EFFECT OF BIOCHAR ON THE PHYSICOCHEMICAL PROPERTIES AND NITROGEN TRANSPORT OF PODZOLIC SOIL IN A BOREAL ECOSYSTEM

By

Ratnajit Saha

A thesis submitted to the School of Graduate Studies

in partial fulfillment of the requirement for the degree of

Master of Science

Environmental Science Program

Memorial University of Newfoundland

August 2020

St. John’s, Newfoundland, Canada

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Approved:

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Supervisor (Dr. Lakshman Galagedara)

Date

Committee member

Dr. Raymond Thomas

Dr. Kelly Hawboldt

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Abstract

This study is aimed at investigating the effects of biochar on the physicochemical properties and nitrogen transport in podzolic soils. Soil samples were collected from a research site in Pasadena, Newfoundland, Canada. Experimental treatments consisted of three types of soils {top, E-horizon and mixed soil (topsoil 2: E-horizon soil 1)}, two biochar types (granular and powder) and four biochar application rates (0%, 0.5%, 1% and 2% on a weight basis). A total of 210 most relevant and latest research articles were reviewed. Ten important physicochemical parameters of soil were investigated through a total of 72 experimental units and 54 leaching column experiments. Metadata analysis showed that only a few studies were conducted on the boreal podzolic soil. Soil porosity, field capacity and plant available water increased by 2.8%, 10%, and 12.9%, respectively compared to control when the soil was treated with powdered biochar. Nitrate leaching was reduced by 36% compared to control soil. Granular and powdered biochar were found to be hydrophobic and hydrophilic, respectively. A 2% biochar application rate showed greater impact in terms of improving hydraulic properties and reducing nitrogen leaching. The findings would be helpful to improve agricultural practices in the boreal podzolic soil.

General Summary

Poor quality soil and nutrient loss from podzolic soil in boreal ecosystem are considered important constraints in agricultural productivity. To overcome the constrain and improve soil properties, a comprehensive laboratory experiment was conducted using soil from Pynn's Brook area, two types of biochar (granular and powder) with four rates: 0, 0.5, 1 and 2% (in weight basis). Lack of experiments on physicochemical properties and nitrogen transportation, were identified through literature review. Application of biochar to podzolic soil improved soil hydraulic properties and granular biochar showed low impact compared to powder biochar in improving availability of plant available water in the tested loamy sand soil. A 2% biochar application rate in soil was found to be the best suitable one among the tested rates to improve physicochemical properties and reduce significant amount of nutrient (nitrogen) loss (as leaching) from soil. The findings would be applicable for farmers, enhance agricultural productivity as well as influence government policy for agricultural practices.

Acknowledgements

I am grateful to almighty God for my strength and grace, so that I am able to successfully complete my MSc Thesis research work. First, I would like to give special thanks and humble honor to my supervisor Dr. Lakshman Galagedara for his continuous supervision, suggestion, and advice at every step of this research. My sincere thanks to my co-supervisor Dr. Raymond Thomas and committee member Dr. Kelly Hawboldt for their guideline, constructive suggestion, and advice in conducting the study.

I am acknowledging the members of Hydrology & Agrophysics Group, Memorial University of Newfoundland- Grenfell Campus for their help and constructive comments during conducting my MSc Thesis research. Also, I am grateful to Dr. Tao Yuan, Lab Coordinator of the Boreal Ecosystem and Research Facility, Grenfell Campus, Memorial University of Newfoundland, for his valuable contribution in conducting analysis, especially on Ion Analyzer (LACHATE), Ion Chromatography, and overall coordinating activities in the lab. I am thankful to Dr. Muhammad Nadeem and Dr. Yeukai Katanda of School of Science and the Environment, Grenfell Campus, Memorial University of Newfoundland for their support during study design and executing experiments.

My wholehearted thanks to my parents, elder sister and sister’s husband and elder brother for their encouragement and support during my study.

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List of abbreviations

BC = Biochar

BD = Bulk density

BET = Brunauer Emmett Teller

BOD = Biochemical Oxygen Demand

BSM = Biochar Stability Measurement

C = Carbon

CEC = Cation Exchange Capacity

CO_2= Carbon Dioxide

COD = Chemical Oxygen Demand

CSPP = Carbon Sequestration Policy and Program

CUE = Carbon Use Efficiency

Disease S. = Disease Susceptibility

DNA = Deoxyribonucleic Acid

DSC = Differential Scanning Calorimetry

EC = Electrical Conductivity

EDX = Energy Dispersive X-ray

EGWMP = Estimating Global Warming Mitigation Potential

ERA = Environmental Risk Assessments

FC = Field Capacity

FTIR = Fourier Transform Infrared Spectroscopy

GHG = Greenhouse Gas

HMDS = Heavy Metal Distribution System

ICP-MS = Inductively Coupled Plasma Mass Spectrometry

K = Potassium

K_{sat} = Saturated Hydraulic Conductivity

K_{unsat} = Unsaturated Hydraulic Conductivity

LECA = Lightweight Expanded Clay Aggregation

LN = Leaf Nutrient

LP = Leaf Porometry

LVFR = Leachate Volume and Flow Rate

MCUE = Microbial Carbon Use Efficiency

mg L^{-1} = Milligram Per Liter

N = Nitrogen

NH_4^+= Ammonia

NMR = Nuclear Magnetic Resonance

NO_3^- = Nitrate

NPK = Nitrogen, Phosphorous and Potassium

NRI = Nitrogen Recovery Index

NUE = Nitrogen Use Efficiency

NUT = Nutrient Uptake

O&G = Oil and Gas

OC = Organic Carbon

OFMSW = Organic Fraction of Municipal Solid Waste

OM = Organic Matter

OMD = Organic Matter Decomposition

P = Phosphorous

PAHs = Polycyclic Aromatic Hydrocarbons

PAW = Plant Available Water

PCA = Principal Component Analysis

PEPM = Plant Eco-physiological Measurements

PLFAs = Phospholipid Fatty Acids

POME = Palm Oil Mill Effluent

RE = Relative Error

RMSE = Root Mean Square Error

RNA = Ribonucleic Acid

SEM = Scanning Electron Microscopy

SHP = Simulating Hydrological Process

SMC = Soil Moisture Curve

SOC = Soil Organic Carbon

SSA = Specific Surface Area

SWRC = Soil Water Retention Curve

TC = Total Carbon

TGA = Thermal Gravimetric Analysis

THPs = Total Petroleum Hydrocarbons

TN = Total Nitrogen

TPH = Total Petroleum Hydrocarbon

T-RFLP = Terminal Restriction Fragment Length Polymorphism

TSS = Total Suspended Solid

VFCWs = Vertical Flow Constructed Wetlands

VPHs = Volatile Petroleum Hydrocarbons

VSMC= Volumetric Soil Moisture Content

w/w = Weight/Weight

WHC = Water Holding Capacity

WR = Water Repellency

XPS = X–ray Photoelectron Spectroscopy

XRD = X-ray Diffraction

Chapter One

Introduction

1.1 Background and rationale

Recent reports in the literature indicate biochar application research across various sectors has been increasing steadily over the last 10 years (Mašeka et al., 2018). Peer-reviewed studies suggested that biochar can improve soil health (soil physical, chemical, and biological properties) and agricultural productivity through increasing nutrient retention, and soil fertility (Amin et al., 2016; Xiong et al., 2017). Biochar application in the soil is also well recognized as a useful potential climate change mitigation strategy (Ashiq et al., 2020; Woolf et al., 2010). Specifically, this mitigation strategy includes decreased erosion potential (Batista et al., 2018), remediation of contaminated water or soil (Han et al., 2013; Kumar et al., 2018; Yuan et al., 2017), and improved agricultural production and ecosystem sustainability (Hardie et al., 2014; Suliman et al., 2017).

In the boreal ecosystem, a cool climate with a short crop growing season is considered a critical limitation to agricultural productivity (Hansen et al., 2016; Hagemann et al., 2017; Jeffery et al., 2011). Other major factors considered for low productivity are low soil pH and fertility, uneven distribution of rainfall (Nadeem et al., 2019), and leaching of the applied nutrients from the root zone which consists of A-horizon (plow layer or topsoil) and E-horizon. A four-year field experiment by Haider et al. (2017) reported that biochar treated soil significantly reduced the amount of nitrate (NO_3^-) leaching and improved the soil moisture content in sandy soil. From the leaching zone of a soil profile, both NO_3^- and ammonia (NH_4^+) leach out, and crops do not have adequate nutrients. Improving soil quality and retaining more nutrients for crops are essential to help ensure food and agricultural quality in a world with a rising population in the boreal regions (Gundale et al., 2016). Modern scientific literature is replete with examples of biochar's ability to improve soil physicochemical properties and agricultural production. Only a small number of studies have been conducted on biochar amendment to improve the soil performance including physicochemical properties of podzolic soil in boreal climates or ecosystems (Altdorff et al., 2019; Ashiq et al., 2020; Vermooten et al., 2019; Wanniarachchi et al., 2019). It is important to note that boreal ecosystem covers approximately 11% of the terrestrial land surface on Earth (Gundale et al., 2016).

Almost all the peer-reviewed studies evaluate a specific application of biochar, such as effects on soil, solute transport, contaminated soil remediation, etc., without having any comprehensive details of merits-demerits, impacts, limitations, and way forward for further studies (Tammeorg et al., 2016). Also, no studies were conducted on biochar application with specific details, co-benefits, environmental sustainability context, and identifying the knowledge gap on the prioritized experiments that need to be done for the overall ecosystem sustainability. However, in the agricultural field, granular and powdered biochar types are commonly used. Biochar stability in agricultural practices and the mechanism of alteration of physicochemical properties in acidic soils as well as the reduction in nitrogen loss from the leaching zone have not been investigated (Rechberger et al., 2017). There is very little information in the current scientific literature on how these modulations affect podzolic soil performance and crop production in boreal ecosystem. Does biochar application retain N-fertilizer (a form of NO_3^- and NH_4^+) on podzolic soil in boreal ecosystem? This has not been yet investigated. There is lack of studies on biochar application in acidic soil and knowledge deficiency on how biochar helps to improve soil physicochemical properties and how much N can be retained by biochar amendment on podzolic soil in boreal ecosystem. Thus, I intended to apply biochar on podzolic soil to investigate the improvement of physicochemical properties and ability to retain N in boreal ecosystem.

The Environmental Science Program at the Memorial University of Newfoundland is an interdisciplinary graduate program. Graduate research is focused on current environmental issues, solving problems, further advancement, and contribution to provincial and federal government policies. Enhancement of agricultural practices by improving soil quality and agricultural production are the prime concerns in Newfoundland. Because around 90% of food and food products are coming from outside of the province, most of the areas are hilly and covered with rock, soils are extremely acidic (boreal podzolic soil) and crop growing season is very short. Besides, expanding global populations in boreal regions necessitate the need for increase agriculture production to reduce challenges with food security. It is important to conduct a scientific investigation to know how biochar application improve soil quality such as physicochemical properties of soil and retain more nitrogen (as a nutrient) on podzolic soil in boreal ecosystem. That could improve agricultural production on podzolic soil in boreal ecosystem.

1.2 Objective of the thesis

The overarching hypotheses of the study were "application of biochar to podzolic soil will improve soil hydraulic properties that helps to increase plant available water in the root zone", "granular biochar is less efficient than powder biochar in improving plant available water that will explain hydrophilic or hydrophobic characteristics of biochar", and "biochar amendment in podzolic soil capable to retain more N and that will indicate enrichment of nutrients in the root zone". The study is aimed to investigate the effects of biochar on the physicochemical properties and N transport of podzolic soil in boreal ecosystem.

The specific objectives of the study were:

1. To identify the knowledge gaps related to biochar application in improving agricultural production systems, environmental sustainability and provide information for addressing the future direction of research on biochar application based on the current findings in the literature, especially in regard to podzolic soil in boreal ecosystem.

2. To investigate the influence of different types and rates of biochar on the physicochemical properties of podzolic soil.

3. To examine the effect of biochar on N transport and hydraulic properties through a simulation study of podzolic soil in boreal ecosystem.

It is expected that the study findings would significantly improve the understanding of biochar application as a soil amendment to improve the physicochemical properties of soil and retain more nutrients in podzolic soil. Also, the findings would be a road map for further scientific exploration of biochar application in different sectors, especially in the agricultural sector. The expected findings would be applicable for farmers to support increased agricultural productivity as well as guide to decision and policies for sustainable agricultural practices.

1.3 Thesis organization

The thesis is presented in manuscript style and divided into five chapters. The thesis has a general introduction chapter, three stand-alone chapters (manuscript format) including abstract, introduction, methodology, results, discussion, conclusion, and references, and overall conclusion chapter. To meet the specific objectives in each chapter, I have conducted extensive literature review, a series of important experiments following standard experimental protocols. All three study chapters were focused to meet the overall objective of the thesis.

Chapter one: This is the introduction chapter of the thesis. It provides the background information, rationale, and objective of the thesis.

Chapter two: This is study one based on literature review of most relevant and recently published articles. The title of the chapter is “Effects of biochar on agricultural and environmental sustainability: A review”. The findings of the literature review indicated the knowledge gap and types of experiment that needs to be done in biochar application-based studies.

Chapter three: The content of this chapter is study two. The title of the chapter is "Investigating the influence of biochar amendment on the physicochemical properties of podzolic soil". The experiment results indicated that the best combination of biochar types and rates with soil for improving physicochemical properties of podzolic soil.

Chapter four: This chapter covers study three. The title of the chapter is "Effect of biochar on nitrogen transport and hydraulic properties of podzolic soil in boreal ecosystem". This chapter described the role of biochar amendment on nitrate (NO_3^-) and ammonia (NH_4^+) retention. Simulation of hydraulic properties of biochar amended podzolic soil was done using Hydrous 1D.

Chapter five: This chapter present an overall concise discussion on the three study findings and conclusion. Also, this chapter provides the recommendations for further studies.

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Co-authorship statement for study one

The study entitled “Effects of biochar on agricultural and environmental sustainability: A review” has been submitted to the *Journal of Cleaner Production* on August 2020 (Ms. Ref. No.: JCLEPRO-D-20-17314). After submission, the manuscript was sent for the peer-review. Ratnajit Saha, the thesis author was the primary and corresponding author of this manuscript. Ratnajit Saha identified the research topic, collected all the relevant articles from reputed journals, analyzed metadata and all the analysis, graphical representation of the dataset and prepared the manuscript. Dr. Lakshman Galagedara (supervisor) was the second author, provided guideline of metadata analysis and term map preparation, contributed to review and editing, and overall supervision of the manuscript. Dr. Raymond Thomas (co-supervisor) was the third author of this manuscript. Dr. Thomas suggested for the schematic diagram – how biochar application ensure agricultural and environmental sustainability, also contributed to organization, review and editing of the manuscript. Dr. Kelly Hawboldt (co-supervisor) was the fourth author of this manuscript. Dr. Kelly gave specific guidelines and structure of the manuscript as well as contributed several times review and editing of the manuscript.

Chapter Two

Study one

Effects of biochar on agricultural and environmental sustainability: A review

Ratnajit Saha[1], Lakshman Galagedara[1,2], Raymond Thomas[2], and Kelly Hawboldt[3]

[1]Environmental Science Program, Faculty of Science, Memorial University of Newfoundland, St. John’s, NL, A1B 3X7, Canada

[2]School of Science and the Environment, Memorial University of Newfoundland, Corner Brook, NL, A2H 5G4, Canada

[3]Department of Process Engineering, Memorial University of Newfoundland, St. John's, NL, A1C 5S7, Canada

Abstract

Biochar, a biomass-derived carbon, is used in various applications, including agriculture, forestry, water purification, and wastewater treatment. In applications related to agriculture and environmental protection, biochar can: (i) improve physicochemical and biological properties of soil, sequester carbon, enhance plant growth, physiological functions and diversify of microbial communities, (ii) control nutrient transport in soil, and (iii) improve compost quality. The overall aim of this review was to explore the applications of biochar in agricultural and environmental protection. A total of 210 of the most relevant published articles related to the impacts and limitations of biochar application in the agricultural and environmental protection sectors were reviewed. A metadata analysis (study location, goal, and outcome) of the studies was done. The research showed that most of the studies were conducted in tropical ecosystems, with only a few studies were done in higher latitude areas, especially in podzolic soils under boreal climates. Most studies suggested that the biochar amendment positively impacted the soil's physicochemical properties and reduced nitrogen leaching from soils. Biochar amendment of soil showed positive impacts on plant growth, including improved production and productivity, enhanced carbon sequestration, and reduced greenhouse gas emissions. Biochar helps to adsorb cadmium, copper, lead, zinc, arsenic, nickel, and mercury from contaminated soils and wastewater. However, the bulk of the extant studies have been conducted over short periods. In contrast, accurate assessment of agricultural implications and the degree of carbon sequestration requires extended study periods consisting of several seasons. Furthermore, the ecosystem response to biochar application is a function of climatic and other conditions, and therefore biochar application (loading) is not clearly defined in many regions across the world. This review-based study explored the priority areas of studies conducted to assess the effects of biochar applications and that will help to explore knowledge gap in conducting experiments to the researcher for further scientific exploration of biochar application for the improvement of agricultural practices and environmental sustainability.

Keywords: Biochar application, the impact of biochar, experimental approaches, agriculture, environment, sustainability.

2.1 Introduction

Biochar is a carbon-rich product. It is produced commercially by the pyrolysis of a wide variety of biomasses such as residues from agriculture and forestry-based materials, organic waste, animal manure, municipal solid, and semi-solid waste. This process occurs in the absence of oxygen or in very low oxygen concentrations, at moderate to high temperatures (Amin et al., 2016; Ojeda et al., 2015; Shaaban et al., 2018). Biochar characteristics are primarily influenced by the feedstock properties, processing temperature and time as well as heating rate (Amin et al., 2016). As such, biochar is very heterogeneous in its chemical and physical composition. The pore size of biochar depends on pretreatment and pyrolysis operating conditions and can vary from nano (<0.9 nm), micro (<2 nm) to macro (>50 nm) pores (Shaaban et al., 2018). The nutrient retention capacity of biochar varies according to surface properties of biochar (Atkinson et al., 2010). The molecular structure of biochar shows a high degree of chemical and physical stability (Atkinson et al., 2010).

As noted above, biochar studies covered areas such as: (i) improvement of soil health (soil physical, chemical, and biological properties) and agricultural productivity through increasing nutrient retention, interactions, and soil fertility; (ii) climate change adaptation and mitigation; (iii) soil remediation; and (iv) wastewater treatment; among other (Amin et al., 2016; Xiong et al., 2017). Biochar application to soil found effective on soil physicochemical properties, nitrogen leaching, soil fertility, plant growth, greenhouse gas emission, remediation of contaminants, etc. (Shaaban et al., 2018; Woolf et al., 2010; Zhang et al., 2018). Biochar application in agricultural practices can play a vital role in altering nutrients dynamics, improving soil health, microbial functions, soil fertilization as well as remediation of contaminants from soil, and wastewater (Guo et al., 2020; Xie et al., 2013).

Ecosystem sustainability can be defined as the ecosystem's capacity to maintain its essential functions and processes while dealing with quantified change in its environmental condition (Dizdaroglu et al., 2012; Stevenson, 1997). An ecosystem relies on soil biota, especially bacteria and fungi, nutrient cycling, soil-water function (water balance), and plant growth. The application of biochar in agriculture can also provide a strategy for climate change mitigation. It acts as a carbon sink (Arbestain et al., 2014) and improves soil water quality (Oliveira et al., 2017). A comprehensive assessment, including examining the physicochemical and microbial properties of compost, can help us better understand the effect of a biochar amendment on the composting process (Agyarko-M et al., 2017; Du et al., 2019). The process of heavy metals generations or cycling in response to changes in the environmental condition that could become a serious global issue in food security and population health (Vithanage et al., 2017). Decreasing heavy metal concentrations from contaminated soil is essential to sustain the ecosystem and reduce environmental health risk (Xu et al., 2018). Biochar could play an important role in heavy metal remediation and promoting ecological sustainability (Chen et al., 2018). For example, biochar application remediates contaminated soil by reducing ecotoxicity to soil-borne organisms. However, the underlying mechanisms for how biochar functionally reduces ecotoxicology in a particular climate/ ecosystem is still not well understood (Zheng et al., 2018). It is crucial to determine how biochar application can ensure agricultural and environmental sustainability in different sectors.

The bulk of the peer-reviewed published soil studies evaluate a specific application of biochar, such as effects on soil, solute transport, and contaminated soil remediation without any comprehensive details of the merits, demerits, impacts, limitations, and ways forward for further studies (Tammeorg et al., 2016). Also, no studies have been conducted on biochar application across different sectors with specific details, including co-benefits, environmental sustainability context, and identifying the knowledge gap on the prioritized experiments that need to be done for the overall ecosystem sustainability. This review work was aimed to (i) identify the knowledge gaps related to biochar application in different sectors, and (ii) explore the underlying mechanisms and limitations of biochar application pattern to enhance agricultural productivity and environmental sustainability. Overall, this information can guide policy decisions for the application of biochar for agricultural and environmental sustainability.

2.2 Methodology

In this review-based study, metadata was collected on biochar application in different sectors from peer-reviewed journals (impact factor ≥ 2). A total of 210 journal articles, focusing on biochar applications related to agriculture and the environment, were reviewed. Among them, 195 (92.9%) of the cited journal articles were published during the last ten years, and 76% of articles were published during the previous five years. The countries and specific location of experimental sites (where biochar applied) were identified through metadata analysis. Based on geographical location, the countries were divided into four regions: tropical (0° - 23.5°), temperate (23.5° - 50°), boreal (50° - 60°), and cold (60° - 90°). Studies were further divided into six sections: (1) Soil physicochemical properties; (2) Soil nutrient cycling (nitrogen transportation); (3) Plant growth, yield and biomass production; (4) Carbon sequestration in soil and greenhouse gas (GHG) emission; (5) Application in composting and microbial activities in soil; and (6) Contaminated soil, wastewater, solid and semi-solid waste remediation (Amin et al., 2016; Tammeorg et al., 2016). A term map based on the latest publications (from the last five years) was prepared using VOSvierwer (1.6.16) software to identify the most usable terms used in the co-occurrence links in the studies (Pallottino et al., 2018). Experimental approaches (including measured variables) were assessed. The prioritized experiments of biochar application in different sectors were identified to facilitate the gap analysis and explore the scope of essential investigations that need to be done in future studies. A comparative and critical review of biochar application in different sectors were done focusing on the study theme, applied methods, results/impacts, limitations, and scope of the further work to achieve this study's aims. Microsoft Excel was used to present results and ArcGIS 10 to visualize the countries' locations where the studies were conducted.

2.3 Results and discussion

2.3.1 Influence of biochar application in different sectors

2.3.1.1 Effects of biochar on physicochemical properties of soil

Metadata

Twenty-eight (28) experiment-based studies on physicochemical properties were reviewed. The bulk of the studies were conducted in the tropical and temperate (0° - 50°) regions of the northern hemisphere (Figure 2.1a). The breakdown of the studies were 18% (n=5) in China (northeast and Shanghai), 11% (n=3) in the USA (around the Pacific Northwest region), 7% (n=2) in Brazil (dry and northeast region), and 7% (n=2) in Taiwan (southern region). Australia, New Zealand, Canada (Pynn's Brook, Newfoundland), Columbia, Costa Rica, Finland, Ghana, Korea, Germany, Poland, Norway, Saudi Arabia, South Korea, Sri Lanka, and Sweden each contributed one study (4% per country).

Impacts, limitations, and scope of further work

Many studies focused on determining the impact of biochar amendment on soil properties, such as soil pH, electrical conductivity (EC), cation exchange capacity (CEC), total carbon (TC), total nitrogen (TN), bulk density (BD), water repellency (WR), porosity, field capacity (FC), water holding capacity (WHC), saturated and unsaturated hydraulic conductivity (K_{sat} and K_{unsat}) and evaporation (Table 2.1). Many studies indicated a range of positive impacts of biochar on soil physicochemical properties. These studies reported that biochar treatment increased soil pH, EC, CEC, TC, TN, WR, Porosity, FC, WHC, and decreased BD, K_{sat} and K_{unsat} (Table 2.1). Biochar treatment is attributed to creating larger pore spaces (macro-porosity and meso-porosity) and improve aggregate stability (Herath et al., 2013; Hardie et al., 2014). Biochar macro-aggregate formation in soil plays a vital role in reducing soil erosion potentials (Jien and Wang, 2013) as well as increased water retention capacity, especially in coarse-textured soils (Villagra-Mendozaa and Horn, 2018). Several studies also examined important biochar characteristics such as SSA, pore diameter, pore-volume, and chemical composition to determine how biochar influences soil conditions. Biochar particle size (surface area) has a significant influence on soil hydraulic properties. For example, the application of smaller diameter biochar (<0.5 μm) in soil can reduce the soil pore volume by blocking natural pore spaces. In contrast, higher diameter biochar (0.5-500 μm) amendment in soil can increase the soil pore volume as it has a higher volume and occupies more space (Zhang et al., 2016; Głąb et al., 2016).

Table 2.1: Effects of biochar on physicochemical properties of soil

Studies on	**Applied methods**	**Results/Impacts**	**Sources**
Physical properties	BC rate: [0.5, 1, 2, and 4% (w/w)], [0, 2.5, 5.0, 7.5, and 10% (w/w)], [0, 15, 22 and 45 Mg ha^{-1}]; [0, 3, 6, 9 and 12 kg·m^{-2}]; [2.5 and 5 Mg ha^{-1}]; [(1, 2.5, and 5 % (w/w)]; [4, 8, 12 and 16 Mg ha^{-1}], BC types: different, SEM analysis; BET surface area; van Genuchten model	Increased porosity (macro-porosity, and meso-porosity), field capacity, total pore volume, permeability (more wet), plant available water, water repellency, water retention; aggregate stability, soil water storage capacities and soil moisture, water use efficiency (increased 50%), and decreased bulk density, K_{sat}.	Abel et al., 2013; Hardie et al., 2014; Głąb et al., 2016; Laghari et al., 2015; Suliman et al., 2017; Herath et al., 2013; Igalavithana et al., 2017; Ibrahim et al., 2013; Wanniarachchi et al., 2019; Ojeda et al., 2015; Zhang et al., 2016; Obia et al., 2016; Fu et al., 2019; Yeboah et al., 2016; Rattanakam et al., 2017; Zheng et al., 2019; Lima et al., 2018
Chemical properties	BC rate: [0, 3.5, 7.0, and 10.5 Mg ha^{-1}]; [0, 0.1, 0.5 and 1% (w/w)]; [0, 5, 10, 20 and 30 Mg ha^{-1}], different types of factors, randomized design, SMC monitoring	Increased pH, CEC, K, P, TN, OC, carbon/nitrogen ratio, available P_2O_5 and reduced acidity and risk of salinization	Pimenta et al., 2019; Zhao et al., 2015; Kang et al., 2018; Zheng et al., 2019; Gamage et al., 2016; Tammeorg et al., 2014

Biological properties	Four factors: control, biochar, straw, chemical fertilizers	Increased soil microbial biomass carbon and nitrogen.	Zheng et al., 2019
Environmental sustainability	BC rate: [0, 2.5, and 5% (w/w)]; [0, 5, 10, and 20 g kg^{-1}]; Simulated rainfall (80 mm h^{-1}); randomized block design	Improved physicochemical and biological properties of highly weathered soils, increased potentiality to overcome extreme hydrological conditions and boreal (agricultural) soil fertility and demonstrated net negative effect of global warming potential.	Jien and Wang, 2013; Villagra-M. and Horn, 2018; Gundale et al., 2016; Laird et al., 2010; Mukherjee et al., 2014

Note: BC–Biochar; BD–Bulk Density; BET–Brunauer Emmett Teller; C–Carbon; CEC–Cation Exchange Capacity; K_{sat}–Saturated hydraulic conductivity; K–Potassium; OC– Organic carbon; P–Phosphorous; SEM–Scanning electron microscopy; SMC–Soil moisture curve; w/w–weight/weight.

Several studies reported no significant differences was observed between the physicochemical properties of biochar amended and non-amended soils. The biochar application pattern determines the hydrological properties of soil (Ojeda et al., 2015). Rattanakam et al. (2017) suggested that biochar characteristics (e.g., hydrophobicity or hydrophilicity) are not the only governing factor in improving soil moisture content. Table 2.1 summarizes the effects of different biochar rates on soil's physicochemical properties. The best treatment combination of biochar-soil for each specific soil type is currently not well defined. However, it is essential to develop ideal combinations for the best agricultural practices. Therefore, specific focus needs to be directed on biochar production design and application rate with respect to specific soil types to improve soil health. Most of the studies were conducted within a short period such as less than one year, which is not sufficient (in most cases) to complete a comprehensive assessment of biochar effects on agriculture and the environment. Long-term studies (considering practical environmental conditions) with robust study-design are needed to investigate biochar's long-term impact on soil physicochemical properties (Xie et al., 2013).

Biochar treated soil needs further analysis at macro-scale and on the capillary development of heterogeneous moisture patterns in different types of soil (Ojeda et al., 2015). Many studies were conducted in different geographic regions focusing on sandy and loamy soils. Only a few studies were found on the biochar application on podzolic soils in boreal ecosystems (Table 2.1 and Figure 2.1a). Considering the population expansion in boreal regions (as the global population grows), more investigation needs to be focused on determining how biochar applications can improve podzolic soils' performance and health in boreal regions to sustain the extension of agricultural practices.

2.3.1.2 Effects of biochar on soil nutrient cycling (nitrogen transport)

Metadata

Twenty-eight (28) studies were reviewed, from different regions, on the effects of biochar on nutrient transport in different soil types. Most of the studies were conducted in tropical region of the northern hemisphere. Only a few studies (n=5) were done at higher latitudes (approximately 50° N), and most of the studies were conducted in temperate ecosystems (Figure 2.1b). Among the studies, 46% (n=13) were conducted in China (e.g. Beijing, Shanxi, Guizhou, Hubei, Liaoning). Only two (2) studies were conducted in Canada (Southern Ontario and Pasadena, Newfoundland).

