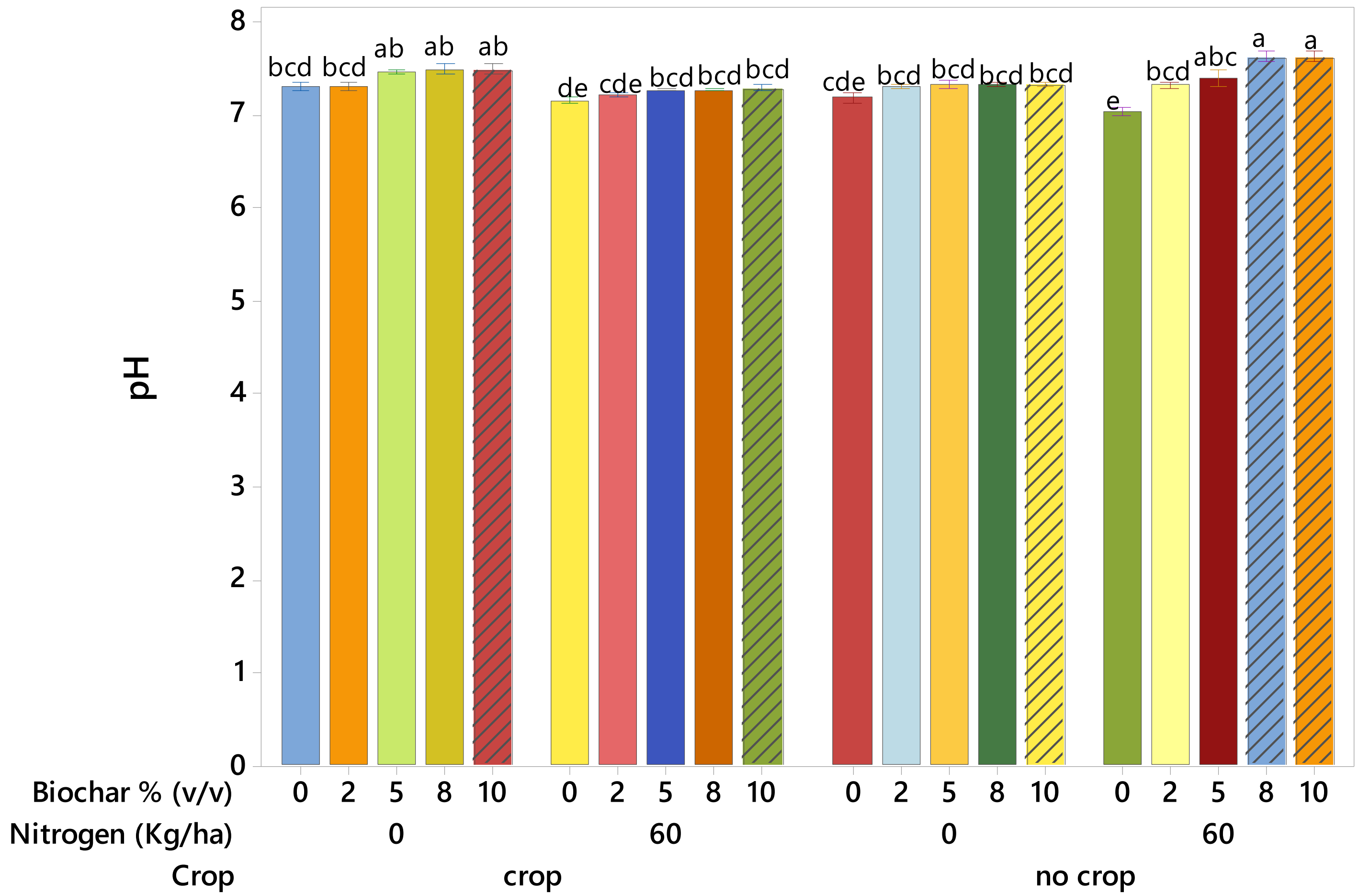


Figure 4-6: Effect of biochar application, nitrogen levels, and crop on soil leachate pH. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM). Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test)

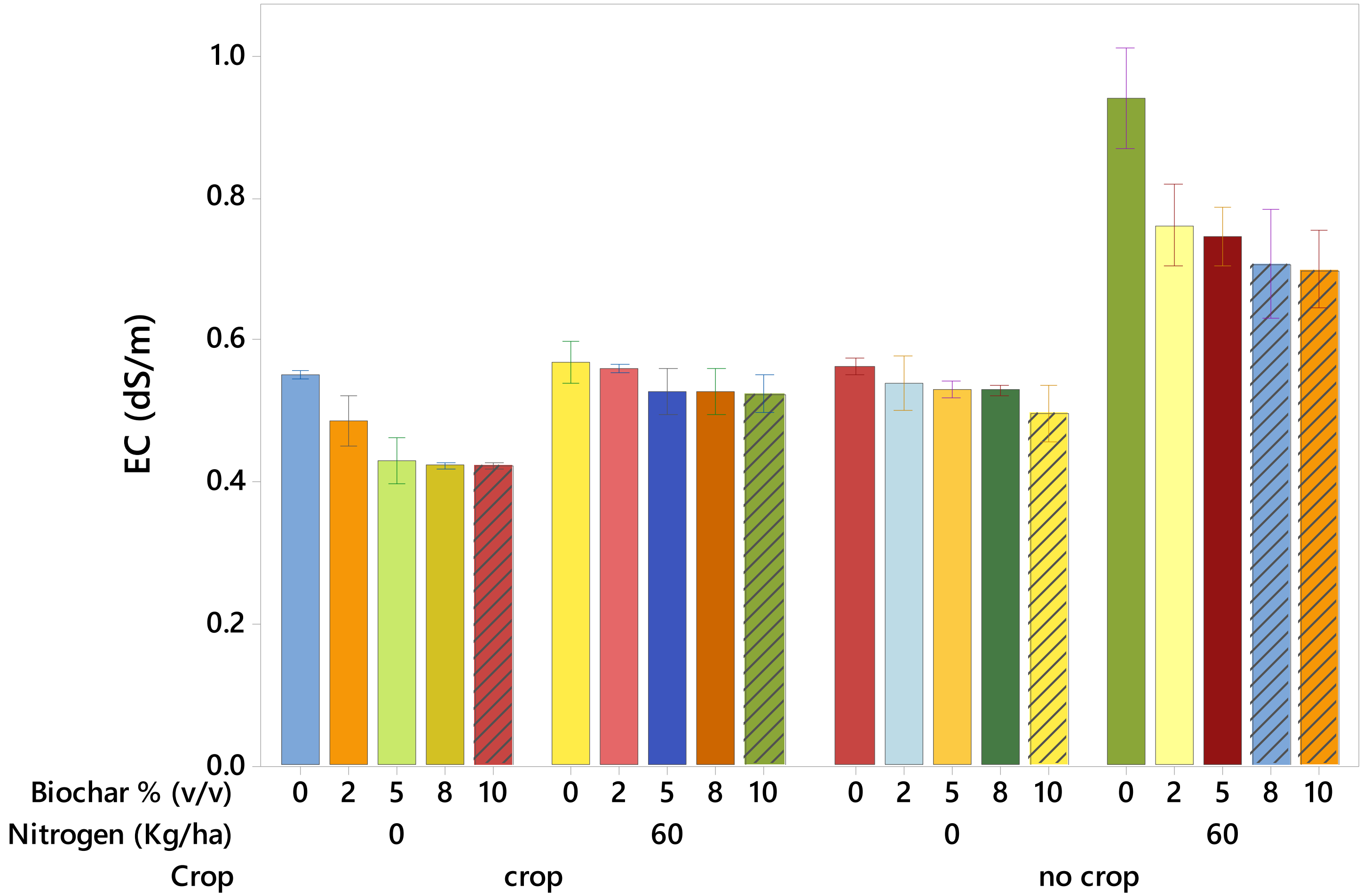


Figure 4-7: Effect of biochar application, nitrogen levels, and crop on soil leachate EC (dS/m). Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 4-2: Analysis of variance (ANOVA) of estimated soil leachate nitrate (mg/L) in response to the main effects of biochar, nitrogen levels, crop, and interactions

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	654.89	163.72	102.60	0.000
N (kg/ha)	1	3630.82	3630.82	2275.43	0.000
Crop	1	2373.68	2373.68	1487.58	0.000
B % (v/v)*N (kg/ha)	4	37.49	9.37	5.87	0.001
B % (v/v)*Crop	4	3.83	0.96	0.60	0.665
N (kg/ha)*Crop	1	0.18	0.18	0.11	0.740
B % (v/v)*N (kg/ha)*Crop	4	24.20	6.05	3.79	0.010
Error	40	63.83	1.60		
Total	59	6788.90			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop.

Table 4-3: Analysis of variance (ANOVA) of estimated soil leachate ammonium (mg/L) in

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	69.899	17.475	55.51	0.000
N (kg/ha)	1	194.965	194.965	619.31	0.000
Crop	1	0.386	0.386	1.23	0.275
B % (v/v) *N (kg/ha)	4	49.712	12.428	39.48	0.000
B % (v/v) *Crop	4	3.002	0.751	2.38	0.067
N (kg/ha) *Crop	1	0.132	0.132	0.42	0.521
B % (v/v) *N (kg/ha)*Crop	4	1.629	0.407	1.29	0.289
Error	40	12.592	0.315		
Total	59	332.318			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop.

response to the main effects of biochar, nitrogen levels, crop, and interactions

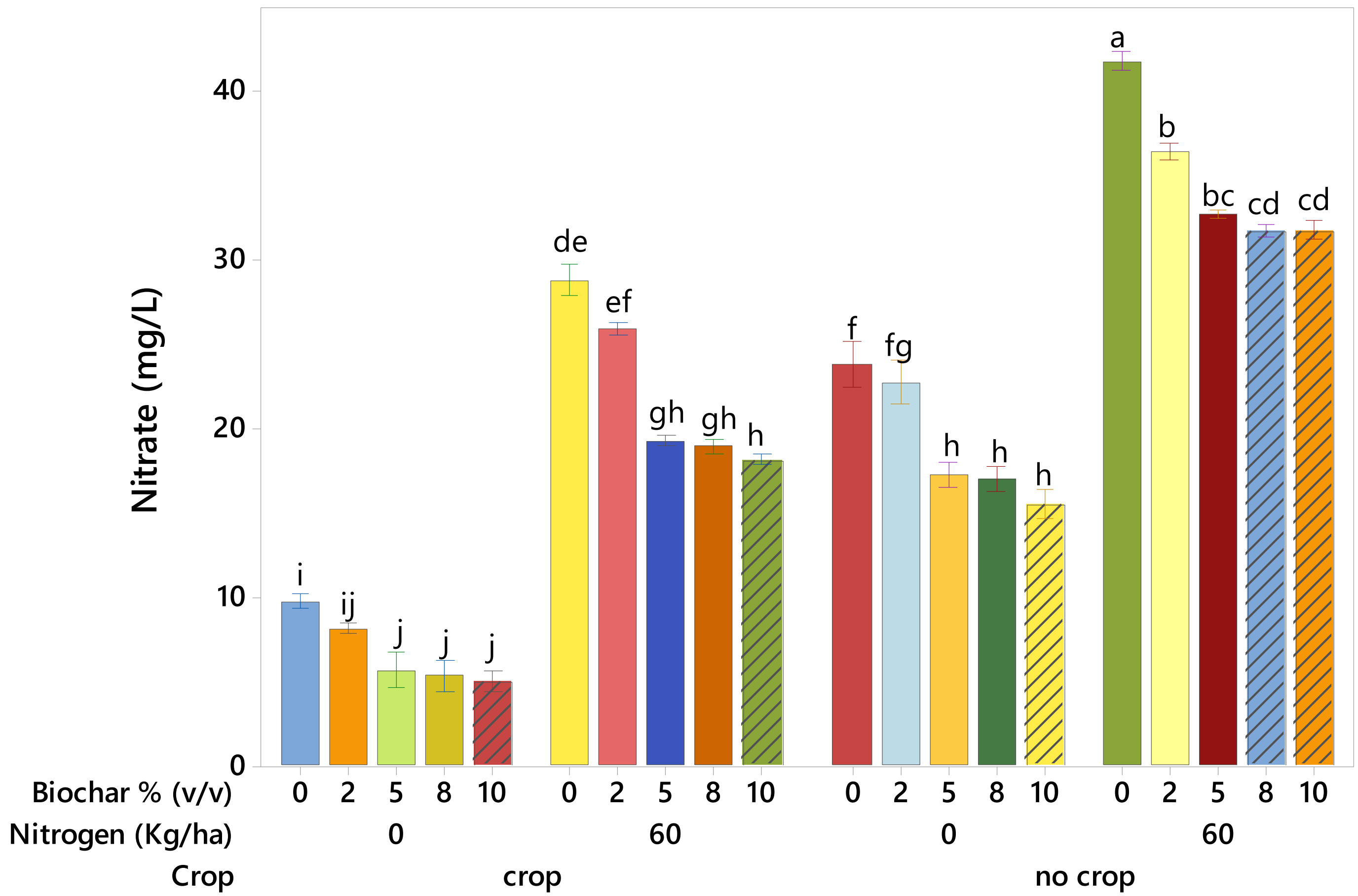


Figure 4-8: Effect of biochar application, nitrogen levels, and crop on soil leachate nitrate. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM). Mean values followed by the same letter within a column are not significantly different ($p < 0.05$, Tukey's test)

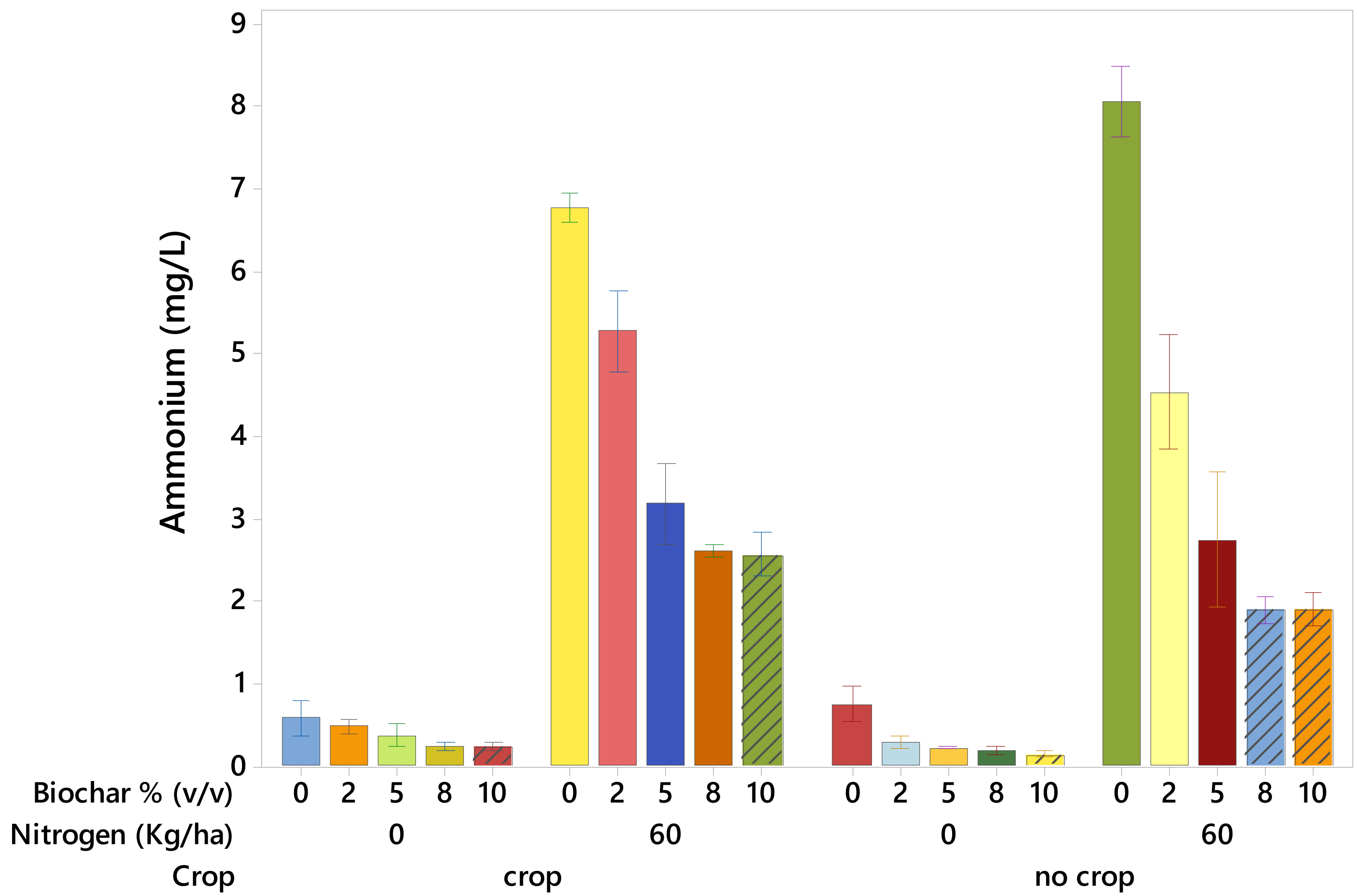


Figure 4-9: Effect of biochar application, nitrogen levels, and crop on soil leachate ammonium. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 4-4: Analysis of variance (ANOVA) of estimated soil leachate total nitrogen (mg/L) in response to the main effects of biochar, nitrogen levels, crop, and interactions

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	6141.1	1535.3	140.19	0.000
N (kg/ha)	1	30260.1	30260.1	2763.20	0.000
Crop	1	8512.3	8512.3	777.30	0.000
B % (v/v) *N (kg/ha)	4	2335.3	583.8	53.31	0.000
B % (v/v) *Crops	4	376.6	94.2	8.60	0.000
N (kg/ha) *Crops	1	2139.5	2139.5	195.37	0.000
B % (v/v) *N (kg/ha) *Crops	4	82.1	20.5	1.87	0.134
Error	40	438.0	11.0		
Total	59	50285.1			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop

Table 4-5: Analysis of variance (ANOVA) of estimated soil leachate dissolved organic carbon (mg/L) in response to the main effects of biochar, nitrogen levels, crop, and interactions

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B % (v/v)	4	15599.8	3900.0	8.86	0.000
N (kg/ha)	1	18596.7	18596.7	42.23	0.000
Crop	1	12000.1	12000.1	27.25	0.000
B % (v/v) *N (kg/ha)	4	283.9	71.0	0.16	0.957
B % (v/v) *Crops	4	1705.6	426.4	0.97	0.435
N (kg/ha) *Crops	1	4092.2	4092.2	9.29	0.004
B % (v/v) *N (kg/ha)*Crops	4	69.7	17.4	0.04	0.997
Error	40	17613.0	440.3		
Total	59	69961.1			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N), and crop

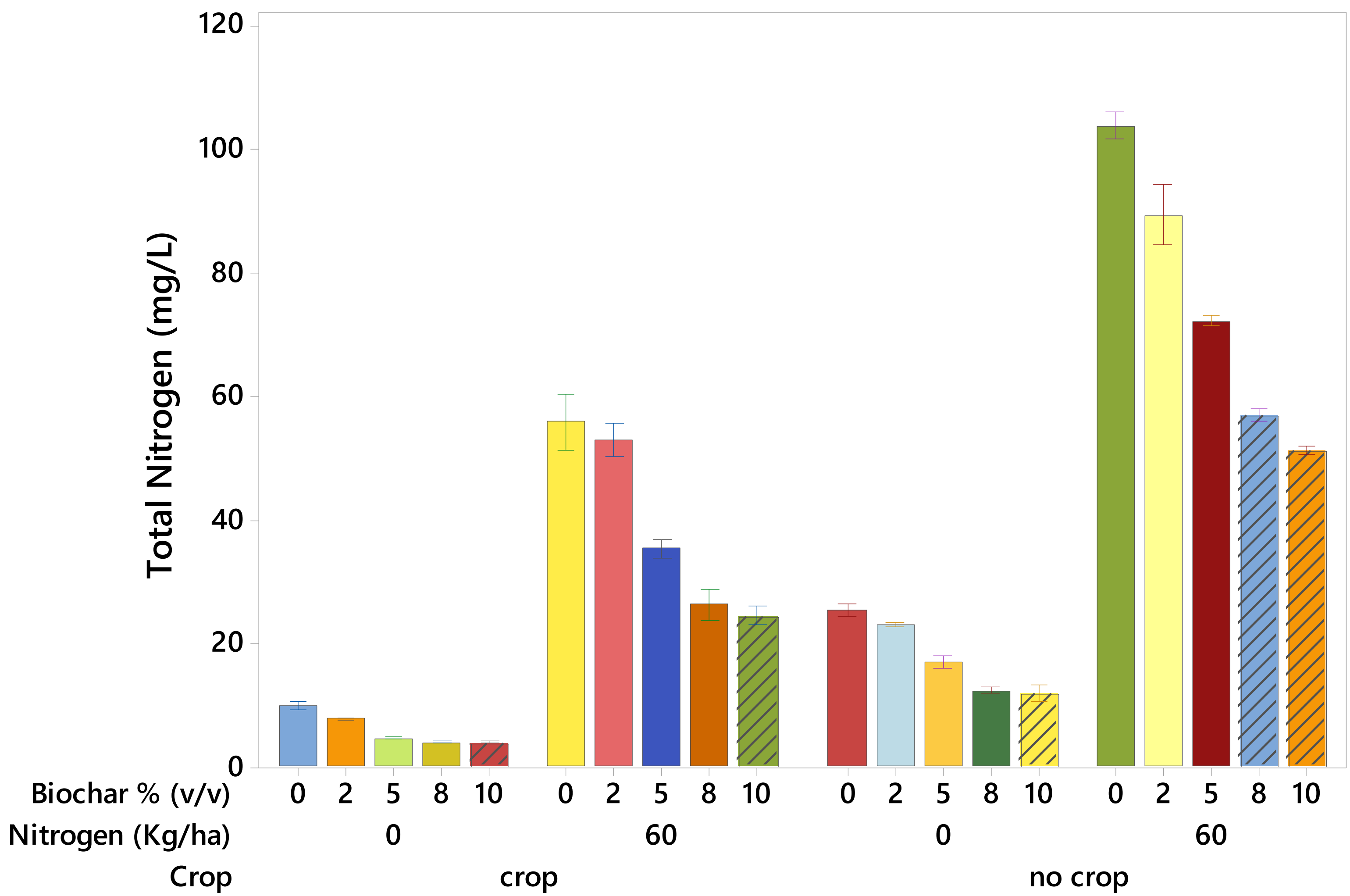


Figure 4-10: Effect of biochar application, nitrogen levels, and crop on soil leachate total nitrogen. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

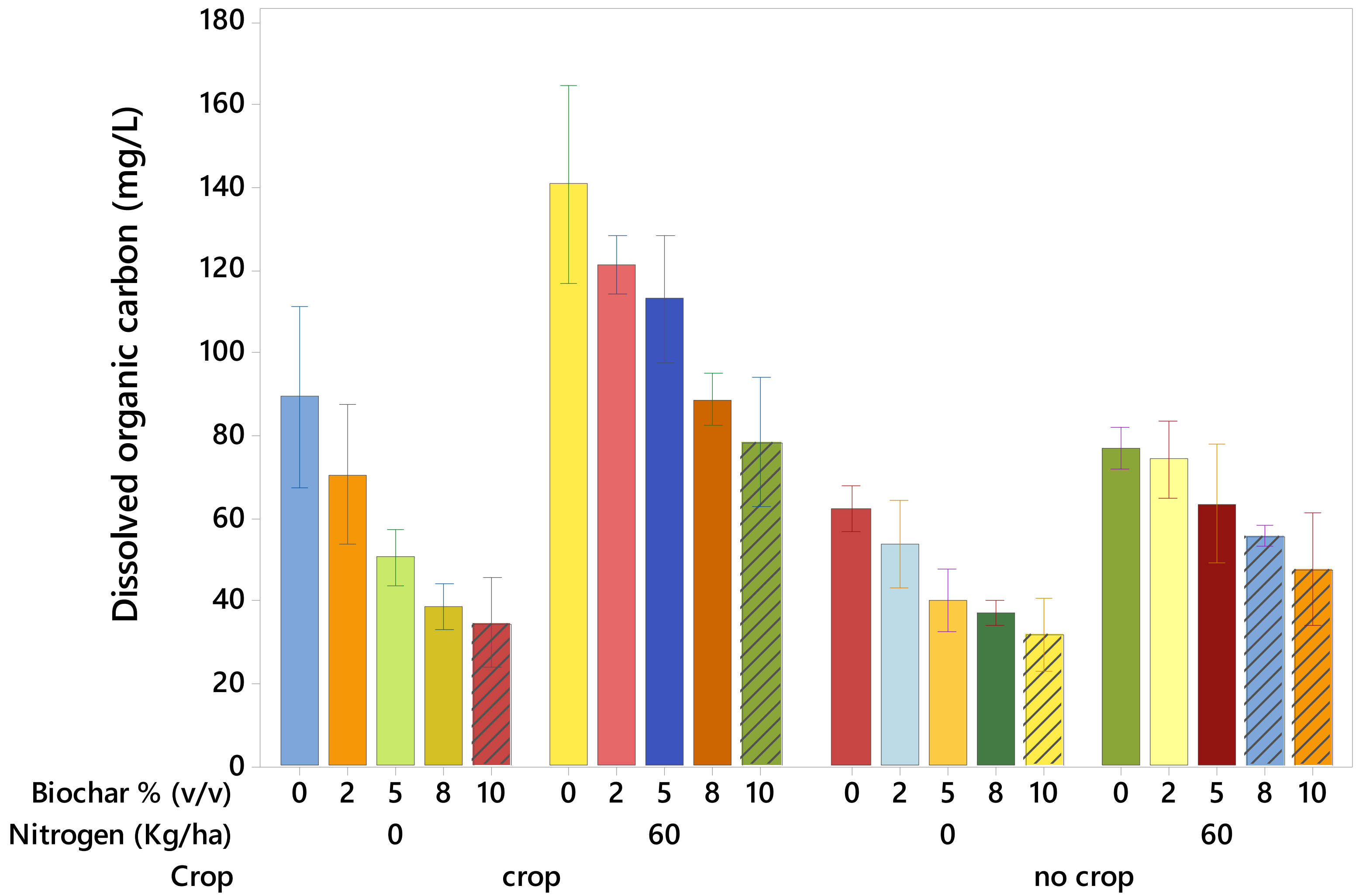


Figure 4-11: Effect of biochar application, nitrogen levels, and crop on soil leachate dissolved organic carbon. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 4-6: Poisson correlation coefficients between the leached parameters, including nitrate, ammonium, total nitrogen, total dissolved carbon, pH, and EC (n = 60)

	Nitrate (mg/L)	Ammonium (mg/L)	Dissolved organic carbon (mg/L)	Total nitrogen (mg/L)	pH
Ammonium (mg/L)	0.691				
	0.000***				
Dissolved organic carbon (mg/L)	0.358	0.668			
	0.005**	0.000***			
Total nitrogen (mg/L)	0.964	0.786	0.467		
	0.000***	0.000***	0.000***		
pH	-0.296	-0.479	-0.573	-0.342	
	0.022*	0.000***	0.000***	0.007**	
EC	0.853	0.573	0.324	0.817	0.198
	0.000***	0.000***	0.012*	0.000***	0.130

*Correlation is significant (p-value < 0.05), **correlation is significant (p-value < 0.01), and ***correlation is significant (p-value < 0.001)

4.5. Discussion

4.5.1. Effect of biochar on soil leachate pH and EC

Soil leachate pH of this study extends from a minimum of 7.03 in the control treatments at biochar rate 0 % [v/v] to a maximum of 7.63 at the biochar treatment rate of 10 % [v/v] (Figure 4-6). The biochar effect on the soil leachate pH was statistically significant, and the pH values increased with increase in the biochar application rates (p-value < 0.001) (Table 4-2). These results were consistent with Angst et al., (2013), and Bradley et al., (2015), who also reported that soil leachate pH significantly increased with the increase in the biochar application rate. The biochar effect on the leachate pH probably originates from the biochar alkalinity, as the pH of the used biochar in this study is quite alkaline (pH = 9.9) (Table 4-1). The high alkalinity of biochar is not only factor for reducing soil acidity; however, carbonates and functional groups including oxides, and organic anions on the biochar's surfaces, are also another factor possible for reducing soil acidity (Yuan et al., 2011). As discussed by Ren-yong et al., (2019) that the exchangeable soil acidity is mainly caused by exchangeable soil Al^{3+}. The reduction of the exchangeable soil Al^{3+} through biochar application can be explained by the biochar high alkalinity effect for balancing soil acidity directly (Yuan and X, 2011). The biochar application induces the change of replaceable Al^{3+} to hydroxyl-aluminum polymerization and precipitation of Al hydroxides through hydrolysis responses (Qian et al., 2016). Availability of base cations such as Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in biochar exchanges with Al^{3+} on soil exchange sites, in turn, release exchangeable Al^{3+} to soil solution which in turn reacts with alkalis of the biochar and results in soil acidity reduction (Yuan and Xu, 2012). Moreover, the formation of an organic component by biochar functional groups and Al also reduces the soil acidity (Qian and Chen, 2014; Shi et al., 2018).

The soil leachate pH was significantly affected by the interaction of nitrogen and crop treatments, in which the soil leachate pH values within the combination of nitrogen 60 kg/ha and no crop treatments were significantly increased more than that in the combination of nitrogen 60 kg/ha and crop treatments (p-value < 0.004) (Table 4-2). The effects of the N fertilizers addition on soil pH in acidic soils depend on the direct impact of the chemical composition of N fertilizers; for instance, the addition of urea increases the soil pH by increasing OH^- and NH_4^+ concentrations as a response to urea hydrolysis (Wang et al., 2020; Zhou et al., 2014). The crop effect in reducing soil pH was possibly attributed to the roots protons (H^+) released when the roots adsorb more cations than anions, while the roots trying to balance the positive charges in their cells (Custos et al., 2020).

The biochar effect on the soil leachate EC was different, where the leachate EC reduced significantly with the increase in the biochar application rates (p-value < 0.001) (Table 4-3). The leachate EC in the control treatment of 0 % [v/v] was significantly higher than the EC of the leachate in other biochar application rates of 2 %, 5 %, 8 % and 10 % [v/v]. The reduction in the EC of the leachate was by 11 %, 15 %, 17 %, and 18 % as the biochar application rate was by 2 %, 5 %, 8 % and 10 % [v/v], respectively, in relative to the control treatment (0 % [v/v]) (Figure 4-7). The reduction of the soil leachate EC under the higher biochar application rates can be attributed to the increase in the cations adsorption capacity by increasing the biochar rates, consequently, these cations become not removable by the leachate water, particularly in the treatments with the higher biochar rates (Ippolito et al., 2014; Thomas et al., 2013). Likewise, improvement of the soil permeability under the higher biochar rate treatments is facilitated by the water movement through the soil profile; this improvement of soil permeability reduces the water retention time under the higher biochar rate treatments and increase it under the control and low biochar rate treatments. The increase of water retention time under the control and low biochar rate treatments allowed more cations to be dissolved and released within the leachate water and therefore increased the EC in the leachate (Buecker et al., 2016; Sika and Hardie, 2014). The soil leachate EC was also significantly affected by the nitrogen and crop levels (Table 4-3), where the maximum EC in the leachate was observed at the lower biochar application rates and higher nitrogen levels with no crop treatments (Figure 4-7). This confirms that the biochar high retention ability of slow-releasing nitrogen fertilizer. The potential mechanism of minimizing the nitrogen fertilizer leaching may be attributed to the biochar's oxygen containing carboxyl, hydroxyl, and phenolic surface functional groups (Cai et al., 2016). Whereas, increasing the leachate EC within the no crop treatments compared to the crop treatments was most likely due to increase in the biochar salt sorption capacity as its rate increased (Thomas et al., 2013), and also due to the crop nutrient (ions) uptake which improved the crop nutrient use efficiency under the combination of biochar and nitrogen fertilizer treatments (Prapagdee and Tawinteung, 2017).

4.5.2. Effect of biochar on soil leachate total nitrogen, nitrate, and ammonium

Generally, the nitrogen leaching losses depend on nitrogen fertilizer management, crop and crop residue management, as well as on the water management (He et al., 2017; Tian et al., 2007; Wang et al., 2007). In the results, the amounts of TN in the leachate follow the N fertilizer applications; the leached TN from the 60 kg N/ha was significantly higher than that from 0 kg N/ha (control) (p-value < 0.001) (Table 4-6 & Figure 4-10). The results also confirmed that nitrate was the main nitrogen form in the leachate, as the Poisson correlation coefficient for nitrate is (R^2 = 0.964 & p-value < 0.001) (Table 4-8), whereas the Poisson correlation coefficient for ammonium is (R^2 = 0.786 & p-value < 0.001) (Table 4-8). These results were in agreement with Tian et al., (2007), and He et al., (2017) who reported that nitrate was the major leached nitrogen form under upland crops.

The nitrate concentration in leachates were significantly affected by biochar application (p-value < 0.001) (Table 4-4 & Figure 4-8). The results indicated that the spruce bark biochar has strong adsorption ability for nitrate. The FT-IR spectra images of the SB550 biochar showed different peaks at different wavelengths, which represent different functional groups on the biochar (Figure 4-2). These functional groups contribute to the nitrate adsorption by the biochar and reduce the nitrate leaching (Lawrinenko and Laird, 2015; Prima et al., 2016). The nitrate leaching amount decreased with increase in the biochar application rates. Regardless of the biochar rate pattern, the results are consistent with previous studies in which biochar application minimized the nitrate concentration in the leachates (Mukherjee and Zimmerman, 2013; Xu et al., 2016). The leachate nitrate reduction may be due to the nitrate adsorption ability of biochar (Mukherjee et al., 2014; Prima et al., 2016). In the current study, the biochar was made from a spruce bark at 550^{o}C, and the pyrolysis temperature impacts the physical and chemical properties of the biochar and in turn its adsorption capacity for nitrate. The pyrolysis temperature created a pore structure; thus, the adsorption of nitrate was prevailing (Jin et al., 2016). Nevertheless, the possible mechanisms associated with that are; (i) the mass flow of nitrate ions into the biochar particles and incorporated within pores onto the surface of the biochar (Fidel et al., 2018; Haider et al., 2016), (ii) the electrostatic interaction between the negative nitrate charge and some of the functional groups or positively charged cationic salts on the biochar surface (Haider et al., 2016; Mukherjee et al., 2011). Other possible mechanisms that could be associated with the nitrate leaching reduction are; (i) reduction in the nitrification rate by biochar ammonium adsorption (Dempster et al., 2012; Xu et al., 2016), which reduces the available exchange sites for nitrification process (Kumar et al., 2016), and (ii) nitrogen immobilization via biochar soluble phenolic high concentration (Mukherjee et al., 2011), or via increased microbial nitrogen uptake either in its inorganic form or organic forms after transforming it to the organic pool (Mukherjee et al., 2014; Yoo and Kang, 2012). Several studies have reported the biochar ability to adsorb ammonium that reduced the nitrate leaching under the soil-biochar amendment, which might be attributed to; (i) the ammonium adsorption by biochar as a response to inhibiting organic nitrogen mineralization and/or ammonium nitrification (Dempster et al., 2012; Troy et al., 2015; Yao et al., 2012), and (ii) the direct effect of biochar on inorganic nitrogen adsorption and immobilization (Liu et al., 2021). These confirmations suggest the biochar's high ability to mitigate nitrate leaching and increase nitrate retaining and the nitrogen fertilizer efficiency in the soil profile.