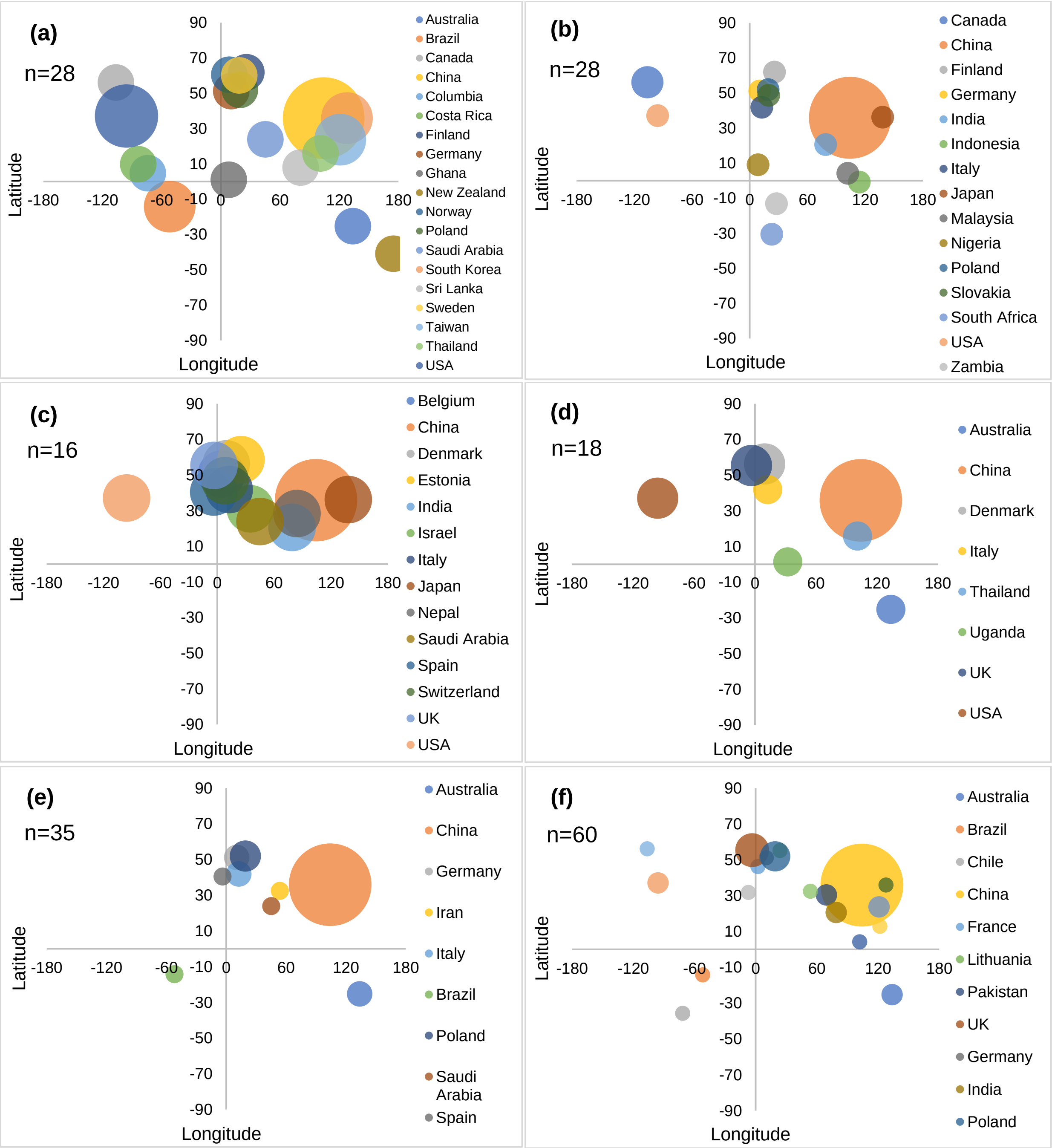


Table 2.1: Total number of experimental studies were conducted on biochar application covering different areas such as: (a) Physicochemical properties, (b) Soil nutrient cycling (nitrogen transport), (c) Plant growth, yield and biomass production, (d) Carbon sequestration and GHG emission, (e) Composting and microbial activities, and (f) Contaminated soil, wastewater, solid and semi-solid waste remediation

Impacts, limitations, and scope of further work

Several studies have been conducted to assess the effect of biochar amendment on solute transport in different soil types. Clough et al. (2013) explain how biochar influences cation-anion exchange reaction, nitrogen (N) fertilizer adsorption, and N immobilization in the biochar amended soils. Nguyen et al. (2017) conducted a meta-analysis to investigate the effect of biochar properties (pore size and distribution pattern) and the interaction between biochar, soil, and fertilization. In most of the studies, leaching column experiments were done in the laboratory. Only a limited number of studies were conducted on N transportation in the agricultural field with large-scale experiments (Dil et al., 2014) (Table 2.2). Biochar amendment in the soil showed a significant influence on the reduction of N leaching from the leaching zone (a combination of A and E-horizon in the soil profile) (Li et al., 2018) and the overall N cycling in agricultural ecosystems (Nguyen et al., 2017; Gul and Whalen, 2016; Clough et al., 2013). Many N related studies (n=12) used standard urea or ammonium nitrate fertilizer in the experiment. Biochar amendment in soil significantly reduced nitrate and ammonia leaching from the soils (Table 2.2). Sun et al. (2017) recommended that biochar treatment in the soil as one of the best options for beneficial agronomic management and long-term nutrient retention in the soil.

In the leaching column experiment, the leaching rate depends on factors such as chemical and physical properties of biochar, biochar application rates, location and depth of the leaching zone, soil texture, amount and types of fertilizer applied, rainfall volume and intensity, and crop type. In different geographic regions, biochar application on the forest soil showed approximately 10% reduction of N leaching (Atkinson et al., 2010; Yao et al., 2012). However, N dynamics in agricultural and forest soil (especially N cycling) is not yet fully understood. A comprehensive study considering N use efficiency, ecotoxicological assessment, runoff, precipitation, and simulation of N leaching from soil has not been done across different ecosystems (Mo'allim et al., 2018; Tafteh and Sepaskhah, 2012). It is essential to know how much N can be retained in the soil by applying biochar. In Canada, only a few studies have been conducted on nutrient leaching from agricultural fields, especially on podzolic soils in boreal ecosystem.

Table 2.2: Effects of biochar on soil nutrient cycling (nitrogen transport)

Studies on	**Applied methods**	**Results/Impacts**	**Sources**
Nutrient leaching	Leaching column, Column percolation and Pot experiments, BC rate: [1, 2 and 4% (w/w)]; [2, 4 and 8% (w/w)]; [0.5, 1, 2 and 4% (w/w)]; [0, 3, 9, and 15% (w/w)]; [2.5% (w/w)]; [0, 0.5, 2.5 and 10% (w/w)]; [0, 2, 4 and 8% (w/w)]; [0, 4, 8 and 16 g kg^{-1}]; [0, 15, 30, and 45 Mg ha^{-1}], BC types: two flow rates (12 and 36 mL/h), 6 weeks simulating heavy winter rainfall, Freundlich sorption isotherm model	Nitrogen leaching was reduced (18.8- 20.2%); Decreased the available nitrogen leaching and storage (14.96 to 21.76 mg·kg^{-1}). Reduced nitrogen loss in podzolic sandy and loamy soil. Biochar application found an effective management option to mitigate nitrate leaching and recovered exchangeability.	Naka et al., 2016; Han et al., 2016; Libutti et al., 2016; Sika and Hardie, 2014; Li et al., 2018a; Li et al., 2018b; Zhang et al., 2017; Sun et al., 2017; Widowati et al.*, 2014;* Xu et al., 2016; Yao et ail., 2012
Nitrogen use efficiency	BC rates: [2 and 4% (w/w)]; [0, 10, 20 Mg ha^{-1}]; [0, 3, 6, and 12 Mg ha^{-1}]; Urea rate: [0, 25, 50, 75 and 100% (w/w)]; [0, 30, 60 and 90 nitrogen kg ha^{-1}]; [0, 40, 80 kg ha^{-1}]; field and Incubation experiments	Increased nitrogen and nutrients use efficiency and availability of P and K in tropical acidic soil. Significant interactive effect found between BC and nitrogen fertilizer (on Alfisol)	Liu et al., 2017; Maru et al., 2015; Oladele et al., 2019; Šimanský et al., 2018

Co-benefit	Field and laboratory experiment; BC rates: [0–10% (w/w)]; [10, 20, 40, 80 Mg ha^{-1}]; [10, 20 and 30 Mg ha^{-1}]; Different types of biochar and soil; Randomized design; Hydrus 1D simulations	Decreased net nitrogen mineralization and urease activity. Increased fertilizer rates (especially concentrations of P, K, Mg, and Fe) and no negative effects were observed. Found a positive effect in Boreal Podzol soil. Reduced cumulative concentration load in runoff of nutrients.	Altdorff et al., 2019; Dil et al., 2014; Kraska et al., 2016; Kuoppamäki et al., 2016; Luo et al., 2017; Martinsen et al., 2014; Singh et al., 2018;
Environmental sustainability	Leaching column and extraction experiments; different types of biochar; ^{15}N-enriched biochar and fertilizer urea; runoff volumes and ratios monitored	Exhibited control erosion (natural) potential and recommended for agronomic managements, efficient nitrate loss and nitrogen retention in the ecosystem, and long-term nutrient retained in the soil. Decreased CH_4 emissions control in the field.	Hagemann et al., 2017; Li et al., 2017; Xie et al., 2013; Yuan et al., 2016

Note: BC–Biochar; CEC–Cation Exchange Capacity; N–Nitrogen; K–Potassium; NPK–Nitrogen, Phosphorous, and Potassium; w/w–weight/weight

2.3.1.3 Effect of biochar on plant growth, yield, and biomass production

Metadata

Sixteen (16) published articles on plant growth were reviewed. All the studies were conducted in tropical and temperate regions of the northern hemisphere, with only a few in higher latitude regions. The studies on plant growth experiments were conducted in China, USA (Washington State), UK (Wales), Japan (Tottori University), Switzerland (Ayent, Valais), India (Lucknow, Uttar Pradesh), and other locations (see Figure 2.1c).

Impacts, limitations, and scope of further work

Several study findings recommended biochar amendment in the soil for increasing inland agricultural productivity (Jeffery et al., 2011; De Tender et al., 2016). Almost all studies reported that biochar amendment in soils significantly influenced plants' growth, biomass production, and land productivity (Kasak et al., 2018; Williams et al., 2016). The study by Graber et al. (2010), biochar applications positively enhanced leaf size and tomatoes' plant height (Graber et al., 2010). Pandit et al. (2018) reported that nutrient stress alleviation could be a crucial the reason why plant growth was positively affected by the biochar application. Biochar helps in seed germination in dry conditions by mixing ratios of 1:1, 2:1, and 4:1 (w/w) by seed weight (Williams et al., 2016). One of the essential co-benefits of biochar application for plant growth is the positive economic effects, especially in organic farming (Table 2.3). Furthermore, biochar amendment in soil was found beneficial for plant growth, especially in scenarios where the availability of plant nutrient is limited (De Tender et al., 2016; Jones et al., 2012; Jeffery et al., 2011).

Again, the bulk of the studies were conducted over a short-term basis and under laboratory conditions. A few studies were done in the long-term over 2-3 years (consecutive field trials). Usually, long-term studies gave more precise information for agronomic management (Jones et al., 2012). In arid and semi-arid regions, seeding effectively restores vegetation under limited soil moisture and high-temperature conditions. A co-benefit of biochar application on plant development is that biochar lowered the plant's heavy metal uptake (Shaaban et al., 2018). Besides, biochar is applied different ways for plant growth and increase productivity. Biochar seed coating help in the restoration of vegetation, influences water that is available to plants at the root zone, and plant growth in different types of soil – the mechanism is yet unknown (Yang et al., 2019; Liu et al., 2018; Usman et al., 2016; Williams et al., 2016; Jones et al., 2012). Also, minimal knowledge exists on the threshold amounts of biochar needed for there to be positive agronomic effects (Schulz et al., 2014).

Table 2.3: Effect of biochar on plant growth, yield, and biomass production

Studies on	**Applied methods**	**Results/Impacts**	**Sources**
Plant growth	Field trial; BC rates: [0, 0.5 and 2% (w/w)]; [1–5% (w/w)]; NPK fertilizer: different dosages.	Significant plant growth (especially in limited nutrient soil condition) and enhanced plant height and leaf size. Improved available nutrients and moisture retention.	De Tender et al., 2016; Graber et al., 2010; Pandit et al., 2018
Plant productivity	BC rates: [0, 10 and 40 Mg ha^{-1}]; [0, 4.0 and 8.0% (w/w)]; [0, 10, 15 and 20 Mg ha^{-1}]; [0, 1.5 and 15 Mg ha^{-1}]; plant tissue analysis; emissions monitored by closed chamber method; lightweight expanded clay aggregation (LECA)	Enhanced crop productivity (even in salty soil); effective plant development and increased biomass yield. Help in root development to capture available micro and macronutrients	Hansen et al., 2016; Kasak et al., 2018; Paneque et al., 2016; Singha et al., 2018; Usman et al., 2016; Uzoma et al., 2011; Zhang et al., 2010
Germination of seeds	BC characterized by FTIR, ^{13}C, and ^{1}H NMR; BC coating used; agronomic traits, growth-related genes, and proteins used as markers; evaluate germination	Facilitate germination in dry condition and seedling growth promoted as well as improved root weight.	Sun et al., 2017; Williams et al., 2016;

			Yang et al., 2019
Co-benefit	Biochar characterization and nutrient saturation; greenhouse experiment; plant tissue analysis	The positive economic effect found in organic farming;	Kizito et al., 2019; Schmidt et al., 2014
Environmental sustainability	BC rates: 0, 25 and 50 Mg ha^{-1}, crop performance assessed in a specific interval	Significantly increased plant performance and changed agroecosystem functioning.	Jones et al., 2012

Note: BC–Biochar; C–Carbon; GH–Greenhouse; FTIR–Fourier-transform infrared spectroscopy; LECA–Lightweight expanded clay aggregation; NPK–Nitrogen, Phosphorous, and Potassium; NMR– Nuclear magnetic resonance; w/w–weight/weight.

2.3.1.4 Effect of biochar on carbon sequestration in soil and GHG emission

Metadata

Eighteen (18) experiment-based studies on the effect of biochar on carbon (C) sequestration and GHG emission were reviewed. Most of the studies (n=12) were conducted in the temperate regions, and only a few studies were found in the tropical (n=2) and boreal regions (n=4). Among 18 studies, 44% (n=8) were conducted in China, one was done in Australia (samples collected from vineyard, vegetable cultivated, arable and sports areas), and another study was done in Italy (data were collected in two consecutive seasons in the Near Pistoia area) (Figure 2.1d).

Impacts, limitations, and scope of further work

In soil, C: N is essential, especially for soil health and climate change issues (Castaldi et al., 2011; Lu et al., 2019; Luo and Gu, 2016; Sheng and Zhu, 2018). Experiments on biochar amendments showed that this can reduce C mineralization in agricultural fields (Bolan et al., 2012; Yousaf et al., 2017) and decrease CO_2 emissions (Sheng and Zhu, 2018). However, Mašek et al. (2019) suggested that adding 256 µmol g^{-1} potassium concentration at the time of biochar production process (pyrolysis) could increase C sequestration potential by up to 45%. If biochar C sequestration potential could increase by that percentage, the global C sequestration potential could be reduced 2.6 Gt CO_2-carbon(eq) yr^{-1}. Biochar characteristics like porosity and SSA have a huge impact on C sequestration (Hansen et al., 2015). Ashiq et al. (2020) mentioned that a higher rate of biochar application reduces more GHG emissions from biochar amended soil. Besides, biochar's biophysical potential has been observed in farming systems (Bolan et al., 2012) and showed a positive impact on soil health. If the biochar market price is low, then the biochar amendment in soil could be beneficial. Index-based (R50) degradation of biochar and economic value of C sequestration in the biochar amended soil was found to be suitable in the context of global warming (Table 2.4).

Wang and Wang (2019) suggested that the C sequestration experiment should be investigated after a certain time period to learn the results' consistency. However, C sequestration potential in the farming system is not comprehensively investigated (Roobroeck et al., 2019). C sequestration in soils might persist for a long time, and there could be an impact on downstream environments. A long-term study design with useful C sequestration measurement is essential to understand biochar's influence on the ecosystem.

Table 2.4: Effect of biochar on carbon sequestration in soil and GHG emission

Studies on	Applied methods	Results/Impacts	Sources
Carbon sequestration	BC rate: [0, 3.2, 16 and 32 Mg ha^{-1}]; BC characterization (SEM, BET), incubation, respiration experiments, stable isotope ($d^{13}C$) approach, carbon mineralization compared to biowaste	Useful for carbon sequestration in the soil as well as soil structure, nutrient and water retention. Reduced carbon-mineralization (sorption of organic carbon) and increased stabilization of carbon. Avoid degradation or erosion of soil.	Bolan et al., 2012; Hansen et al., 2015; Hansen et al., 2016; Lin et al., 2015; Sheng et al., 2016; Wu et al., 2016; Yousaf et al., 2017
Global warming potential	BC rates: [0.5%, 1%, 2 and 5% (w/w)]; [6.25, 12.50, 18.75 and 25.00 Mg ha^{-1}]; [low – 2%, 4% and 6%; and high– 8%, 12% and 18% (w/w)]; Raman spectra measurements; stable carbon content analysis; randomized complete block design	Good options for the mitigation of climate change. Decrease greenhouse gas (CO_2) emissions. Increase carbon sequestration potential up to 45% [over 2.6 Gt CO_2-carbon(eq) yr^{-1}]	Ashiq et al., 2020; Mašek et al., 2019; Sheng and Zhu, 2018; Thammasom et al., 2016
Co-benefits	BC rates: [0, 0.5, 1.0 and 2.0% (w/w)]; [0, 30, 60, and 90 Mg ha^{-1}]; [30 and 60 Mg ha^{-1}]; BC characterization; household surveys; beneficial and potential impact studies	Significant biophysical potential for carbon sequestration in farming systems observed. Positive impact on a microbiological and molecular level of the soil.	Christopher et al., 2012; Dong et al., 2018; Luo and Gu, 2016; Roobroeck et al., 2019;

			Vaccari et al., 2011
Economic value	Recalcitrance index (R50) assessment; economic model; Carbon offset price scenarios: farm profit estimated with different types of biochar	Biochar application is found to be profitable (if the market price is low or carbon offset market exists). Index-based (R50) degradation and economic model provided a suitable framework.	Galinato et al., 2011; Harvey et al., 2012

Note: BC–Biochar; BET–Brunauer-Emmett-Teller; C–Carbon; OC–Organic carbon; PLFAs–Phospholipid fatty acids; SEM–Scanning electron microscopy

2.3.1.5 Effect of biochar on composting and microbial activities in soil

Metadata (composting)

Twenty (20) experiment-based studies on the effect of biochar on composting were reviewed. Most of the studies (n=14) were conducted in the temperate region. In the boreal and tropical regions, 4 and 2 studies were carried out, respectively. Among these studies, 55% (n=11) were completed in China (across the country), and 15%(n=3) were conducted in Poland. One study was found in Australia (New South Wales) and another study in Brazil (the Federal University of Lavras, in minas Gepais State) (Figure 2.1e).

Impacts, limitations, and scope of further work (composting)

Composting is one of the most effective ways to treat various organic wastes and destroy harmful pathogens, and the converted byproduct can be used as organic fertilizer (Liu et al., 2017; Wu et al., 2017; Jain et al., 2018). Many studies recommended biochar amendment as a beneficial additive and bulking agent in composting. Several of these studies reported that biochar has positive impacts on the composting process. For example, biochar helps to increase the decomposition rate of organic matter, rate of nitrification, ecological and economic values of compost. Biochar also influence to reduce nutrient losses (Ca, Mg, N), GHG emission, and total compost processing time (Hagemann et al., 2018; Sanchez-Monedero et al., 2018; Godlewska et al., 2017; Liu et al., 2017; Malińska et al., 2014). Wang et al. (2017) found that biochar reduced a significant amount (by 27%) of N losses in the composting process. As well, the addition of biochar during composting reduced the health risk of heavy metals (Cu, Pb, Cd) in the product (Zhou et al., 2018). In different studies, the vermicompost was recommended as a growing medium because of its high-quality fertilizer properties (Ashiq et al., 2020; Malińska et al., 2017; Hagemann et al., 2018). In summary, biochar reduces compost toxicity and waste density, exhibits higher moisture content, reduces health risks of heavy metals exposure, and benefits the microbial environment (Table 2.5).

During composting, optimum dosages of biochar must be determined to ensure pollutant prevention, compost toxicity reduction, and to mitigate toxic gas emissions. Sanchez-Monedero et al. (2018) mentioned that biochar pores' structure and properties may change during the composting process (Sanchez-Monedero et al., 2018). Thus, it is essential to know how these changes occur and their impacts on the composting process. The best biochar-compost combination for the soil improvement and plant growth needs to be addressed (Hagemann et al., 2018; Godlewska et al., 2017). During composting, long-term biochar stability and C sequestration potential need to be investigated in the future.

Metadata (microbial activities in soil)

Fifteen (15) studies focusing on biochar's effects on microbial communities in soil were reviewed. Most of the studies (n=12) were conducted in the temperate regions, and only a few (n=3) studies were done in the boreal region. The identified countries where the studies were conducted include Australia (Barossa Valley Region, n=1), China (n=10), Germany (n=1), Iran (Alborz Province, n=1), and Italy (Tuscany region, n=2) (Figure 2.1e).

Impacts, limitations, and scope of further work (microbial activities in soil)

Soil microorganisms play a vital role in nutrient cycling, including C transformation and immobilization. The soil microbiome is very sensitive to environmental stresses, nutrient cycling, and impacting terrestrial ecosystem functioning (Liu et al., 2018; Rutigliano et al., 2014; Xu et al., 2018). All the studies were conducted with different biochar application rates in various soil types under laboratory or field conditions (experimental plots). Table 2.5 described the biochar amendment in soil improved microbial processes such as functional diversity of microbes, changes in bacterial community structure and composition, and increased diversity of soil bacterial communities. Khadem and Raiesi (2017) reported that biochar types, application rates, and soil texture are major influencers of the microbiological properties in the soil. Biochar stimulates nitrification and denitrification processes and functional diversity of the microbial community in soil (Rutigliano et al., 2014; Senbayram et al., 2019; Xu et al., 2014; Xu et al., 2018). As a co-benefit, biochar application improved soil quality, nutrients (AMF/SF ratio, SOC, nitrogen, and P), and OM content in the soil profile. Biochar reduces heavy metals' bioavailability, mitigates soil microorganisms' biotoxicity, and maintains microbial stability in soil (Table 2.5).

However, biochar's application could negatively impact beneficial microbes directly or indirectly (Huang et al., 2017). There is a lack of information on how C (released from biochar) stimulates biological activities (Kizito et al., 2019) in different types of soil in various ecosystems and could maximizes benefits on microbial community structure diversity. Biochar influences soil biological communities, specifically the rhizosphere microbiome which are beneficial for plant growth. In drylands, it is uncertain how long biochar affects soil microbial community and diversity (Luo et al., 2017).

Table 2.5: Effect of biochar on composting and microbial activities in soil

Studies on	Applied methods	Results/Impacts	Sources
Composting			
Composting process	BC rates: [0, 5, 10, and 20% (w/w)]; [2.5, 5 and 10% (w/w)]; [2, 4, 8 and 12% (w/w)]; [10% (v/v)]; BC characterization; 16S rRNA high-throughput sequencing	Better degradation of compost particle, improved compost quality (especially for the light humified fraction) and higher composting rate. Recommended feasible approach for biosolids composting.	Awasthi et al., 2018; Cui et al., 2016; Jain et al., 2018; Liu et al., 2017b; Malińska et al., 2016

OM composting	Laboratory experiment; BC rate: 6%, 12% and 18% (w/w); different types of BC; BC characterization (SEM); used bioreactor system	Increased organic matter decomposition (especially in increased temperature). Sometimes the addition of sludge is recommended for organic fraction degradation.	Du et al., 2019; Malińska et al., 2014; Zhang et al., 2014
Nitrogen losses	BC rates: [0, 10, 15, and 30% (w/w)]; [0, 5, 10 and 15% (w/w)]; [0, 1, 3, 5 and 7% (w/w)]; Other factors: sludge, straw, zeolite and lime	Reduce significant nitrogen losses (27%) and efficient in preserving nitrogen in mature compost that increased compost quality to attend manure standard. Mitigation of GHG emissions.	Awasthi et al., 2016; Dias et al., 2010; Liu et al., 2017a; Wang et al., 2017
Co-benefit	BC rate: 10 and 15% (w/w); 16S rRNA and 18S rDNA technology; FTIR, ^{13}C NMR, Principal Component Analysis.	Vermi-composts has good fertilizing properties and that were recommended for growing medium. No alteration on carbon speciation and sustainable, slow-release fertilizer could be produced.	Ashiq et al., 2020; Hagemann et al., 2018; Malińska et al., 2017; Waqas et al., 2018
Environmental sustainability	BC rate: 0%, 1.5%, 3% and 5% (w/w); BC types: different like sawdust charcoal and wheat straw charcoal BC.	Reduced compost toxicity, lower waste density, exhibited higher moisture content and increased health risk (Cu, Pb, Cd). Beneficial for the microbial environment.	Agyarko-M. et al., 2017; Malinowski et al., 2019; Zhou et al., 2018
Microbial community			
Composition / structure	BC rate: [0.5, 1, 2, and 5% (w/w)]; [0, 2, 4 and 8% (w/w)]; [0, 5, and 10% (w/w)]; [0.5 and 1% (w/w)]; functional	Improved microbial processes and attributes, impact on microbiological properties, alter functional diversity of microbes,	Khadem and Raiesi, 2017; Liu et al., 2018; Rutigliano et al., 2014;

	microbial diversity; soil DNA extraction; 16S rRNA–based T–RFLP approach; simulation; redundancy analysis	changed bacterial community structure and compositions, and increased diversity of soil bacterial communities. Increased mean substrate-induced respiration of microbes.	Sheng and Zhu, 2018; Wong et al., 2019; Xu et al., 2014; Yao et al., 2017;
Co-benefit	Field experiment; BC rate: 0, 10, 30 and 50 Mg ha^{-1}; incubation; PLFA, correlation and redundancy analysis (RDA)	Improved soil quality and nutrient (AMF/SF ratio, SOC, nitrogen and P) available in semi-arid farmland. Organic matter content explained the majority (45%) of the variation in bacterial profiles.	Huang et al., 2017; Jia et al., 2018; Luo et al., 2017; Zhang et al., 2018
Environmental Sustainability	Field experiment; BC rates: [3 or 6 kg m^{-2}]; [5% w/w]; incubation; Measured fluxes: N_2O, CH_4 and CO_2; carbon and microbial biomass ratio	Reduced heavy metal (Cd) bioavailability and mitigated biotoxicity of soil microorganisms. Found minimal impact on greenhouse gas flux. Maintained microbial stability and highlighted micro-ecology.	Castaldi et al., 2011; Li et al., 2018; Steinbeiss et al., 2009; Xu et al., 2018

Note: BC–Biochar; N- nitrogen; C–Carbon; DNA–Deoxyribonucleic acid; FTIR–Fourier-transformed infrared; RNA–Ribonucleic acid; SEM–Scanning electron microscopy; NMR–Nuclear magnetic resonance; PLFAs–Microbial phosphor-lipid fatty acid; T-RFLP–Terminal restriction fragment length polymorphism; w/w–weight/weight

2.3.1.6 Effect of biochar on contaminated soil, wastewater, solid and semi-solid waste remediation

Metadata

Twenty-one (21) experiment-based studies on heavy metal retention in soil were reviewed. Most of the studies were conducted in the northern hemisphere's temperate region, and only a few studies were done in the southern hemisphere. More than half (57%, n=12) of the studies on heavy metal were conducted in China. In Australia, two studies were conducted in the Barossa Valley Region, (South Australia) and in the UK, two studies were conducted in Wales and Kidsgrove, Staffordshire. There was one study (n=1) conducted in each of the following countries: Brazil, Chile, France, Lithuania, and Pakistan (Figure 2.1f). On petroleum remediation, twelve (12) experiment-based studies were reviewed worldwide, and all the studies were conducted during the last five years. Almost all the studies on petroleum remediation were conducted in the tropical and temperate region (0° - 50° N) of the northern hemisphere, and one study was found in the higher latitude area. China conducted six studies (at different sites across the country like the Dagang oil field, Tianjin, and more areas). The UK conducted two studies in Dorest, and one study was conducted in Saskatchewan, Canada. Other countries like Iran (Gachsaran oil field of Kohgiluyeh and Boyer Ahmad Province in Southwest Iran), Malaysia, and Pakistan conducted one study each (n=1) on petroleum remediation using biochar (Figure 2.1f). In solid and semi-solid waste purification, a total of twelve (12) studies were reviewed. All the studies were conducted in the temperate regions of the northern hemisphere. Several countries like India, Morocco, Philippines, Taiwan, the UK, and the USA conducted one study (n=1). On wastewater purification, fifteen (15) studies were reviewed, and among them, China conducted six studies out of fifteen (Figure 2.1f). Almost all the studies were conducted in the temperate region of the northern hemisphere. Only a few studies were done in the tropical region of the northern hemisphere. No information was found on the application of biochar on wastewater purification from countries in the southern hemisphere. Among the studies on wastewater purification through the application of biochar, China conducted 40% (n=6) studies. In Poland, 27% (n=4) studies were done at experiment farms in the southeast part of the country, especially the Bezek farm on Podzolic soils. Other countries like Germany, India, South Korea, Taiwan, and the USA conducted a minimal number of studies (n=1) (Figure 2.1f).

Impacts, limitations, and scope of further work (contaminated soil remediation)

Many studies have been conducted on heavy metal retention and reducing the bioavailability of metal for plant uptakes (Yin et al., 2017; Zhang et al., 2017). Biochar has been used to remediate heavy metal contaminated soils through immobilization and phytoextraction (Moore et al., 2018; Li et al., 2018; Li et al., 2017; Beesley and Marmiroli, 2011). Komkiene and Baltrenaite (2016) mentioned that biochar treatment effectively removed heavy metals, like Cd, Cu, Pb, and Zn, from a diluted aqueous solution. Biochar capacity for heavy metal extractability and enzyme activity (of microbes) varied with the biochar type, application rate, and particle size (Yin et al., 2017; Vithanage et al., 2017). In the context of environmental sustainability, biochar application was found to be beneficial for the management of degraded landscapes and an effective method to reduce environmental risks related to heavy metals exposure (Table 2.6).

Overall, biochar amendment can decrease soil toxicity. However, limited information exists on biochar about the long-term effects of soil pollutants, distribution pattern of contaminants, and persistence of pollutants in the soil (Lu et al., 2018; Lucchini et al., 2014). There is also inadequate information found on biochar and metalloid interaction in soil. Most of the studies were conducted on the short-term effects of metal extractability. There is a need to investigate the long-term effects of biochar amendment (with different types and rates) on heavy metal remediation and soil health improvement (Yin et al., 2017) to sustain agriculture and the environment.

Impacts, limitations, and scope of further work (petroleum remediation)

Several studies suggested that the application of biochar was effective in biodegradation of total petroleum hydrocarbon (TPH) (Li et al., 2019). For example, biochar accelerates Polycyclic Aromatic Hydrocarbons (PAHs) biodegradation in petroleum-polluted soil (Kong et al., 2018) (Table 2.6). Different types and rates of biochar can be used to remediate petroleum-contaminated soil. For example, bulrush straw powdered biochar could be an effective type of biochar which remediates petroleum contaminated soils (Wang et al., 2017). Biochar, produced from raw materials like banana and orange peel, can be used as an adsorbent to treat palm oil mill effluent (Lam et al., 2018). Also, wheat straw biochar amendments can be applied to remove PAHs from contaminated soils (Cao et al., 2016).

Bushnaf et al. (2011) reported that biochar reduced the number of monoaromatic hydrocarbons, which influence the biodegradation of the petroleum compounds. That is one of the limitation of biochar application in petroleum remediation. Many laboratory-based studies demonstrated that the carbonaceous sorbents have high potentials to reduce PAHs' bioavailability, such as hormones and organic pesticides, from contaminated soils. Biochar characteristics, such as porosity and SSA, greatly influence the petroleum retention time and reduce the leaching potential into groundwater (Shaaban et al., 2018). From an environmental sustainability viewpoint, using plant *ryegrass* could be an effective remediation strategy to mitigate TPH. Besides, biochar treatment may be suitable for the phytoremediation of contaminated soils, including TPH (Han et al., 2016) (Table 2.6). A comprehensive study combining phytoremediation and biochar amendment in soil needs to be done in the future to learn the effectiveness of this treatment for TPH remediation strategy.

Impacts, limitations, and scope of further work (wastewater treatment)

Agricultural runoff is a critical issue for environmental health and agroecological systems (Wei et al., 2018). Many water-scarce countries use wastewater for irrigation that possesses high contamination risks for farmers and consumers (Werner et al., 2018). Biochar characteristics like its surface area, porous structure, functional group, and mineral composition facilitate high efficiency removal of pollutants from the aqueous solutions (Tan et al., 2015). Specifically, biochar SSA facilitates high adsorption capacity of contaminants (like Pb and Cu) from wastewater (Shen et al., 2018). Biochar application in agricultural wastewater purification was found to be effective in reducing the release of excess nutrients from agricultural runoff (Ghezzehei et al., 2014). Furthermore, biochar amendment reduced PAHs, nutrient leaching and pathogen loads in wastewater (Tan et al., 2015; Kończak and Oleszczuk, 2018; Stefaniuk et al., 2018; Tan et al., 2016; Zama et al., 2017; Werner et al., 2018). Biochar increased Ni (II) and Cd (II) ions removal efficiency from aqueous solutions (Bogusz et al., 2017; Li et al., 2017) (Table 2.6). Wastewater treatment by biochar suffers certain drawbacks (e.g., low mechanical properties and low sorption capacity of ions) that limit its applicability (Tan et al., 2016; Vikrant et al., 2018; Zhou et al., 2017). This is an area that need more research to address strategies for further improvement (Wei et al., 2018).