Biochar can be an ammonium retaining additive, as several studies have reported that (Cai et al., 2016; Mandal et al., 2018; Xu et al., 2016). Urea is converted into ammonium bicarbonate when applied to the soil as a result of the urease enzyme, at that point, the ammonium is commonly translated to nitrate through nitrification; whereas, biochar application decreased nitrate and ammonium in the leachate. (Xu et al., 2016). Thus, in the current study, the ammonium reduction was significantly affected by the biochar application and followed a similar trend of biochar nitrate reduction (p-value < 0.001) (Table 4-5 & Figure 4-8). The biochar application rates are directly proportional to the ammonium reduction as 10 % [v/v] biochar rate has the highest ammonium reduction. Likewise, the correlation analysis between the ammonium and nitrate in the leachate showed a Pearson's correlation coefficient of 0.691 (p-value < 0.001) (Table 4-8), which indicates a significant positive correlation between them. Nevertheless, in comparison to nitrate leaching reduction, the percentage of ammonium leaching reduction was higher (Figure 4-8 & Figure 4-9). The percentage of ammonium leaching reduction ranged from 34.65 to 70.04 % for the 2 % and

10 % biochar rates, respectively, compared to the nitrate leaching reduction that ranged from 11.61 to 47.75 % for the 2 % and 10 % biochar rates, respectively. The ammonium leaching reduction may be attributable to (i) the low nitrification rate as nitrification processes were inhibited by biochar (Dempster et al., 2012), which may confirm the high ability of the used biochar for inhibiting the nitrification processes, as different biochar feedstock could affect the nitrification processes differently (Mandal et al., 2018). (ii) ammonium retention by biochar adsorption as a result of the high CEC (Clough et al., 2013), which referred to high concentrations of negatively charged and oxygen-containing functional groups including carboxyl, carbonyl, and phenol on the biochar surface adsorption sites (Wang et al., 2016; Zeng et al., 2013). The CEC value of the used biochar in this study is 28.8 cmol/kg, which probably increased the CEC value of the soil. Thus, the increment in the soil CEC value (14.6-18.6 cmol/kg) (Table 3-4) by biochar may be an important factor being responsible for the observed ammonium leaching reduction (Sika and Hardie, 2014; Zheng et al., 2013). Furthermore, some other studies have also concluded that the biochar surface area is another essential factor that can influence ammonium adsorption, thus reduce total ammonium leaching (Prima et al., 2016; J. Yang et al., 2017). Accordingly, Saleh et al., (2012) proposed that the physical entanglement of ammonium into biochar pore structures might be another possible factor for ammonium adsorption by biochar. The ionic diameter of an ammonium ion is 286 pm (Späth and König, 2010). In contrast, the range of biochar pore diameters is from 1000 to 0.0001 μm (Yu et al., 2019), which may confirm the theory of the physical entanglement mechanism for ammonium's adsorption into the biochar pores.

4.5.3. Effect of biochar on soil leachate dissolved organic carbon

DOC is a common component of the soil organic carbon, which consists mainly of organic materials obtained from different biological transformations (Tiefenbacher et al., 2020). DOC fraction represents about 1 % of the total carbon pool in the soil, characterized as an organic molecules continuum of various size and structure, which can pass through a filter pore size of 0.45 mm (Royer et al., 2007). As shown in (Table 4-5 & Figure 4-11), biochar application has significantly decreased the DOC in the leachate (p-value < 0.001). This result is in line with other studies that reported that biochar application reduced DOC leaching in the agricultural field (Eykelbosh et al., 2015; Lei et al., 2018; Mukherjee and Zimmerman, 2013; Waters et al., 2011). The biochar effect on the DOC reduction can be attributed to: (i) the change in the soil properties by biochar (Lehmann et al., 2011). The high surface areas of the biochar may enhance the adsorption capacities (Kasozi et al., 2010), and the increase in pH and CEC in acidic soils by biochar can increase the adsorption capacities, which in turn decrease the DOC leaching (Lei et al., 2018; Waters et al., 2011). (ii) The great incorporation between soil and added biochar has been reported to enhance the stability of biochar in soil by reducing microbial and chemical decomposition, which in turn reduces the biochar light fraction transportation rate, hence DOC leaching (Eykelbosh et al., 2015; Waters et al., 2011). The ANOVA analysis of DOC also showed significant interaction effects between nitrogen and crop levels (p-value < 0.01) (Table 4-7). The increment of DOC leaching under the 60 kg N /ha and crop treatments may be attributed to the effect of nitrogen fertilizer on the increase in the fine roots of *Festulolium* forage, roots decomposition, poor root exudates, and in turn on its residue's incorporation. Similarly, Royer et al., (2007) found that the incorporation of corn residues in soil has increased DOC concentrations as an effect of liquid hog manure applications. Also, Chibuike et al., (2019) reported that the decomposition of the roots under agrochemicals application was considered as a possible mechanism for increased DOC in the leachate. Salazar et al., (2019), pointed out that the leaching

DOC concentration was low under bare soil, which was attributed to the shortage of organic matter application and poor root exudates.

Furthermore, the results also showed a significantly positive Poisson correlation coefficient between the DOC and TN (Table 4-8). The DOC concentration in the leachate followed the same tendency of nitrogen-based fertilization; this was mostly attributed to biological mechanisms for producing and consuming DOC under nitrogen application in nitrogen-limited ecosystems (Lu et al., 2013). The main biological mechanisms of increase in DOC are: (i) derived from the organic substrates production changes in the soil (Pregitzer et al., 2004). (ii) increase in enzymatic activity, which leads to an increment in releasing more DOC in the soil solution (Bragazza et al., 2006; Wang et al., 2015). (iii) decrease the organic carbon mineralization by nitrogen addition may lead to a decrease in DOC decomposition/consumption through DOC accumulation in the deeper soil profile (Ouyang et al., 2008). Conversely, Tiefenbacher et al., (2020), suggested that nitrogen-based fertilizers decrease the leachate DOC concentration through the DOC mineralization, which in turn, leads to DOC concentration reduction. Nitrate can induce the conversion of organic carbon to carbon dioxide, which leads to a decrease in DOC leaching. However, this result showed an increment DOC concentration in leachate under nitrogen fertilizer treatments; thus, the above-mentioned biological mechanisms are most likely responsible for reducing the DOC in the leachate.

4.6. Conclusion

Biochar application in the soil is generally an effective approach to improve soil fertility by reducing nutrient leaching and sequencing more carbon. Spruce bark biochar (SB550) application at the high rates of 5, 8, and 10 % [v/v] have significantly reduced nitrate (NO_3^-), ammonium (NH_4^+), total nitrogen (TN), and dissolved organic carbon (DOC) leaching losses. The finding from this study suggests that the SB550 biochar has relatively good adsorption capacity. The results indicated that SB550 biochar has significantly reduced NO_3^-, NH_4^+, TN, and DOC in the leachate. The SB500 biochar reduced NO_3^- leaching by 11.61 %, 38.93 %, 42.50 %, and 47.75 %, NH_4^+ leaching by 34.65 %, 59.65 %, 69.55 %, and 70.04 %, TN by 11.31 %, 33.18 %, 48.95, and 52.95 %, and DOC by 13.43 %, 27.70 %, 40.33 %, and 74.26 %, at the biochar rates of 2 %, 5 %, 8 %, and 10 % [v/v], respectively, in comparison to that of the control treatment (0 % [v/v]). In conclusion, the study reveals that SB550 biochar improves nitrogen and carbon retention, which could enhance nitrogen fertilizer use efficiency and carbon sequestration in the eastern Newfoundland podzolic soil.

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Chapter 5

Effect of Hardwood Biochar and Nitrogen Applications on Greenhouse Gas Emission from the Agricultural Forage Crop System in the Eastern Newfoundland podzolic soil

Abstract

It is extensively understood that human activities, including agriculture, are causing significant changes to the global climate due to increased emissions of anthropogenic greenhouse gases (GHG), including carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4). Nitrogen (N) fertilizer is the most common nutrient that needs to be added to improve soil fertility and crop production. The global total nitrogen fertilizer demand increased by 1.5 % per year and reached 188.31 million tonnes in 2020 (FAO, 2017). The intensive increase of nitrogen fertilizer application may increase GHG emissions, in particular, N_2O emission. The application of biochar in the agricultural soil is known as a novel concept for mitigating soil GHG emissions. Thus, a field experiment was conducted during the 2019 growing season at St. John's Research and Development Centre, Newfoundland and Labrador (NL), Canada to investigate the biochar application ability to improve soil fertility, crop productivity and reduce GHG emissions from the eastern Newfoundland podzolic soil. The experimental design consisted of four rates of biochar applications including, 0% (control), 5, 8 and 10% biochar rates [v/v], and with three levels of nitrogen fertilizer applications (Urea 46-0-0) that applied at the rates of 0 and 65 and 130 N kg/ ha to the *Festulolium* forage crop field. The design ended up with 12 treatments using a Randomized Complete Block Design (RCBD). Three replications of each treatment resulted in a total of 36 experimental plots. Biochar application has significantly reduced CO_2 emission by 12, 23 and 42%, CH_4 emission by 59, 75 and 76% and N_2O emission by 22, 38 and 43%, for the biochar rates

of 5 %, 8 %, and 10 % [v/v], respectively. Likewise, biochar application significantly increased the *Festulolium* fresh yield by 15.0 %, 17.5 %, and 30.3 %, and dry matter yield by 18.2 %, 26.3 %, and 33.8 % for the biochar application rates of 5 %, 8 % and 10 % [v/v] respectively. Thus, the study concluded that biochar application could be an alternative strategy that can reduce the GHG emissions from the *Festulolium* forage crop field; however, further research is needed to understand the biochar mechanisms involvement in mitigating soil GHG emission.

Keywords: *agriculture, biochar, greenhouse gas emission, forage crop production*

5. Introduction

5.1. Background

Agriculture contribution is about 23 % of the total anthropogenic greenhouse gas emissions (GHG) (IPCC, 2020). It accounts for around 50 % of the anthropogenic N_2O emissions, as the second-largest sector contributing through fertilization (Robertson and Vitousek, 2009), which may increase as a response to intensive agricultural activities worldwide (Z. Chen et al., 2016; Smith et al., 2007). According to Fisheries, Forestry and Agriculture of Newfoundland and Labrador (NL), NL's soil is Podzol; it has low quality, high acidity, low soil organic matter (SOM), low soil cation exchange capacity (CEC), very coarse soil texture with a significant proportion of stones and gravels, which creating an inappropriate soil status that could affect forage crops production. The NL’s government has decided to increase local food production by extending its agricultural land base (Abedin, 2018; Government of Newfoundland and Labrador 2017).

One crucial factor in boosting local food production is adding nitrogen-based fertilization (Naeem et al., 2017). However, increasing the nitrogen-based fertilizer application may lead to an increase in GHG emissions, particularly N_2O emissions (Cheng et al., 2015; Dai et al., 2013; Hoben et al., 2011; Shen-yan et al., 2017), by increase the inorganic nitrogen availability in the soil

(Inselsbacher et al., 2011; Kostyanovsky et al., 2019; Troy et al., 2017). These emissions can be reduced by improving nitrogen use efficiency (P. Smith et al., 2008). Hence, applying biochar as a soil amendment to such soil could be an alternative strategy to mitigate climate change by reducing GHG emissions (Ashiq et al., 2020; Shrestha et al., 2018; Steiner et al., 2010).

Biochar is a carbon-rich material, solid, produced by pyrolysis of agricultural or other residual biomass under a limited supply of oxygen at temperatures from 300 to 700 °C (Ren-yong et al., 2019). Application of biochar in the agricultural soil is known as a novel concept for establishing a long-term sink for atmospheric CO_2 (Fowles, 2007; Lehmann et al., 2006; Steiner et al., 2007), and potentially increasing CH_4 uptake from the atmosphere. In addition to the advantage of biochar application to mitigate climate change, biochar application has other benefits of increasing soil CEC, soil pH of the acidic soil (Berihun et al., 2017; Gong et al., 2019; Ippolito et al., 2016; Yu et al., 2019; Yuan et al., 2011), improve nutrient retention capacity (Taghizadeh-toosi et al., 2012; Wan et al., 2014; Yuan et al., 2016), soil organic matter content (Ippolito et al., 2016; Mao et al., 2013; Tian et al., 2016; Wan et al., 2014; Yu et al., 2019), and SOC content (Ippolito et al., 2016; Mosier et al., 2006; P. Smith et al., 2008; Tian et al., 2016; Yu et al., 2019). Biochar application can also decrease soil bulk density (Abrol et al., 2016; Oduor et al., 2016; Xiao et al., 2016), increase soil porosity (Cayuela et al., 2014; Torbert et al., 2015), improve soil structure (Burrell et al., 2016), increase water holding capacity (Farkas, 2019; Oduor et al., 2016; Zheng et al., 2013), soil moisture content (Haider et al., 2017), and physicochemical soil properties (Saha et al., 2020). Therefore, biochar application can improve soil fertility and crop production (Agegnehu et al., 2017; Ashiq et al., 2020; Mao et al., 2013; Stavi and Lal, 2013).

In the province of NL, two studies were done to check the impact of biochar application on GHG emissions. The first study conducted in Labrador by Abedin (2017) and the second study was conducted on the west coast of Newfoundland by Ashiq et al. (2020). The study hypothesized that biochar application could improve soil physicochemical properties and carbon sequestration, reduce GHG emissions and increase forage crop production. Thus, this study was conducted to investigate the biochar application's capability to improve soil fertility, crop productivity and reduce GHG emissions from the eastern Newfoundland podzolic soil.

5.2. Materials and methods

5.2.1. Biochar production and characterization

Due to the lack of availability of the required quantity of the used biochar (SB550) in previous experiments at the time of conducting this field study, biochar (HW500) was used in this experiment as the lowest NO_3^- adsorption among the other biochars. This type of biochar was collected from GECA Environnement, Quebec, Canada. Neroval biochar produced from hardwood (75% sugar maple) at 500 °C (HW500) using the Proton Power Inc technology, in the USA, certified by the International Biochar Initiative (IBI), and physicochemical properties were determined as shown in (Table. 1). Detailed information about the biochar preparation and characteristics are presented elsewhere (Allaire, 2018; Lange and Allaire, 2018). Whereas the Scanning electron microscopy (SEM) images of the biochar (Figure 5-1) showed the morphologies and porous structures, and different minerals compounds such as Fe, Mg, Al, Si, K and Ca on the HW500 biochar surface (Figure 5-2).

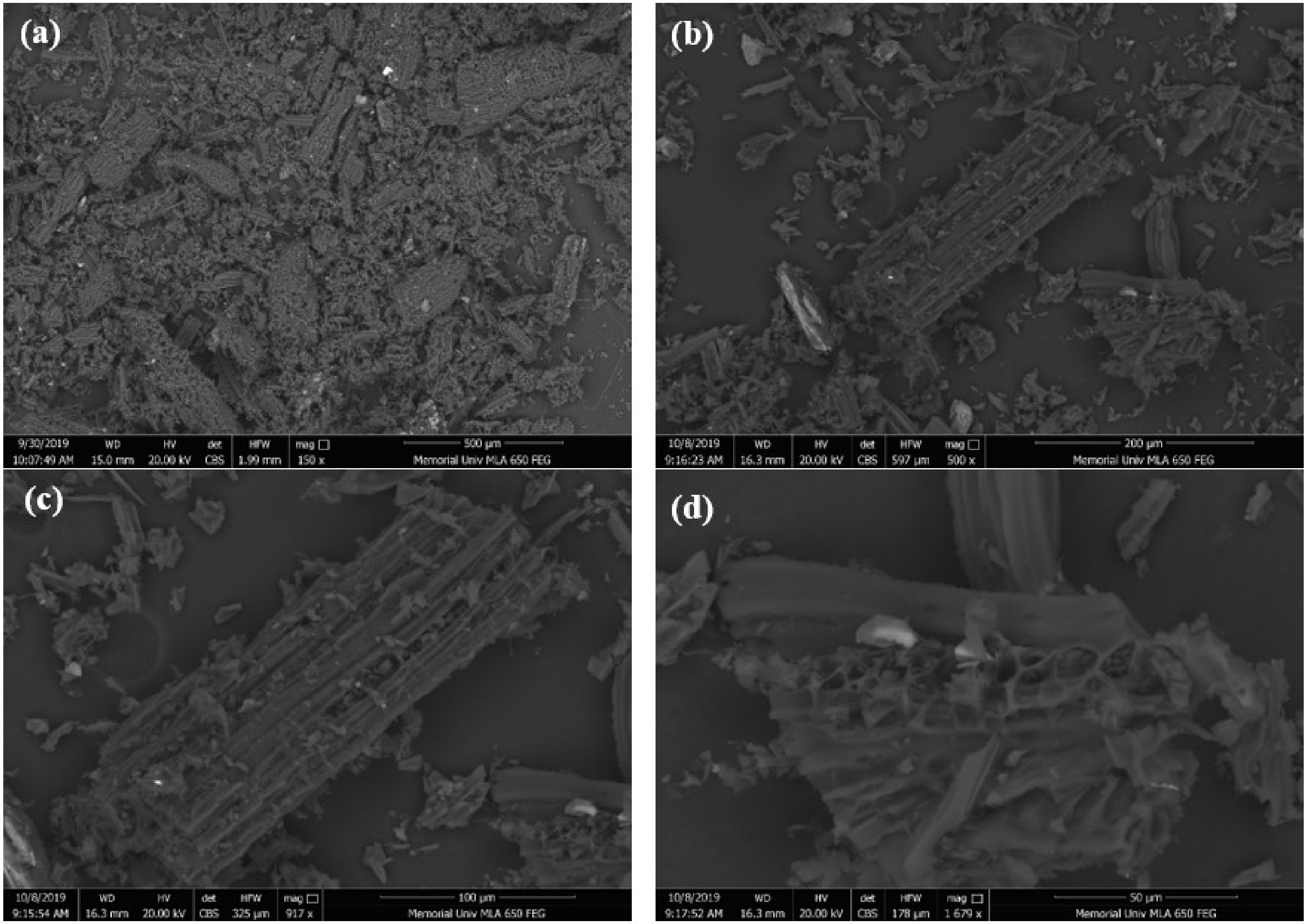


Figure 5-1: SEM images of hardwood (75% sugar maple) (HW500) biochar at different scales, including (a) 500 µm, (b) 200 µm, (c) 100 µm, and (d) 50 µm

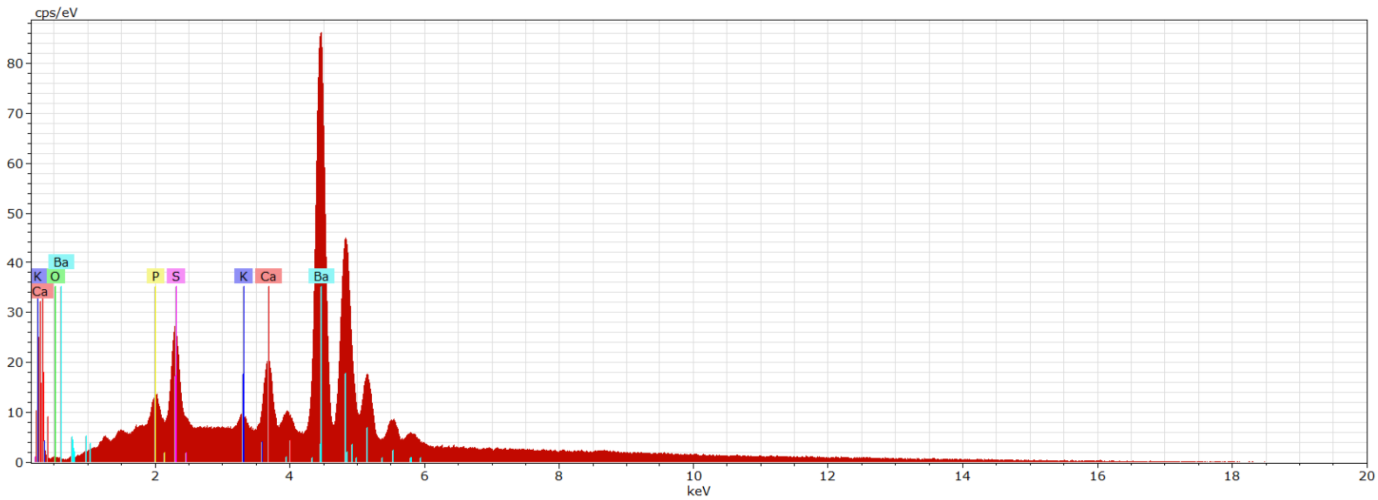


Figure 5-2: Different minerals compounds such as Fe, Mg, Al, Si, K and Ca on the HW500 biochar surface

Table 5-1: Moisture Content, pH, CEC, Total Nitrogen, Total Carbon, Total Phosphorus, Total Calcium, and Total Magnesium of the HW500 biochar

Analysis	HW500
Moisture Content (%)	2.6
pH	11
Total Nitrogen, N (%)	0.54
Total Carbon, C (%)	92.8
Total Phosphorous, P (%)	0.052
Total Calcium, Ca (%)	1.93
Total Magnesium, Mg (%)	0.17
CEC cmol/kg	22.3

Basic properties of HW500 biochar

5.2.2. Soil sampling and analysis

A composite soil sample was collected at 0-20 cm depth from the field (15) at St. John's Research and Development, using soil sampling auger stainless steel (76 mm) diameter and (305 mm) length (AMS. USA). The soil samples were then placed in a cooler and transported immediately to St. John's Research and Development centre facility. The composite sample was air-dried, sieved by

2-mm mesh and analyzed before any soil amendment for texture, pH, SOM, CEC, total N, total C, and available nutrients of P, K, Ca, Mg, S, Zn, Cu, Na, Fe, B, Mn, and Al. Soil texture was determined to be described by 27.3% sand, 16.9% clay, and 55.8 % silt particles (silt loam), slightly acidic soil pH (6.2), moderate levels of SOM, and high CEC (Table 5-2). The extractable concentrations of P, K, Ca, Mg, S, Zn, Cu, Na, B, and Mn are shown in (Table 5-3). Soil bulk density (ρb) was determined using the core method, and total soil porosity (S_t) was calculated based on (ρb) and particle density (ρs) by the equation (1):

$$S_t = 1 - \frac{\rho b}{\rho s} \qquad (1)$$

(Carter and Gregorich, 2008)

The water-filled pore space (WFPS) was calculated by the following equation (2):

$$\text{WFPS (\%)} = \frac{\text{volumetric water content } (\text{cm}^3/\text{cm}^3)}{\text{total soil porosity}} * 100 \qquad (2)$$

WFPS was calculated using calculated bulk density (ρb) and assuming a mineral particle density (ρs) of 2.65 g/ cm^3 (Li et al., 2015).

Chemical analyses were conducted after sieving sub-samples of soil using a 2-mm sieve. Soil pH was measured, and the measurements were done on 1:1, soil: water ratio (m:v) using a pH meter (Thermo Fisher Scientific accumet™ XL250 pH, Canada). CEC was calculated using a buffer pH (Adams and Evans, 1962). Other extractable elements, P, K, Ca, Mg, S, Zn, Cu, Na, Fe, B, Mn, and Al, were extracted by the Mehlich 3 extraction solution method (Carter and Gregorich, 2008) using a Teledyne Prodigy ICP instrument. Whereas the physical analysis such as the soil particle size distribution was performed using the hydrometer method (Carter and Gregorich, 2008), soil bulk density (Core segment method) (Carter and Gregorich, 2008), and soil organic matter was tested by loss on ignition method (Ball, 1964). Electrical conductivity (EC), soil moisture, and soil temperature at 5 cm were checked regularly in the pots using GS3 VWC, temperature, ECw and ProCheck Sensor Read-Out and Storage System (METER Group, Inc. USA). Soil temperature at 20 cm was checked regularly using Traceable Digital Pocket High-Accuracy, 11.5" Long-StemThermometer (Cole-Parmer Scientific, Canada).

Table 5-2: Mean of soil texture and means of pH, CEC, % N, and % C before any soil amendments

Treatments	% Sand	% Clay	% Silt	Soil pH	% N	% C	% SOM	CEC (cmol/Kg
Original Soil	27.3	16.9	55.8	6.2	0.6	7.9	8.98	14.7

Table 5-3: Mean of soil extractable nutrient concentrations before any soil amendments

Parameters	P	K	Ca	Mg	S	Zn	Cu	Na	Fe	B	Mn	Al
	mg/L											
Original soil	96	261	1371	277	17	2.5	3.5	24	144	0.3	16	1156

5.2.3. Experimental set-up and design

A field experiment was conducted during the 2019 growing season at St. John's Research and Development Centre (47° 31’ N; 52° 47’ W; 115 m above sea level), NL, Canada (Figure 5-3). Average temperature and rainfall during 2019 the growing season were 12.5 °C and 597 mm, respectively (Figure 5-4). Soil volumetric moisture content and soil temperature at 5 and 20 cm depths for each treatment are presented in (Figure 5-8a, b & c). The set-up of the study site was done through different agricultural operations, including soil loosening using a moldboard plow to turn over sod, soil softening using a power harrow, soil-biochar mixing manually using steel farming rake14 teeth, field *Festulolium* seeding using Brillion Landscape Seeder, and greenhouse gas collars installation as shown in (Figure 5-5). The *Festulolium* was developed by crossing Meadow or Tall Fescue with Perennial or Italian Ryegrass. The experimental design consisted of four rates of biochar applications including, 0% (control), 5, 8 and 10% biochar rates [v/v], which were applied in the top 10 cm of the soil, and with three levels of nitrogen fertilizer applications (Urea 46-0-0) that applied at the rates of 0 and 65 and 130 N kg/ ha to the *Festulolium* forage crop field. The design ended up with a total of 12 treatments (Figure 5-6) within a Randomized Complete Block Design (RCBD), with three replications of each treatment, resulting in a total of 36 experimental plots, and the net plot size was 2 meters * 2 meters as shown in the experimental layout (Figure 5-6).

5.2.4. Gas sampling and analysis

GHG measurements were taken from the soil surface. The CO_2, CH_4 and N_2O fluxes were calculated using the gas samples based on Closed-chamber method (Rolston, 1986) and gas chromatography method from June to October 2019. Gas samples were taken from the opaque chamber using a 30 ml syringe connected with a two-way stopcock at 0, 10, 20, and 30 min after placing the designed cover on the chamber. Chamber was 20.3 cm in diameter and 15 cm in height, fitted on a 10 cm collar inserted 5 cm in the soil. The top of the chamber is equipped with a vent tube to minimize changes in the temperature during the sampling period. Gas sampling were taken at mid-day between 9:00 a.m. to 2:00 p.m. Newfoundland local time biweekly during the study period. When the gas samples were analysed, 8 ml of the gas sample was manually injected into a Gas Chromatograph (Scion 456-GC, Bruker Ltd., Canada) equipped with Thermal Conductivity Detector (TCD), Flame Ionization Detector (FID) for the analysis of CO_2 and CH_4, and Electron Capture Detector (ECD) for the analysis of N_2O. The fluxes are then calculated using Eq. (1): (Holland et al., 1999; Luan et al., 2019).

$$F = dc/dt \times \rho V/A \qquad (1)$$

Where F is fluxes, dc/dt is the rate of change in concentration with time (t), which is derived from the linear regression of the four gas samples against time over 30 min of the gas sampling period (citations); ρ is the density of air in mol m^{-3}, V is the volume of air within the chamber in m^3, A is the surface area within the chamber in m^2. Any data with a regression coefficient (r^2) less than 0.8 were excluded, which resulted in 10 % of the data removed from any further analysis.

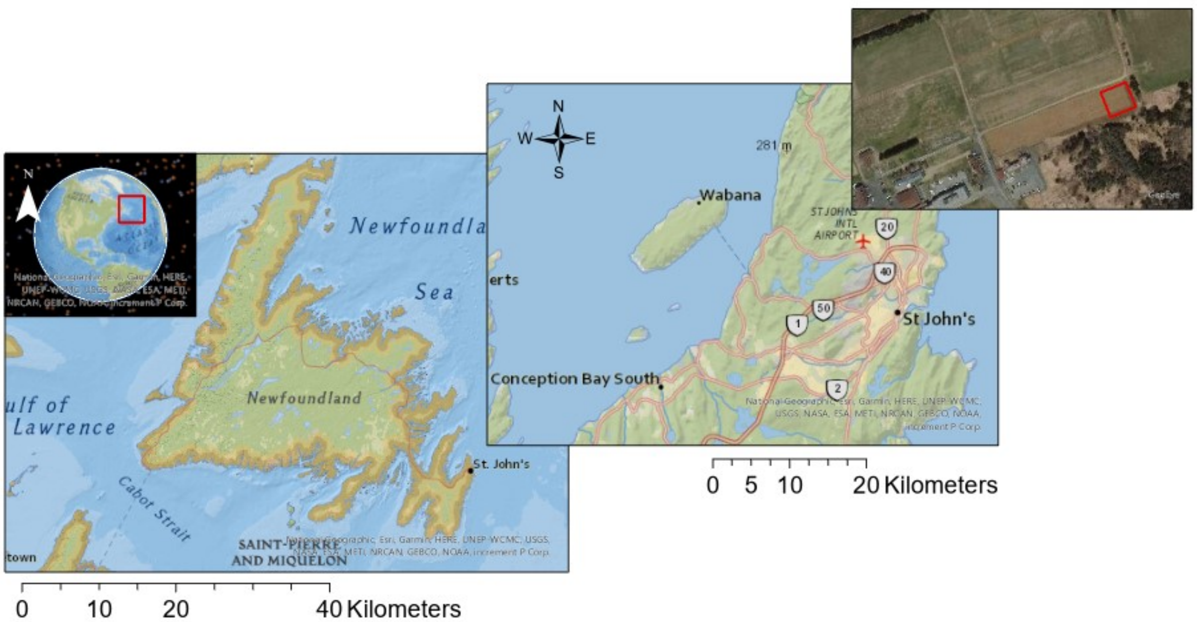


Figure 5-3: The study location at St. John's Research and Development Centre (47° 31' N; 52° 47' W; 15 m above sea level), Newfoundland and Labrador (NL), Canada. The image was obtained using the geographic information system ArcGIS 10.8.1software on Aug 2020, where the red square indicated the study site

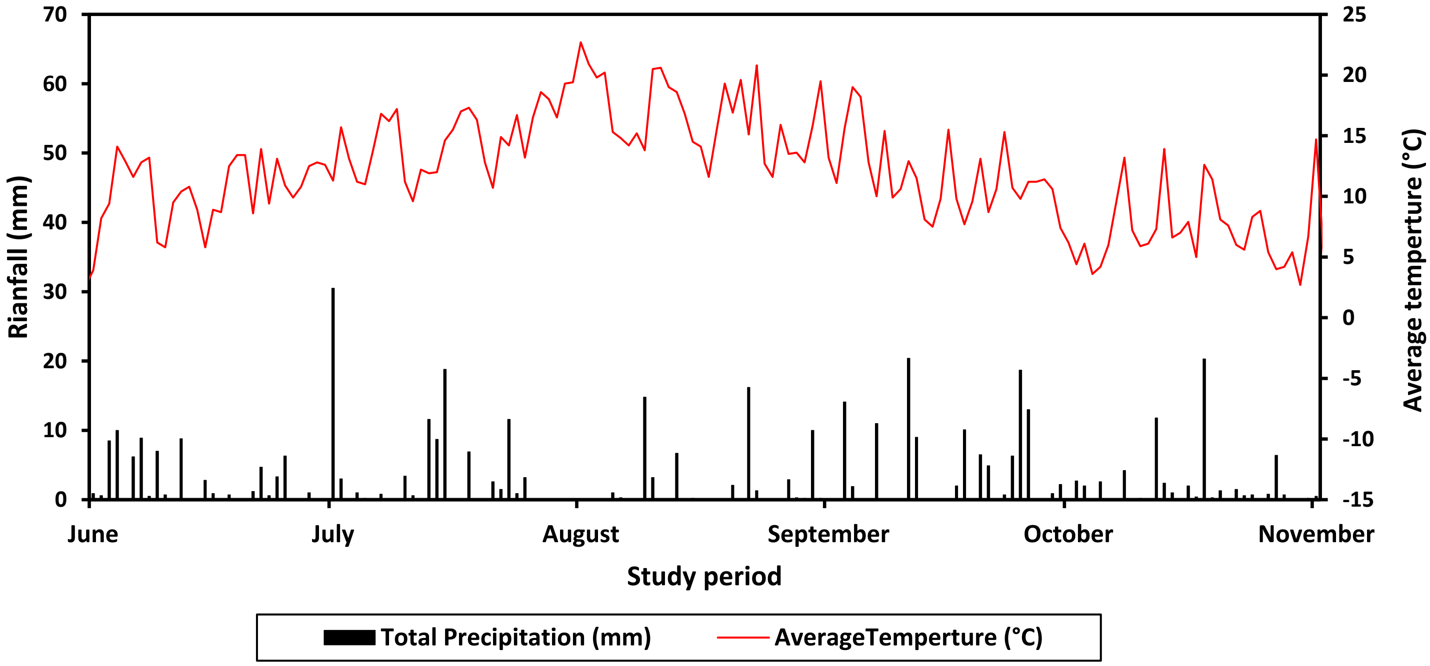


Figure 5-4: The average temperature (°C, (solid red line), and total rainfall (mm, vertical bars) during the 2019 growing season of the study at St. John's Research and Development Centre

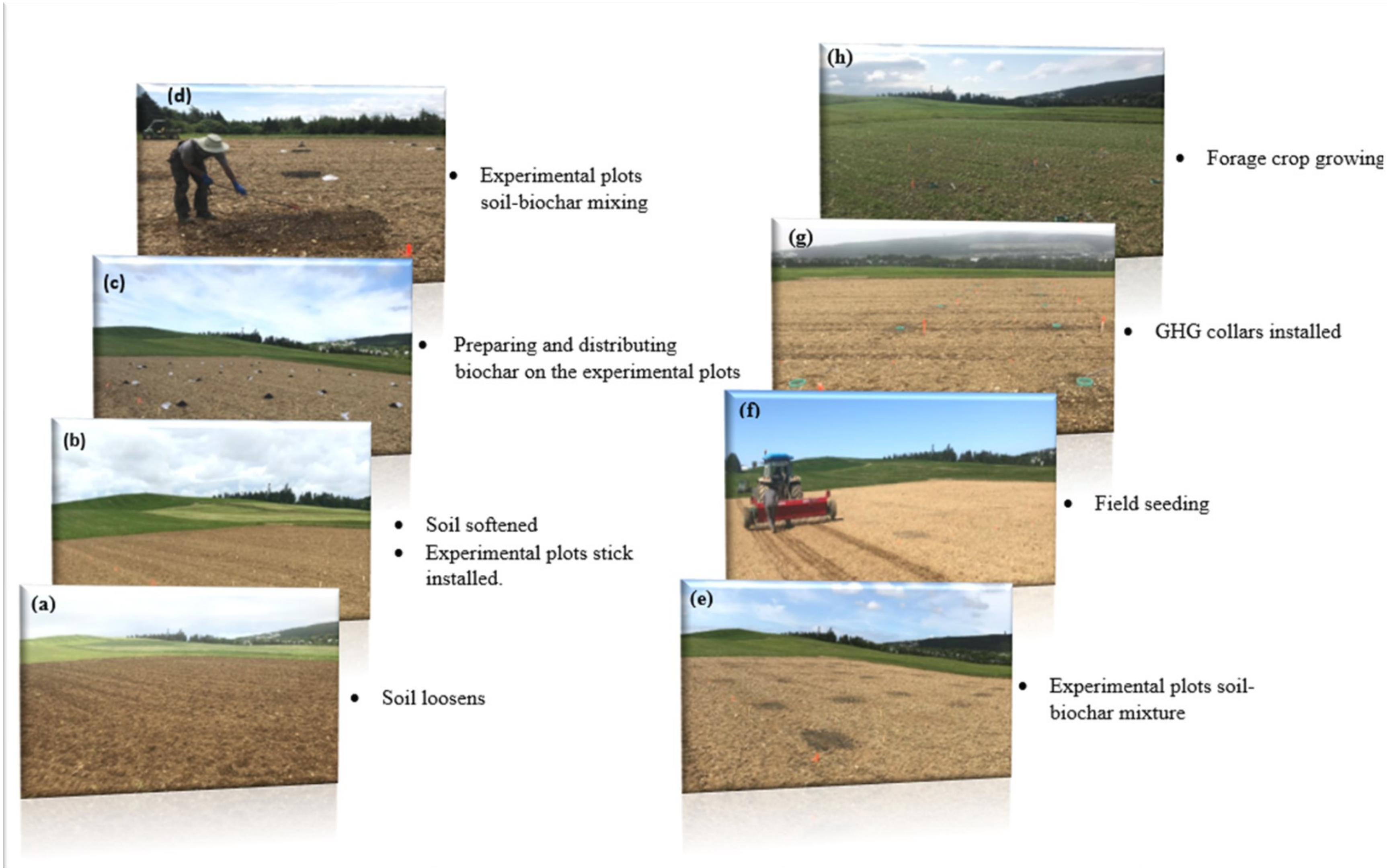
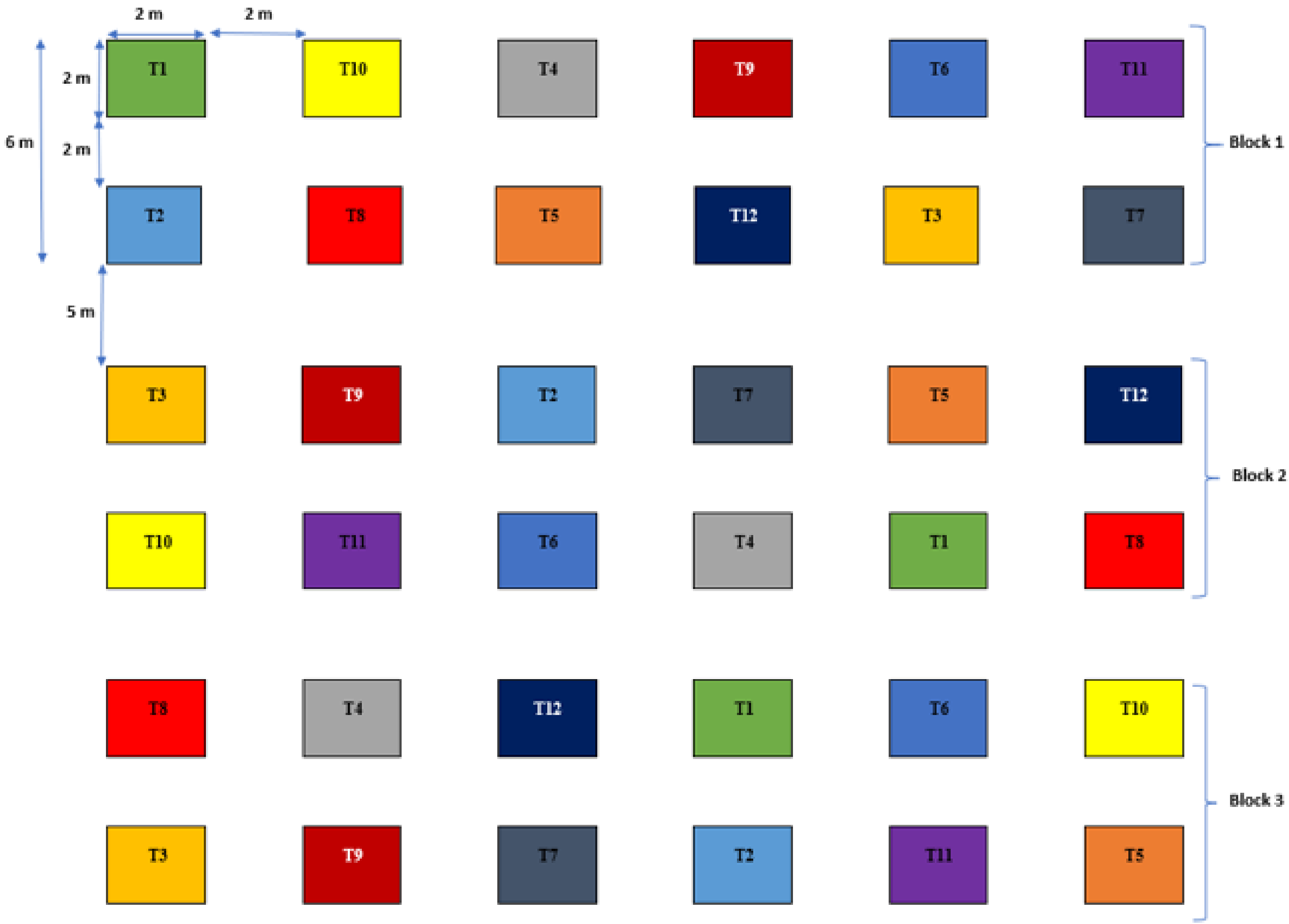