Impacts, limitations, and scope of further work (solid and semi-solid waste remediation)

Randolph et al. (2017) proposed that biochar, produced from mixed solid waste, can be used in solid waste management. For example, biochar produced from municipal solid waste was found to be useful for heavy metal (Cu and Hg) retention in the purification of solid and semi-solid municipal wastes (Li et al., 2015; Sumalinog et al., 2018) (Table 2.6). One of the crucial co-benefits is that biochar can decrease the volume of waste (Li et al., 2018; Milla et al., 2013). Another benefit is that the application of biochar to organic fraction of municipal solid waste (OFMSW) reduced methanogen loss from anaerobic digesters (Qin et al., 2017). From the viewpoint of environmental sustainability, OFMSW treated with biochar has some fertilizer value that may improve the quality of depleted soils (e.g., improving hydraulic properties). Solid and semi-solid waste is generally composed of a wide variety of materials, and these wastes treated with biochar possess a low potential for ecological risk. Further, a comprehensive assessment is needed to identify the most significant source material and biochar application ratio which will provide the best solid and semi-solid waste remediation solution.

Table 2.6: Effect of biochar on contaminated soil, wastewater, solid and semi-solid waste remediation

Studies on	**Applied methods**	**Results/Impacts**	**Sources**
Heavy metal retention			
Heavy metal retention	BC rate: [0, 1 and 5% (w/w)]; [0, 10 and 20 Mg ha^{-1}]; [30 and 60 Mg ha^{-}1]; BC characterization (BET, FTIR, XRD and SEM-EDX); incubation experiment; Column leaching experiment; Batch sorption experiment; R_{50} using TGA analysis; randomized block design	Successful retention of heavy metals (Cd, Cu, Pb, Zn), mobility and transfer of As in soil. Increased Cd sorption on both saturated (59–71%) and upland (57–84%) contaminated soils. Reduced bioavailable of Cu fraction (up to 10 times) in soil. High efficiency of Zn remediation found through phytoextraction in the polluted soil.	Beesley and Marmiroli, 2011; Gonzaga et al., 2018; Huang et al., 2018; Khan et al., 2018; Li et al., 2018; Lu et al., 2012; Moore et al., 2018; Rehman et al., 2017; Qi et al., 2017; Qiu et al., 2018; Yin et al., 2017; Zhang et al., 2017
Co-benefit	Long-time field experiment (6, 12 and 18 months); BC rate: [5% (w/w)]; [0,1, and 5 % (w/w)]; incubation; enzyme activity analysis; PLFAs and microbial CUE were extracted and analyzed; toxicity assessment	Decreased metal bioavailability of heavy metals in soil and enzyme activities (depends on factors) and mitigate biotoxicity to soil microorganisms. Pb adsorption capacity could be enhanced by the chemical treatment of sludge-based biochar.	Kończak and Oleszczuk, 2018; Wongrod et al., 2018; Xu et al., 2018; Yang et al., 2016
Environmental sustainability	Long-term field experiment [repeat-applications (two years later)]; BC rate: [0, 2.5, 5 and 10% (w/w)]; [25 and 50 Mg ha^{-1}]; [8 - 10% (w/w)]; BC structure and morphology analysis	Biochar made from forest residue low in heavy metals as caused by metal fractionation. Found an effective method to reduce environmental risk related to heavy metals. Beneficial for the management of degraded landscapes.	Bogusz and Oleszczuk, 2018; Lu et al., 2018; Lucchini et al., 2014; Zhang et al., 2018

Petroleum degradation			
PAHs degradation	BC rate: 3% (w/w); 2% (w/w); different types of BC; BC characterization (SEM); Batch and column experiments; assessment of degradation	Remediated efficiently petroleum-contaminated soil - higher degradation of THPs up to 78.9%. Biochar-amended soils degrade PH under snowy conditions. High degradation efficiency is found with mineral nutrition and phosphorus.	Bushnaf et al., 2011; Karppinen et al., 2017; Li et al., 2019; Wang et al., 2017; Zhang et al., 2016
Co-benefit	BC rate: 5% (v/v); Compost rate: 5% (v/v); Column and batch experiments; extraction and quantification of PAHs; molecular analysis; fate model for VPHs	Efficient removal of POME and reduced concentration of BOD, COD, and TSS. Plant-microbe interactions with organic soil amendments remediate hydrocarbons. Found to be economically beneficial.	Hussain et al., 2018; Kong et al., 2018; Lam et al., 2018; Meynet et al., 2014
Environmental sustainability	Greenhouse experiment; Amendment and incubation design; extraction and analysis of Phenanthrene; bioremediation strategies	The increased degradation rate of contaminants, planting ryegrass is an effective phytoremediation strategy of contaminated soil.	Abbaspour et al., 2020; Cao et al., 2016; Han et al., 2016
Wastewater purification			
Contaminants removal from wastewater	BC characterization (FTIR, SEM–EDX, and XRD); different types of BC; examined adsorption kinetics, capability, and isotherms	Successfully removed Cd (II), Cu (II), Pb (II), Zn (II), Ni (II) ions, and OM from aqueous solutions/ wastewater. BC properties (functional groups, ions, minerals) controlled sorption significantly. Adding biochar to aerated VFCWs found to be an effective strategy for wastewater treatment.	Bogusz et al., 2017; Ho et al., 2017; Komkiene and Baltrenaite, 2016; Lee et al., 2018; Li et al., 2017; Shen et al., 2018; Wang et al., 2015; Yoon et al., 2017; Zama et al., 2017; Zhou et al., 2017

Environmental sustainability	BC rate: 2.5, 5 or 10% (w/w); Long-term field experiment; batch sorption experiments; catalytic ozonation process	Recovered essential nutrients from dairy wastewater and improved soil fertility. Efficiently reduced pathogen load (P, K, and Mg during filtration) attributed to the P fertilizer effect.	Chen et al., 2019; Ghezzehei et al., 2014; Stefaniuk et al., 2018; Werner et al., 2018
<u>Solid and semi-solid waste purification</u>			
Solid and semi-solid waste purification	BC rate: 0.25, 0.75, 1.5, 2.25, and 3% (w/w); BC and MSWF characterization (SEM, BET, ICP-MS, XPS); Batch experiments; used 6S rRNA and 18S rDNA technology; Gompertz model; PCA, TGA and DSC analysis	Prevented loss of methanogens (25% was absorbed) in the anaerobic digesters. Microwave activation and NH_4Cl modification enhanced Hg^0-removal capacity. Contaminant adsorption found significantly effective, and maximum removal 99.9%	Ashiq et al., 2020; Boumanchar et al., 2017; Li et al., 2015; Li et al., 2018a; Lu et al., 2012; Lu et al., 2019; Qin et al., 2017; Sumalinog et al., 2018
Environmental sustainability	BC characterization; different types of BC; speciation evolution; leaching toxicity; environmental risk assessment	Improved soil fertility, quality of depleted soil, minimized volume of waste, potential GHG mitigation, very low leaching toxicity (risk index), and low potential ecological risk.	Li et al., 2018b; Milla et al., 2013; Randolph et al., 2017

Note: BC–Biochar; BET–Brunauer-Emmett-Teller; BOD–Biochemical oxygen demand; COD–Chemical oxygen demand; O&G–Oil and Gas; *CUE*–Carbon use efficiency; DNA–Deoxyribonucleic acid; DSC–*Differential Scanning Calorimetry;* FTIR–Fourier-transform infrared spectroscopy; SEM– Scanning electron microscopy; GHG–Greenhouse gas; EDX–Energy-dispersive X-ray; ICP-MS– Inductively coupled plasma mass spectrometry; PAHs–Polycyclic aromatic hydrocarbons; THPs–Total petroleum hydrocarbons; TSS–Total suspended solid; PLFAs–Phospholipid fatty acids; VFCWs–Vertical Flow Constructed Wetlands; VPHs–Volatile petroleum hydrocarbons; PCA–Principal component analysis; RNA–Ribonucleic acid; TGA–Thermal gravimetric analysis; POME–Palm oil mill effluent; XRD-X–ray diffraction; XPS-X-ray photoelectron spectroscopy

2.3.2 Integrated experimental approaches on biochar applications for agricultural and environmental sustainability

In the above section, six important areas of biochar application were discussed, focusing on experimental approaches, results or impacts, co-benefits, enhancement of agricultural productivity, and how biochar ensures agricultural and environmental sustainability. It is essential to know the most important terms in biochar application used in the reviewed articles. The term map (Figure 2.2) outlines the most important and common words used in a total of 160 reviewed articles (out of 210) based on the titles, abstracts, and keywords. The most frequently occurring terms and co-occurrence links are visible in the term map. During the last five years, authors mostly used words such as biochar, soil amendment, soil types, agricultural soil, nitrogen, nutrients, nitrate, biochar properties (surface area), hydrological properties of soil (water retention), soil quality (acidity), carbon sequestration, plant growth, microbial community, soil pollutants (lead, zinc, copper), remediation and wastewater treatment. Knowledge of highlighted terms in the biochar application-based studies would help to understand researchers about the appropriate use of essential factors in the experiment-based studies.

Most of the studies on biochar applications were conducted in temperate and tropical regions worldwide (Figure 2.3). Out of 210 studies, a total of 80 (38%) studies were conducted in China (in Asia). Only a few studies were found in countries like the USA (n=9), Poland (n=9), the UK (n=8), Australia (n=6), Germany (n=5), Italy (n=5) and India (n=5). Other countries such as Brazil, Canada, Denmark, Saudi Arabia, South Korea, Taiwan, Japan, Finland, and Iran conducted less than 5 (2.4%) studies on biochar research in various sectors.

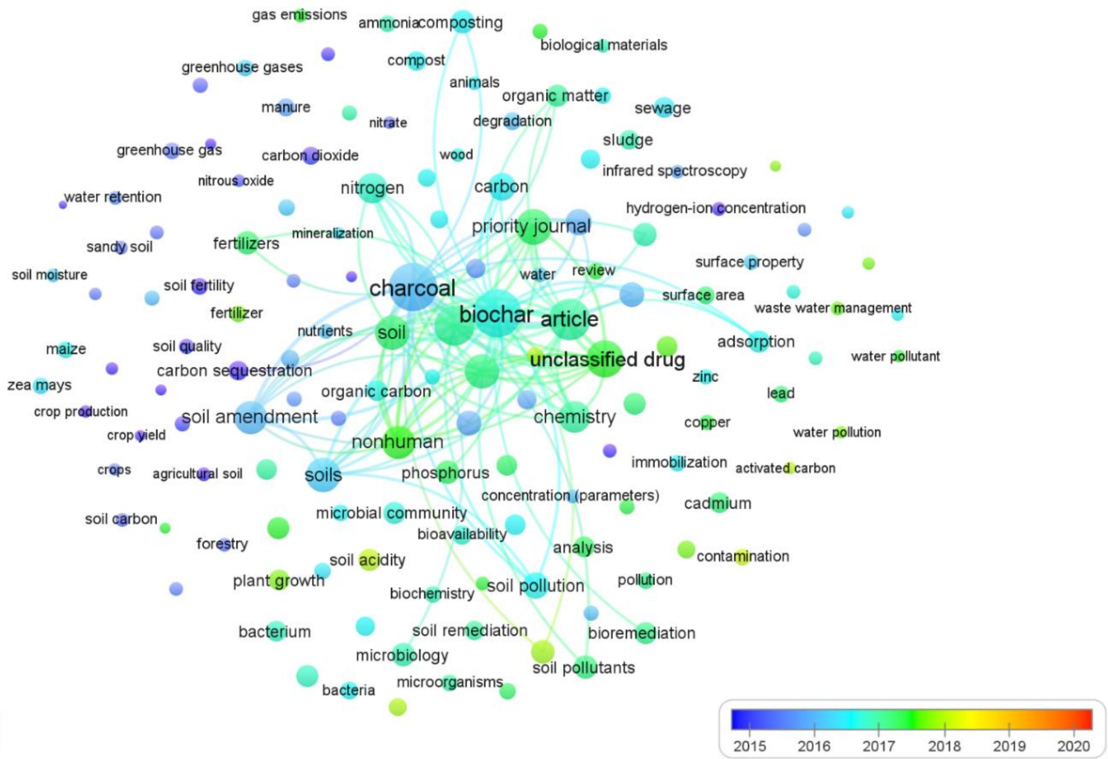


Figure 2.2: Term maps based on 160 publications focusing on biochar application since 2015-2020. The minimum number of occurrence of keywords ten and maximum lines (100) indicates co-occurrence links between the terms.

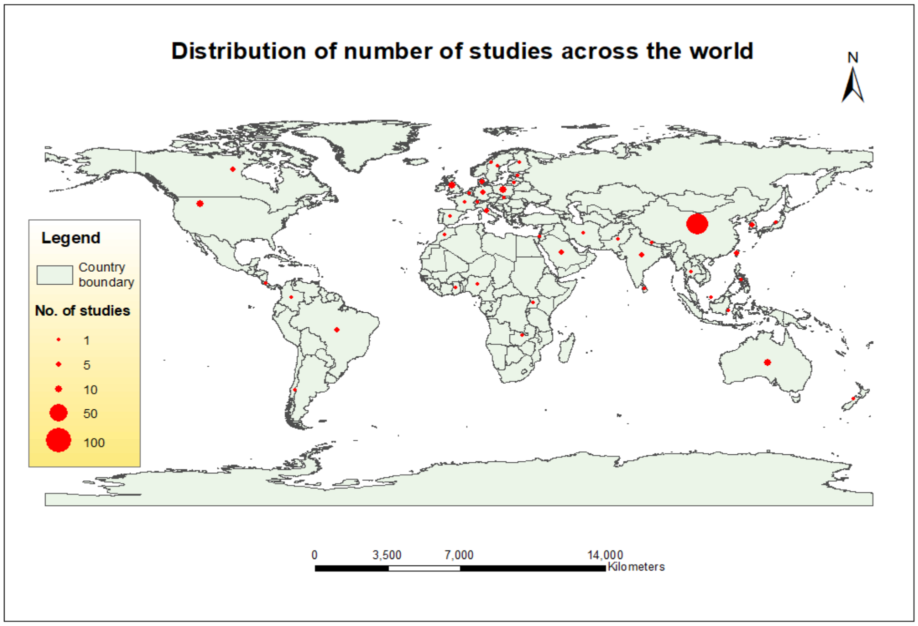
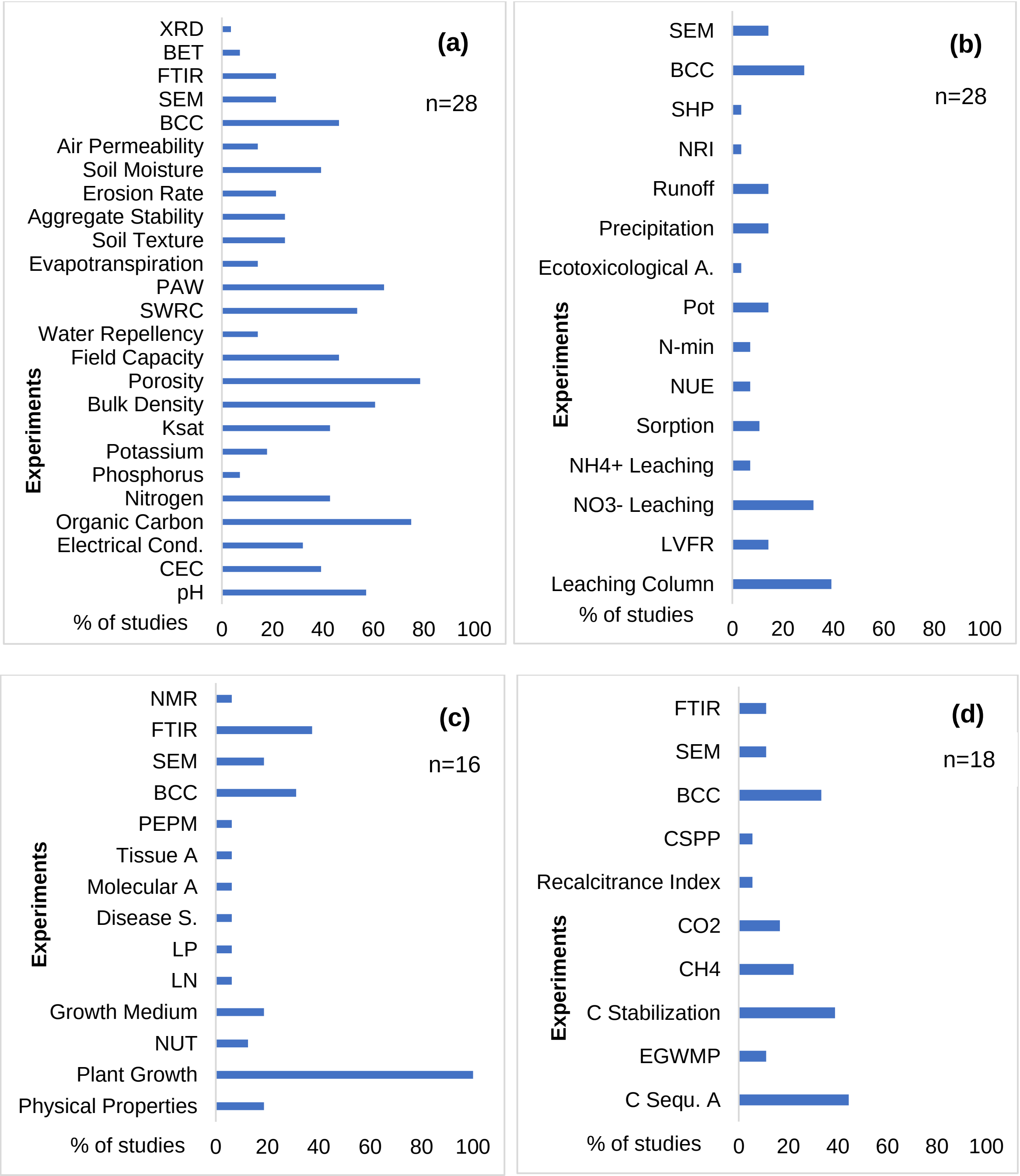


Figure 2.3: Distribution of number of studies based on biochar application conducted across the world and reported in this review

Figure 2.4 describes the experimental approaches applied in different sectors and helps to explore the knowledge gap in conducting experiments in each sector (as discussed in the biochar application in six sectors). In the case of the effect of biochar on the physicochemical properties of soil, most of the studies examined physical properties of soil like porosity 79% (n=22), PAW 75% (n=21), BD 61% (n=17) studies and around half of the studies conducted experiments on biochar characterization 46% (n=13). In the previous studies, authors conducted experiments on water repellency, erosion rate, and aggregate stability as the least prioritized experiments (Figure 2.4a). In the case of the effect of biochar on soil nutrient cycling (N transportation), a significant number of studies were conducted using leaching column experiments [39% (n=11)] and biochar characterization [29% (n=8)]. The number of studies on nitrate leaching was 9 (32%). Figure 2.4b indicated that only 4% (n=1) of the studies conducted experiments on N recovery index and ecotoxicological assessment. In the studies related to plant growth, yield, and biomass production, 100% (n=16) of the studies conducted experiments on plant growth, and a significant number of studies [31%(n=5)] were done on biochar characterization using SEM image. In past, authors conducted experiments on plant tissue analysis, disease susceptibility, but plant eco-physiological measurements were the least prioritized experiments (Figure 2.4c). In the case of C sequestration in soil and GHG emission studies, most experiments were conducted on C sequestration assessment [44% (n=8)], and C stabilization in soil [39% (n=7)]. A significant number of studies [33% (n=6)] were conducted on biochar characterization. The least priority experiments were done on global warming mitigation potential [11% (n=2)] and recalcitrance index [6% (n=1)] (Figure 2.4d). A total of 66% (n=23) of these studies conducted experiments on bacterial community structure analysis, 17% (n=6) studies were on microbial biomass assessment and enzyme activity assays. However, only 11% (n=4) of the studies completed assessment on organic matter (OM) decomposition. The identified least prioritized experiments were phytotoxicity test [9% (n=3)], compost kinetics [9% (n=3)], and microbial C use efficiency [3% (n=1)] (Figure 2.4e). In the case of the effect of biochar on contaminated soils, wastewater, solid and semi-solid waste remediation, higher percentage of studies conducted experiments on adsorption [22% (n=13)], and heavy metals retention (As, Cd, Cu, Hg, Ni, Pb, and Zn) [15% (n=9)], (PAHs) degradation [13% (n=8)] and OFMSW removal [13% (n=8)]. The least prioritized experiments were conducted on the pathogen removal [8% (n=5)], TPH removal [5% (n=3)], modelling [5% (n=3)], environmental risk assessments [5% (n=3)] and flow cytometry analysis [2% (n=1)] (Figure 2.4f).

Figure 2.5 describes the experimental approaches of biochar applications in agricultural and environmental sustainability. Biochar applications improve soil health, including physicochemical properties and biotic properties. Biochar helps to reduce N leaching in soil, enhance physical properties to overcome extreme hydrological conditions, and improve agroecosystem functioning. The plant gets more nutrients from biochar-treated soil, which will ultimately increase agricultural productivity. Ecotoxicological assessment of biochar indicated that biochar is a sustainable application option for agricultural and environmental needs.


(a)
n=28
Experiments
XRD
BET
FTIR
SEM
BCC
Air Permeability
Soil Moisture
Erosion Rate
Aggregate Stability
Soil Texture
Evapotranspiration
PAW
SWRC
Water Repellency
Field Capacity
Porosity
Bulk Density
Ksat
Potassium
Phosphorus
Nitrogen
Organic Carbon
Electrical Cond.
CEC
pH
% of studies
0
20
40
60
80
100
(b)
n=28
Experiments
SEM
BCC
SHP
NRI
Runoff
Precipitation
Ecotoxicological A.
Pot
N-min
NUE
Sorption
NH4+ Leaching
NO3- Leaching
LVFR
Leaching Column
% of studies
0
20
40
60
80
100
(c)
n=16
Experiments
NMR
FTIR
SEM
BCC
PEPM
Tissue A
Molecular A
Disease S.
LP
LN
Growth Medium
NUT
Plant Growth
Physical Properties
% of studies
0
20
40
60
80
100
(d)
n=18
Experiments
FTIR
SEM
BCC
CSPP
Recalcitrance Index
CO2
CH4
C Stabilization
EGWMP
C Sequ. A
% of studies
0
20
40
60
80
100

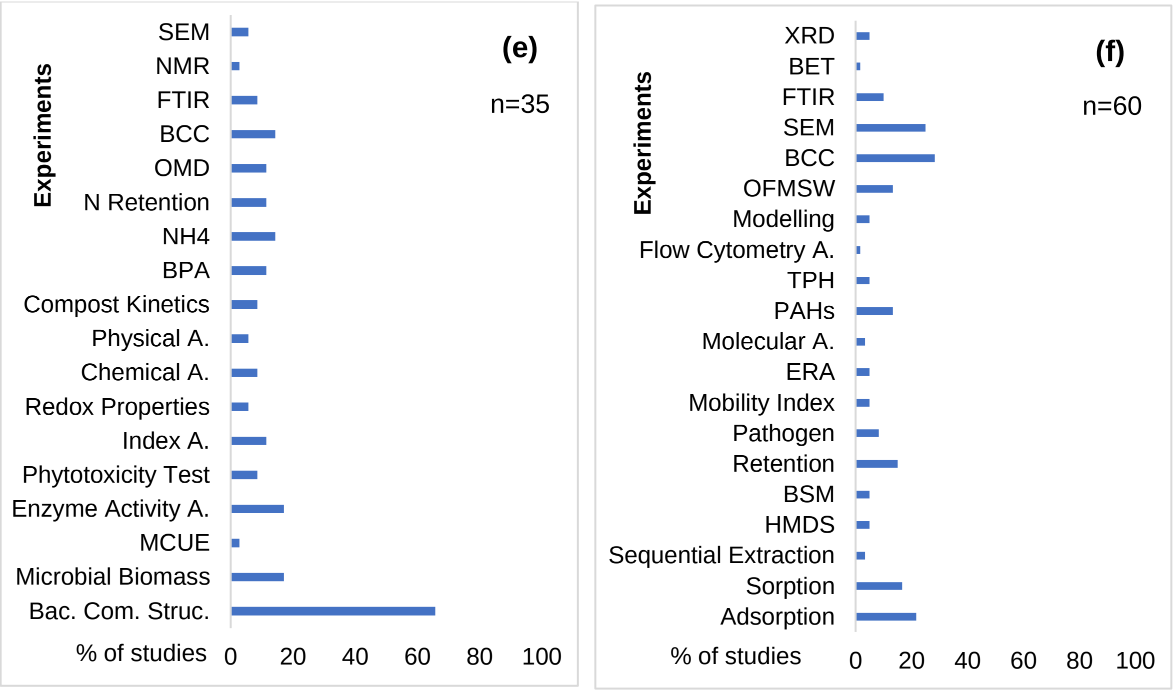


Figure 2.4: Priority areas of studies conducted to assess the effects of biochar applications. These priority areas include: (a) physicochemical properties; (b) nitrogen transport; (c) plant growth; (d) soil carbon sequestration and greenhouse gas emission; (e) soil microbial activities and composting, and (f) contaminated soil-wastewater-semisolid and solid waste purification.

[Note: Bac. Com. Struc. –Bacterial Community Structure; BCC–Biochar Characterization; BET–Brunauer-Emmett-Teller Theory; BPA–Biological Property Analysis; BSM–Biochar Stability Measurement; C Sequ. A–Carbon Sequestration Assessment; CEC–Cation Exchange Capacity; CSPP–Carbon Sequestration Policy and Program; Disease S. –Disease Susceptibility; EGWMP–Estimating Global Warming Mitigation Potential; ERA–Environmental Risk Assessments; FTIR–Fourier Transform Infrared *Spectroscopy;* HMDS–Heavy Metal Distribution System; K_{sat}–Saturated Hydraulic Conductivity; LN–Leaf Nutrient; LP–Leaf Porometry; LVFR–Leachate Volume and Flow Rate; MCUE–Microbial Carbon Use Efficiency; N-min–Nitrogen Mineralization; NMR–Nuclear Magnetic Resonance Spectroscopy; NRI–Nitrogen Recovery Index; N Retention–Nitrogen Retention; NUE–Nitrogen Use Efficiency; NUT–Nutrient Uptake; OFMSW–Organic Fraction of Municipal Solid waste Removal; OMD–Organic Matter Decomposition; PAW–Plant Available Water; PAHs–Polycyclic Aromatic Hydrocarbons degradation; PEPM–Plant Eco-physiological Measurements; Retention- Retention (Cd, Pb, Zn, Cu, As, Ni, Hg); SEM–*Scanning Electron Microscope*; SHP–Simulating Hydrological Process; SWRC–Soil Water Retention Curve; TPH–Total Petroleum Hydrocarbon Removal; XRD–X-ray Diffraction]

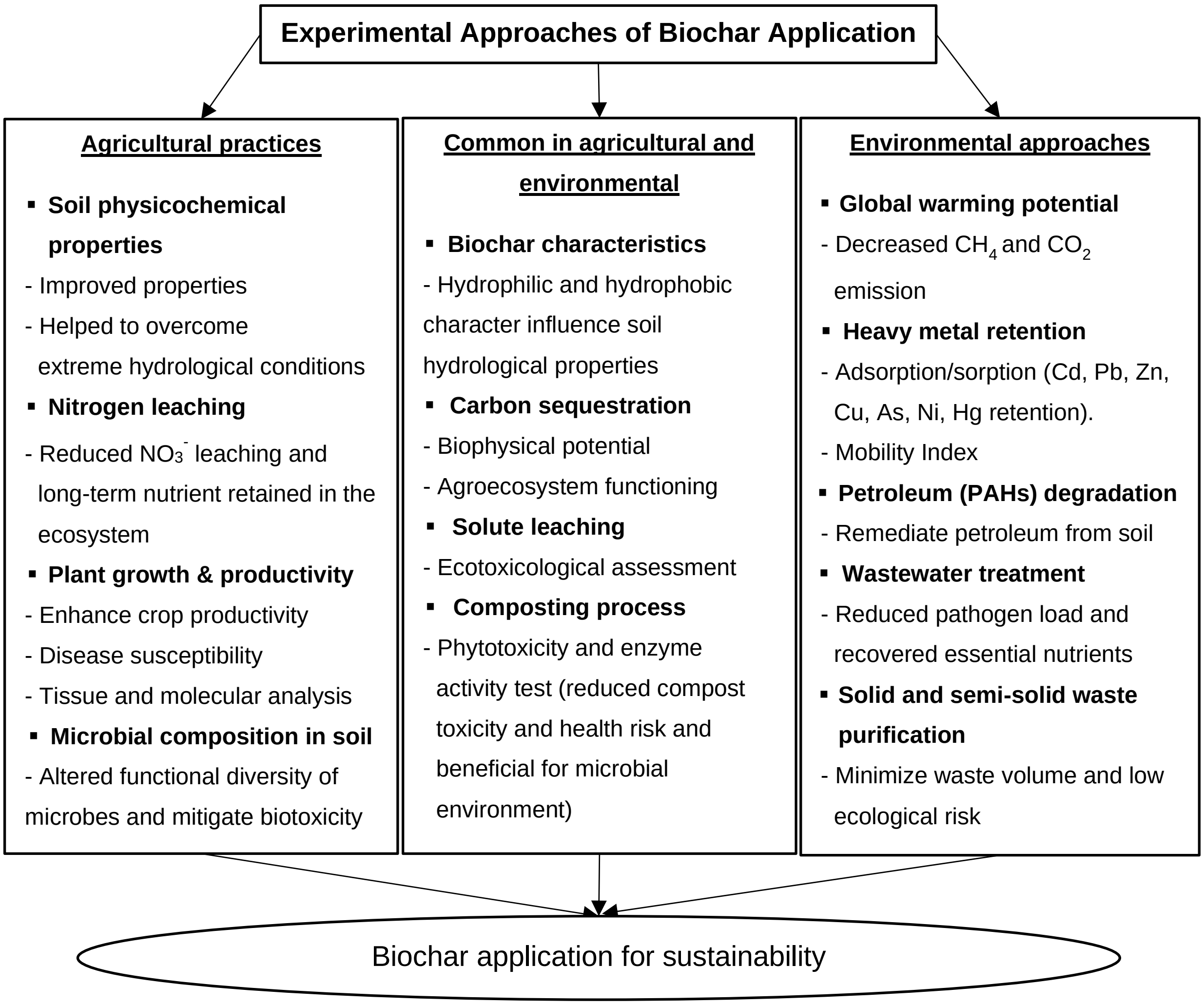


Figure 2.5: A schematic diagram of experimental approaches of biochar application for agricultural and environmental sustainability

Over the last decade, biochar has been applied as a vital additive for the positive impact to the ecosystem. In 2016, Tammeorg et al. prepared a research priority index focusing on the use of biochar as a unique theme. The priority index indicated that more research is needed to assess disease suppression of plants, and population dynamics related to ecotoxicological assessment. Before using biochar in any sector, analysis of biochar characteristics is required as this will directly influence study objective achievement as well as to better understand how agricultural and environmental sustainability may be achieved. Appropriate selection of analytical techniques to investigate biochar characteristics is also essential (Amin et al., 2016; Oliveira et al., 2017). Xiong et al. (2017) suggested that biochar research should focus on biochar characteristics, desirable/undesirable reactions for highly efficient and sustainable applications, and co-benefits. However, several mechanisms play a vital role in determining the best possible impact of biochar in different ecosystems and areas associated with agricultural sustainability. For example, an assessment of soil enzyme activities in biochar-amended soils would be beneficial for an in-depth understanding of ecological performance (Chen et al., 2018) and potential toxicity of biochar on microorganisms (Wang et al., 2019). The agronomic benefits of biochar application would be an important area (Oliveira et al., 2017) for the beneficial management practices to increase agricultural productivity while minimizing the negative environmental impacts from agricultural inputs. Atkinson et al. (2010) informed that biochar's potential influence on agricultural practices, especially in the tropical and temperate regions, has been identified. But still, comprehensive studies with sufficient scientific information have not yet been investigated under boreal climatic conditions. Therefore, further studies are essential to critically examine the role of biochar for the sustainability of different ecosystems.