Figure 5-5: The set-up of the study site through different agricultural operations including (a) soil loosens, (b) soil softens and experiment plots stick installed, (c) preparing and distributing biochar on the experimental plots, (d) soil-biochar mixing, (f) field *Festulolium* seeding, and (g) greenhouse gas collars installation



Number of treatments (t) = 12
Number of replications per treatment (r) =3
Sample size (n) = 36

Levels of biochar application = 4 (B0%, B5%, B8%, B10%)
Levels of nitrogen fertilizer = 3 (N1, N2, N3) N1= 0, N2= 0.5 R, and N3=R

Treatments codes	Treatment descriptions	Treatments codes	Treatment descriptions	Treatments codes	Treatment descriptions	Treatments codes	Treatment descriptions
T1	B0-N0	T4	B10-N0	T7	B8-N65	T10	B5-N130
T2	B5-N0	T5	B0-N65	T8	B10-N65	T11	B8-N130
T3	B8-N0	T6	B5-N65	T9	B0-N130	T12	B10-N130

Figure 5-6: The experimental layout showed the study's treatment descriptions within a Randomized Complete Block Design (RCBD)

5.3. Statistical analysis

Statistical analysis of variances (ANOVA) was performed using a general linear model in the Minitab 19 software (Minitab, 2019). To test the degree of the significance of the biochar effect, the nitrogen fertilizer effect, and the interaction between these two factors on the CO_2, CH_4 and N_2O emissions at $\alpha \leq 0.05$, taking the experimental design (RCBD) into consideration. The normality of distribution and homogeneity of variance were tested before ANOVA analysis was conducted, and all assumptions were met. The data for the GHG fluxes followed a normal distribution, which had the similar distribution to the other studies (Ashiq et al., 2020; Gong et al., 2019). The arithmetic averages were calculated from the gas fluxes to represent the seasonal average for each treatment, and the standard error of the mean was directly calculated from the gas fluxes for each treatment. Correlations between gas fluxes and environmental parameters were tested with a Pearson correlation test. Significant differences between the treatment means were analyzed using Tukey's test at a 95% significance level ($P < 0.05$). A two-way analysis of variances (ANOVA) was performed according to a linear model (2) (Dunn and Smyth, 2018).

$$Yijk=\mu+Ai+ Bj+(AB)ij+\varepsilon ijk \qquad (2)$$

Where Yijk is the dependent variable of CO_2, CH_4 and N_2O emissions, μ is the overall mean, Ai and Bj are the effects of ith (biochar rates), jth (nitrogen levels), respectively, and εijk is the random error terms within the experiment.

5.4. Results

5.4.1. CO_2 emissions

The soil CO_2 emissions were increased with the growing season, followed by seasonal trends with the lowest values in August, ranged from 6.3 to 20.3 mg CO_2 m^{-2} h^{-1}, and the highest values in

October, ranged from 106 to 185.2 mg CO_2 m^{-2} h^{-1} as shown in (Figure 5-7a, b & c). There was a significant positive correlation of the seasonal CO_2 emission related to soil moisture, $r(5) = 0.926$, $p < 0.001$, (Table 5-4 & Figure 5-9), and soil temperature at 5 cm, $r(5) = 0.926$, $p = 0.002$, (Table 5-4 & Figure 5-9), whereas, a significant negative correlation of the seasonal CO_2 changes related to soil temperature at 20 cm, $r(5) = -0.868$, $p = 0.025$, (Table 5-4 & Figure 5-9). However, the observation showed a higher seasonal trend of CO_2 emissions from treatments with lower biochar application rates compared to treatments with higher biochar application rates as shown in Figure (5-7a, b & c). The statistical analysis of CO_2 emissions is shown in Table (5-5) stating that biochar application and nitrogen fertilizer significantly affected CO_2 emissions (p-values < 0.05). The Tukey's test results indicated a significant reduction in the CO_2 emissions followed by an increase in the biochar application rate, in which all biochar rates, including 5 %, 8 %, and 10 % [v/v], were significantly different than the control (0 % [v/v]) (p-value < 0.001) (Table 5-5). The CO_2 emissions were reduced dramatically by 12 %, 23 %, and 42 % for the biochar rate of 5 %, 8 %, and 10 % [v/v], respectively, in comparison to that for the control treatment (p-value < 0.001) (Table 5-5 & Figure 5-7). The nitrogen fertilizer rate had a significant impact on CO_2 emissions (p-value = 0.011) (Table 5-5). The CO_2 emissions were increased by 6.50 % and 21.14 % for the 65 and 130 kg N/ha, respectively, compared to that of the control treatment (0 kg N/ha) (Table 5-5 & Figure 5-10). The CO_2 emissions were also positively related to soil bulk density and negatively related to soil porosity (Table 5-13).

4.5.2. CH_4 emissions

Negative values of CH_4 emissions were observed from all treatments. The seasonal CH_4 emissions followed a reduction trend with lower values ranging from -132.8 to 30.7 µg CH_4 m^{-2} h^{-1} in September, and the highest values in October, ranging from -8.8 to -1.0 µg CH_4 m^{-2} h^{-1} as shown in (Figure 5-7d, b & f). There was a significant negative correlation between the seasonal CH_4 emissions and soil moisture, *r (5) = -0.757, p = 0.081*, (Table 5-4 & Figure 5-9), and significant negative associations between the seasonal CH_4, and soil temperature at 5 cm, *r (5) =-0.893, p = 0.016,* while and significant positive associations between the seasonal CH_4 and soil temperature at 20 cm *r (5) = 0.969, p = 0.001* as shown in (Table 5-4 & Figure 5-9). Lower seasonal CH_4 emission was observed in the treatments with higher biochar application compared to the control. The analysis of variance (ANOVA) of CH_4 emissions was significantly changed by biochar application and nitrogen fertilizer rates (p-values < 0.05) (Table 5-6). The Tukey's test results indicated that biochar application had significantly reduced the CH_4 emissions by 59 %, 75 %, and 76 % for the biochar rates of 5 %, 8 %, and 10 % [v/v], respectively, compared to the control treatment (p-value < 0.031) (Table 5-6 & Figure 5-11). However, the CH_4 emissions were influenced by the nitrogen fertilizer rates; the CH_4 emissions were increased by 33 % and 44 % for the 65 and 130 kg N/ha, respectively, compared to that of the control treatment (0 kg N/ha) (Table 5-6 & Figure 5-11).

5.4.3. N_2O emissions

The N_2O emission followed seasonal trends with lower values of 1.36 μg N_2O m^{-2} h^{-1} in September and higher values of 8.94 μg N_2O m^{-2} h^{-1} in October, as shown in (Figure 5-7g, h & i). N_2O emissions had significant positive associations related to soil moisture *r (5) = 0.863, p = 0.027*, and soil temperature at 5 cm *r (5) = 0.875, p = 0.022,* while the N_2O emissions had significant negative correlation related to soil temperature at 20 cm *r (5) =-0.874, p = 0.023* as shown in (Table 5-4 & Figure 5-9). The ANOVA analysis of N_2O emissions indicated that both biochar application and nitrogen fertilizer rates had significantly affected the N_2O emissions (p-value < 0.05) (Table 5-7 & Figure 5-9). Nitrogen fertilizer rates had increased the N_2O emissions by 10 %

and 17 % for the fertilizer rate of 65 and 130 kg N/ha, respectively, in comparison to that of the control treatment (0 kg N/ha) (Table 5-7 & Figure 5-12). However, the overall N_2O emissions were decreased by 22 %, 38%, and 43 % for the biochar rate of 5 %, 8 %, and 10 % [v/v], respectively, compared to that of the control treatment (p-value < 0.001) (Table 5-7 & Figure 5-12).

5.4.4. Soil temperature and soil moisture and their impacts on GHG emissions

Generally, soil temperature at 5 cm and 10 cm depths have decreased from July to October across all treatments (Figure. 5-8). Soil temperatures may affect the soil GHG emissions by affecting the soil responsible microbial activities and soil respiration (Oertel et al., 2016), nitrification and denitrification (Signor and Cerri, 2013) and methanogenesis and methanotrophic (Das and Adhya, 2012; Serrano-Silva et al., 2014). There was a significant positive correlation of soil temperature at 5 cm with the seasonal CO_2 emission, $r(5) = 0.926, p = 0.002$ (Table 5-4 & Figure 5-9), whereas soil temperature at 20 cm had a significant negative correlation with the seasonal CO_2 changes, $r(5) = -0.868, p = 0.025$, (Table 5-4 & Figure 5-9). Likewise, there was significant negative correlation between soil temperature at 5 cm and the seasonal CH_4 emissions, $r(5) = -0.893, p = 0.016$, while a significant positive correlation between soil temperature at 20 cm and the seasonal CH_4, $r(5) = -0.969, p = 0.001$ was detected, as shown in (Table 5-4 & Figure 5-9). Furthermore, there were positive significant correlations between soil temperature at 5 cm and the seasonal N_2O emissions, $r(5) = 0.875, p = 0.022$, and a significant negative correlation between soil temperature at 20 cm and the seasonal N_2O emissions, $r(5) = -0.874, p = 0.023$ as shown in (Table 5-4 & Figure 5-9).

The soil moisture effects varied with GHG. Soil moisture had a significant positive correlation with the seasonal CO_2 emission, $r(5) = 0.926, p < 0.001$, (Table 5-4 & Figure 5-9), a significant negative correlation with the seasonal CH_4 emissions, *r (5) = -0.757, p = 0.081*, (Table 5-4 & Figure 5-9), and significant positive correlation with the seasonal N_2O emission, *r (5) = 0.863, p = 0.027*, as shown in (Table 5-4 & Figure 5-9).

5.4.5. *Festulolium* forage yield

The *Festulolium* fresh and dry matter yields were influenced by both biochar application rates and nitrogen fertilizer levels. An increment in the *Festulolium* fresh and dry matter yields followed the increment in both biochar application rates and nitrogen fertilizer levels. The ANOVA analysis of *Festulolium* fresh and dry matter yields indicated that both biochar application rates and nitrogen fertilizer levels had significantly affected the *Festulolium* fresh and dry matter yields (p-values < 0.05) (Tables 11 & 12). The *Festulolium* fresh yield increased by 15.0 %, 17.5 %, and 30.3 % for the biochar application rates of 5 %, 8 % and 10 % [v/v] compared to that of the control treatment (p-value = 0.022) (Table 5-11 & Figure 5-16). Likewise, the nitrogen fertilizer levels have increased the *Festulolium* fresh yield by 45.0 % and 88.5 % for the fertilizer levels of 65 and 130 kg N/ha, respectively, in comparison to that of the control treatment (0 kg N/ha) (p-value = 0.000) (Table 5-11 & Figure 5-16). The *Festulolium* dry matter yield increased by 18.2 %, 26.3 %, and 33.8 % for the biochar application rates of 5 %, 8 % and 10 % [v/v] compared to that of the control treatment (p-value = 0.033) (Table 5-12 & Figure 5-17). While the nitrogen fertilizer levels have increased the *Festulolium* dry matter yield by 37.7 % and 72.0 % of the fertilizer levels of 65 and 130 kg N/ha, respectively, in comparison to that of the control treatment (0 kg N/ha) (p-value < 0.001) (Table 5-12 & Figure 5-17).

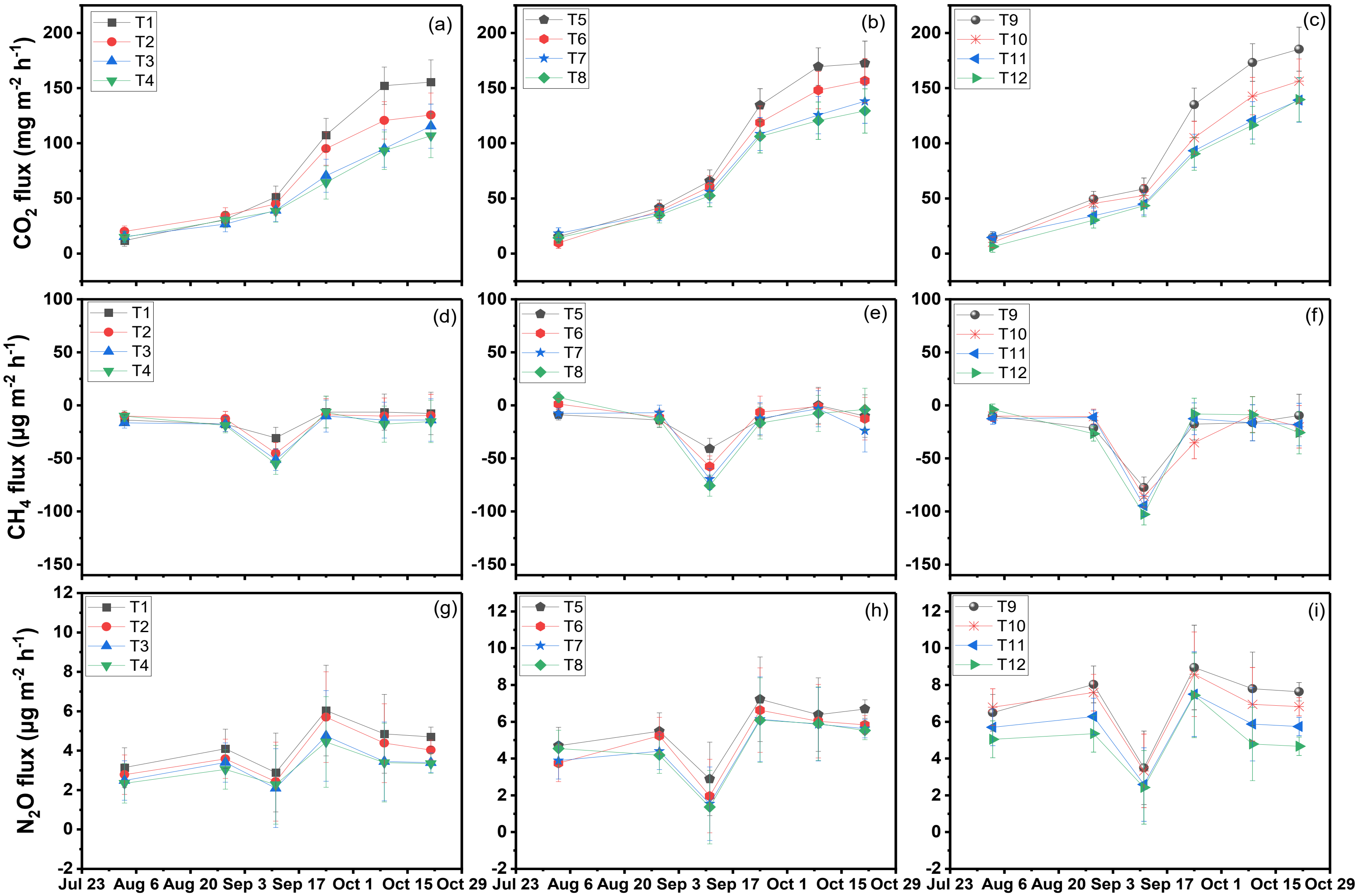


Figure 5-7: Temporal patterns for soil CO_2 (a,b,c), CH_4 (d,e,f) and N_2O (g,h,i) emissions during 2019 of *Festulolium* forage crop growing under different treatments, including T1 (B0-N0), T2 (B5-N0), T3 (B8-N0), T4 (B10-N0), T5 (B0-N65), T6 (B5-N65), T7 (B8-N65), T8 (B10-N65), T9 (B0-N130), T10 (B5-N130), T11 (B8-N130) and T12 (B10-N130)

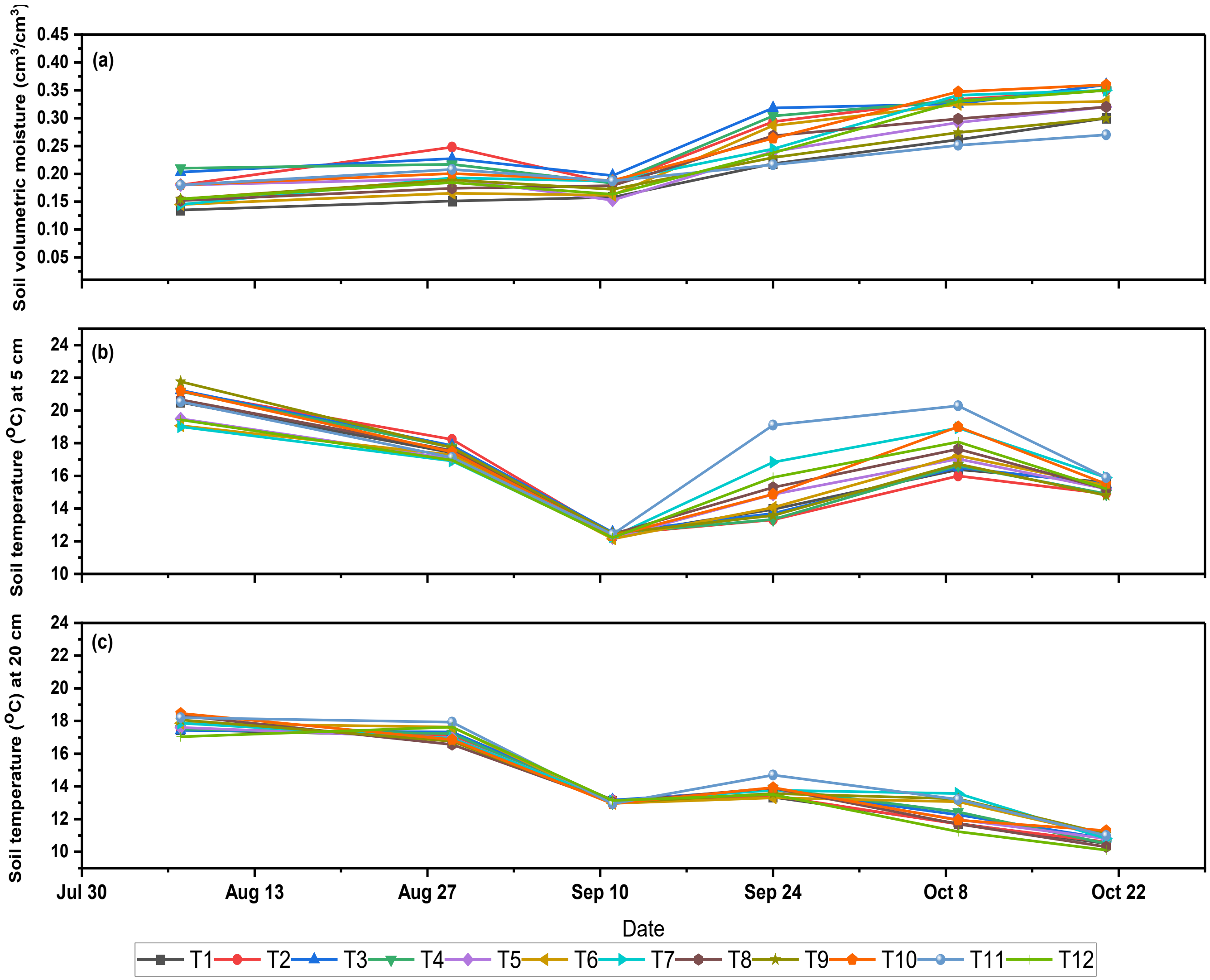


Figure 5-8: Mean of soil volumetric moisture content (a), soil temperature at 5 cm depth (b), and soil temperature at 20 cm depth (c) in experimental treatments during the growing season of the study at St. John's Research and Development Centre. Legend represents the experimental treatments of the study, including T1 (B0-N0), T2 (B5-N0), T3 (B8-N0), T4 (B10-N0), T5 (B0-N65), T6 (B5-N65), T7 (B8-N65), T8 (B10-N65), T9 (B0-N130), T10 (B5-N130), T11 (B8-N130) and T12 (B10-N130)

Table 5-4: Poisson correlation coefficients of CO_2 flux, CH_4 flux, and N_2O flux, soil moisture, soil temperature at 5 cm, and soil temperature

	CO_2 (mg/m^2/h)	CH_4 (µg/m^2/h)	N_2O (µg/m^2/h)	Moisture (m^3/m^3)	Soil temperature at 5 cm (^oC)
CH_4 flux (µg/m^2/h)	-0.857				
	0.029*				
N_2O flux (µg/m^2/h)	0.926	-0.941			
	0.008**	0.005**			
Soil moisture (m^3/m^3)	0.983	-0.757	0.862		
	0.000***	0.081*	0.022*		
Soil temperature at 5 cm (^oC)	0.962	-0.893	0.875	0.931	
	0.002**	0.016*	0.027*	0.007**	
Soil temperature at 20 cm (^oC)	-0.868	0.969	-0.874	-0.786	-0.945
	0.025*	0.001***	0.023*	0.064	0.004**

*Correlation is significant (p-value < 0.05), **correlation is significant (p-value < 0.01), and ***correlation is significant (p-value < 0.001).

at 20 cm

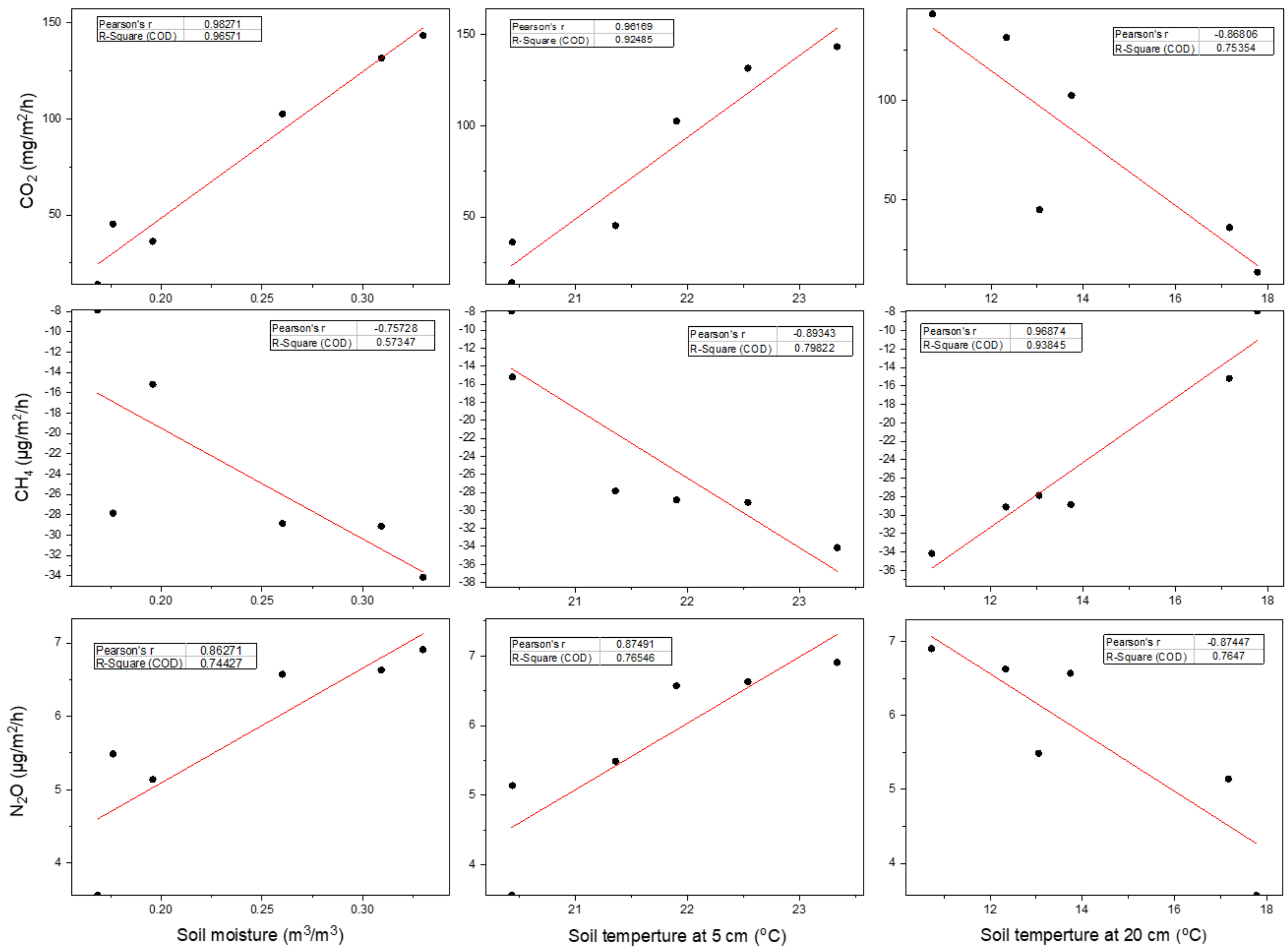


Figure 5-9: Correlation coefficients of CO_2 flux, CH_4 flux, and N_2O flux, with soil moisture, soil temperature at 5 cm, and soil temperature at 20 cm

Table 5-5: Analysis of variance (ANOVA) of estimated CO_2 emissions in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	9837.0	3279.0	20.09	0.000
N (kg/ha)	2	1790.3	895.1	5.48	0.011
Biochar (v/v) *N (kg/ha)	6	947.9	158.0	0.97	0.468
Error	24	3917.6	163.2		
Total	35	16492.8			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N)

Table 5-6: Analysis of variance (ANOVA) of estimated CH_4 emissions in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	43954	14651	3.48	0.031
N (kg/ha)	2	65996	32998	7.84	0.002
Biochar (v/v) *N (kg/ha)	6	17788	2965	0.70	0.649
Error	24	100955	4206		
Total	35	228692			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N)

Table 5-7: Analysis of variance (ANOVA) of estimated N_2O emissions in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	146.929	48.9763	36.97	0.000
N (kg/ha)	2	13.307	6.6534	5.02	0.015
Biochar (v/v) *N (kg/ha)	6	2.956	0.4926	0.37	0.890
Error	24	31.792	1.3247		
Total	35	194.983			

Statistically significant difference ($P < 0.05$). Source of variance codes, including biochar (B), nitrogen (N)

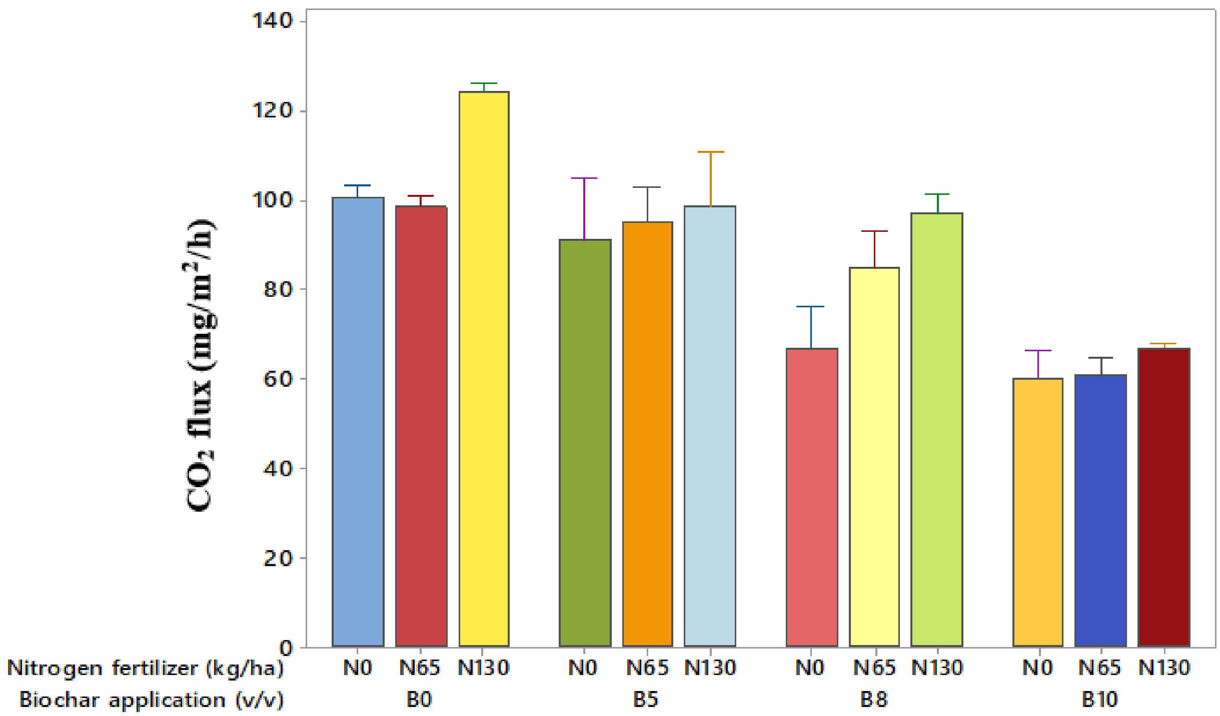


Figure 5-10: Effect of biochar application and nitrogen fertilizer levels on CO_2 emissions (mg/m^2/h). Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

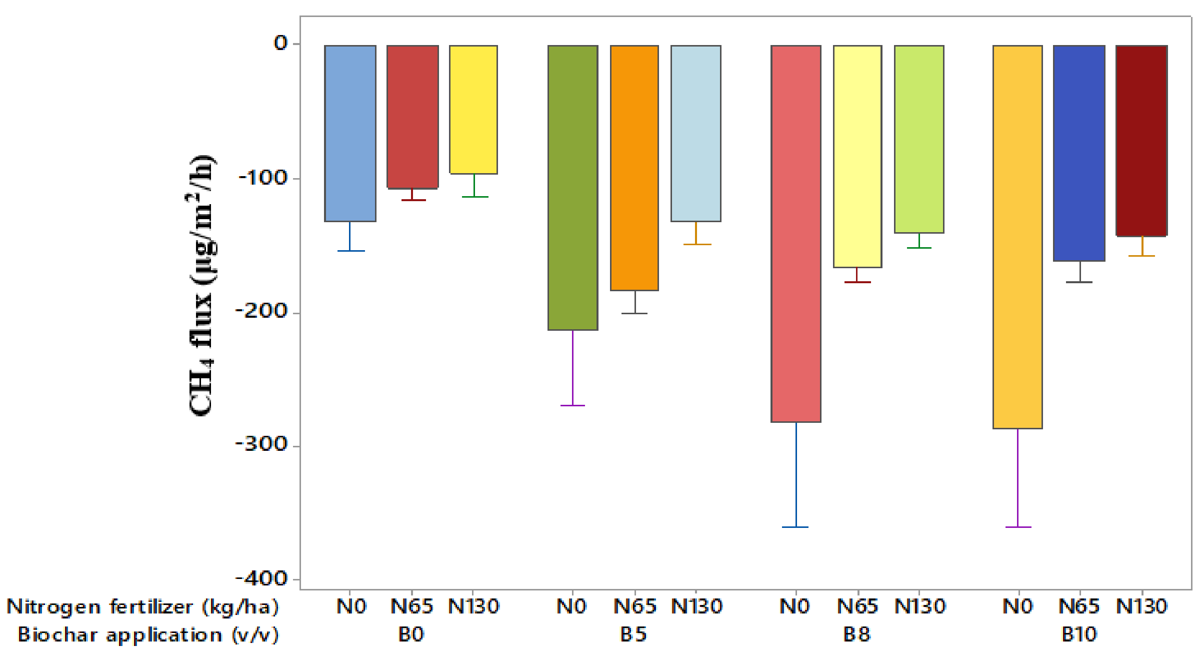


Figure 5-11: Effect of biochar application and nitrogen fertilizer levels on CH_4 emissions (µg/m^2/h). Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