Based on this review, a few key areas need to be further studied:

- Long-term field experiments would be essential on biochar-amended sites to integrate physicochemical and biological processes in soil management.

- Biochar will have significant impacts on soil-water nutrient cycling. Thus, biochar impacts on nutrient losses and soil-water retention needs to be investigated under different soils, climate, and management practices.

- Climatic conditions have an enormous influence on ecosystem functioning, especially when applying biochar for agricultural practices. It is important to know how climate influences biochar effect on improving soil health, nutrient cycling in the ecosystem, microbial community structure, pathogen removal, and heavy metal retention.

2.4 Conclusion

Currently, biochar has a wide range of applications in various sectors across the world. Metadata analysis showed that most of the studies on biochar applications were conducted in the temperate region. In contrast, only a few studies providing sufficient critical details were done in high latitude areas, especially in podzolic soil in boreal ecosystems. The variation of the study findings based on geographical location was not found to be very high. A substantial increase in water use efficiency was observed in the temperate and boreal ecosystems compared to other areas. Application of biochar in soil can influence the soil's physicochemical properties, reduced a significant amount of N leaching from the soil as well as improved soil health in agroecological systems. Biochar application enhanced plant growth, productivity, biomass production and improved microbial processes (diversity and functions) in soils, increased carbon sequestration, may be a potential strategy for mitigating greenhouse gases, facilitated organic matter degradation, and reduced waste toxicity, volume, and density during composting. Biochar application has been found useful in wastewater purification, heavy metals retention from contaminated soil, and biodegradation of Polycyclic Aromatic Hydrocarbons in petroleum-polluted soils. Most of the studies, reported in the literature, were conducted over the short-term (less than one year). Therefore, long-term studies need to be considered in different soil, management, and ecological conditions. The threshold amounts of biochar that need to be applied for the positive agronomic effects and environmental sustainability still needs to be addressed in different ecosystem. Experiments on the results of biochar on agricultural practices and impacts on the ecosystem need to be re-investigated after a certain period to learn the long-term effects of biochar, the consistency of the impact, and a way forward for further improvement. The focus of biochar research on podzolic soils would be beneficial under the potential northward shift of agriculture which is mainly due to climate change. A comprehensive assessment of ecosystem functioning on the impact of biochar in different regions across the world would be essential to better understand how biochar applications may contribute to the sustainability of agricultural practices and the environment.

Acknowledgment

The authors are grateful to the authorized bodies and different journal sites whose dataset and information were used in this review-based research article. Authors acknowledge researchers of Hydrology and Agrophysics Research Group, Memorial University of Newfoundland, for their inspiration and contribution during the manuscript's preparation. Authors appreciate the contribution of Dr. Muhammad Nadeem, Postdoctoral Fellow, School of Science and the Environment, Memorial University of Newfoundland, in time of the manuscript preparation.

Special thanks go to Mr. Gabriel Grunwald, Department of Naval Architecture, Marine Institute of Memorial University of Newfoundland, Canada, for copy-editing this manuscript. Thanks to a few distinguished researchers who have given their valuable comments and suggestions at the manuscript's preparation stage.

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Co-authorship statement for study two

The study entitled "Investigating the influence of biochar amendment on the physicochemical properties of podzolic soil" has been published in *Agriculture* Journal [Impact Factor: 2.072]. Reference of the published research article – "Saha, R.; Galagedara, L.; Thomas, R.; Nadeem, M.; Hawboldt, K. Investigating the Influence of Biochar Amendment on the Physicochemical Properties of Podzolic Soil. *Agriculture* **2020**, *10*, 471. https://doi.org/10.3390/agriculture10100471". Ratnajit Saha, the thesis author was the primary and corresponding author of the manuscript. Ratnajit Saha collected samples, prepared study design, executing all the experiments, analyzed the experimental data, visualized the experiment results through graphs and prepared the manuscript. Dr. Lakshman Galagedara (supervisor) was the second author and contributed in study design, data analysis, especially on soil moisture release curve to get permanent wilting point using the van Genuchten (VG) model, helped in interpretation of the results, provided expert opinion in presenting experiment results, review and edited of the manuscript and overall supervision from conceptualization of the experimental study to manuscript preparation. Dr. Raymond Thomas (co-supervisor) was the third author and contributed in study design especially on using a scanning electron microscope (SEM), to provide detail about physicochemical, elemental, and morphological properties of biochar, also participated in review and editing of the manuscript. Dr. Muhammad Nadeem was the fourth author of the manuscript. Dr. Nadeem contributed to executing some experiments (like temporal effect on pH and electrical conductivity) in the lab, helped in principal component analysis and manuscript preparation and review of the manuscript. Dr. Kelly Hawboldt (co-supervisor) was the fifth author and Dr. Kelly contributed to organize the write-up, review and editing of the manuscript.

Chapter Three

Study two

Investigating the influence of biochar amendment on the physicochemical properties of podzolic soil

Ratnajit Saha [1], Lakshman Galagedara [1,2], Raymond Thomas [2], Muhammad Nadeem [2] and Kelly Hawboldt [3]

[1] Environmental Science Program, Faculty of Science, Memorial University of Newfoundland, St. John's, NL A1B 3X7, Canada

[2] School of Science and the Environment, Memorial University of Newfoundland, Corner Brook, NL A2H 5G4, Canada

[3] Department of Process Engineering, Memorial University of Newfoundland, St. John's, NL A1C 5S7, Canada

Abstract

Research into biochar, as an amendment to soil, has increased over the last decade. However, there is still much to understand regarding the effects of biochar type and rates on the physicochemical properties of different soil types. This study aimed to investigate the effects of biochar application on the physicochemical properties of podzolic soils. Podzolic soil samples were collected from a research site in Pasadena, Newfoundland, Canada. Experimental treatments consisted of three

types of soils (topsoil, E-horizon soil and mixed soil (topsoil 2: E-horizon soil 1)), two biochar types (granular and powder) and four biochar application rates (0%, 0.5%, 1% and 2% on a weight basis). Ten physicochemical parameters (bulk density (BD), porosity, field capacity (FC), plant available water (PAW), water repellency (WR), electrical conductivity (EC), pH, cation exchange capacity (CEC), total carbon (TC), and nitrogen (N)) were investigated through a total of 72 experimental units. Biochar morphological structure and pore size distribution were examined using a scanning electron microscope, whereas surface area was assessed by the Brunauer−Emmett−Teller method. The result indicated that the E-horizon soil was highly acidic compared to control (topsoil) and mixed soils. A significant difference was observed between the control and 2% biochar amendment in all three soil mixtures tested in this experiment. Biochar amendments significantly reduced the soil BD (E-horizon: 1.40–1.25 > mixed soil: 1.34–1.21 > topsoil: 1.31–1.18 g cm^{-3}), increased the CEC (mixed soil: 2.83–3.61 > topsoil: 2.61–2.70 > E-horizon: 1.40–1.25 cmol kg^{-1}) and total C (topsoil: 2.40–2.41 > mixed soil: 1.74–1.75 > E-horizon: 0.43–0.44%). Waterdrop penetration tests showed increased WR with increasing biochar doses from 0 to 2% (topsoil: 2.33–4.00 > mixed soil: 2.33–3.33 > E-horizon: 4.00–4.67 s), and all the biochar–soil combinations were classified as slightly-repellent. Significant effects of biochar application were found on soil water retention. Porosity increased by 2.8%, FC by 10%, and PAW by 12.9% when the soil was treated with powdered biochar. Additionally, the temporal effect of biochar (0 to 2% doses) were examined on pH and EC and observed an increase in pH (4.3–5.5) and EC (0.0–0.20 dS/m) every day from day 1–day 7. Collectively the study findings suggested that 2% powder biochar application rate is the best combination to improve the physicochemical properties of the tested mixed podzolic soil. Granular and powdered biochar was found to be hydrophobic and hydrophilic, respectively. These findings could be helpful to better understand

the use of biochar for improving the physicochemical properties of podzolic soils when used for agricultural practices in boreal ecosystems.

Keywords: granular biochar; powder biochar; biochar rates; topsoil; E-horizon soil; mixed soil

3.1 Introduction

For more than a decade, research into the diverse applications of biochar has been increasing [1]. This increase is primarily driven by potential applications for biochar in agricultural practices [2–6]. Biochar refers to the solid carbonaceous product [7] produced naturally and commercially [8] via pyrolysis and gasification [9] from organic biomass. Biochar production process temperature range between 300 and 1000 °C under minimum or no oxygen conditions [10,11]. A variety of feed stocks are considered as source material for biochar production including residues produced in agricultural, forestry, and municipal operations [12,13].

Biochar has been well studied as a soil amendment [6,13] and some of these study findings suggest biochar can improve soil physicochemical properties. For example, increasing values of cation exchange capacity (CEC) was reported in [14], soil water interaction, and retention (including degraded soils) [15], saturated hydraulic conductivity [16], soil aggregation and stability [17] following soil amendment with biochar. Furthermore, biochar has also been reported to influence soil health by enhancing microbial abundance and diversity in the rhizosphere, as well as modifying the favorable microbial environments by adjusting nutrients, increasing soil pH [18–20] and modifying plant growth performance through improved fertility, and direct supply of carbon (C) rich substrates [21,22]. Biochar application or amendment is also well recognized as a useful potential climate change mitigation strategy [23,24]. Specifically, this mitigation strategy includes decreased erosion potential [13], remediation of contaminated water or soil [25–27], and improved agricultural production and ecosystem sustainability [10,28].

Biochar application may have a positive or negative impact on soil texture and soil hydrological properties such as field capacity (FC) and plant available water (PAW) [8,29] depending on whether the biochar applied is hydrophilic or hydrophobic. If biochar has hydrophobic characteristics, then soil nutrient distribution and retention capacity could be negatively affected, whereas hydrophilic biochar could increase interactions with soil solution [30]. Biochar amendment can influence soil hydraulic properties such as porosity and water retention in three ways: (1) increased total porosity i.e., contributes to pore distribution; (2) modification of compaction between soil and biochar as well as surrounding aggregation; and (3) increased aggregate stability or reduced soil erosion potential by improving pore space persistence [10,31]. Biochar helps to mitigate extreme hydrological conditions (such as very low moisture content), thus acting as a soil amendment for sustainable farming practices that aim to conserve soil and water [32,33]. Biochar can also positively or negatively impact the soil hydrological properties depending on the intensity of its application [34]. Therefore, characterization of biochar before its application is important as it influences the soil moisture content (MC), water holding capacity (WHC), PAW (larger pores retain water weakly under gravity and smaller pores do not have enough space to hold water in a plant-accessible form), ability to absorb water, nutrients, and agricultural chemicals [10,15,35–38]. Pore size distribution is very important to study if biochar is to be used as a soil amendment [10,16]. Determination of pore size and pore distribution pattern from different angles in biochar is essential to understand the effects on WHC and nutrient absorption capacity. Biochar characteristics like surface area and porosity depend on the temperature of pyrolysis and the raw materials used for biochar production [4,39]. Pore sizes can be used to further characterize biochar where pores less than 2 nm in size are referred to as micropores, 2–50 nm as mesopores, and larger than 50 nm as macro-pores [27,40]. Biochar properties such as elemental composition, pH, redox potential (Eh), CEC, and surface functional groups control the interaction between soil and biochar properties [20,41–43] and can modulate soil performance. There is very little information in the current scientific literature on how these modulations affect podzolic soil performance and crop production in the boreal ecosystem.

In the boreal ecosystem, a cool climate with a short crop growing season is considered a critical limitation to agricultural productivity [44–46]. Major factors that result in poor productivity are low soil pH and fertility, and uneven rainfall distribution. Potential toxicity from soluble forms of Al, Mn, and Fe, are also factors that can negatively impact the physical properties of podzolic soils [47]. Sandy soil is prone to high nutrient leaching due to continuous spring, summer and fall rainfall, and large spring thaw. Innovation in production systems and a better understanding of crop adaptation strategies are therefore critical for sustaining agricultural productivity in boreal regions. Improving soil quality is essential to help ensure food and agricultural quality in a world with a rising population in the boreal regions [48]. Modern scientific literature is replete with examples of biochar's ability to improve soil physicochemical properties and agricultural conditions. However, only a small number of studies have been conducted on the biochar amendment to improve the soil performance including physicochemical properties of podzolic soil in boreal climates or ecosystems [23,49–51]. This is important to note considering the boreal ecosystem is facing an increase in agricultural production and covers approximately 11% of the terrestrial land surface on Earth [48]. In 2019, Wanniarachchi et al. [52] reported that biochar application influences some properties of podzolic soil (e.g., water repellency—WR). However, biochar stability in agricultural practices and the mechanism of alteration of physicochemical properties in acidic soils has not been investigated [30].

Because of the lack of studies on biochar application in acidic soils, biochar was applied on podzolic soil to investigate further. In the agricultural field basically two types of biochar are used: granular and powder biochar. The overarching hypotheses were "application of biochar to podzolic soil will improve soil hydraulic properties" and "granular biochar is less efficient than powder biochar in improving availability of PAW". The objective of the study was to investigate the influence of biochar amendment on the physicochemical properties of podzolic soil. Overall, the goal of the study was to evaluate the effects of different types of biochar on important soil physicochemical properties that can influence crop performance when cultivated on podzolic soils in boreal ecosystem. The experiments were conducted focusing on several research questions such as: What are the effects of different biochar types and application rates on the physicochemical properties of topsoil, E-horizon when separated, and when mixed? Are there any temporal effects of the biochar amendment on the physicochemical properties of podzolic soils (pH, electrical conductivity (EC), MC, and WR)? What are the impacts of granular and powder biochar on the podzol soil water retention curve (SWRC)? How do biochar characteristics (pH, EC, CEC, surface area, pore size, and distribution pattern) influence the physicochemical properties of podzolic soil? It is expected that the study findings significantly improve our understanding of how biochar application used as a soil amendment and improve soil health, as well as agricultural productivity of podzols, in the boreal ecosystem.

3.2 Materials and Methods

3.2.1 Sampling site, sample collection from field and sample preparation

To conduct the study, soil samples were collected from the agricultural experimental station managed by the Department of Fisheries, Forestry and Agriculture of the Government of Newfoundland and Labrador in Pasadena (49°5′38.63” N and 57°32′9.32” W), Newfoundland, Canada, on June 19, 2019. Topsoil and E-horizon soil samples were collected from 0 to 15-cm depth and brought to the Boreal Ecosystems Research Facility (BERF) of Grenfell Campus, Memorial University of Newfoundland. Soil samples were air-dried for seven days at room temperature, then sieved using a 2-mm sieve. During soil sampling from the field, I observed that the average depth of topsoil was around 10 cm, while the below E-horizon soil was around 5 cm thick. Before cultivation, soil is usually ploughed forming a horizon consisting a mixed of topsoil and E-horizon. Based on these observations, the mixed soil was prepared combing topsoil and E-horizon soils with a ratio of 2 (topsoil): 1 (E-horizon soil)—according to the average soil layers in the field. Three soil types were evaluated: topsoil, E-horizon soil, and the mixed soil. Two types of biochar: granular biochar (Market Product—Yellow Pine, Pinus Spp. at 500 °C 30 min, Air Terra Inc., Alberta, Canada), and powdered biochar (Market Product—Maple Hardwood 450 °C, ABRI Tech Inc., Quebec, Canada) were used in the experiment. Soil samples were amended with four biochar rates (weight basis): 0% (control), 0.5% (5 g kg soil), 1% (10 g kg soil), and 2% (20 g kg soil) based on literature review and general application rates in the agricultural soils. If it is assumed that the average bulk density (BD) of 1.25 gcm^{-3}, and biochar incorporation at a soil depth of 0.1 m, these tested rates would be equal to 6.25, 12.5 and 25.0 Mg of biochar per ha. Ten important physicochemical parameters of the soil (BD, porosity, FC, PAW, WR, EC, pH, CEC, total carbon (TC), and nitrogen (N)) were analyzed in this study. A total of 72 experimental units, including all treatments and parameter combinations (3 types of soil, 2 types of biochar with 4 rates, 10 physicochemical properties, and 3 replications), were conducted to assess the effects of biochar on physicochemical properties of podzolic soil (Figure 3.1).

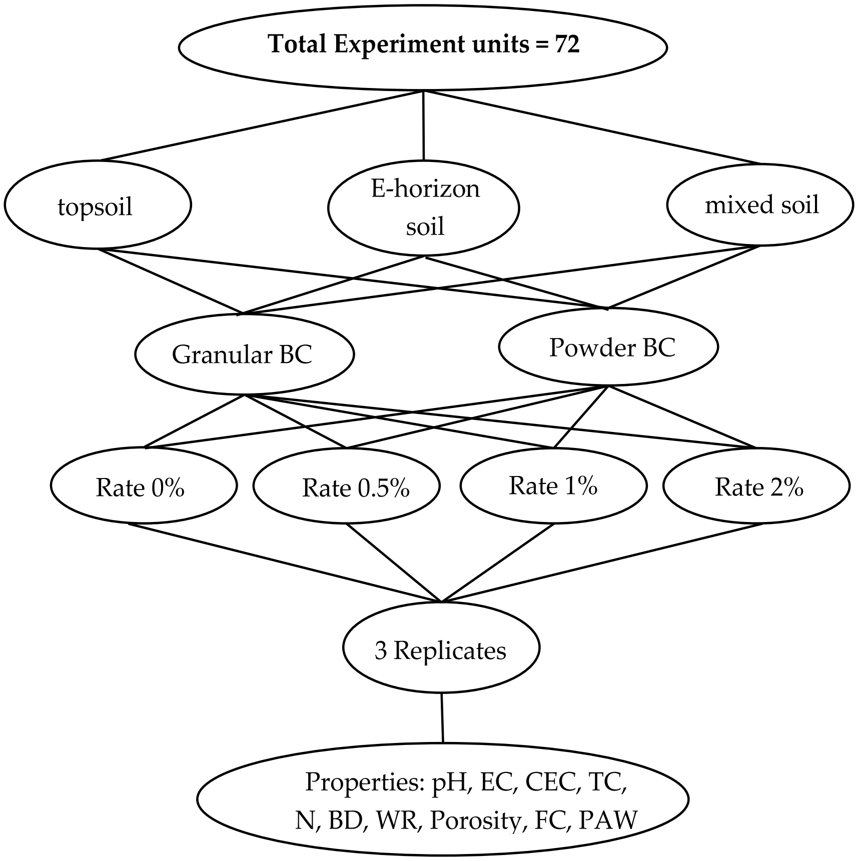


Figure 3.1: Flow chart of investigating the effect of biochar type and different rates on physicochemical properties of podzolic soils. Abbreviations: EC—electrical conductivity; CEC—cation exchange capacity; TC—total carbon; N—nitrogen; BD—bulk density; WR—water repellency; FC—field capacity; PAW—plant available water.

3.2.2 Biochar characterization

The surface of granular and powder biochar was analyzed using a scanning electron microscope (SEM), to provide detail about physicochemical, elemental, and morphological properties [53,54]. High-resolution images from 1 mm to 2 μm (magnification 100× to 49,999× with the pressure 4.96×10^{-6} mbar to 4.67×10^{-6} mbar) for both biochar types to identify the diameter and availability of the pore space were taken using SEM [13,53]. Biochar specific surface area was analyzed by the Brunauer−Emmett−Teller (BET) N_2 (0.162 nm^2) method and used a NOVA-2000E surface area analyzer [55,56].

3.2.3 Soil particle size analysis

The hydrometer method was used for soil particle size analysis following the procedures of the Bouyoucos method [57]. Topsoil and E-horizon soil samples were analyzed and calculated the particle size in the mixed soil according to the mixing ratio of topsoil (2): E-horizon soil (1). The percentages of clay (<0.002 mm), silt (0.002–0.05 mm), and sand (0.05–2 mm) were calculated following Equations (1) – (3).

$$\%\ \text{Clay} = \text{Hydrometer reading at 6 h. and 52 min.} \times 100/\ \text{wt. of samples} \quad (1)$$

$$\%\ \text{Silt} = \text{Hydrometer reading at 40 s.} \times 100/\ \text{wt. of samples} - \%\ \text{clay} \quad (2)$$

$$\%\ \text{Sand} = 100\% - \%\ \text{Silt} - \%\ \text{Clay} \quad (3)$$

3.2.4 Bulk Density (BD)

The BD was measured in the samples for each treatment. For this, 86.7 cm^3 volume metal containers were filled (tapped three times on the table) with soil and biochar samples (three replications). The samples were oven-dried for 24 h at 105°C in a forced air-dried oven (SHEL LAB, SHELDON Manufacturing. Inc., Cornelius, NC, USA). Then BD of the samples (dry sample mass/volume of sample) was calculated. The BD of all the treatment combinations were calculated following Equation (4) [52].

$$BD = \frac{100}{[\left(\frac{x}{\rho 1}\right)+\left(\frac{100-x}{\rho 2}\right)]} \tag{4}$$

where BD, ρ_1, and ρ_2 are the bulk densities (gcm^{-3}) of the biochar: soil mixtures, biochar only, and soil only, respectively, and x is the biochar rate (%) by weight.

3.2.5 Water Repellency (WR)

A water drop penetration time (WDPT) test was conducted in a 3.85 cm height and 5.81 cm diameter cylindrical plastic container. The bottom of each container was covered by a geotextile cloth to hold the samples. To conduct the WDPT test, about 78.64 ± 0.1 to 92.03 ± 0.1 g of samples were placed in each container. Same samples were used for both WR and BD measurements. A 50-µL volume burette was used in the WDPT test, and one drop of deionized water (50 ± 1 µL) was placed on the top of the sample surface from about a 10-mm height. A stopwatch was used to record the penetration time after placing the water drop. The time was recorded carefully when the drop of water penetrated the surface layer of the sample to ensure accuracy. The WR measurement values were categorized following Leelamanie et al. [58] who suggested the following WR categories: non-repellent (≤1 s), slightly repellent (1–60 s), strongly repellent (60–600 s), severely repellent (600–3600 s) and extremely repellent (≥3600 s). Each sample container was covered with a lid to protect sample from evaporation during the experiment. To measure the temporal effects, soil MC at FC and WDPT test were done. After that, samples were kept in a forced air-dried oven (SHEL LAB, SHELDON Manufacturing. Inc, Cornelius, USA) at 28° C, and sample weights were measured from day 1 to day 6 to estimate the SMC and conducted the WDPT test.

3.2.6 pH and Electrical Conductivity (EC)

A portable pH/EC/TDS/Temperature meter (HANNA—HI9813–6 with CAL Check, ON, Canada) was used to measure pH and EC in all sample treatments. A 15-g air-dried sample from each biochar-treated soil was diluted in 30 mL of de-ionized water (1:2 ratio) in 50-mL prewashed polypropylene tubes (VWR, ON, Canada). Each vial containing the sample was stirred for one hour at 100 RPM speed. Samples were then left in the vials for 30 min to settle. pH and EC measurements were taken continuously for 7 days, and updated measurements were taken almost at the same time each day [50,59].

3.2.7 Cation Exchange Capacity (CEC)

For all soil amendments, CEC was measured chromatographically by changing sodium acetate with soil or biochar cations [50]. Ion chromatography (Dionex ICS-5000 + DC-5 detector/chromatography module) was used to analyze the amount of sodium concentration in the sample solutions. Interference among sodium (Na) and ammonium (NH_4^+) peaks were observed, and the values were corrected to get the actual concentration of Na (cmolkg^{-1}) using the following Equation (5):

$$\text{Exchangeable amount of Na} = \frac{a \times b \times mcf}{(d) \times (23) \times s} \quad (5)$$

where a = Na concentration (ppm); mcf = the moisture correction factor of oven-dried soil; s = the weight of air-dried sample (g); b = amount of ammonium acetate solution (33 mL); d = the conversion factor (10) from ppm to cmol kg^{-1}; 23 = the molecular weight of Na.

3.2.8 Total Carbon (TC) and Nitrogen (N)

TC and N were determined by elemental combustion analysis [41,60]. Three types of soil (topsoil, E-horizon soil, and mixed soil) and two types of biochar (granular and powder) with three replications were homogenized as follows: the samples were ground well to make the particle size very fine, then around 5 mg samples were taken in the designated capsule and the percentage of TC and N contained in the sample were measured using the CHNS Analyzer (Series II CHNS/O Analyzer 2400, PerkinElmer, Folio Instruments, Inc. CT, USA). Based on the estimated % of TC and N of topsoil, E-horizon soil, granular, and powder biochar, % of TC and N values for all the combinations using 0, 0.5, 1, and 2% biochar rates were calculated.

3.2.9 Soil Water Retention Curve (SWRC)

3.2.9.1 Porosity and Field Capacity (FC)

A pressure plate apparatus system (0700CG23F1 Manifold and 0505V# Compressor, model 1600, Soil Moisture Equipment Corp., CA, USA) was used for developing the SWRC. Soil (control) and soil amended with biochar (treatments) weights needed for the sampling ring was calculated based on the predetermined BD, ring volume (21.53 cm^3), and the moisture factor of the respective sample. The total weight of each sample (including filter paper, plastic ring, and sample) was taken. Samples were saturated for 3 days using a shallow plastic plate and maintained a water height just below the top of the plastic ring (around 0.2 cm). Once the samples were assumed to reach saturation (when a film of water on the soil surface was observed), sample weights were measured (Ws) and samples were then arranged on 50 kPa ceramic plates and placed at the 500 kPa pressure chambers. The initial data point was taken at 10 kPa. Once the water release from the chamber stopped and samples reached a constant weight at the set pressure, the weight of samples was measured. Then samples were placed in the chamber again, and the pressure was increased to 20 kPa. The procedure was repeated subsequently for 30, 40, 50, 70, 100, 300, 400, 500, 600, and 700 kPa pressure levels. The porosity was calculated using Equation (6) at 0 kPa and FC was estimated at 10 kPa using Equation (7) [59].

$$\text{Porosity (p)} = \frac{\mathrm{Ws}-\mathrm{Wp}}{\mathrm{Vt}} \times 100 \qquad (6)$$

$$\text{Field Capacity (FC)} = \frac{\text{Wd}-\text{Wp}}{\text{Vt}} \times 100 \qquad (7)$$

where Ws is the saturated soil core weight, Wp is the dried soil core weight, Wd is the drained soil core weight and Vt is the core volume.

3.2.9.2 Plant available water (PAW)

All gravimetric water contents at each pressure level (ψ) to volumetric soil moisture contents (VSMC) (θ) were converted using calculated BD of the samples. Then, VSMC (θ), and pressure (ψ) were fitted to the van Genuchten (VG) model [61], Equation (8) [62]. Usually, VG model describes the SWRC of unsaturated soils. A VG function was used to predict how the value would change from 800 to 1500 kPa (Equation (8) using measured data acquired up to 700 kPa. The VSMC at the permanent wilting point (PWP) was predicted using the fitted VG equation, with the pressure being set at 1500 kPa.

$$\theta(\psi) = \frac{(\theta_s - \theta_r)}{[1+\propto (\psi)^n]^m} + \theta_r \qquad (8)$$

where $\theta(\psi)$ is the VSMC (cm^3cm^{-3}) at a given matric potential ψ(kPa); θ_s is the saturated water content (cm^3cm^{-3}) when ψ the 0 kPa; θ_r is the residual water content (cm^3cm^{-3}). At $\psi \geq -1500$ kPa (0.05–0.07) and $\propto$, n, and m shape parameters of the VG equation (Equation (8). The Mualem constant ($m = 1-1/n$) was adopted to increase model parsimony [28,61,63,64].

SWRC of measured values vs. predicted values were prepared using the VG equation up to PWP at 1500 kPa. Additionally, a 1:1 line graph of measured and predicted value was created to check whether the slope is equal to 1 and the intercept is equal to 0. The root means square error (RMSE) was calculated between estimated and predicted values to check the accuracy of the prediction.

PAW or water storage available for plant use was calculated as the difference between VSMC at field capacity (θ_{FC}) and permanent wilting point (θ_{PWP}) (Equation (9).

$$\text{Plant Available Water (PAW)} = \theta_{FC} - \theta_{PWP} \tag{9}$$

3.2.10 Statistical analysis

To assess and quantify the effects of different biochar types and application rates on the physicochemical properties of three soils, a general analysis of variance (ANOVA) was conducted. Fisher’s least significant difference (LSD) test was used to compare control (only soil without biochar) and treatment groups at alpha = 0.05 to know the significant effect of different variables in different treatment [36]. Descriptive statistical analysis was performed using the software STATA 12.0 version and MS Excel. Graphical visualizations were done through MS excel. Principal Component Analysis (PCA) of data was carried out using XLSTAT (Premium 2017, Version 19.5, Addinsoft, New York, NY, USA).

3.3 Results

3.3.1 Basic physicochemical properties of soil and biochar

The basic physicochemical properties of these two biochar types are shown in Table 3.1.

Table 3.1: Physicochemical properties of soil and biochar.

Physicochemical Parameters	**Unit**	**Topsoil**	**E-horizon Soil**	**Mixed Soil**	**Granular Biochar**	**Powder Biochar**
pH		5.3 ± 0.00	4.3 ± 0.00	5.6 ± 0.00	9 *	8.9 *
EC	dSm^{-1}	0.15 ± 0.02	0.00 ± 0.00	0.00 ± 0.00	5.2*	1.3*
CEC	$cmolkg^{-1}$	4.99 ± 0.09	2.61 ± 0.27	3.61 ± 0.17	11.07 ± 0.70	5.76 ± 0.31
BD	gcm^{-3}	1.31 ± 0.10	1.40 ± 0.00	1.34 ± 0.00	0.20 ± 0.00	0.35 ± 0.00
WR	S	1.67 ± 0.58	4.00 ± 0.00	3.00 ± 0.00	-	-
TC	%	2.40 ± 0.00	0.43 ± 0.00	1.74 ± 0.00	24.53 ± 1.24	58.63 ± 4.60
N	%	0.05 ± 0.00	0.07 ± 0.00	0.06 ± 0.00	0.04 ± 0.01	0.1 ± 0.04
Porosity	%	0.52	39.63	48.41	-	-
FC	%	29.18	27.86	30.33	-	-
Surface Area	m^2g^{-1}	-	-	-	Almost nonporous	12.9
Clay	%	16	10	14	-	-
Silt	%	24	32	27	-	-
Sand	%	60	58	59	-	-

Note: Top, E-horizon and mixed soil, granular and powder biochar (n = 3) and abbreviations: CEC—cation exchange capacity; EC—electrical conductivity; BD—bulk density; WR—water repellency; TC—total carbon; N—nitrogen; FC—field capacity.
* Source: Wanniarachchi et al., 2019b [52].

3.3.2 Characteristics of granular and powder biochar (BET and SEM image analysis)

The surface area (SA) of powdered biochar was found to be 12.9 m^2g^{-1}, and granular biochar SA was very low (almost non-porous). A high-resolution SEM image (100×–49,999× mag) taken showed morphological and well-defined pore structure and distribution pattern (arrangement of pore space), helping to differentiate the granular from the powdered biochar (Figures 3.2 and 3.3).

In granular biochar images, the pore space was found only on one side (Figure 3.2c), whereas on the other sides, surface walls contained no pore spaces (Figure 3.2(d,e)). Some pore space entrances were found to be collapsed with fragments (Figure 3.2(d_2,e_1)). In the granular biochar samples, pore sizes were not evenly distributed or appeared uniform. Pore spaces were observed on different sides with diameters larger than 10 µm (Figure 3.2(e_2)). It was observed that pore spaces were blocked (partially) by the fragments (Figure 3.2f). According to the observation in Figure 3.2g, pore diameters were found to be <2 µm and 2–5 µm (app.) at different sides of the granular biochar surface, with a non-uniformly distributed number of pores.

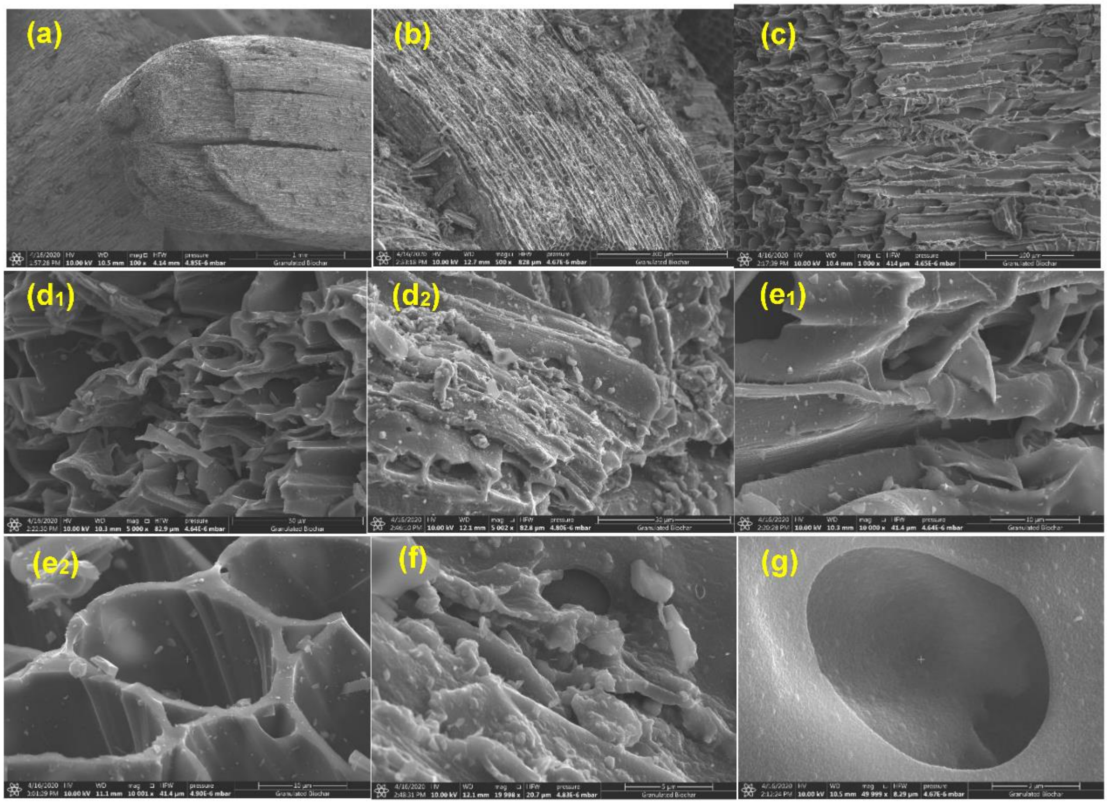


Figure 3.2: Scanning electron microscopy image of granular biochar at different magnifications and scales: (a) 100× mag—1-mm scale; (b) 500× mag—300-µm scale; (c) 1000× mag—100-µm scale; (d_1) 5000× mag—30-µm scale; (d_2) 5000× mag—30-µm scale; (e_1) 10,000x mag—10-µm scale; (e_2) 10,001× mag—10-µm scale; (f) 19,998× mag—5-µm scale; (g) 49,999× mag—2-µm scale.

The percentage of pore space in powdered biochar was low (Figure 3.3($c_{1,2}$)). Pore spaces were found on only one side, and other sides were occupied by mobile components (like system fragments) in the powder biochar (Figure 3.3d). On the other side, the surface was not smooth at 5000× magnification with a 30-µm scale (Figure 3.3($e_{1,2}$)). Based on the image scale at different angles, uneven distribution of pore space and size were observed in powdered biochar. The image showed the average pore size was larger than 5 µm (or around 10 µm), with some pores being blocked by the fragments (Figure 3.3($f_{1,2}$)).

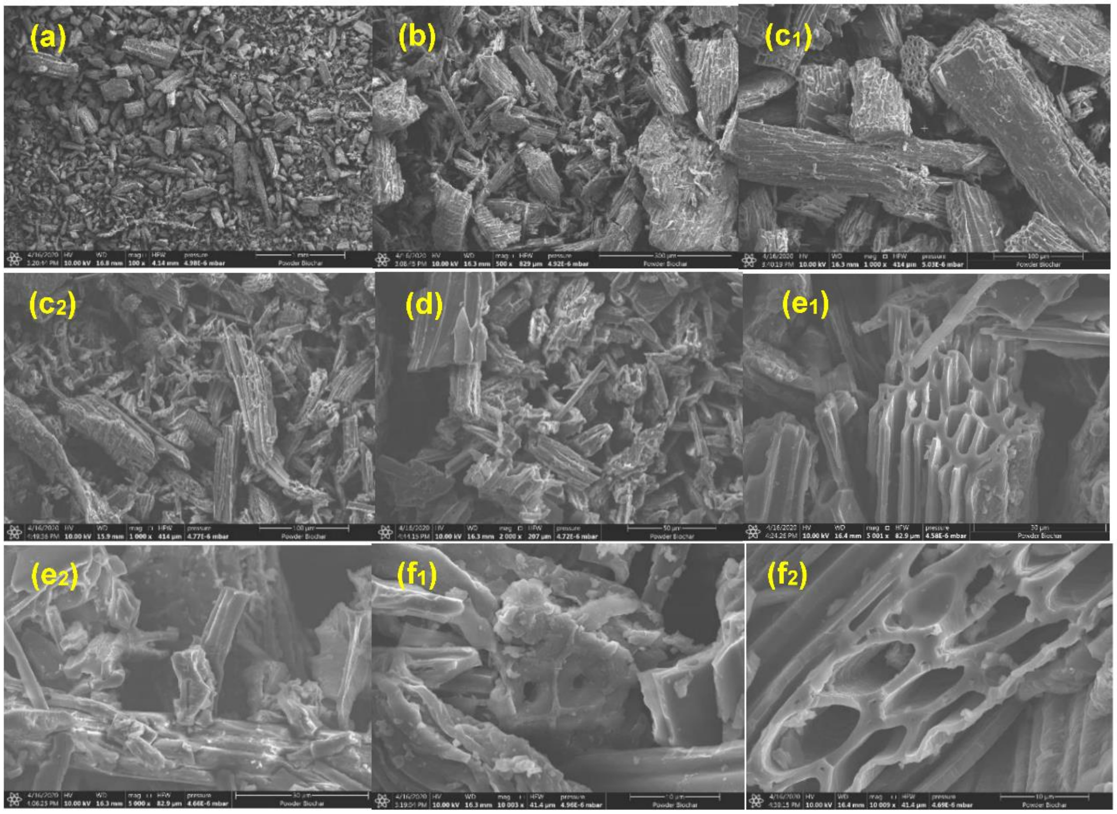


Figure 3.3: Scanning electron microscopy image of powder biochar at different magnification and scale: (a) 100× mag—1-mm scale; (b) 502× mag—300-µm scale; (c_1) 1000× mag—100-µm scale; (c_2) 1000× mag—100-µm scale; (d) 2000× mag—50-µm scale; (e_1) 5001× mag—30-µm scale; (e_2) 5000× mag—30-µm scale; (f_1) 10,001× mag—10-µm scale; (f_2) 10,000× mag—10-µm scale.

Surface morphologies of both granular and powder biochar showed very heterogeneous and structurally complex pore size and shape distribution. In both granular and powder biochar samples, some of the micropores (as visible in the SEM image at different angles) were slightly blocked by the system fragments (as mobile components), damaging micropores. The wall structures of both types of biochar were smooth. Both biochar types surface had a rough surface, even at different angles, perhaps due to the collapse of the pore space becoming filled with system fragments (Figures 3.2 and 3.3).

3.3.3 Soil particle size distribution

Soil particle size distribution showed a higher percentage of sand-size particles in topsoil (60%) and E-horizon soil (58%) than clay size particles. Topsoil, E-horizon soil, and mixed soil were found to be loam, sandy loam, and sandy loam, respectively (Table 3.1).

3.3.4 Bulk Density (BD)

Biochar types and varying application rates had significant ($p < 0.05$) effects on BD across all three soil combinations. When granular biochar was applied in the topsoil, BD was reduced in the following order: control (1.31 gcm^{-3}) > 0.5% (1.28 gcm^{-3}) > 1% (1.24 gcm^{-3}) > 2% (1.18 gcm^{-3}). The same sequence was found (from the calculated BD) when powder biochar was added in the topsoil; control (1.31 gcm^{-3}) > 0.5% (1.29 gcm^{-3}) > 1% (1.28 gcm^{-3}) > 2% (1.24 gcm^{-3}). BD trends were highly correlated to applied biochar ratio (Table 3.2), which was expected. Granular biochar had significant ($p < 0.05$) effects on BD of E-horizon soil (control (1.40 gcm^{-3}) > 0.5%

(1.36 gcm^{-3}) > 1% (1.32 gcm^{-3}) > 2% (1.25 gcm^{-3}). When powder biochar was applied in E-horizon soil, BD also reduced (1.38, 1.36 and 1.32 gcm^{-3} with biochar rate 0.5%, 1% and 2%, respectively) compared to the control (1.40 g cm^{-3}). Both granular and powder biochar-amended mixed soil BD were decreased (1.30, 1.27 and 1.21 gcm^{-3} with the granular biochar and 1.32, 1.30, 1.27 gcm^{-3} with the powder biochar rate of 0.5%, 1% and 2%, respectively) when compared to the control (1.34 gcm^{-3}).

3.3.5 Water Repellency (WR)

The WR of granular biochar-amended topsoil slightly increased (2.33, 3.00, and 3.00 s with 0.5%, 1%, and 2% biochar application rates, respectively) compared to the control topsoil (1.67 s). Both granular and powder biochar-amended E-horizon soil increased WR characteristics (4.33, 4.67, 4.67 s when applied with 0.5%, 1%, and 2% biochar, respectively) compared to the control (4.00 s). No significant difference was found for WR when 1% and 2% powder biochar applied on mixed soil. Overall, WR increased with the biochar application rate in the treatment combination. The experimental results indicated that the biochar amendment increased small WR (by the order of seconds). All the treatments were classified as a slightly-water repellent, as the WDPT was below 5 s in most of the cases at air-dried conditions.

Table 3.2: Effect of biochar type and application rates on bulk density, water repellency, cation exchange capacity and total carbon, nitrogen on podzolic soil.

Sl. No	**Soil Type**	**Biochar**		**Bulk Density (gcm^{-3})**	**WR (s) [*p*]**	**CEC ($cmolkg^{-1}$) [*p*]**	**Total C (%)**	**Nitrogen (%)**
1	Top soil	GBC	0%	1.31 ± 0.1	1.67 ± 0.58	4.99 ± 0.09	2.40 ± 0.0	0.05 ± 0.0
2			0.5%	1.28 ± 0.0	2.33 ± 0.58 [0.39]	4.92 ± 1.26 [0.20]	2.40 ± 0.0	0.05 ± 0.0
3			1%	1.24 ± 0.0	3.00 ± 0.00	4.57 ± 0.85 [0.20]	2.40 ± 0.0	0.05 ± 0.0
4			2%	1.18 ± 0.0	3.00 ± 0.00	5.09 ± 1.76 [0.20]	2.40 ± 0.0	0.05 ± 0.0
5		PBC	0%	1.31 ± 0.1	2.33 ± 0.58	4.93 ± 0.08	2.40 ± 0.0	0.05 ± 0.0
6			0.5%	1.29 ± 0.0	3.00 ± 0.00	5.34 ± 0.60 [0.20]	2.40 ± 0.0	0.05 ± 0.0
7			1%	1.28 ± 0.0	2.67 ± 0.58 [0.08]	5.24 ± 0.10 [0.20]	2.41 ± 0.0	0.05 ± 0.0
8			2%	1.24 ± 0.0	4.00 ± 0.00	4.99 ± 0.18 [0.20]	2.41 ± 0.0	0.05 ± 0.0
9	E-horizon soil	GBC	0%	1.40 ± 0.0	4.00 ± 0.00	2.61 ± 0.27	0.43 ± 0.0	0.07 ± 0.0
10			0.5%	1.36 ± 0.0	4.67 ± 0.58	2.39 ± 0.34 [0.20]	0.43 ± 0.0	0.07 ± 0.0
11			1%	1.32 ± 0.0	4.67 ± 0.58	2.35 ± 0.49 [0.20]	0.43 ± 0.0	0.07 ± 0.0
12			2%	1.25 ± 0.0	4.67 ± 0.58	2.70 ± 0.31 [0.20]	0.43 ± 0.0	0.07 ± 0.0
13		PBC	0%	1.40 ± 0.0	4.00 ± 0.00	2.28 ± 0.49	0.43 ± 0.0	0.07 ± 0.0
14			0.5%	1.38 ± 0.0	4.33 ± 0.58	1.71 ± 0.41 [0.20]	0.43 ± 0.0	0.07 ± 0.0
15			1%	1.36 ± 0.0	4.00 ± 0.00	1.43 ± 0.06 [0.20]	0.44 ± 0.0	0.07 ± 0.0
16			2%	1.32 ± 0.0	4.67 ± 0.58	1.53 ± 0.07 [0.22]	0.44 ± 0.0	0.07 ± 0.0
17	Mixed soil	GBC	0%	1.34 ± 0.0	3.00 ± 0.00	2.83 ± 1.32	1.74 ± 0.0	0.06 ± 0.0
18			0.5%	1.30 ± 0.0	3.67 ± 0.58	3.64 ± 0.45 [0.20]	1.74 ± 0.0	0.06 ± 0.0
19			1%	1.27 ± 0.0	3.00 ± 0.00	3.49 ± 0.41 [0.20]	1.74 ± 0.0	0.06 ± 0.0
20			2%	1.21 ± 0.0	3.00 ± 0.00	3.61 ± 0.22 [0.20]	1.74 ± 0.0	0.06 ± 0.0
21		PBC	0%	1.34 ± 0.0	2.33 ± 0.58	3.61 ± 0.17	1.74 ± 0.0	0.06 ± 0.0
22			0.5%	1.32 ± 0.0	2.33 ± 0.58[0.08]	3.59 ± 0.15 [0.20]	1.74 ± 0.0	0.06 ± 0.0
23			1%	1.30 ± 0.0	3.00 ± 0.00	3.38 ± 0.30 [0.20]	1.75 ± 0.0	0.06 ± 0.0
24			2%	1.27 ± 0.0	3.33 ± 0.58 [0.39]	3.35 ± 0.13 [0.20]	1.75 ± 0.0	0.06 ± 0.0

Abbreviations: GBC–granular biochar; PBC—powder biochar; WR—water repellency at air dried condition; Total C—total carbon. Note: *p* value—treatment values compared to control. All the treatment combinations of bulk density, total C and nitrogen were calculated values based on experimental values of three types of soil and two types of biochar as mentioned in the method.

3.3.6 Cation Exchange Capacity (CEC)

In the experiment, when soil was amended with different types and rates of biochar, topsoil (4.99–5.09 cmolkg^{-1}) showed higher CEC values than E-horizon soil (2.61–2.70 cmolkg^{-1}) and mixed soil (2.83–3.61 cmolkg^{-1}) (Table 3.2). Both granular and powder biochar had almost no effect on the CEC of E-horizon soil; 2% granular biochar application in the mixed soil showed higher CEC than the control (2.83 cmolkg^{-1}). Biochar-amended topsoil slightly increased CEC with high variabilities.

3.3.7 Total Carbon (TC) and Nitrogen (N)

The TC content of granular biochar was 24.53 ± 1.24%, while for powder biochar it was 58.64 ± 0.04% (Table 3.1). In the experiment, 0.5%, 1%, and 2% of both types of biochar were applied in the podzolic soil. Powder biochar amendment slightly impacted TC content in the treated topsoil. The soil–biochar treatment combinations were found to be 2.40% C with 0.5% biochar, 2.41% C with 1% biochar, and 2.41% C with 2% biochar, with the control topsoil C content being 2.40%. The percentage of C slightly increased from 0.43 to 0.44% with the application of powder biochar (0–2%) in E-horizon soil. In the case of powder biochar-amended mixed soil, the percentage of C content increased by 1.74% (with 0% biochar) and 1.75% (with 2% biochar).

The sample biochar contained only a low level of nitrogen (N), at 0.04% (granular biochar), and 0.1% (powder biochar) (Table 3.1). In all types of biochar-treated soils, the N levels increased when the biochar application rate increased.

3.3.8 Soil Water Retention Curve (SWRC)

Figure 3.4 compares measured and predicted (using VG equation) values in the SWRC. Table 3.3 outlines the co-efficient of determination (R^2) for all the treatment combinations. SWRC showed the changes in the characteristics of three types of soils (top, E-horizon, and mixed soil) after amendment with two biochar types (granular and powder) at different rates (0%, 1%, and 2%) (Figure 3.4). The powder biochar amendment increased SWR compared to the control soil and high-water retention capacity compared to granular biochar amended soil. In the experiment, important physical parameters such as porosity, FC, and PAW increased with the increasing rates of powder biochar amendment in the podzolic soil.

3.3.8.1 Porosity and Field Capacity (FC)

In the topsoil amended with powder biochar, porosity increased slightly by 1.1% (with 1% biochar rate) and by 1.6% (with 2% biochar rate), compared to the control. In the case of granular biochar application to the topsoil, porosity showed a slightly decreasing trend compared to the control. For example, porosity decreased by 3.1% with a 1% biochar rate. In the powder biochar-treated E-horizon soil, porosity increased by 2.4% (with 1% biochar rate) and by 5.0% (with 2% biochar rate) when compared to the control E-horizon soil. In the E-horizon soil, porosity decreased by 4.2% with the application of 2% granular biochar. In the case of mixed soil, porosity increased by 2.8% with a 1% powder biochar rate. In the mixed soil, porosity decreased by 2.6% (with 1% granular biochar rate) and by 16.5% (with 2% granular biochar rate) compared to the control mixed soil (Figure 3.5). The results imply that using powder biochar as a soil amendment would be suitable to increase soil moisture content in all three types of soil.

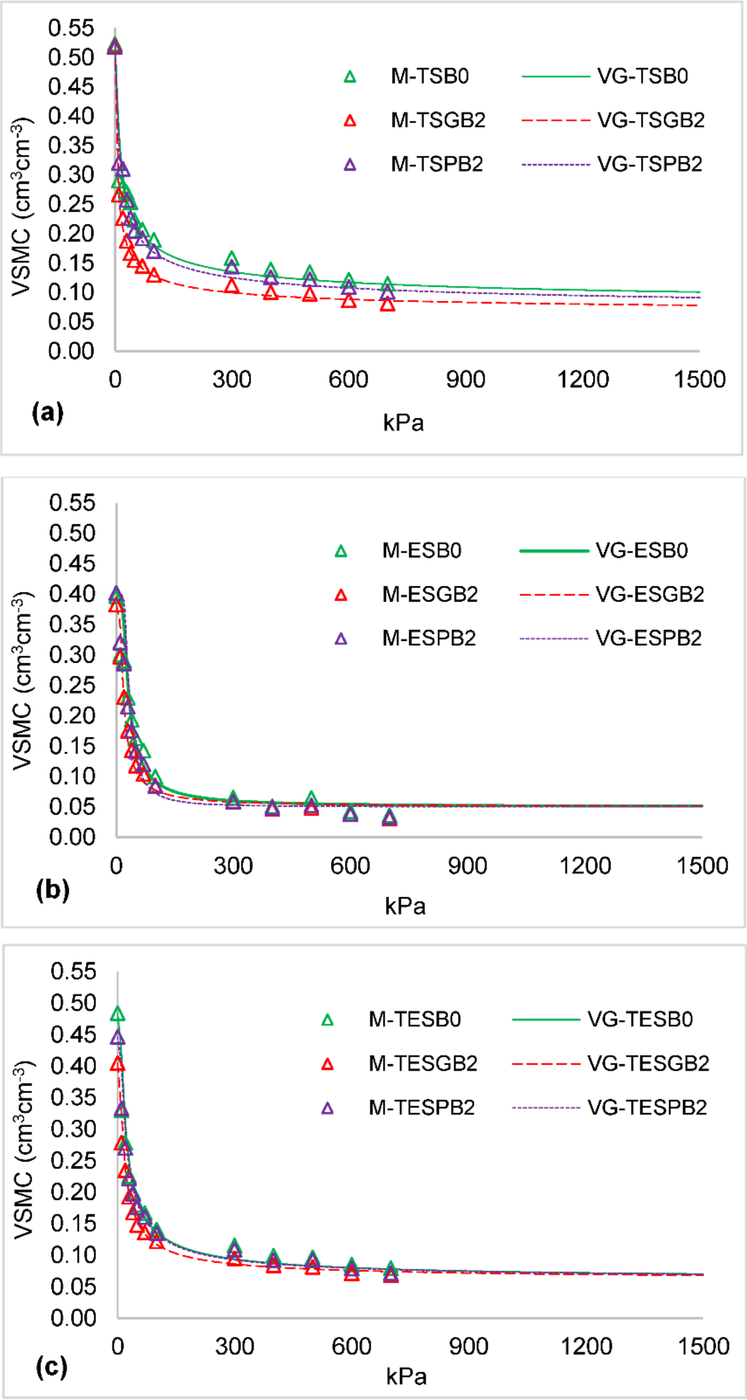


Figure 3.4: Soil water retention curve (SWRC) of measured (M) values vs. predicted values using van Genucthen (VG) equation up to permanent wilting point (PWP) at 1500 kPa for: (a) topsoil, (b) E-horizon soil and (c) mixed soil. Abbreviations: VSMC —

volumetric soil moisture content; M-TSB0 — measured topsoil with 0% biochar; VG-TSB0 — predicted topsoil with 0% biochar; M-TSGB2 — measured topsoil with 2% granular biochar; VG-TSGB2 — predicted topsoil with 2% granular biochar; M-TSPB2 — measured topsoil with 2% powder biochar; VG-TSPB2 — predicted topsoil with 2% powder biochar; M-ESB0 — measured E-horizon soil with 0% biochar; VG-ESB0 — predicted E-horizon soil with 0% biochar; M-ESGB2 — measured E-horizon soil with 2% granular biochar; VG-ESGB2 — predicted E-horizon soil with 2% granular biochar; M-ESPB2 — measured E-horizon soil with 2% powder biochar; VG-ESPB2 — predicted E-horizon soil with 2% powder biochar; M-TESB0 — measured mixed soil with 0% biochar; VG-TESB0 — predicted mixed soil with 0% biochar; M-TESGB2 — measured mixed soil with 2% granular biochar; VG-TESGB2 — predicted mixed soil with 2% granular biochar; M-TESPB2 — measured mixed soil with 2% powder biochar; VG-TSPB2 — predicted mixed soil with 2% powder biochar.

Table 3.3: Fitted and measured values of the saturated and residual water content and parameters of the fitted values of the soil water retention model.

Sl. No	**Soil type**	**Biochar**		**θ_s (cm^{3}cm^{-3})**		**θ_r (cm^{3}cm^{-3})**	**α**	**n**	**R^2**
		Type	**Rate**	**a**	**b**				
01	Top Soil	GBC	0%	0.52	0.52	0.07	1.98	1.81	0.9534
02			1%	0.51	0.51	0.06	3.37	1.89	0.9889
03			2%	0.52	0.52	0.06	4.75	1.89	0.9973
04		PBC	0%	0.52	0.52	0.06	1.74	1.75	0.9549
05			1%	0.53	0.53	0.06	1.95	1.68	0.9652
06			2%	0.52	0.52	0.06	2.27	1.76	0.9857
07	E-horizon soil	GBC	0%	0.39	0.39	0.05	0.49	5.65	0.9421
08			1%	0.39	0.39	0.05	0.45	6.95	0.9612
09			2%	0.38	0.38	0.05	0.90	4.85	0.9714
10		PBC	0%	0.40	0.40	0.05	0.49	5.65	0.9543
11			1%	0.41	0.41	0.05	0.85	4.32	0.9693
12			2%	0.40	0.40	0.05	0.41	8.27	0.9514
13	Mixed soil	GBC	0%	0.48	0.48	0.06	0.95	2.87	0.9677
14			1%	0.47	0.47	0.06	1.25	2.81	0.9784
15			2%	0.41	0.41	0.06	1.20	2.75	0.9851
16		PBC	0%	0.44	0.44	0.06	0.90	2.85	0.9601
17			1%	0.46	0.46	0.06	0.90	2.95	0.9685
18			2%	0.45	0.45	0.06	0.90	2.85	0.9826

Abbreviations: GBC—granular biochar; PBC—powder biochar; θ_s — the saturated water content (cm^{3}cm^{-3}) when $\psi \leq -3$ kPa; θ_r — the residual water content range 0.05–0.07 (cm^{3}cm^{-3}) at $\psi \leq -1500$ kPa; α, and n — shape parameters of the van Genuchten (1980) model [61]. Van Genuchten parameters were fitted to the data between ≈1.8 and 1500 kPa only. The parameters are therefore only valid for this water potential range. a — the measured values of θs; b — the fitted values of θs.

In the powder biochar-amended topsoil, FC increased by 3.3% with a 1% rate and by 6.7% with a 2% rate compared to control topsoil. In contrast, with the application of granular biochar to the topsoil, FC decreased by 3.4% (with 1% biochar rate) and by 8.3% (with 2% biochar rate) compared to the control topsoil. Similarly, with the application of power biochar in E-horizon soil, FC increased by 3.3% (with 1% biochar rate) and by 6.7% (with 2% biochar rate) compared to the control E-horizon soil. However, FC in the granular biochar-amended E-horizon soil decreased slightly by 0.8% (with 1% biochar rate) and by 5.3% (with 2% biochar rate) compared to the control E-horizon soil.

As for the powder biochar-amended mixed soil, FC increased by 4.1% (with 1% biochar rate) and by 10.0% (with 2% biochar rate) compared to the control mixed soil. In the case of mixed soil amended with granular biochar, FC showed a decreasing trend, decreasing by 6.6% with a 1% biochar rate and by 15.5% with a 2% biochar rate compared to the control mixed soil (Figure 3.5). These results suggest that the powder biochar amendment in the podzolic soil was found to be suitable in increasing FC. Thus, the WHC in the powder biochar-treated soil was found to be higher than the WHC in the granular biochar-treated soil. Overall, the experiment results indicated that applied granular biochar possesses hydrophobic characteristics, and powder biochar possesses hydrophilic characteristics.

Table 3.3 summarizes van Genucthen (1980) [61] parameters and residual water content. All SWRC fitted parameters had a very high coefficient of determination (R^2) and were close to the unit (Figure 3.4 and Table 3.3) that showed the accuracy of the VG model for predicting the SWRC in the soil amended with granular and powder biochar.

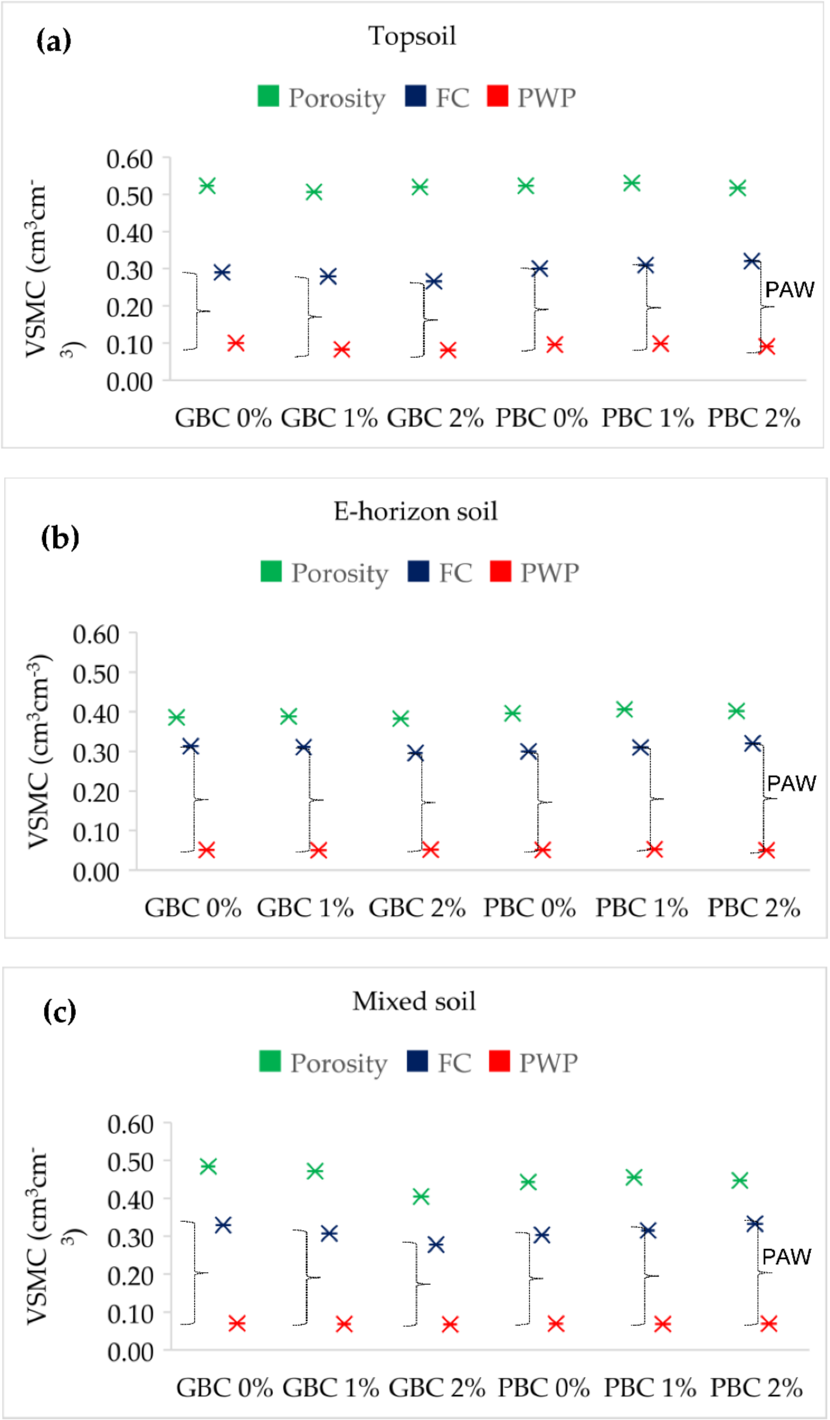


Figure 3.5: Effect of biochar amendment on porosity, field capacity (FC), permanent wilting point (PWP) and plant available water (PAW) in different types of soil: (a) topsoil; (b) E-horizon soil and (c) mixed soil. Abbreviations: GBC—granular biochar; PBC—powder biochar; VSMC—volumetric soil moisture content; the symbol "}" indicated PAW which is the difference between FC and PWP.

This indicates that the fitting of the proposed interpolation equation to the experimental data was highly acceptable. Saturated and residual water contents of the treatment combination influenced by the types of biochar. For example, the powder biochar amendment influenced an increase in saturated and residual water content, while granular biochar induced a decrease in VSMC in the biochar-treated soil.