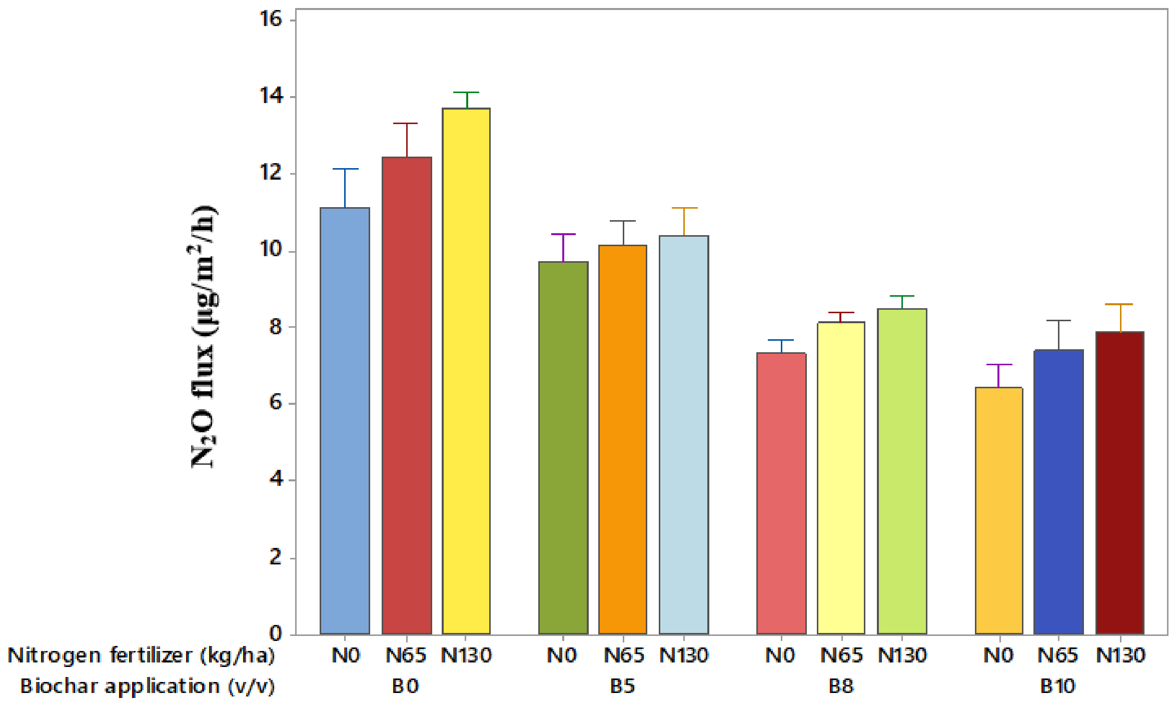


Figure 5-12: Effect of biochar application and nitrogen fertilizer levels on N_2O emissions (µg/m^2/h). Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 5-8: Analysis of variance (ANOVA) of estimated soil bulk density in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	0.507320	0.169107	91.52	0.000
N (kg/ha)	2	0.005313	0.002657	1.44	0.257
Biochar (v/v) *N (kg/ha)	6	0.025707	0.004285	2.32	0.066
Error	24	0.044344	0.001848		
Total	35	0.582685			

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B), nitrogen (N)

Table 5-9: Analysis of variance (ANOVA) of estimated soil total porosity in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	268.93	89.644	24.10	0.000
N (kg/ha)	2	14.83	7.417	1.99	0.158
Biochar (v/v) *N (kg/ha)	6	17.18	2.864	0.77	0.601
Error	24	89.28	3.720		
Total	35	390.24			

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B), nitrogen (N)

Table 5-10: Analysis of variance (ANOVA) of estimated soil water-filled pore in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	151.70	50.567	16.43	0.000
N (kg/ha)	2	10.21	5.103	1.66	0.212
Biochar (v/v) *N (kg/ha)	6	42.11	7.019	2.28	0.070
Error	24	73.88	3.079		
Total	35	277.91			

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B), nitrogen (N)

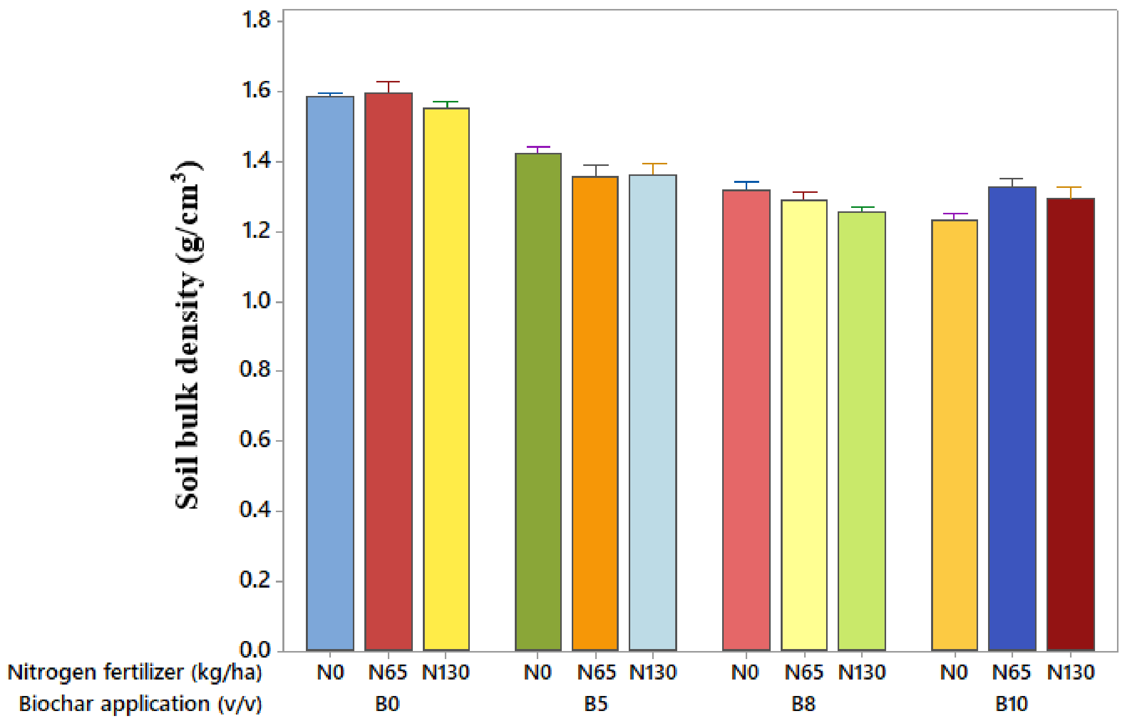


Figure 5-13: Effect of biochar application and nitrogen fertilizer levels on soil bulk density. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

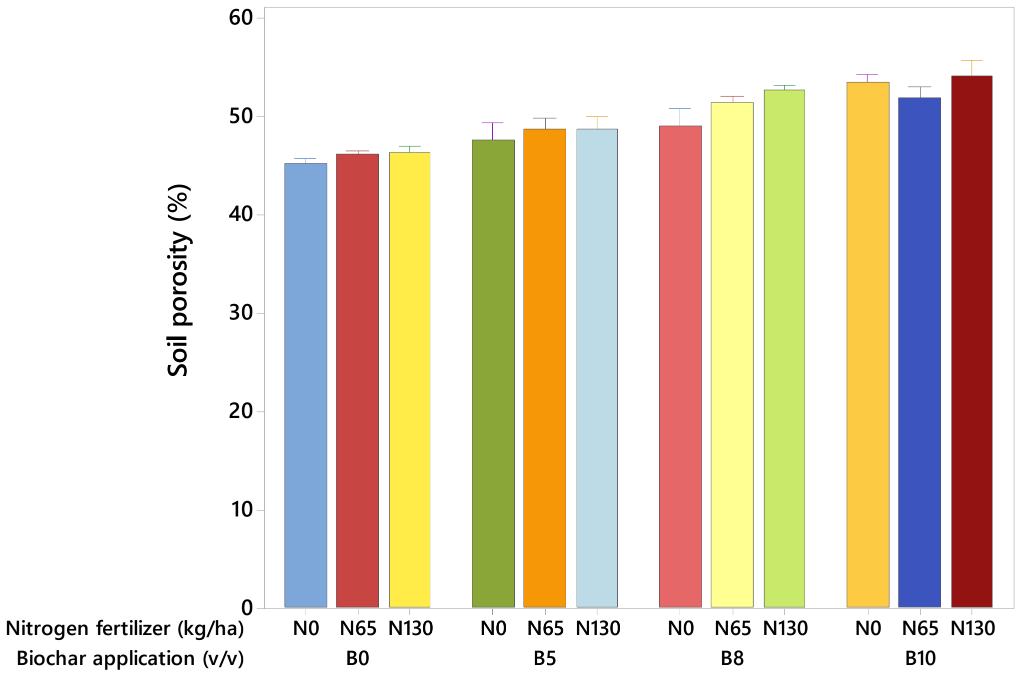


Figure 5-14: Effect of biochar application and nitrogen fertilizer levels on soil porosity. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

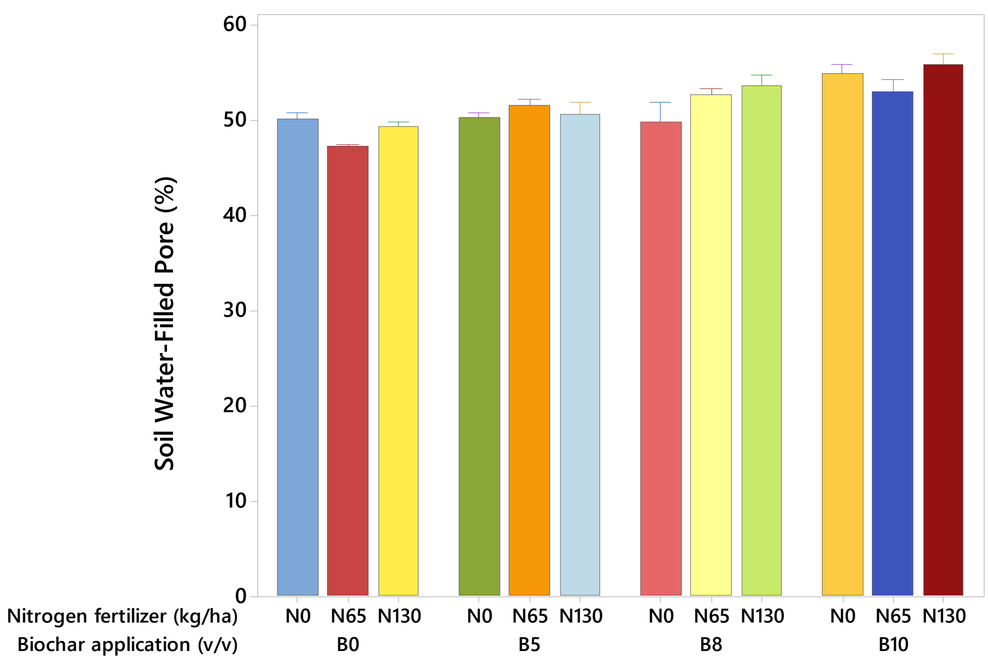


Figure 5-15: Effect of biochar application and nitrogen fertilizer levels on soil water-filled pore. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 5-11: Analysis of variance (ANOVA) of estimated fresh yield in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	25391672	8463891	3.84	0.022
N (kg/ha)	2	183172310	91586155	41.58	0.000
Biochar (v/v)*N (kg/ha)	6	4600984	766831	0.35	0.904
Error	24	52867464	2202811		
Total	35	266032431			

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B), nitrogen (N)

Table 5-12: Analysis of variance (ANOVA) of estimated dry matter yield in response to the main effects of biochar, nitrogen levels, and biochar and nitrogen interaction

Source of Variance	*df*	*Adj SS*	*Adj MS*	*F-Value*	*P-Value*
B (v/v)	3	1122722	374241	3.44	0.033
N (kg/ha)	2	4706589	2353294	21.66	0.000
Biochar (v/v)*N (kg/ha)	6	70714	11786	0.11	0.995
Error	24	2607507	108646		
Total	35	8507531			

Statistically significant difference (P < 0.05). Source of variance codes, including biochar (B), nitrogen (N)

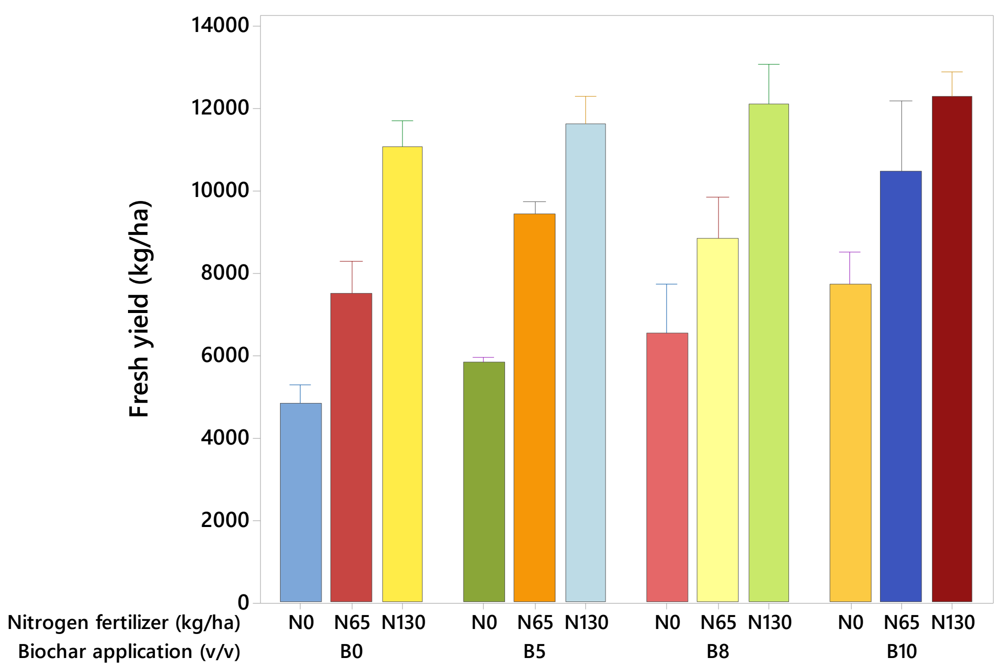


Figure 5-16: Effect of biochar application and nitrogen fertilizer levels on fresh yield. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

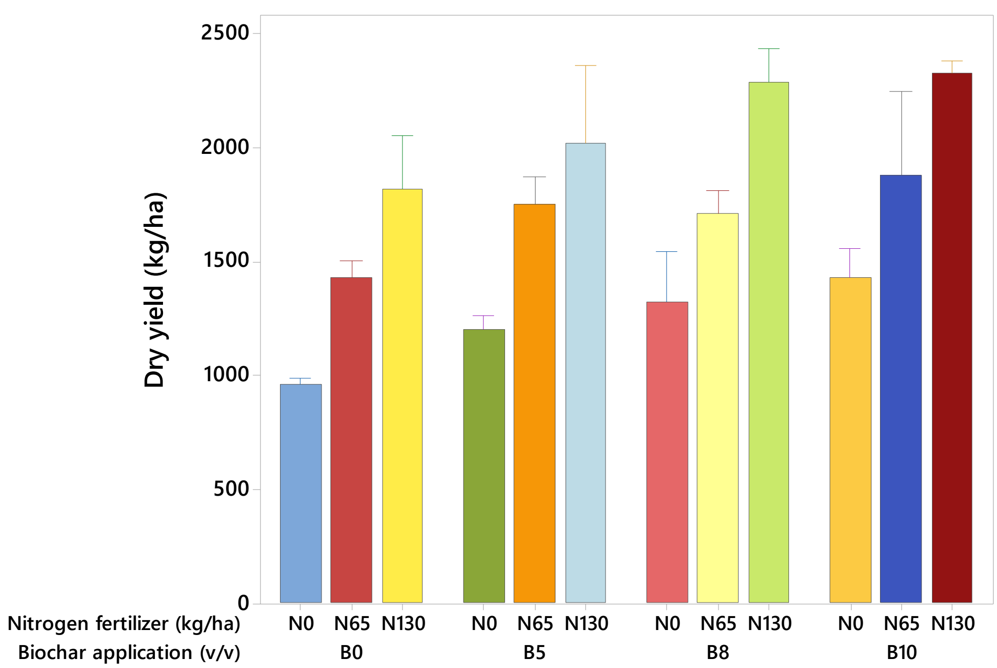


Figure 5-17: Effect of biochar application and nitrogen fertilizer levels on dry matter yield. Each bar interprets the mean (n=3), and vertical error bars are standard error of the mean (SEM)

Table 5-13: Correlation coefficients of CO_2 flux, CH_4 flux, N_2O flux, bulk density, soil porosity, soil water-filled pore, and porosity

	CO_2 flux (mg/m^2/h)	CH_4 flux (µg/m^2/h)	N_2O flux (µg/m^2/h)	Bulk Density (g/cm^3)	Soil porosity (%)	Soil Water-Filled pore (%)	Soil Air-Filled porosity (%)
CH_4 flux (µg/m2/h	0.303						
	0.072						
N_2O flux (µg/m2/h	0.719	0.508					
	0.000***	0.002***					
Bulk Density (g/cm^3)	0.629	0.359	0.751				
	0.000***	0.032*	0.000***				
Soil porosity (%)	-0.631	-0.135	-0.717	-0.834			
	0.000***	0.374	0.000***	0.000***			
Soil Water-Filled pore (%)	-0.536	-0.017	-0.632	-0.740	0.900		
	0.001***	0.921	0.000***	0.000**	0.000***		

*Correlation is significant (p-value < 0.05), **correlation is significant (p-value < 0.01), and ***correlation is significant (p-value < 0.001)

5.5. Discussion

5.5.1. CO_2 emissions

The *Festulolium* forage crop growth has affected the CO_2 emissions at all sampling events for all treatments, as shown in (Figure 5-7a, b & c). The lowest values of CO_2 emissions that were measured in August, ranged from 6.3 to 20.3 mg CO_2 m^{-2} h^{-1}, and the highest values were in October, ranged from 106 to 185.2 mg CO_2 m^{-2} h^{-1}. Different variations of CO_2 emissions were noticed among treatments, in which the higher CO_2 emissions were obtained from treatments with lower biochar application rates (p-value < 0.001) (Table 5-5 & Figure 5-10). The seasonal trends of CO_2 emissions increased along with the forage crop growth, which may be attributed to the increase in shoot, and root biomass. Thus, CO_2 emissions from green biomass (shoot respiration) were also included. The amount of CO_2 emission from the soil surface can be determined through root (autotrophic) respiration and microorganisms (heterotrophic) respiration (Kuzyakov and Larionova, 2006). About 40-45% of the CO_2 emission is related to root-derived respiration, and 55-60% is associated with the microbial decomposition of root exudates and other rhizodeposits (Kuzyakov and Larionova, 2005).

The *Festulolium* growth was affected by nitrogen fertilizer levels. CO_2 emissions showed a significant response to nitrogen fertilizer levels (p-value = 0.011) (Table 5-5). Higher nitrogen fertilizer levels resulted in increased CO_2 emissions. In addition to its function of increase crop growth, it can also represent the energy input to the ecosystem, which can be used by soil microorganisms for SOM decomposition (De Oliveira et al., 2013), thus, increased CO_2 emissions were observed under higher nitrogen fertilizer levels (Figure 5-6). Moreover, when applying urea to the soil as a nitrogen supply, with the presence of water and urease enzymes, the urea is converted into NH_4^+, OH^-, and HCO_3^-. In the end, the formed HCO_3^-, breakdown into CO_2 and water (Snyder et al., 2009); and thereby increases CO_2 emissions from treatments with higher nitrogen levels ((Figure 5-10).