The 1:1 comparison of the measured and predicted values of VSMC for all the combinations are shown in Figure 6. Both measured and predicted values of porosity found in 1:1 line with $R^2 = 1$, and the values were statistically significant ($p = 0.000$). For FC, both measured and predicted values were found to be very close to the 1:1 line with a high value of $R^2 = 0.9962$, and the values were statistically significant ($p = 0.012$). VSMC at −700 kPa, both measured and predicted values lie in 1:1 line with high $R^2 = 0.9699$ and the values found statistically significant ($p = 0.002$). The results of all three VSMC parameters found a good fit in the 1:1 line.

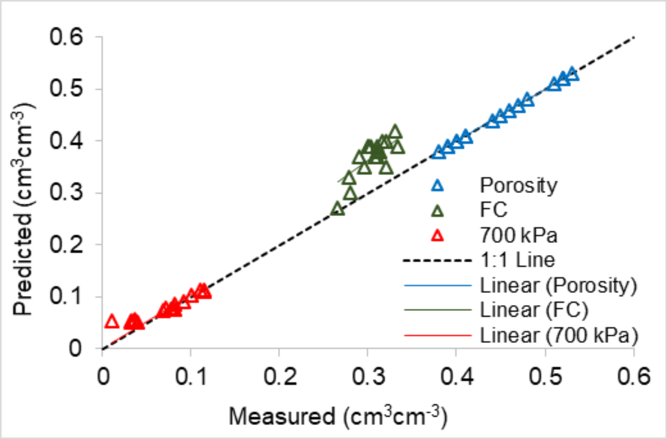


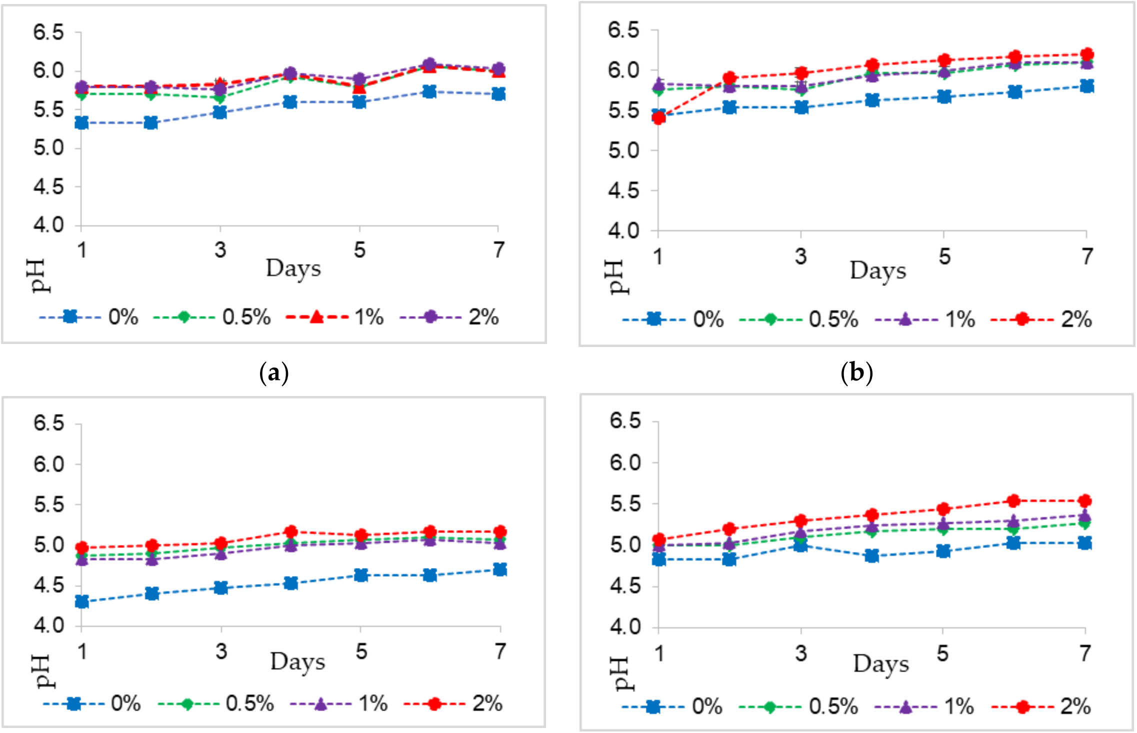
Figure 3.6: 1:1 Line graph of measured and predicted values of the porosity, field capacity (FC) and water content at −700 kPa. Abbreviation: VSMC — volumetric soil moisture content.

3.3.8.2 Plant Available Water (PAW)

PWP values of all the treatment combinations were calculated using predicted values from the van Genucthen (1980) model [61]. After determining the PWP values, PAW was found for each treatment combination. In the powder biochar-amended topsoil, PAW increased by 3.7% (with 1% biochar rate) and by 12.5% (with 2% biochar rate) when compared to the control topsoil. In contrast, PAW decreased by 2.9% in the topsoil with a 2% granular biochar amendment. In the case of powder biochar-amended E-horizon soil, PAW increased by 3.4% (with 1% biochar rate) and by 8.4% (with 2% biochar rate) when compared to the control. With the application of granular biochar in the E-horizon soil, PAW decreased very slightly (0.6%) with a 1% biochar rate and decreased by 6.3% with a 2% biochar rate. In the powder biochar-treated mixed soil, PAW increased by 5.8% (with 1% biochar rate) and by 12.9% (with 2% biochar rate). On the other hand, in the mixed soil, adding 1% granular biochar decreased PAW by 7.8% while adding 2% granular biochar decreased PAW by 19% when compared to the control mixed soil (Figure 3.5). These results suggested that granular biochar would not be suitable for increasing PAW, and the powder biochar can be applied to increase PAW at the crop root zone of podzolic soil in boreal ecosystem.

3.3.9 Temporal effects of treatments on soil pH

The temporal effects of biochar (from day 1–day 7) on pH are shown in Figure 7. In the topsoil, granular biochar amendment increased from pH 5.7 to 6.0 (with 0.5%), 5.8 to 6.0 (with 1%), and 5.8 to 6.0 (with 2%) biochar rates from day 1 to day 7 where control topsoil pH was found to be 5.3 at day 1. There was a slightly increasing trend observed in the temporal effect of pH amended with granular biochar in the topsoil (Figure 3.7a). Similarly, a slightly increasing trend was found when powder biochar was applied to the topsoil. However, E-horizon soil pH was found to be very low (pH = 4.3) in the control of E-horizon soil. After applying powder biochar to the E-horizon soil, pH increased from 4.3 to 5.5 from day 1 to day 7 with the biochar rate of 0.5–2% (Figure 3.7c, d). Increasing trends of pH were observed with the increasing rate of both granular and powder biochar in the E-horizon soil. Also, Figure 3.7e, f indicates a slightly increasing trend of pH in the mixed soil when both granular and powder biochar were applied at different rates. The initial pH of the mixed soil was 5.6, and after seven days, the pH increased to 6.1 (with 2% granular) and 6.3 (with 2% powder) after biochar application.

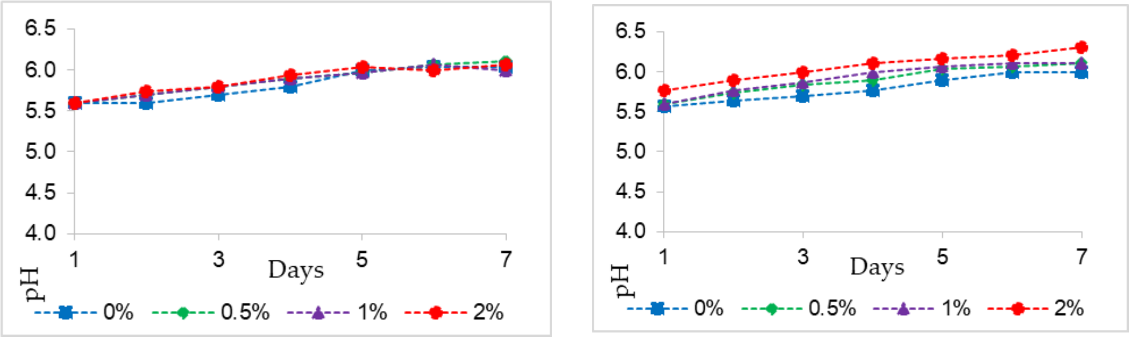


(a)

(b)

(c)

(d)

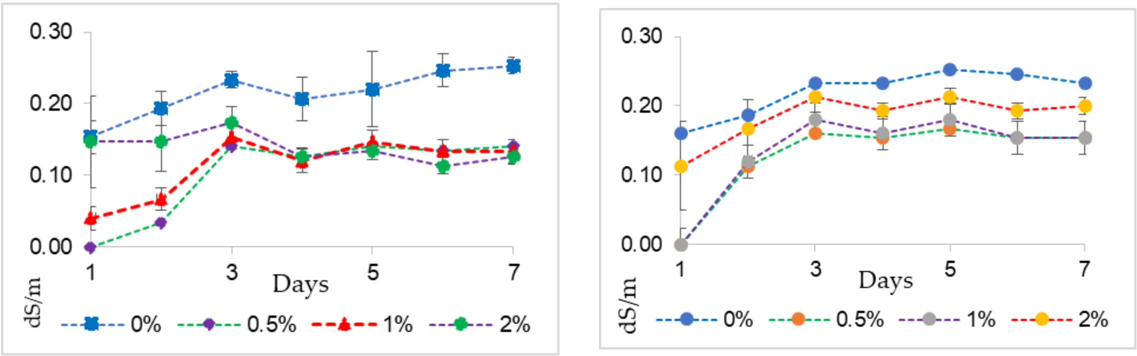


(e) (f)

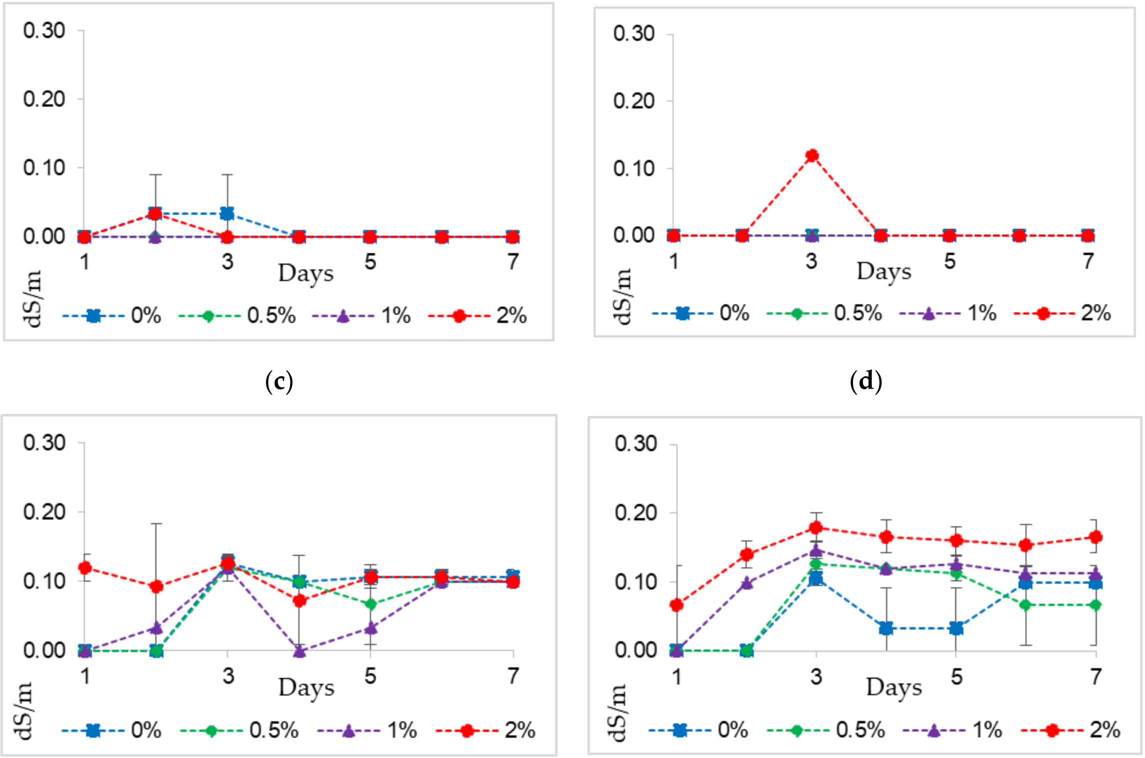
Figure 3.7: Temporal effect of biochar on pH: (a) topsoil with granular biochar; (b) topsoil with powder biochar; (c) E-horizon soil with granular biochar; (d) E-horizon soil with powder biochar; (e) mixed soil with granular biochar; (f) mixed soil with powder biochar.

3.3.10 Temporal effect on Electrical Conductivity (EC)

Figure 3.8 shows the temporal effect of different types and rates of biochar application on different types of soils from day 1 to day 7. In the topsoil, granular biochar amendment increased EC from 0.0 to 0.13 dS/m, while powder biochar increased EC from 0.0 to 0.20 dS/m from day 1 to day 7 with 0.5 to 2% biochar rates. Factually, there was no impact of biochar observed on EC in the E-horizon soil. In the mixed soil, EC increased 0.0 to 0.10 dS/m (with granular biochar) and 0.0 to 0.17 dS/m (with powder biochar) when applying biochar at different rates from day 1 to day 7.



(a) (b)



(c)

(d)

(e)

(f)

Figure 3.8: Temporal effect of biochar on electrical conductivity (EC): (a) topsoil with granular biochar; (b) topsoil with powder biochar; (c) E-horizon soil with granular biochar; (d) E-horizon soil with powder biochar; (e) mixed soil with granular biochar; (f) mixed soil with powder biochar.

3.3.11 Temporal effect on water repellency vs. moisture content

Figure 3.9 showed the temporal effect of granular and powder biochar on MC vs. WR. The effect of biochar application on WR and MC was observed at FC level from day 1 to day 6. In the biochar (both granular and powder) treated topsoil, MC instantly dropped from FC on day 1. After a declining trend of MC and WR was observed from day 1 to day 3, the trend was found to be almost flat from day 4 to day 6. In the case of biochar-treated (both granular and powder) E-horizon soil, a huge drop of MC and WR was observed from FC level to after day 1.

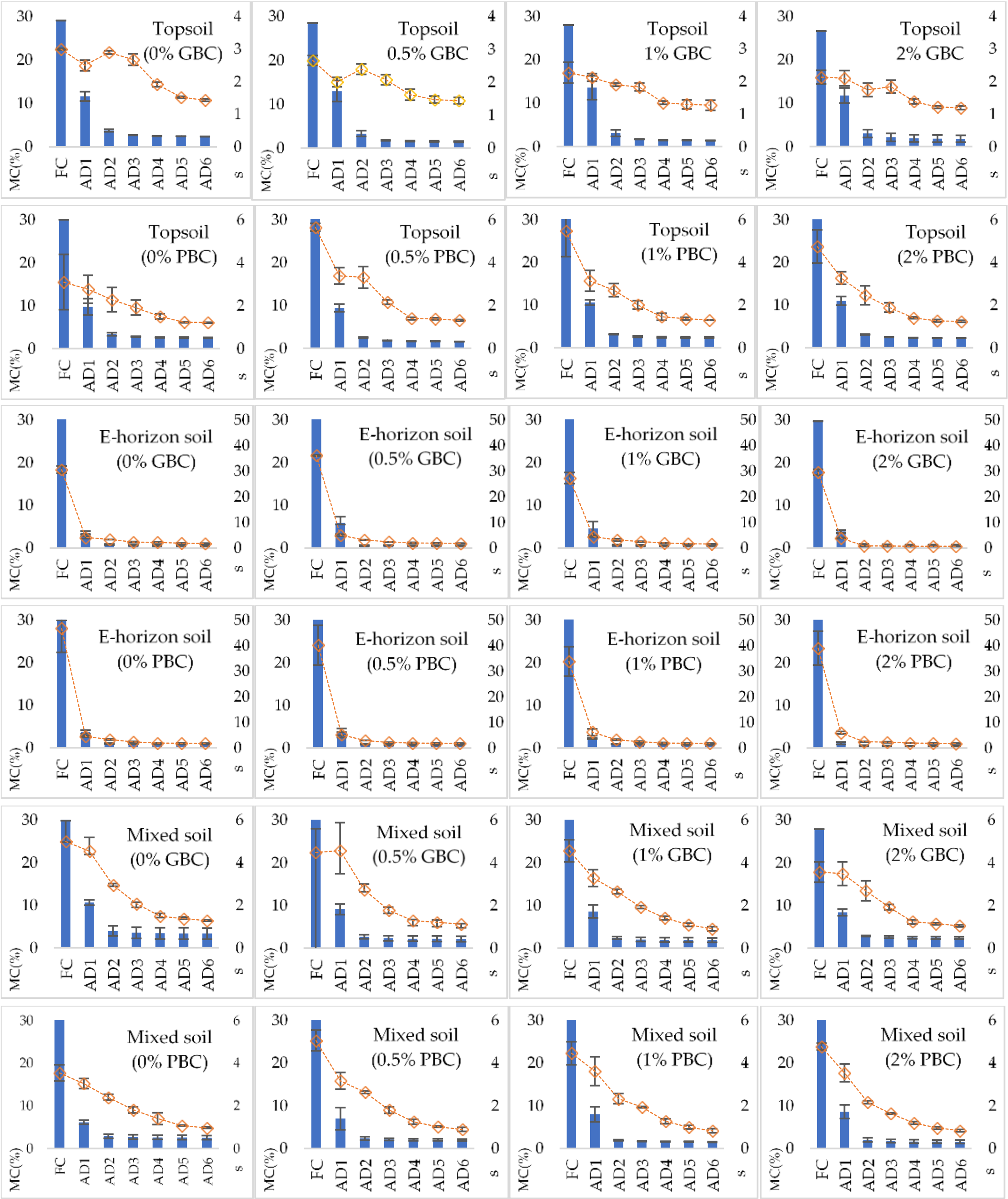


Figure 3.9: Temporal effect on moisture content (MC) vs. water repellency (WR) in biochar-amended soil. Samples were placed in the oven at 28°C after field capacity level from day 1 to day 6. Abbreviations: GBC—granular biochar; PBC—powder biochar.

The slope of the curve was found to be almost flat from day 1 to day 6. In the case of both types of biochar-amended mixed soil, a continuous declining trend was observed in both MC and WR. After 6 days drying at 28 °C in the oven, the moisture content (maximum 3.35% and minimum 0.42%—described in Figure 3.10) was found to be below the permanent wilting point (around 5–9%). Overall, MC and WR showed declining trends from day 1 to day 6 with different types and rates of biochar amendment in all types of soil (Figure 3.10).

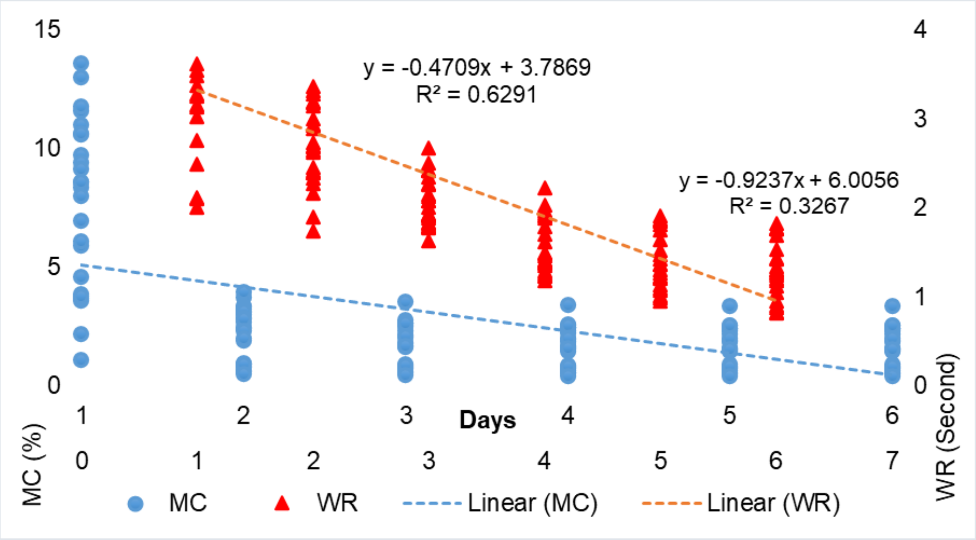


Figure 3.10: Combined temporal effect on moisture content (MC) vs. water repellency (WR) in biochar-amended soil from day 1 to day 6.

3.3.12 Principal Component Analysis

Principal component analysis (PCA) showed the relationship of shared physicochemical properties of three types of soil that were amended with two types of biochar with different rates (Figure 3.11a, b). PCA explained 72.20% of the total variability in the data set, where component 1 displayed 50.81% and component 2 displayed 21.37%, respectively, for variability. Different physicochemical properties were observed in different quadrants of the PCA biplot. Two biochar types were grouped in different quadrants based on different physicochemical properties of the three types of soil found in the PCA observation plot (Figure 3.11a). A clear grouping of three types of soil was observed due to different variables under the study (Figure 3.11b). Topsoil and E-horizon soils were observed in opposite quadrants, whereas mixed soil is noted in between topsoil and E-horizon soil, which is expected due to the mixing of both types of soils (Figure 3.11b). The distribution pattern of parameters in different quadrants explained their associations, confirming strong positive or negative correlations between the parameters. The PCA results determined that strong and positive correlations exist among chemical properties such as EC, pH, CEC, TC, and all the parameters found in quadrant A. In the case of physical properties, strong positive relationships were observed between FC and PAW (exist in the same quadrant D). In addition, positive relationships were found among BD, FC, and PAW. However, strong negative relationships were observed between porosity and WR; BD and EC; TC and N; and CEC and N, as all relational data were found in the exact opposite quadrants. PCA delineated that variables of quadrant A were moderately and strongly connected with quadrant D. The findings from PCA suggest that different physicochemical properties, such as EC, pH, CEC, TC, and BD, FC, and PAW, had a strong relationship, while other parameters such as porosity and WR, and CEC and N had no relationship after applying biochar in podzolic soil in the boreal ecosystem.

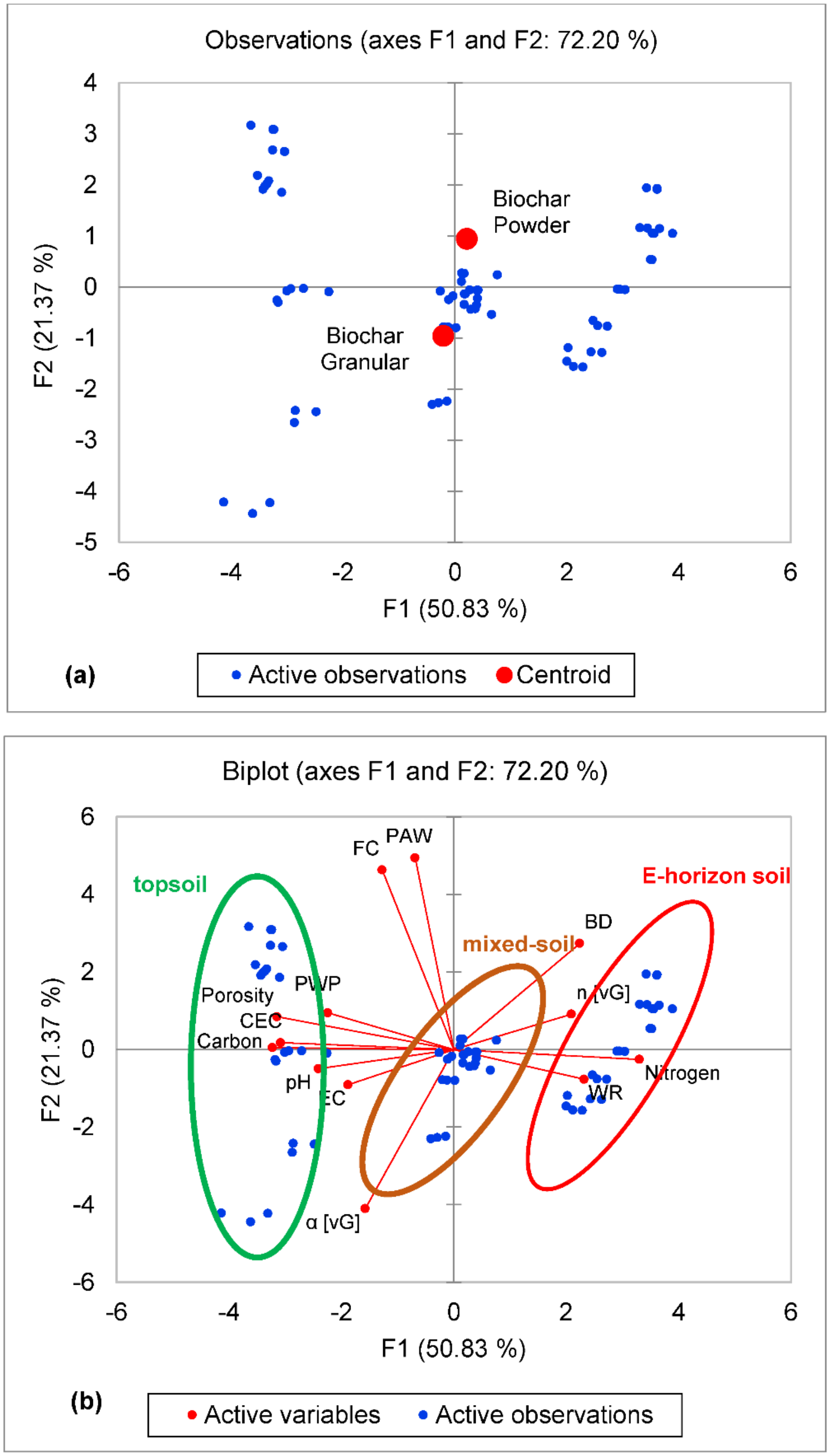


Figure 3.11: Principal component analysis (PCA) output of (a) observation and (b) biplot are showing the effects of biochar on the physicochemical parameters of podzolic soil.

3.4 Discussion

The study findings indicate that the biochar amendment significantly affects the physicochemical properties of the top, E-horizon, and mixed soil. The physicochemical properties of biochar-amended soil correlated with the biochar types and rates. A higher percentage of biochar rates showed lower BD and increased hydraulic properties like porosity, FC, and PAW, especially when powder biochar applied to the top, E-horizon, and mixed soil. In 2019, Fu et al. [65] also found similar effects for biochar, suggesting that it significantly increased total porosity and decreased BD in biochar-amended soil. The effect of biochar on soil properties varied based on soil types. The findings from experiments signaled that biochar application in the mixed soil showed better consistency in improving physicochemical properties with respect to biochar rates compared to the biochar topsoil and E-horizon soil.

Biochar characteristic is highly influential on biochar function in the biochar-amended soil [2,66]. The pore size in biochar is considered one of the important characteristics that can increase PAW and improve nutrient retention in the soil. Combined biochar pore size and SA help to describe biochar capacity for adsorption of nutrients and retention of heavy metals. As water attraction of biochar is influenced by its SA, pore size and distribution pattern on the surface, it can be assumed that powder biochar would be more likely to possess hydrophilic characteristics (attracting more water in the soil), while granular biochar would be more likely to possess hydrophobic characteristics (preventing water release and entrance in the pores). The physical structure of biochar (e.g., pore size, SA, and particle morphology) is an important factor when changing soil physicochemical properties [67]. The morphological characteristics of both types of biochar, such as surface roughness and pore radius, could have a greater influence on the hydrological properties of biochar-treated soil. If the biochar possesses hydrophilic (wetting characteristics) or hydrophobic characteristics, the treatment combination will show that type of properties. Mandal et al. [55] mentioned that biochar usually has a microporous structure with higher pore volume and defined pore diameter with the surface area of 576.1 m^2g^{-1}. In the study, it was reported that granular biochar did not have any SA (which is non-porous), while SA of powder biochar was 12 m^2g^{-1}. The pore arrangement on the biochar surface was visible in the SEM image and BET analysis. Identified SA was located on the surface and inside of the biochar particles. Pore size and distribution pattern of granular and powder biochar were visible in the SEM image, which identified SA for both types of biochar. The SEM image indicated that both granular and powder biochar share similar surface characteristics. Some important biochar properties, such as high total porosity, number of micropores, and SA, can potentially improve soil physical properties and create a better environment for plant root growth and nutrient uptake. Small size biochar particles, especially with diameter < 0.5 µm, can reduce the volume of soil pores by filling the available larger pore spaces. On the other hand, larger biochar particles with a range of 0.5–500 µm can increase the total pore volumes by increasing macropores between particles and micropores within particles. It is suggested that SWR properties specifically depend on pore size, where water can be stored, and the size of the biochar particles [10]. Thus, podzolic soil's SWR properties influenced by the characteristics of applied biochar.

Biochar could have hydrophilic and hydrophobic characteristics depending on the source materials and types. Hydrophilic biochar is usually providing superior wettability to soil [8]. Hydrophobic biochar surfaces may obstruct the uptake of water into biochar pores without considering pore size, distribution pattern, and structure. This may have a huge impact on WR (as WR depends on both biochar rates and soil particle size) that subsequently affects water infiltration in soil, SWR capacity as well as plant growth [16]. Rattanakam et al. [8] mentioned that hydrophobicity or hydrophilicity is not the most important governing factor of the SWR ability of soil.

Studies suggested that biochar pore sizes are classified as storage pores if the pore size ranges from 0.5 to 50 µm, which helps to increase water retention capabilities—thus increasing SWR, PAW, and nutrients retention in the soil [68]. However, we need to check the biochar pore distribution pattern on different sides and at different angles. If the percentage of the pore with the range 0.5 to 50 µm is found to be high compared to non-porous size, then the biochar could show hydrophilic characteristics. The pore size distribution of biochar may influence water storage capacity and pore sizes range from 1 to 10 µm are defined as macro-porosity. The study by Hardie et al. [10] found that almost all (95%) pore size of the applied biochar was <0.002 µm. Studies indicated that smaller size pore diameter (<0.2 µm) biochar is expected not to alter water storage capacity significantly in the sandy soil because smaller pore size of biochar has a very little contribution in variation with regards to particle size distribution of the biochar soil mixture [33]. However, many factors influence the SWR characteristics of biochar-amended soil. The biochar application rate is recognized as one of the most important factors that affects hydraulic properties [15]. Biochar amendment in soil could have both direct and indirect impacts on SWR in the soil. Biochar amendment can directly impact the SWR in the soil due to its ability to create a larger surface area and a higher number of residual pores on the biochar where water can be retained through capillarity. The direct impact of biochar application in the agricultural field are improve total porosity in soil, increase SMC, decrease water mobility in soil, and reduce water stress in plants' root zone. The experiment results indicated that application of powder biochar in three types of soil improve PAW that is a direct positive impact of biochar amendment to improve water stress condition. Fine biochar particles could directly contribute to increasing PAW by increasing porosity, generating more accommodation of pores, or by improving aggregate stability in the biochar-treated soil [10,33]. Biochar application in sandy soil can increase SWR and PAW. In the study, the applied soils were loam and sandy loam and soil's physicochemical properties increased, especially SWR and PAW in the treatment combinations. However, in the clay soil, both SWR and PAW properties may be reduced through biochar application. Besides, the indirect impact of biochar in soil includes improvement of aggregate stability and structural composition in the soil, and consequently affecting the capacity of SWR in the biochar-amended soil [13,69].

Specifically, soil amended with higher porosity biochar has been shown to improve SWR [15]. The study data suggested that biochar with larger pore volume and average pore diameter has better SWR capacity. Rattanakam et al. [8] reported that the biochar amendment on sandy soil increased SWR by 15.9% when compared to the control. More water can be retained in sandy soil when biochar is applied in a single layer [70]. If biochar is mixed non-uniformly within the soil, then the chance of high SWR capacity could be disrupted. In the experiment, the soil amended with granular biochar, porosity showed a slight decline with increasing biochar rates compared to powder biochar. Usually, granular biochar shape is not uniform and when added to a soil, it can creates more void spaces in different shapes and sizes within the soil as well as within biochar particles resulting a higher overall porosity. However, SEM image showed that some of the granular biochar walls were smooth with uniform angles in some instances. Additionally, the granular biochar showed hydrophobic characteristics. These could be the potential reasons why granular biochar-treated soil showed slightly decreasing trend in porosity. Biochar particle size has a significant influence on the hydraulic properties of biochar-treated soil. Biochar amendment in agricultural soil maximizes the water use efficiency, even in sandy loam and sandy soils. Thus, biochar application on podzolic soil would enhance agricultural production in boreal ecosystem [29].

Biochar amendment in agricultural soil may be one of the most suitable and sustainable options to provide long-lasting improvements in soil fertility, especially in sandy soils where agricultural practices face constraints due to low SWR and its tendency to leach high amounts of soil nutrients. Jeffery et al. [16] and Villagra-Mendozaa and Horn [33] mentioned that biochar properties such as SSA and total pore volume, play an important role in WHC capacity. In the study, it was found that powder biochar application increased field capacity the treated soil compared to control soil. Thus, the hydraulic properties (WHC) improved in the biochar-amended podzolic soil. But application of granular biochar in the soil showed slightly decreased WHC compared to control soil. The results confirm that the applied powder biochar could possess hydrophilic characteristics while granular biochar showed hydrophobic properties.

Results from our experiments showed that both types of biochar have a significant influence on soil properties, including increasing pH, EC, CEC, TC: N ratio, WR, porosity, FC, and PAW and decreasing BD when biochar dosage increases. In the biochar-treated podzolic soil, the improvement of hydrological properties could be attributed to the micro-porosity in powder biochar and macro-porosity in the granular biochar. Biochar addition enhances the physical and hydraulic properties of soil because it is a porous substance [33]. Even though biochar increased porosity in the soil, SWR capacity and PAW would sometimes remain unchanged [10]. Biochar-amended soil posits strong SWR 28–32% in the sandy loam soil [15] and secures available nutrients in the soil that may enhance sandy soil quality [71,72]. Głąb et al. [73] indicated that the application of the finest biochar particles in sandy soil increased PAW and WR slightly, even though it was classified as non-repellent. In the study, WDPT test also confirmed that all the treatment combinations were classified as slightly-water repellent.

Besides improving physical properties of soil, biochar amendment usually improves the chemical properties of soil. In 2016, Gamage et al. [74] found significant changes in soil physicochemical properties at 1% with 0.5% biochar application rates. Different studies across the world found similar effects for the biochar amendment on the soil properties in their region. For example, biochar application showed potential ameliorating acidic sandy soils by increasing pH and CEC, especially for sandy loam soil [74]. In the E-horizon soil (sandy soil), pH of the control soil was 4.3. After adding 2% powder biochar, pH increased up to 5.5 in the treated E-horizon soil. In granular biochar-treated E-horizon soil and mixed soil, CEC showed a slightly decreasing trend compared to the powdered biochar treatment. The CEC of powdered biochar (5.76 ± 0.31 cmolkg^{-1}) was found to be low compared to granular biochar (11.07 ± 0.70 cmolkg^{-1}) resulting in lower CEC values in soils treated with powdered biochar. Besides, the mixed soil consists of topsoil and E-horizon soils with a ratio of 2:1. CEC of E-horizon was found to be very low (2.61 ± 0.27 cmolkg^{-1}). This could be another reason why the CEC value of powder biochar-treated mixed soil was low compared to granular biochar-treated mixed soil. Additionally, in the experiment, it was found no significant changes on EC in the E-horizon soil (which was a sandy loam soil). Gamage et al. [74] also indicated that there was no significant impact on EC in the biochar-amended sandy loam soils. There was no significant increase in EC in either soil or biochar treatment that indicates no threat of salinity in the boreal podzolic soil.

In the experiment, applied biochar contained 60% of TC, which was close to the percentage used in the Laird et al. [75] study where they used biochar with 71.5% of TC. Study findings confirmed that the biochar amendment in soil exhibited a prominent effect on soil TC through an increased C: N ratio. In 2019, Majumder et al. [76] indicated that biochar increased the amount of C in the treated soil. In addition, Laghari et al. [17] found that higher doses of biochar improved C: N ratio in sandy desert soils. They recommended biochar as a suitable option for desert soil application to aid in sustainable agricultural development. Thus, the biochar amendment in soil was found to be beneficial with C stability, N cycling, and the addition of N fertilizer as well [77]. The study results found in PCA analysis highlighted several interesting interrelationships among the physicochemical properties of soil after being amended with biochar. Additionally, in PCA analysis, different properties provided consistent results with the cluster wise analysis of the properties [3].

In this study, the biochar amendment in the three types of soil had a significant impact on the alteration of several physicochemical soil properties – the similar impact of biochar application in soil was observed by Arbestain et al. [78]. Ojeda et al. [34] mentioned that three important soil functions, nutrient release, water, and carbon storage are influenced by the biochar amendment. Biochar plays an important role in binding material to form stable micro-aggregates in the soil. The micro-aggregates facilitate the formation of capillaries in the treated soil and thereby increased

SWR properties [29]. When biochar is added to the soil, organic matter (humic substances), microorganisms, heavy metals, etc., — all expected to occupy the volumes of unoccupied pores [13]. Biochar micropores generally play a vital role in increasing the soil matrix micropores and increasing the diameter of the pore space (macropores), which could lead to increase earthworm burrowing—as an assumption by Hardie et al. [10]. Thus, biochar pore size and distribution patterns are considered crucial factors for the formation of hydraulic properties in the biochar-treated soil, especially in sandy soil [70] and sandy loam soil [29,20]. In the experiment, biochar application found to be beneficial on loam and sandy loam podzolic soil in the boreal ecosystem. The experiment confirmed that the powder biochar amendment in soil, especially with 2% rate, more efficient in improving availability of PAW. This could be able to improve water stress situation and enhance soil–water–plant interaction. In a study, Suliman et al. [28] also mentioned that biochar application in podzolic soil could be considered a sustainable option for improving soil fertility for the long-term, especially in sandy soil. Study findings from Villagra-Mendozaa and Horn [33] recommended that the biochar amendment in sandy soil is beneficial for soil health, as well as plant growth, especially in climate-sensitive (cool) conditions. These findings suggest that biochar is proven to be a long-lasting sustainable option as a soil amendment.

Based on the experimental findings and discussion, future points to be considered are:

- Hydrological functions of biochar-amended soil need to be investigated at different environmental conditions (field experiments), which will help to predict potential effects of different types and rates of biochar, especially higher doses on SWR. In addition, the agronomic benefits of biochar application in the soil need to be evaluated [79].

- Application of more than 2 % (w/w) rate of biochar in the soil need to be further investigated to know the impacts on physicochemical properties of different soils including podzolic soil.

- The physicochemical properties of biochar may change after a period of environmental exposure. For example, porosity (surface structural characteristics) is likely to be gradually altered by 4 years of exposure [36,80]. This can affect the properties of biochar-amended soil and make it a challenge to predict ecosystem services in the long-term. Thus, the long-term stability of biochar in soil and its impact on soil physicochemical properties need to be investigated.

- Quantitative risk assessment of biochar application on human health and ecosystem [81] is very important to ensure proper safety, development, and sustainability if biochar application use is to increase in boreal agricultural system.

3.5 Conclusion

The experiment results indicated that the biochar amendment significantly improved physicochemical properties of podzolic soil. The basic physical properties of biochar-treated soils, such as porosity and field capacity, were found to be dependent on biochar rate, morphology, and granulated/powdered structure. Granular biochar was determined to be slightly hydrophobic, and powder biochar was determined to exhibit hydrophilic characteristics. This study provided strong evidence that supports the positive impact of the biochar amendment in podzolic soil. For example, biochar application increased pH (especially in the E-horizon soil), electrical conductivity, cation exchange capacity, and the total carbon: nitrogen ratio in the soil while reducing bulk density. In this study, water repellency was found to be slightly increased with the different rates of biochar treatment, but the treatment combinations were still classified as slightly-repellent. The biochar amendment showed great ability in improving soil water retention. Both types of biochar amendments increased porosity in the treatment combinations. However, the field capacity and plant available water increased more in the powder biochar-amended soil than the granular biochar-amended soil. The study results suggested that the application of 2% powder biochar could have a beneficial influence on the physicochemical properties of podzolic soil. The overall experimental findings indicated that the application of biochar in mixed soil showed better improvement in physicochemical properties in response to increasing biochar rates, compared to the improvements found in its application to the topsoil and E-horizon soil. Further chemical and structural analyses are needed to accurately calculate the percentage of pore space changed through biochar application. Biochar application as soil amendments in podzols needs to be investigated more to better understand its effects in improving soil physicochemical properties in boreal ecosystem. The long-term ecotoxicological effects of biochar need to also be examined to ensure ecological sustainability in the future.

Acknowledgments

Authors acknowledge members of Hydrology & Agrophysics Group, Grenfell Campus-Memorial University of Newfoundland for their help and constructive comments during the study. Authors gratefully acknowledge Tao Yuan, Lab Coordinator of the Boreal Ecosystem and Research Facility, Grenfell Campus, Memorial University of Newfoundland, for his valuable contribution in conducting analysis, especially on Ion Chromatography, and overall coordinating activities in the lab. Special thanks go to Muhammad M. Farhain and Gayantha S. Perera for their help during soil sampling and sample preparation. Authors are also thankful to Yeukai Katanda, Postdoctoral Fellow, School of Science and the Environment, Grenfell Campus, Memorial University of Newfoundland, for her support given during the experiments, especially on methodology and execution of the experiments. Authors also acknowledge Gabriel Grunwald, Department of Naval Architecture, Marine Institute of Memorial University of Newfoundland, Canada for copy-editing of this manuscript.

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Co-authorship statement for study three

The study entitled “Effect of biochar on nitrogen transport and hydraulic properties of podzolic soil in boreal ecosystem” was prepared and formatted following the instructions of *Journal of Soil Science and Plant Nutrition* especially on abstract, text with citation and references. The manuscript is in the process of submission to the above journal. Ratnajit Saha, the thesis author was the primary and corresponding author of the manuscript. Ratnajit Saha conceptualized the study, prepared the study design and leaching column, executed leaching column experiment in the lab and used Hydrous 1D model for the simulation of soil moisture content, analyzed nitrate and ammonia concentration in the Ion analyzer, analyzed the data and prepared the manuscript. Dr. Lakshman Galagedara (supervisor) was the second author and contributed in study design, provided specific guideline for the simulation of soil moisture content using Hydrous 1D software, also suggested on findings visualization, review and editing of the manuscript, and overall supervision of the study. Dr. Raymond Thomas (co-supervisor) was the third author. Dr. Thomas contributed to overall study design, review and editing of the manuscript. Dr. Kelly Hawboldt (co-supervisor) was the fourth author and Dr. Kelly contributed to review and editing of the manuscript.

Chapter Four

Study three

Effect of biochar on nitrogen transport and hydraulic properties of podzolic soil in boreal ecosystem

Ratnajit Saha[1], Lakshman Galagedara[1,2], Raymond Thomas[2], and Kelly Hawboldt[3]

[1]Environmental Science Program, Faculty of Science, Memorial University of Newfoundland, St. John’s, NL, A1B 3X7, Canada

[2]School of Science and the Environment, Memorial University of Newfoundland, Corner Brook, NL, A2H 5G4, Canada

[3]Department of Process Engineering, Memorial University of Newfoundland, St. John's, NL, A1C 5S7, Canada

Abstract

Purpose: Nitrogen (N) leaching is considered the most important constraint on agricultural production in boreal ecosystem. The study is aimed to investigate the effect of biochar on N transport and simulation of hydraulic properties in podzolic soil.

Methods: Soil samples were collected from an agricultural research field in Pasadena, Newfoundland, Canada. Three types of leaching columns were prepared with two types of biochar (granular and powder) application rate {0%, 1%, and 2% (w/w)}: (1) topsoil, (2) top & E-horizon soil, and (3) mixed soil (topsoil 2: E-horizon soil 1). A total of 270 experimental units were executed including leaching column experiment and Hydrous 1D simulation on soil hydraulic properties. The amount of nitrate and ammonia in the leachate were analyzed by Ion Analyzer (LACHAT Instruments).

Results: The amount of NO_3^- leached ranged from 4.96 to 12.03 mgL^{-1} with a mean 8.63 mgL^{-1}. The application of powder biochar reduced NO_3^- leaching by 36% compared to control soil. The amount of NH_4^+ leached varied from 0.18 to 2.02 mgL^{-1} with the mean amount of 0.88 mgL^{-1}. The powder biochar application reduced the volume of leachate by 46% compared to control. Simulated volumetric soil moisture content in the biochar treated soil increased by 6.97% (in the topsoil) and 8.56% (in the mixed soil).

Conclusion: Of the four biochar rates and two biochar types tested in this study, a 2% powder biochar application rate was found to be most effective at reducing significant amounts of N leaching from podzolic soil. This finding could be helpful to better understand the effective use of biochar to retain more nutrients within the root zone when podzolic soil is used for agricultural production in boreal ecosystem.

Keywords: Biochar, nitrogen transportation, leaching column, hydraulic properties, Hydrous 1D, podzolic soil

4.1 Introduction

Nutrient leaching and water stress place major constraints on agricultural practices (Li et al., 2018). Nitrogen (N) is one of the most important elements of soil health and plant growth (Liu et al., 2017). N fertilization, such as application of urea, in the agricultural field is a common practice without considering environmental consequences to get high yield. In agricultural fields, applied urea is converted to ammonium bicarbonate by urease enzyme. Then through nitrification, ammonia (NH_4^+) is usually transformed to nitrate (NO_3^-) (Xu et al., 2016; Sun et al., 2017). In the soil profile, N may be present in different forms as NO_3^-, NH_4^+, and organic N. The NO_3^- form is known to be highly soluble in soil-water solution and has the highest mobility and may contributes to groundwater contamination (Iqbal et al., 2020a). NO_3^- and NH_4^+ can leach from the root zone (leaching zone) for several reasons. These include excessive application of N-fertilizer, high amounts of rainfall, sandy soil, and agricultural production on sloping land (Libutti et al., 2016). Leaching is considered a leading sink of nutrients loss from the crop root zone. Consequently, crops are losing a significant amount of nutrients required for productivity from the crop root zone (Iqbal et al., 2020b). Excessive amount of N fertilizer is being applied to agricultural fields to achieve maximum productivity. The use of fertilizer in the agricultural field is a major reason for the release of huge amount of N to surrounding aquatic systems that contributes to eutrophication (Iqbal et al., 2020a; Yao et al., 2012). Excess leaching of N from soil decreases soil fertility, increases soil acidity, reduces productivity, and increase the cost of agricultural production due to additional fertilizer. The risk of eutrophication of environmental health could be increased algae growth and decreased the concentration of dissolved oxygen in water, as a result death of fish in the aquatic system (Xu et al., 2016; Yao et al., 2012). Scientific solutions to reduce N leaching and improving hydraulic properties are very important for the sustainability of the ecosystem (Li et al., 2018).

Biochar, a carbon-based material, can reduce N leaching and improve soil hydraulic properties (Li et al., 2018; Yao et ail., 2012). The application of biochar in agricultural practices has been increasing due to its multi-functionality and ecological compatibility (Chang et al., 2018; He et al., 2018; Ibrahim et al., 2013; Kang et al., 2018; Yang et al., 2018). An important pursuit of biochar treated soil is the improvement of the physicochemical properties, especially the hydraulic properties of the soil. These improvements will aid in reducing nutrient leaching from the leaching zone of soil (Shaaban et al., 2018). Biochar's porous structure may increase the water holding capacity of biochar treated soil (Dil et al., 2014; Qiao-Hong et al., 2014; Han et al., 2016). Furthermore, use of biochar for agricultural practices has been proposed as a viable strategy to mitigate climate change as it acts as a carbon sink (Arbestain et al., 2014; Zhang et al., 2017) as well as improves soil water quality (Oliveira et al., 2017; Chen et al., 2018).

Altdorff et al. (2019) mentioned that very little information exists on how biochar affects soil system's hydraulic properties. Numerical simulation of water movement is a useful technique in assessing the effect of biochar on hydraulic properties and findings could be used to simulate occurrence under field conditions as well as improve our knowledge how biochar applications modulate hydraulic properties in practical field situations (Mailhol et al., 2011). Hydrous 1D software is a valuable tool to predict hydrological responses in biochar amended soil (Altdorff et al., 2019; Zheng et al., 2017). Hydrous 1D is a gravitational flow model, based on Richards' equation (Caiqiong and Jun, 2016; Tafteh and Sepaskhah, 2012), and is capable of simulating water, heat, and solute movement in different saturated and unsaturated porous medium (Jiménez-Martínez et al., 2009). Hydrous 1D also used for the entire modeling of the hydrological processes, including precipitation, evapotranspiration, irrigation, deep drainage, etc. (Caiqiong and Jun, 2016). This is a reliable tool compared to other models to evaluate water movement and fluxes in the soil system (Iqbal et al., 2020b). Pal et al. (2014) applied the Hydrous 1D model to simulate soil columns (depth 20 – 60 cm) and found that the simulated results were very close to the experimental findings. Also, Mo'allim et al. (2018) applied a Hydrous 1D model successfully to simulate solute transport at different soil depths. Initial calibration of hydrological parameters would be a good strategy to get an accurately simulated dataset (Ursulino et al., 2019). The model's input data sets need to be appropriately focused on study objectives and would help to achieve the desired outcome (Hou et al., 2016).

However, in a four-year field experimental study, Haider et al. (2017) indicated that biochar treated soil significantly reduced the amount of NO_3^- leaching and improved the soil moisture content in sandy soil. The knowledge of the status of hydraulic properties, like moisture content and hydraulic conductivity, of podzolic soil used for agricultural production in boreal ecosystem is very important. Very little attention has been given to the application of biochar in reducing nutrient leaching and improving hydrological processes of podzolic soil in boreal ecosystem (Li et al., 2018; Dil et al., 2014). Only a few studies on soil hydraulic properties and N leaching from agricultural fields were conducted separately in the different regions (e.g., tropical, temperate, and boreal). The elucidation of soil water movement and N retention capacity on the biochar treated podzolic soil in boreal ecosystem need to have a robust study design with specific details.

In the boreal ecosystem, a cool climate with a short crop growing season is one of the important challenges for higher agricultural productivity (Hansen et al., 2016; Hagemann et al., 2017; Jeffery et al., 2011). The root zone in boreal ecosystem typically consist of an A-horizon (plow layer or topsoil) and E-horizon. Low soil pH and fertility, uneven distribution of rainfall (Nadeem et al., 2019), and leaching of the applied nutrients from the root zone. These are considered major factors which govern poor productivity of podzolic soil in boreal ecosystem. Therefore, scientific investigation on water flow movement and identify the way of reducing N loss from leaching zones is critical for sustaining agricultural productivity in the boreal region. Is the biochar application on podzolic soil in boreal ecosystem retain N – fertilizer (a form of NO_3^- and NH_4^+)? That question has not yet been investigated.

The overarching hypotheses were as follows: the application of biochar in podzolic soil will improve properties like soil moisture content and retain more N (ionic form) in the boreal ecosystem. The study is aimed to investigate the effect of biochar on N transport and hydraulic properties of podzolic soil in boreal ecosystem. The experiments focused on several research questions: (i) What were the differences in simulated soil moisture content in different biochar treatment combinations? (ii) Was the simulated and experimental time to leach matched? (iii) Did the application of biochar increase or decrease the volume of leachate from the treated soil? (iv) What was the optimal biochar quantity to retain the maximum amount of NO_3^- and NH_4^+ in the podzolic soil? It is anticipated that the study's findings will provide guidelines for the use of biochar on podzolic soil in boreal ecosystem to retain N in the leaching zone. The anticipated results will be applicable both in increased agricultural productivity and in informing decision making for sustainable agricultural practices.

4.2 Methodology

4.2.1 Sampling site, sample collection from field and sample preparation

Soil samples were collected from the agricultural experimental station managed by the Department of Fisheries and Land Resources of the Government of Newfoundland and Labrador in Pasadena (49° 5'38.63"N and 57°32'9.32"W), Newfoundland, Canada in June, 2019. Topsoil and E-horizon soil samples were collected from 0 – 15 cm depth (where topsoil from 0 – 10 cm and E-horizon soil from 11 – 15 cm) in the plowed and forest area and brought to the laboratory of Boreal Ecosystems Research Facility (BERF) of Grenfell Campus, Memorial University of Newfoundland. Soil samples were air-dried for seven days at room temperature and sieved using a 2 mm sieve. Three types of soil: topsoil, E-horizon soil, and mixed soil (2:1 topsoil: E-horizon soil ratio according to the average soil layer thickness in the field) were considered for the further analysis. Two types of biochar: (i) granular biochar (Market Product – Yellow Pine, Pinus Spp. at 500°C 30 min, Air Terra Inc., Alberta, Canada) and (ii) powdered biochar (Market Product – Maple Hardwood 450°C, ABRI Tech Inc., Quebec, Canada) were used in this experiment. The basic physicochemical properties of the two biochar types are given in Table 4.1. Soil samples were amended with three biochar rates (weight basis); 0% (control), 1% (10 g per kg soil), and 2% (20 g per kg soil). If it is assumed that the average bulk density of 1.25 gcm^{-3} and biochar incorporation soil depth of 0.1 m, these rates would be equal to 12.5 and 25.0 Mg of biochar per ha, respectively.

4.2.2 Soil particle size analysis

The hydrometer method was used for soil particle size analysis following the standard procedure (Bouyoucos, 1962). Topsoil and E-horizon soil samples were analyzed, and the percentage of clay, silt, and sand were calculated using Eq.1 -3.

% Clay = Hydrometer reading at 6 h. and 52 min. x 100/ wt. of samples (Eq. 1)
% Silt = Hydrometer reading at 40 sec. x 100/ wt. of samples - % clay (Eq. 2)
% Sand=100% - % Silt - % Clay (Eq. 3)

4.2.3 Bulk density

The bulk density (BD) was measured in prepared soil amendments considering soil and biochar types, and treatment combinations. For this, metal containers having 86.7 cm^3 of volume were filled (tapped three times on the table during the filling) with soil and biochar samples (three replications). The samples were oven – dried for 24 h at 105°C in the forced air – dried oven (SHEL LAB, SHELDON Manufacturing. Inc, Cornelius, USA). Then BD of the samples was calculated. After that, BD of all the treatment combinations was calculated following Eq. 4 (Wanniarachchi et al., 2019).

$$\text{Bulk Density} = \frac{100}{[\left(\frac{x}{\rho 1}\right)+\left(\frac{100-x}{\rho 2}\right)]} \quad \text{(Eq. 4)}$$

Where ρ_1, and ρ_2 are the bulk densities (gcm^{-3}) of the biochar: soil mixtures, biochar only, and soil only, respectively and x is the biochar rate (%) by weight.

4.2.4 Porosity and field capacity (FC) of soil samples

A pressure plate apparatus system (0700CG23F1 Manifold and 0505V# Compressor, model 1600, Soil Moisture Equipment Corp., California, the USA) was used to develop the soil water retention curve (SWRC). The weight of the soil (control) and soil amended with biochar (treatments) were calculated based on the BD of the mixture and ring volume (21.53 cm^3). Each sample's total weight (including filter paper, plastic ring, and sample) was taken. Samples were saturated for 3 days using a shallow plastic plate and maintained a water height just below the top of the plastic ring (around 0.2 cm). Once the samples were assumed to reach at the saturation level (observed a film of water on the soil surface) the samples weight were measured (Ws) and samples were arranged on 50 kPa ceramic plates and placed in the 500 kPa pressure chambers. The initial data point was taken at 10 kPa.

Samples' weight was measured right after the chamber stopped releasing water and samples reached a constant weight at the set pressure. The porosity was calculated using Eq. 5 at 0 kPa and FC was calculated at 10 kPa using Eq. 06 (Canadian Society of Soil Science, 2008).

Porosity (p) = $\frac{Ws-Wp}{Vt} \times 100$ (Eq. 5)

Field Capacity (FC) = $\frac{Wd-Wp}{Vt} \times 100$ (Eq. 6)

Where Ws is the saturated soil core weight, Wp is the dried soil core weight, Wd is the drained soil core weight and Vt is the core volume.

4.2.5 Preparation of leaching column

The leaching column calculated volume was 433.52 cm^3, where column radius (r) = 2.35 cm and height (h)= 25 cm, and the surface area was 17.34 cm^2 (0.001734 m^2).

A total of fifty-four (54) leaching columns were prepared to test all treatment combinations representing three types of soil (top, E-horizon, mixed), two types of biochar (powder and granular), three biochar rates (0%, 1%, and 2%) with three replications (Figure 4.1). Three types of leaching column were executed in the experiment. The leaching column were: (a) topsoil column: a combination of topsoil and biochar from 0 – 25 cm (Figure 4.2a), (b) top & E-horizon soil column: a combination of topsoil and biochar from 0 – 16.5 cm and only E-horizon soil (without biochar) from 16.5 – 25 cm (Figure 4.2b), and (c) mixed soil column: a combination of mixed soil and biochar from 0 – 25 cm.

These leaching columns were prepared to understand the natural condition in the field as three types of situations exist during plowing and biochar mixing within the plow layer. A schematic diagram of the three types of leaching columns with the listed materials is shown in Figure 4.2. The materials used in the leaching column were transparent polymethyl methacrylate cylindrical pipes as column (30 cm where 25 cm was filled with samples and 5 cm was blank to add Deionized water) (Li et al., 2018), stand for keeping the column, column holder with stand, funnel, filter paper used on the top of the funnel, urea, soil-biochar treatment combinations, 250 mL beaker for collecting leachate, measuring cylinder for a calculated volume of leachate, 15 mL vials for storing leachate until the ion concentration analysis.

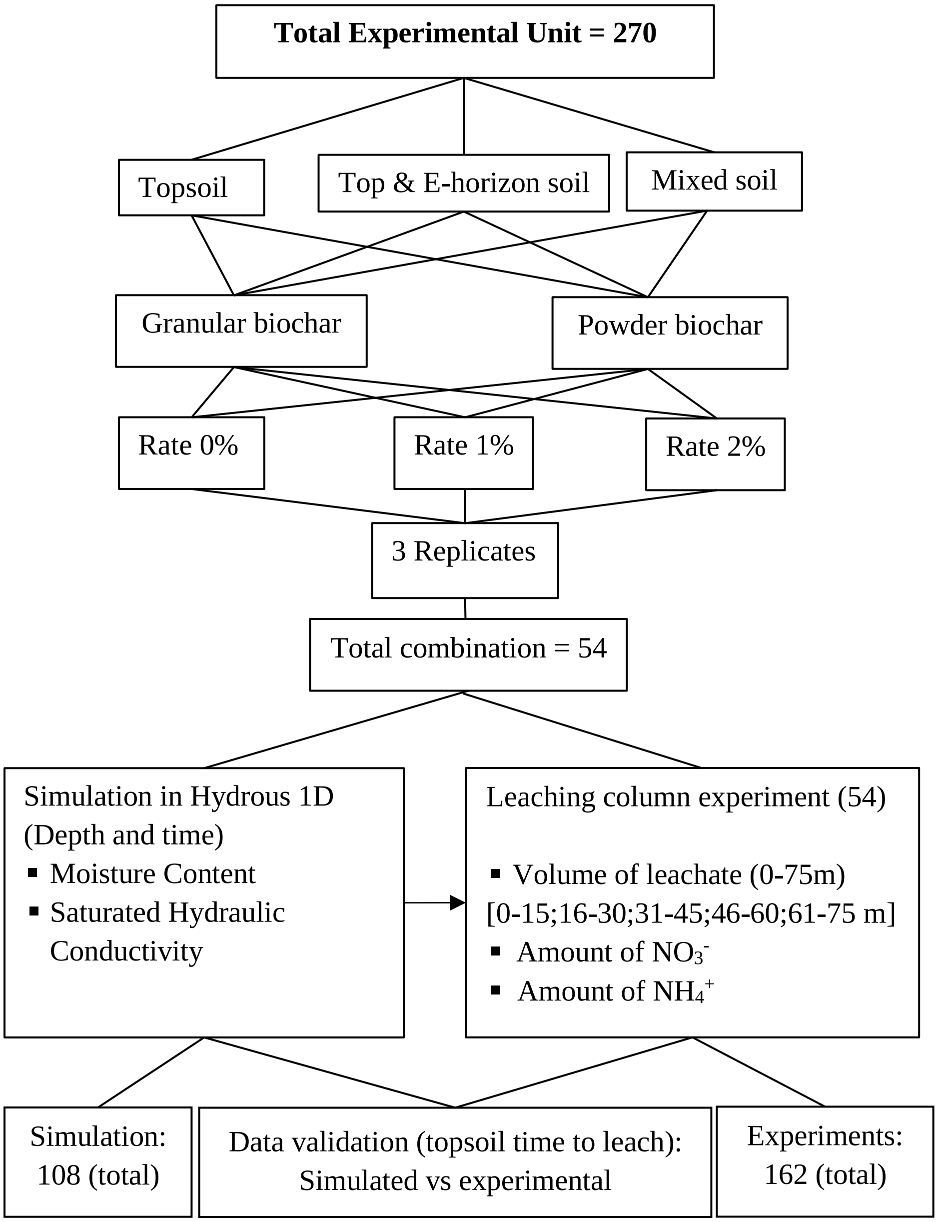

Figure 4.1: Flow chart showing the effects of biochar type and rates on hydraulic properties and nitrogen transport in podzolic soil

According to the Government of Newfoundland and Labrador, Canada, urea is applied at 115 kg ha^{-1} in agricultural fields in June. Based on the surface area of the leaching column (0.001734 m^2), 0.20±0.01 g of urea was added on the top of each leaching column.

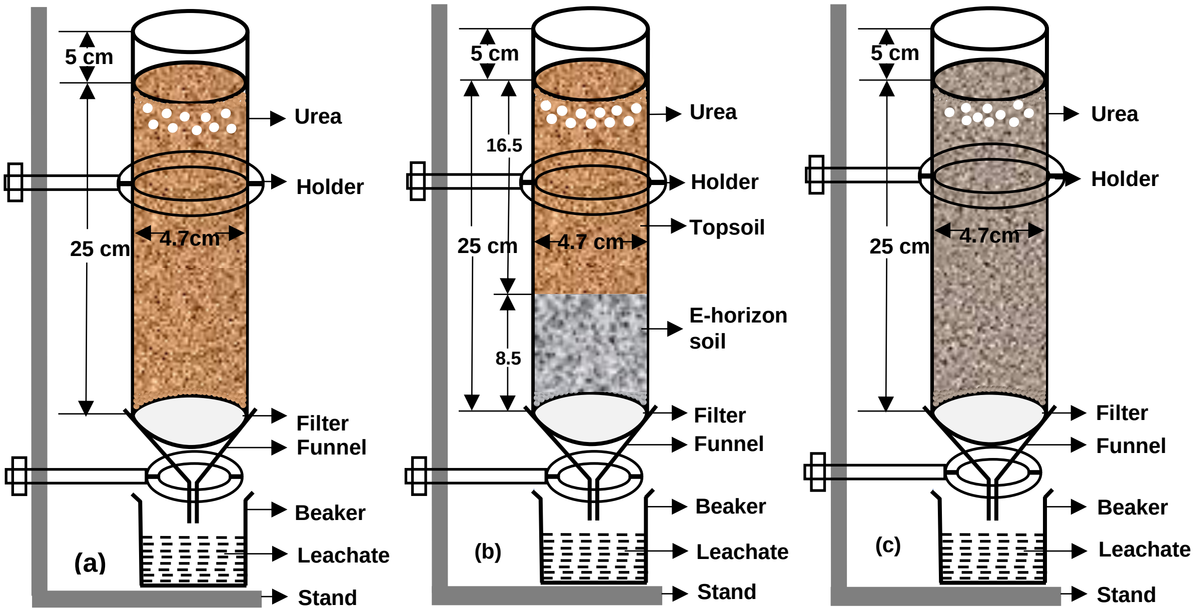

Figure 4.2: A schematic diagram of the leaching column: (a) topsoil; (b) top & E-horizon soil and (C) mixed soil

4.2.6 Application of Hydrous 1D for hydraulic properties in the leaching column

Hydrous 1D, a one-dimensional numerical model, was used to simulate hydraulic properties (moisture content and hydraulic conductivity) of biochar treated soil in the leaching columns. In the simulated leaching column, soil water movement from the surface to the bottom has been described (modified Richards equation) in the model as follows Eq. 7 (Iqbal et al., 2020; Zheng et al., 2017; Tafteh and Sepaskhah, 2012).

$$\frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial z}\ [k(h)\left(\frac{\partial h}{\partial z} + 1\right)] - S(z, t) \text{ (Eq. 7)}$$

Where, θ = Volumetric soil moisture content (cm^3cm^{-3}), h= soil water pressure head (cm), t= time (hour), z= maximum soil depth (cm), K= Unsaturated hydraulic conductivity (cmh^{-1}) and S= Source/sink term of the flow equation.