Moreover, CO_2 emissions can be significantly affected by nitrogen fertilizer due to its impact on the soil microbial communities (Ren et al., 2020). Inselsbacher et al. (2011) reported that nitrogen fertilization has increased CO_2 emissions substantially in the cropped ecosystem, but not in the uncropped soil, which indicated that the microorganisms motivated the root's exudation and the growth of the crop. In contrast, the organisms in the uncropped soil were carbon limited. However, it was reported that biochar has a high resistant ability to soil microbial activity, which slows down soil organic matter (SOM) decomposition rate and reduces the soil CO_2 emissions (Stavi and Lal, 2013; J. Wang et al., 2016). Likewise, the functional groups' presence on the biochar surface may enhance CO_2 adsorption, which may minimize CO_2 emissions from the biochar amended soils (Ashiq et al., 2020; Brennan et al., 2015; Sheng and Zhu, 2018; Zheng et al., 2018). Furthermore, stabilization of root exudates by forming organo-mineral combinations under the biochar amended soil which reduces the autotrophic respiration (Pokharel and Chang, 2019).

5.5.2. CH_4 fluxes

About 10-90% of CH_4 produced in the soils through methanogenic activities and consumed by methanotrophic microbes (Aimen et al., 2018; Oertel et al., 2016; Serrano-Silva et al., 2014). The nitrogen fertilizer effect on the CH_4 emissions can either stimulate or inhibit CH_4 emissions (Banger et al., 2012), based on the site-specific factors, such as nitrogen fertilizers form (Dattamudi et al., 2019), and rates, microbial communities and activities, and soil carbon (Ashiq et al., 2020; Banger et al., 2012). The nitrogen element is a fundamental nutrient for methanotrophs, as methane-oxidizing bacteria which could be stimulated by nitrogen addition. Thus, nitrogen limitation can inhibit the CH_4 oxidation in soils (Bodelier and Laanbroek, 2004). Previous studies have reported that CH_4 emissions stimulation by nitrogen fertilizers may be attributed to the inhibition of methanotrophs activities that led to lower CH_4 oxidation and more significant CH_4 emissions in agricultural ecosystems. In this study, negative CH_4 emissions were observed from all experimental treatments, while a significant increment in the CH_4 emissions followed the higher nitrogen fertilizer levels (p-value < 0.05). Treatments with 130 kg N/ha showed higher CH_4 emissions (Figure 5-11), which can be explained by nitrogen fertilizer stimulation. Aronson and Helliker (2010) demonstrated that nitrogen fertilizer application of higher than 100 Kg N/ha suppressed methanotrophs activities and resulted in lower CH_4 oxidation in soils (Jeffery et al., 2016). Likewise, urea fertilizer application of 200 - 400 Kg N/ha stimulated the soils' CH_4 oxidation process (Bodelier et al., 2000). Therefore, stimulation of methanotrophs was the primary mechanism of increasing CH_4 emissions under higher nitrogen fertilizers levels.

Biochar application had a significant reduction in the CH_4 emissions (p-value < 0.05) (Table 5-6 & Figure 5-11). Biochar depresses methanogenesis activities and increases the soil's methanotrophic activities, leading to decreased CH_4 emissions by increasing biochar application rates (Ashiq et al., 2020; Feng et al., 2012; Han et al., 2016). Biochar also can adsorb CH_4 due to its large surface area and sizeable porous structure (Figure 5-1). Generally, increased nitrogen fertilizer levels turning treatments functioning as a net source of CH_4 emissions, although increased biochar application rate made treatments performing as a net sink of atmospheric CH_4 during the 2019 growing season. In agreement with this study, Ashiq et al., (2020) have reported that biochar application at 20 tons/ha has significantly depressed CH_4 emission from a silage corn field.

5.5.3. N_2O fluxes

Nitrogen fertilizer rate is an important factor affecting soil N_2O emission (Bing et al., 2006; Wang et al., 2016; Xuejun and Fusuo, 2011; Yi et al., 2017). In this study, it was found that nitrogen fertilizer level significantly increased the soil N_2O emissions (p-value = 0.015) (Table 5-7 & Figure 5-12). Increase in the N_2O emissions with increase in the nitrogen application rate (Cheng et al., 2015; Dai et al., 2013; Hoben et al., 2011; Yi et al., 2017) may be attributed to increase in the inorganic nitrogen concentration in the soil (Inselsbacher et al., 2011; Kostyanovsky et al., 2019; Troy et al., 2017). This may enhance N_2O production mechanisms by nitrification and denitrification (Cheng et al., 2015; Oertel et al., 2016; Rivett et al., 2008; Troy et al., 2017).

The N_2O emissions were significantly reduced by biochar application (p-value < 0.001) (Table 5-7 & Figure 5-12), increased biochar rates and gradually decreased the N_2O emissions. The possible underlying mechanisms of reducing the soil N_2O emissions by biochar are; (i) increase in soil pH by incorporation of alkaline biochar (Zhang et al., 2011) can identify the primary mechanisms for N_2O production through the threshold pH which suppresses denitrification rate, when the denitrification was dominated by N_2O emission at the threshold pH below 4.5 (Cheng et al., 2015; Obia et al., 2015). Likewise, increase in soil pH by biochar increases the N_2O-reductase activity by N_2 formation and raises N_2: N_2O ratios through a complete reduction of NO_3^- to N_2 instead of N_2O (Ashiq et al., 2020; Borchard et al., 2019). (ii) increase in soil aeration due to the highly porous structure of biochar (Cayuela et al., 2014; Torbert et al., 2015), decrease in soil bulk density (Table 5-8 & Figure 5-13) and increasing soil porosity (Table 5-9 & Figure 5-14), which suppress denitrification because of higher oxidation rate in the biochar amended soil (Clough et al., 2013; Singh et al., 2010; Taghizadeh-toosi et al., 2011; Troy et al., 2017). (iii) Nitrate (NO_3^-) retention onto the biochar surface (Cayuela et al., 2014; Cheng et al., 2008) could reduce the N_2O emissions

(Ameloot et al., 2013; Karhu et al., 2011), through adsorption of ammonium (NH_4^+) and NO_3^- by biochar (Cornelissen et al., 2013), which decrease the nitrogen availability for nitrifiers and denitrifiers and lead to N_2O emissions reduction (Bhatia et al., 2010; Clough et al., 2013; Singh et al., 2010).

Moreover, biochar application to the soil could increase specific organisms' abundance in the biochar amended soil (e.g. Bradyrhizobiaceae and Hyphomicrobiaceae communities), reduce N_2O emissions, supporting denitrification and converting NO_3^- to N_2 (Anderson et al., 2011; Ashiq et al., 2020; Clough et al., 2013). Furthermore, biochar application may add considerable amounts of labile C that can be easily used by soil organisms (Smith et al., 2010), which result in N_2O reduction via microbial growth and N immobilization (Bruun et al., 2012).

Although the higher nitrogen fertilization increased N_2O emissions, the N_2O emissions peaks followed the increase of soil moisture and topsoil temperature at the same time (Figures. 5-7g-i and 5-8a and b), N_2O emissions peaks observed in the fourth sampling event. A significant positive correlation of N_2O emissions with soil moisture and topsoil temperature was observed (Table 5-4). However, the results showed that water-filled pore space (WFPS) in the soil was about 55 % on average among all treatments (Figure 5-15), which may confirm suppressing denitrification. Bateman and Baggs (2005) demonstrated that nitrification was the primary process of N_2O emissions at 35-60 % WFPS, whereas denitrification was the main source of N_2O in soils at 70% WFPS. The first sampling events were done after about two weeks of nitrogen fertilizer addition, which may be the main reason that no N_2O peaks after nitrogen fertilizer addition was not observed.

In general, adding biochar with nitrogen fertilizer combination to the Newfoundland podzolic soil has reduced the N_2O emissions (Figure 5-12). That reduction of soil N losses through volatilization perhaps enhances N use efficiency and significantly mitigates agricultural N_2O emissions.

5.5.4. *Festulolium* forage yield

The fresh and dry matter yields were significantly increased by both nitrogen fertilizer levels and biochar application rates (p-values < 0.05) (Table11&12). The treatments with a combination of higher nitrogen fertilizer level and biochar application rate recorded the highest forage crop yields. Lower results were observed in the control treatments (Figures 5 -16 & 5 -17). Nitrogen is a primary nutrient element necessary for all plants to achieve optimal growth and yield production (Naeem et al., 2017). Biochar application can improve soil fertility (Adekiya et al., 2020; Prapagdee and Tawinteung, 2017; Reichenauer et al., 2009), reduce soil bulk density and increase soil porosity and water holding capacity. Also, biochar application was reported to enhance soil nutrient, soil cation exchange capacity, soil structure, nutrient use efficiency, decrease soil acidity, and carbon sequestration (Ndor et al., 2015). These improvements of soil physical and chemical characteristics as a result of biochar application may be the reasons that *Festulolium* forage yields increased by improving roots penetration and enhancing nutrient absorption (Adekiya et al., 2020).

However, by comparing the results of *Festulolium* forage yields in chapter 3 (Figure 3-6) and chapter 5 (Figures 5 -16 & 5 -17), the results showed that *Festulolium* forage yield grown under the greenhouse condition was significantly higher than the *Festulolium* forage yield grown in the field. For instance, under the greenhouse condition, the yield of the *Festulolium* forage reached 20000 kg/ha at the B5-N60 treatment. Whereas, in the field the yield of the *Festulolium* forage was about 10000 kg/ha at the B5-N65 treatment. The tendency of the results thus obtained are compatible with Padmanabhan et al., (2015) who stated that plants production under greenhouses is around 15 times more per acre than under field conditions. These results most likely provide an explanation of the ideal suited ecosystem in the greenhouse space for the forage growth. The growth in greenhouse spaces has many advantages compare to the growth under field conditions. In the greenhouse the plants grow under careful monitoring and proper maintenance techniques, for instance, in the greenhouse eco-system the temperature is more controlled, and the atmosphere is very humid which is very useful for plants growth (Padmanabhan et al., 2015).

5.6. Conclusions

An intensive increase of nitrogen fertilizers applications to the soil to improve soil fertility and crop production may cause a serious threat to the environment by increasing GHG emissions. Biochar application has been found to have significant potential to boost biomass production and decrease GHG emissions from agricultural ecosystems. Thus, a field experiment was conducted to evaluate the impact of biochar on *Festulolium* forage crop production and GHG emissions. The experimental design consisted of four rates of biochar applications including, 0% (control), 5, 8 and 10% biochar rates [v/v], and with three levels of nitrogen fertilizer applications (Urea 46-0-0) that were applied at the rates of 0 and 65 and 130 N kg/ ha. Biochar application showed a significant reduction in CO_2, CH_4, and N_2O emissions and higher forage crop production. Thus, the study concludes that biochar application has great potential benefits in reducing GHG emissions and enhancing agricultural cropping systems. However, further research is required for additional understanding of the biochar involved mechanisms in mitigating GHG emissions from the eastern Newfoundland podzolic soil.

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Chapter 6

6. Synthesis, conclusions, and future research

6.1. Overview of Study Objectives

The studies reported in this thesis will help to comprehend the effect of biochar application to the eastern Newfoundland podzolic soil by identifying the biochar nitrate adsorption capacity and determining the associated mechanism of nitrate adsorption onto biochar, which will help to improve the soil's physical and chemical properties, forage production and quality, and nutrient uptake. Biochar was found to reduce NO_3^-, NH_4^+, TN, and DOC leaching losses, subsequently improve nitrogen and carbon retention, which could enhance nitrogen fertilizer use efficiency and carbon sequestration. Biochar also reduced GHG emissions including, CO_2, CH_4, and N_2O from the eastern Newfoundland podzolic soil. The specific objectives of this thesis were:

(i) To determine the effectiveness of biochar on nitrate removal from aqueous solutions, identify the highest nitrate adsorption capacity among four types of biochar, and determine the associated mechanism of nitrate adsorption onto biochar.

(ii) To investigate the capability of biochar application for improving the soil fertility, forage production and quality, and nutrient uptake in the podzolic soil of Newfoundland.

(iii) to examine the impact of biochar application on reducing leaching losses of N and C from the eastern Newfoundland podzolic soil.

(iv) to investigate the capability of biochar application to improve soil fertility, crop productivity and reduce GHG emissions from podzolic soil.

Four studies have been conducted as a part of this thesis research to achieve these objectives including laboratory, greenhouse, and field experiments.

In summary, despite the research limitation such as biochar availability, soil testing, and funding availability, this thesis has provided a deep understanding of biochar application effect on biochar nitrate adsorption, soil physical and chemical properties, forage production and quality, and nutrient uptake, NO_3^-, NH_4^+, TN, and DOC leaching losses, and GHG emissions in the eastern Newfoundland podzolic soil. Thus, this research can be used as a model by the NL provincial agriculture sector to support the development of the boreal agriculture industry while mitigating climate change impacts from agricultural development and improve food and animal feed production in the province.

6.2. Synthesis of research results

6.2.1. The nitrate adsorption capacity of biochar varies with biochar feedstock

The biochar properties are dependent on the biochar feedstock. Although the four-biochar feedstock, including spruce bark biochar (SB550), hardwood biochar (HW500), softwood biochar (SW500), and fir/spruce biochar (FS427), had profoundly affected the nitrate adsorption capacity, the SB550 biochar was the highest among all. The maximum adsorption capacity of SB550 for nitrate was found to be 184 mg/g. The results also demonstrated that the nitrate removal rate was directly proportional to the initial nitrate concentration and inversely proportional to the initial solution pH. This study confirmed the high nitrate adsorption capacities of the four biochar types and highlighted the effect of feedstock as a critical factor on nitrate adsorption by biochar.

6.2.2. Improve soil fertility, nutrients uptake, and *Festulolium* forage crop productivity and quality by spruce bark biochar application in the eastern Newfoundland podzolic soil

Applying SB550 biochar along with nitrogen application had resulted in significant improvements in soil fertility and *Festulolium* forage crop productivity and quality. Under the greenhouse condition, SB550 biochar application to the eastern Newfoundland podzolic soil had improved soil pH, SOM, CEC, and soil nutrients availability such as Ca, Mg, K, P, S, Zn, Mn, and B, which enhanced the *Festulolium* nutrients uptake, improved its growth and its quality. Thus, based on the study results, the combination of biochar and nitrogen applications can improve soil nutrition, forage nutrient uptake, and forage growth and quality.

6.2.3. Spruce bark biochar reduced leaching loss of nitrate, ammonium, total nitrogen, and dissolved organic carbon in the leachate from the eastern Newfoundland podzolic soil

The study found that SB550 biochar application at the rates of 5, 8, and 10 % [v/v] significantly reduced total nitrogen, nitrate, ammonium and dissolved organic carbon leaching losses. The finding suggested that the SB550 biochar has a relatively good adsorption capacity, reducing nutrients leaching loss (particularly N). Thus, this study concluded that applying SB550 biochar to the eastern Newfoundland podzolic soil under greenhouse condition has improved N and C retention, which could enhance nitrogen base fertilizers use efficiency and carbon sequestration in the soil.

6.2.4. Hardwood biochar reduced greenhouse gas emissions and improved the forage crop yield in the eastern Newfoundland podzolic soil

A field experiment was conducted to evaluate the impact of hardwood biochar application on *Festulolium* forage crop production and GHG emissions. Biochar application caused a significant reduction in GHG emissions and increment in the *Festulolium* forage crop production. Therefore, the study concluded that biochar application has a high potential to reduce GHG emissions and increase forage crop production.

6.3. Application recommendation

The research results including soil analyses (chapter 3), water leaching analyses (chapter 4), and GHG emissions (chapter 5) showed the biochar treatments at 8 % and 10 % rates had the most effective results for improving soil fertility, and *Festulolium* forage crop quality and reducing GHG emissions compared to the other biochar treatments of 0 %, 2 % and 5 % rates. However, the results also indicated that the biochar treatments of 8 % and 10 % rates were not significantly different. Thus, in terms of soil sustainable management, and economic perspective, this study recommends the biochar treatments of 8 % [v/v] as the best biochar application rate that can be applied for soil and forage qualities enhancement and GHG emissions reduction in the eastern Newfoundland podzolic soil.

6.4. Suggestions for Future Research

6.4.1. Effects of biochar and dairy manure on soil quality, crop production, and GHG emissions from the eastern Newfoundland podzolic soil

Farm dairy manure is an essential source of plant nutrients (e. g., N, phosphorus (P), potassium (K), and sulphur (S). Thus, it has high potential to improve soil fertility and crop productivity (Goss et al., 2013; Maillard and Angers, 2014). Dairy manure also has a negative environmental effect such as N leaching and GHG emissions, including CO_2, CH_4 and N_2O (Bolan et al., 2004; Huang et al., 2017; Luo et al., 2008; M. Zhou et al., 2014). Biochar is known to influence N transformation and GHG emissions from soil. However, these effects of biochar and dairy manure are not constant. These effects can be varied based on the relationships between fertilizer type and rates (Demurtas et al., 2016; Zhang et al., 2015) and soil type and cropping systems (Barros et al., 2015; Jabloun et al., 2015), rainfall patterns (Fang et al., 2014), and irrigation (Jamali et al., 2015). Also, the impact of biochar and organic nitrogen application (e.g., dairy manure) combination on the soil quality, crop production, and GHG emissions from the eastern Newfoundland agricultural soil have not yet been determined. Thus, a study should be conducted on such soil to determine the effects of biochar-dairy manure application on soil quality, crop production and quality, nitrate leaching and GHG emissions.

6.4.2. Effects of biochar on soil microbial communities

In this study, biochar application improved soil fertility, increased soil pH, and improved nutrients retention through cations adsorption (particularly N), enhanced crop growth and productivity. Crop growth and production can also be affected by soil microorganisms (e.g., bacteria and fungi). Biochar has also shown changes in soil microbial communities, structure, and abundance (Kim et al., 2007; Lehmann et al., 2011; Liang et al., 2010; O'Neill et al., 2009; Yang et al., 2018). However, there is not much attention regarding the impact of biochar application on microbial communities in the Newfoundland podzolic soil. Thus, further research is needed to check the effects of biochar on soil microorganisms under field conditions in the cool climatic region of Newfoundland.

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