Preliminary simulations were done using the topsoil to get the desired flux rate and simulation time for Hydrus 1D and leaching column. In the Hydrous 1D model, a maximum depth of soil 25 cm, the number of soil layer 1 or 2 (based on the types of leaching column as described in Figure 4.2), simulation time 6 h, water flux -1.5 cmh^{-1}, ("-" sign represent downward movement in Hydrus 1D) and the initial soil water pressure head of -5000 cm (-500 kPa) were used for all the simulated leaching columns. In the simulated individual leaching column, measured values of soil textural class, BD, and FC of the respective sample were used.

4.2.7 Executing leaching column experiments in the laboratory

In the air-dried biochar treated soil samples, volumetric soil moisture content (VSMC) was 2.67 cm^3cm^{-3}. Based on the background soil water potential of -5000 cm of water (-500 kPa), the VSMC should be around 13% in the topsoil. 50 mL Di-ionized (DI) water was added on each sample (before packing in the leaching column) as a calculated volume to increase the moisture content of all air-dried treatment combinations up to 13%. According to the Hydrous 1D simulation, a total of 156 mL DI water was added from 0 – 6 h (26 mL DI water was added per hour for all leaching columns to maintain water flux of 1.5 cmh^{-1} as of the simulation study). Then, the time to leach (total time was taken for the wetting front to reach the bottom and start leaching) with the topsoil leaching column's simulated and experimental values were validated. After collecting the leachate, the samples were kept in the -20°C freezer until samples were analyzed in the Ion analyzer (NO_3^- and NH_4^+ analyzer).

4.2.8 Validation of simulated and measured values

The Hydrous 1D model results from time to leach of topsoil column were validated with the topsoil leaching column's experimental values. Two statistical indicators: Root Mean Square Error (RMSE) (Eq. 7) and relative error (RE) (Eq. 8) were used to perform the validation of the experimental and simulated results. RMSE and RE's low value indicates a good match between the experimental and simulated values (Haj-Amor and Bouri, 2019).

$$\mathrm{RMSE} = \sqrt{\sum \frac{(Si - Mi)^2}{n}} \text{ (Eq. 8)}$$

$$\mathrm{RE}\ (\%) = \frac{1}{n} \sum_{i=0}^{n} \frac{Si - Mi}{Mi} \times 100 \text{ (Eq. 9)}$$

Where, Mi = measured time to start leaching at the time i, Si = simulated time to start leaching at the same time, and n = number of measurements.

4.2.9 Analysis of NO_3^- and NH_4^+

The amount of NO_3^- and NH_4^+ in the leachate were analyzed by Ion Analyzer (LACHAT Instruments), XYZ Autosampler (ASX – 520 Series), Quick Chem QC8500 Series 2, HACH, Loveland, CO USA (Shaaban et al., 2018).

4.2.10 Statistical analysis

To assess and quantify the effects of different biochar types and application rates, a general analysis of variance (ANOVA) was done. A least significant difference (LSD) test was conducted to know the significant difference between the control and treatment at the 0.05 alpha level (Sorrenti et al., 2016). Descriptive statistical analysis and Pearson correlation were performed using software STATA 12.0 version and MS Excel. Graphical visualizations were done through MS excel.

4.3 Results

4.3.1 Basic physical and chemical properties of soil and biochar

Table 4.1 describes the results of the physicochemical properties of soil and biochar. Topsoil was loam, E-horizon soil was sandy loam, and mixed soil was also sandy loam.

Table 4.1: Physicochemical properties of soil and biochar

Physicochemical Parameters	**Unit**	**Topsoil**	**E-horizon soil**	**Mixed soil**	**Granular Biochar**	**Powder Biochar**
Bulk Density	gcm^{-3}	1.31±0.10	1.40±0.00	1.34±0.00	0.20±0.00	0.35±0.00
Water Repellency	sec	1.67±0.58	4.00±0.00	3.00±0.00	-	-
Porosity	%	0.52	39.63	48.41	-	-
Field Capacity	%	29.18	27.86	30.33	-	-
Clay	%	16	10	14	-	-
Silt	%	24	32	27	-	-
Sand	%	60	58	59	-	-

4.3.2 Simulated hydraulic properties

4.3.2.1 Soil moisture content

The Hydrous 1D model simulated VSMC from 0 – 6 h in the leaching column (depth 0 –25 cm) under different treatment combinations which are shown in Figure 4.3. Simulation indicated that granular and powder biochar treated topsoil increased VSMC from 0.13 (the background moisture) to 0.43 cm^3cm^{-3} after 6 h with the constant flux of 1.5 cmh^{-1}. In the simulated topsoil leaching column, VSMC increased by 6.97% with 2% granular biochar compared to control, while VSMC increased by 4.65% with 2% powder biochar treated topsoil compared to control (topsoil with 0% biochar). In the top & E-horizon soil leaching column, control column VSMC varied from 0.13 to 0.39 cm^3cm^{-3} from 0 to 5 h (as soil saturated at 5 h). The simulation indicated that both granular and powder biochar amendments decreased VSMC in top & E-horizon soil. In the mixed soil leaching column, VSMC was found to be 0.12 cm^3cm^{-3} and after 5 h, the control soil became saturated at 0.41 cm^3cm^{-3}. VSMC increased by 8.56% at 6 h with 2% granular biochar compared to the control mixed soil column. VSMC increased by 6.83% at 6 h with 2% biochar addition compared to the control mixed soil column. Overall, when applied granular and powder biochar with soil in the leaching column, Hydrous 1D simulation indicated that application of granular and powder biochar increased VSMC in the topsoil and mixed soil leaching column except in top & E-horizon soil leaching column.

4.3.2.2 Hydraulic conductivity

Hydrous 1D model simulation of hydraulic conductivity (*k*) in the leaching column was done under different treatment conditions. In the control topsoil leaching column, simulated *k* found to be 0.00 – 1.42 cmh^{-1} from 0-6 h. Simulation indicated that *k* increased by 4.22% with 2% granular biochar and by 9.15% with 2% powder biochar compared to control topsoil. In the control top & E-horizon soil leaching column, simulated *k* was 0.00 – 1.08 cmh^{-1} from 0 – 5 h. The simulation indicated that with the addition of 2% granular and powder biochar, *k* decreased by 6.4% and 21.29%, respectively, compared to control top & E-horizon columns. In the mixed soil columns, *k* found to be varied 0.00 – 1.29 cmh^{-1} from 0 – 5 h. The simulation indicated that *k* increased by 14.72% and 19.37% with the addition of 2% granular and 2% powder biochar, respectively.

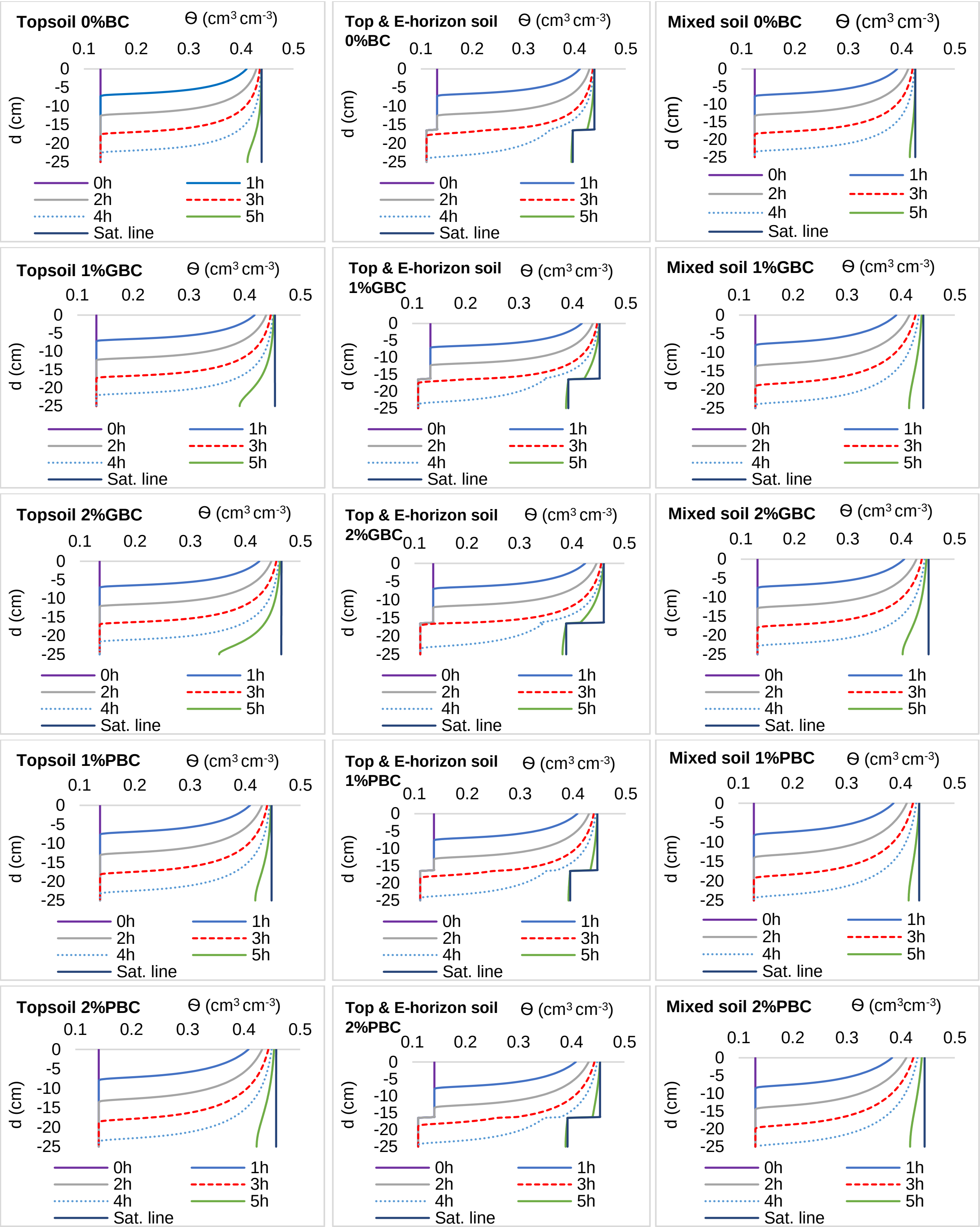

Figure 4.3: Simulated effect of biochar on volumetric soil moisture content vs. depth in the leaching column. [Note: d – depth of simulated leaching column in cm; BC – biochar; GBC- granular biochar; PBC – powder biochar; Sat. line – Saturated line]

4.3.3 Validation of time to leach (experimental vs simulated time)

The time to leach of simulated and experimental values were almost the same. In the control topsoil, the mean time difference was only 12 min. The time to leach of experimental and simulated powder biochar treated topsoil values were found less than granular biochar treated topsoil (Figure 4.4). Experimental and simulated values were found statistically non-significant (p=0.220). RMSE and RE were calculated from simulated and experimental values of time to leach. In the control topsoil, RMSE=0.12 h and RE=1.5%, in 1% granular biochar treated topsoil RMSE=0.2 h and RE=2.7%, in 2% granular biochar treated topsoil RMSE=0.6 h and RE=8.9%, in 1% powder biochar treated topsoil RMSE=0.06 h and RE=0.7%, and in 2% powder biochar treated topsoil RMSE=0.27 h and RE=3.1%. Overall, the difference in time to leach between simulated and experimental values was not so high. But the comparison graph of biochar treated soil showed that the experimental time to leach increased while the simulated time to leach decreased.

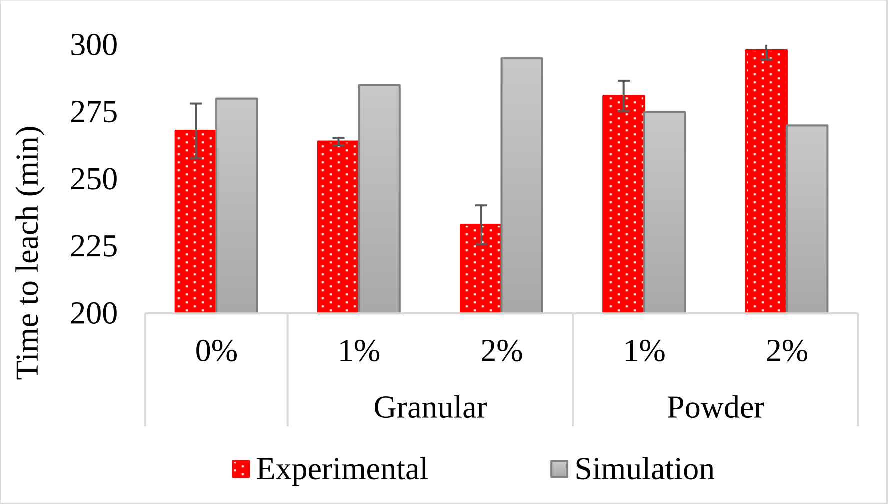

Figure 4.4: Total time taken to start leaching in the topsoil: Experimental time vs simulated time.

4.3.4 Nitrate leaching

The amount of NO_3^- leached under different treatments are shown in Figure 4.5. The range of the NO_3^- amount leached is from 4.96 to 12.03 mgL^{-1} with the mean value of 8.63 mgL^{-1}. Compared to the control topsoil, the amount of NO_3^- reduced by 6% with 1% and 2% granular biochar amendment. With the application of 1% powder biochar in the topsoil, the amount of NO_3^- leaching reduced by 6%, and with 2% powder biochar amendment, the amount of NO_3^- leaching reduced by 10% compared to the control topsoil. In the top & E-horizon soil, the control column released 7.70 mgL^{-1} of NO_3^-. Compared to the top & E-horizon control soil, the amount of NO_3^- leaching decreased by 4% with 1% and 2% granular biochar amendment. The amount of NO_3^- leaching reduced by 35% with 1% powder biochar amendment in the top & E-horizon soil. With the application of 2% powder biochar, NO_3^- leaching reduced by 36% compared to the control top & E-horizon soil leaching column. Approximately 8.77 mgL^{-1} of NO_3^- leached from mixed soil control leaching columns. NO_3^- leaching reduced by 1% with 1% granular biochar amendment compared to the control mixed soil columns. The amount of NO_3^- leaching reduced by 26% with 2% granular biochar addition. In the mixed soil column, NO_3^- leaching reduced by 4% with the addition of 1% powder biochar. NO_3^- leaching reduced by 9% with the amendment of 2% powder biochar compared to the control mixed soil. Generally, the application of different types and rates of biochar showed a significant reduction of NO_3^- amount (1 to 46%) in all the biochar treated leaching columns. Notably, a higher percentage of NO_3^- leaching was reduced when soil was treated with powder biochar.

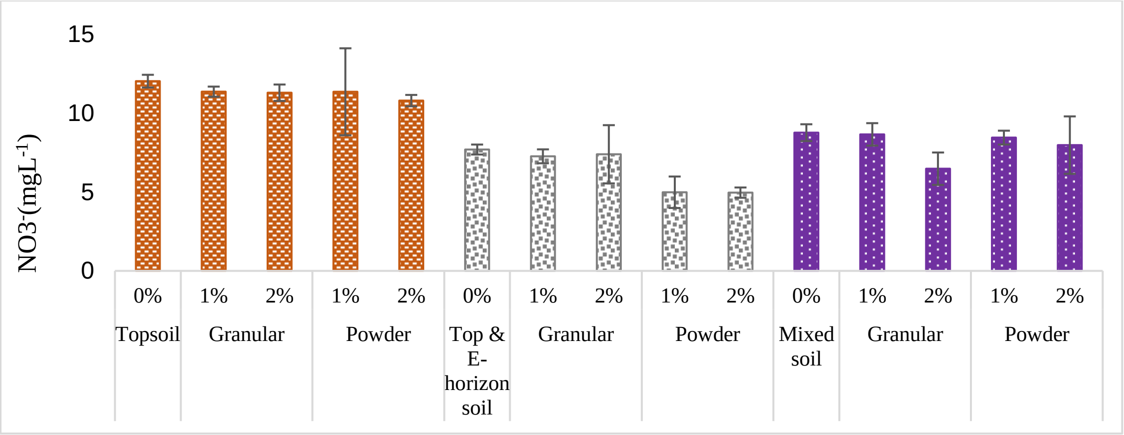

Figure 4.5: NO_3^- leached during each treatment. The values are arithmetic mean of three replicates and the error bars are the standard deviation.

4.3.5 Ammonia leaching

The effect of different types and rates of biochar on NH_4^+ leaching in the leaching columns is shown in Figure 4.6. The range of the amount of NH_4^+ leached was 0.18 – 2.02 mgL^{-1} and the mean amount of NH_4^+ was 0.88 mgL^{-1}. In the control topsoil, the amount of NH_4^+ leached was 0.51 mgL^{-1}. NH_4^+ leaching reduced by 9% with 1% granular biochar added in the topsoil compared to control topsoil. With the application of 2% powder biochar, NH_4^+ leaching reduced by 57% compared to the control topsoil. Meanwhile, in the leachate, NH_4^+ leaching reduced by 7% with 1% powder biochar, and NH_4^+ leaching reduced by 1% with 2% powder biochar compared to control topsoil. In the control top & E-horizon soil, the amount of NH_4^+ leached was 1.42 mgL^{-1}. With the application of 1% granular biochar, NH_4^+ leaching increased by 26% compared to the control top & E-horizon soil. With the addition of 2% granular biochar, NH_4^+ leaching increased by 14%. In the meantime, with the addition of 1% powder biochar, NH_4^+ leaching increased by 15%. The addition of 2% powder biochar NH_4^+ leaching also increased by 42% compared to the control top & E-horizon soil. Besides, 0.66 mgL^{-1} of NH_4^+ was released from the control mixed soil. With the application of 1% granular biochar, NH_4^+ leaching increased by 75% and with 2% powder biochar, NH_4^+ leaching reduced by 33% compared to the control mixed soil. Meanwhile, NH_4^+ leaching decreased by 66% with the addition of 1% powder biochar and NH_4^+ leaching reduced by 72% with the application of 2% powder biochar compared to control mixed soil. Overall, a significant percentage of NH_4^+ leaching reduced with biochar amendment in soil. In the biochar treated topsoil, NH_4^+ leaching reduced by 57%, and in the biochar treated mixed soil, NH_4^+ leaching reduced by 72%.

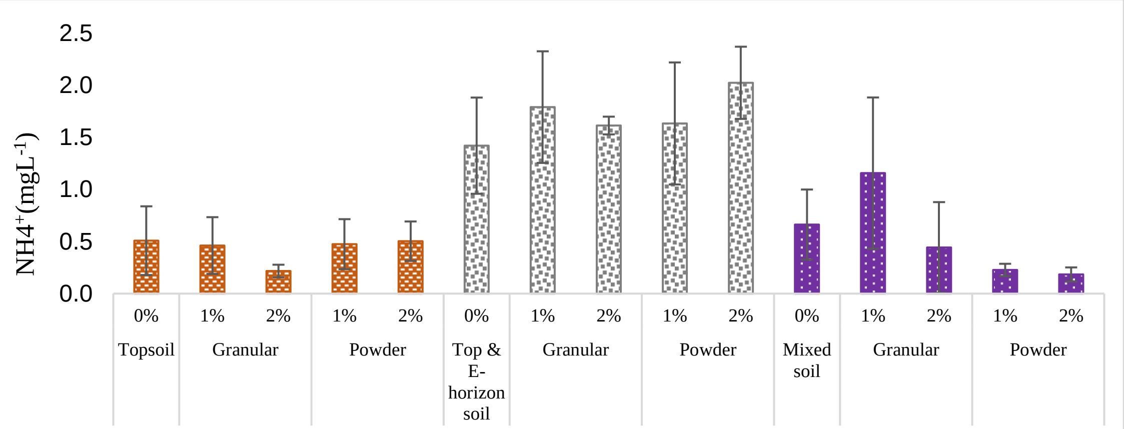

Figure 4.6: NH_4^+ leached during each treatment. The values are arithmetic mean of three replicates and the error bars are the standard deviation.

4.3.6 Volume of leachate

The total amount of leachate from the different leaching columns are presented in Figure 4.7. The leachate volume range was from 27 to 68 mL in the entire leaching columns, and the mean volume of leachate was 50.53 mL. In the control topsoil, the total volume of leachate was 68 mL. With the addition of 1% granular biochar, the volume of leachate decreased by 1% while it was decreased by 4% with 2% granular biochar compared to the control topsoil. In the topsoil, 27% volume of leachate decreased with 1% powder biochar, and 25% volume of leachate decreased with the application of 2% powder biochar compared to the control topsoil. In top & E-horizon soil, a 40 mL of leachate was found from the control column. With the addition of 1% granular biochar, the volume of leachate increased by 20%. With the addition of 2% granular biochar, leachate volume increased by 29% compared to the control column.

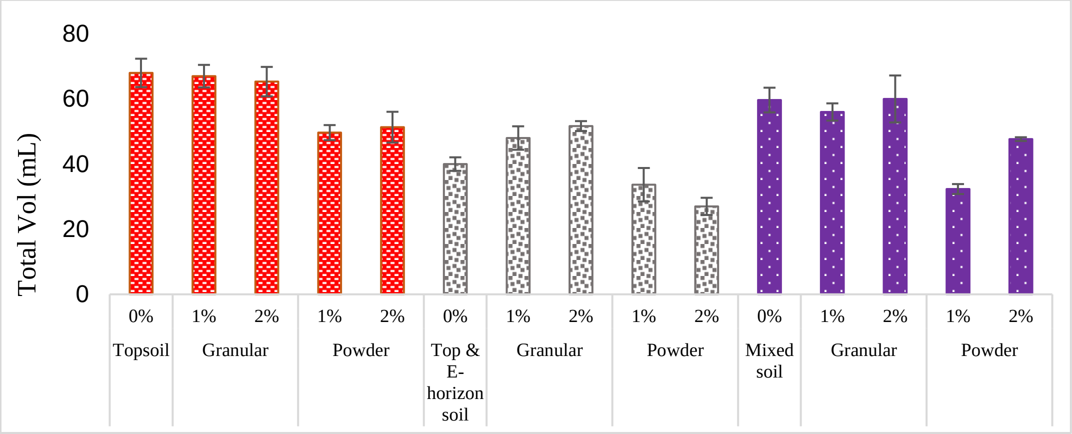

Figure 4.7: Total volume of leachate from 0 to 75 minute

The volume of leachate decreased by 16% with 1% powder biochar. The leachate volume decreased by 33% compared to the control top & E-horizon soil with 2% powder biochar. A total of 60 mL leachate was found in the controlled mixed soil. When 1% granular biochar was added with soil, the leachate volume decreased by 6% and with the addition of 2% granular biochar, the volume of leachate increased by 1% compared to the control mixed soil. When 1% powder biochar was added with soil, the volume of leachate decreased by 46%, and with the addition of 2% powder biochar, the leachate volume decreased by 20% compared to control mixed soil. Overall, the granular biochar amendment increased the volume of leachate by 29%, and powder biochar application in the soil reduced the volume of leachate by 46%.

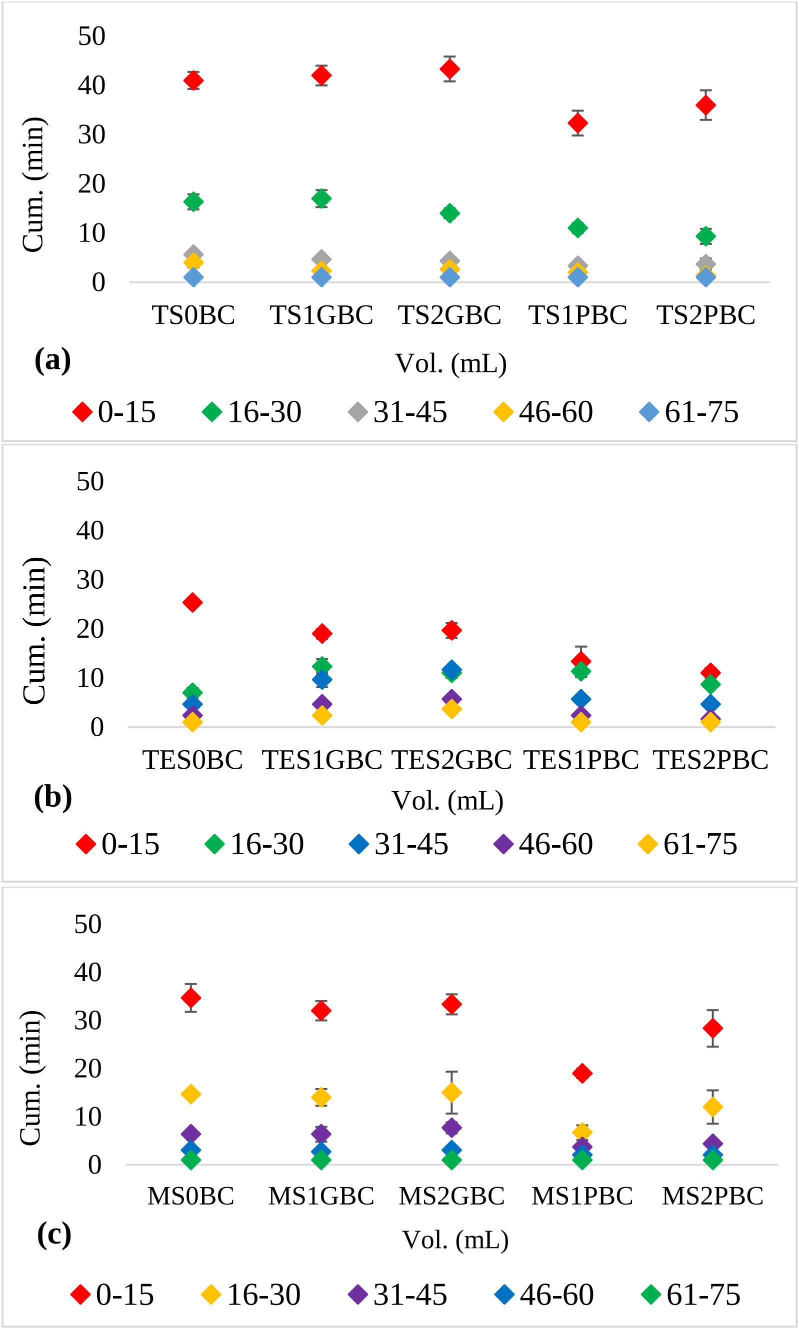

Figure 4.8: Biochar effect on the volume of leachate with time in the leaching column experiment: (a) topsoil; (b) top & E-horizon soil; and (c) mixed soil.

[Abbreviation: TS0BC=topsoil with 0% biochar; TS1GBC=topsoil with 1% granular biochar; TS2GBC=topsoil with 2% granular biochar; TS1PBC=topsoil with 1% powder biochar; TS2PBC=topsoil with 2% powder biochar; TES0BC= top & E-horizon soil with 0% biochar; TES1GBC= top & E-horizon soil with 1% granular biochar; TES2GBC= top & E-horizon soil with 2% granular biochar; TES1PBC= top & E-horizon soil with 1% powder biochar; TES2PBC= top & E-horizon soil with 2% powder biochar; MS0BC= mixed soil with 0% biochar; MS1GBC= mixed soil with 1% granular biochar; MS2GBC= mixed soil with 2% granular biochar; MS1PBC= mixed soil with 1% powder biochar; MS2PBC= mixed soil with 2% granular biochar]

Figure 4.8 describes the effect of biochar on leachate volume from 0 – 75 minutes on a certain (156 mL) amount of water. From 0 – 15 min, the leachate volume was found 32 – 43 mL in the topsoil leaching column, where 2% powder biochar treated soil leached 32 mL and 2% granular biochar treatment leached 43 mL water. From 16 – 30 min, about one-fourth volume of leachate was found from 2% powder biochar treated soil compared to the amount of leachate from 0 – 15 min. In the top & E-horizon soil leaching column, 11 – 25 mL of leachate was found within 0 – 15 min period, which was about half of the leachate of topsoil in the 1st 15 min. The control top & E-horizon soil leached 25 mL of water while 2% powder biochar treated soil leached only 11 mL of leachate from 0 – 15 min. In mixed soil, the range of leachate volume was found to be 19 – 35 mL in the 1st 15 min. Powder biochar treated mixed soil leached less amount of leachate compared to granular biochar treated mixed soil. Overall, biochar treated top & E-horizon soil leached less amount of leachate compared to topsoil and mixed soils.

4.3.7 Correlation among leachate ion concentration and volume

The correlation among the amount of NO_3^- and NH_4^+ and the total volume of leachate are presented in Table 4.2. Notably, the amount of NO_3^- positively correlated with the volume of leachate ($p=0.250$). But the amount of NH_4^+ showed a negative correlation with the leachate volume ($p=0.250$). However, the amount of NO_3^- was negatively correlated with the amount of NH_4^+ in the leachate ($p=0.234$).

Table 4.2: Correlation among NO_3^- (mgL^{-1}), NH_4^+ (mgL^{-1}), and total volume of leachate (TVL) (cm^3)

	NO_3^-	NH_4^+	TVL
NO_3^-	1.0000		
NH_4^+	-0.6817	1.0000	
TVL	0.6945**	-0.5195	1.0000

4.4 Discussion

The leaching column study's experimental design focused on how biochar influence to reduce N leaching and improve soil hydraulic properties of podzolic soil in boreal ecosystem. A comparatively greater amount of NO_3^- retention was observed in the top & E-horizon soils. In the case of NH_4^+ retention, the topsoil showed a greater capacity to hold the positive ion. The study findings indicated that the leachate volume decreased by 46% with powder biochar application. The amount of NO_3^- in the leachate demonstrated a positive correlation with the volume of leachate. The results indicated that the biochar amendment in the soil is an effective tool to reduce N leaching from the agricultural soil.

Liu et al. (2017) mentioned that the exact mechanisms underlying N retention in biochar treated soils are not well defined, but some potential reasons were proposed in many studies. The reasons were as follows: (1) biochar has higher cation and anion exchange capacities, (2) physical retention in soil as N able to dissolve to the soil solution easily, and (3) biochar treated soil has a higher water holding capacity (WHC) - that might help to retain more N in the soil (Xu et al., 2016; Hagemann et al., 2017). As biochar increased WHC, it reduced the total volume of leachate from the leaching column (Liu et al., 2017). Similar responses were found in the leaching column study

– biochar treated top & E-horizon soils reduced almost 50% of leachate volume compared to control. Biochar has a high erosion potentiality that could be one of the reasons why biochar amended soil contains a greater amount of N in the soil (Dil et al., 2014).

Biochar particles have a strong capacity to adsorb free NH_4^+ ions as it has high cation exchange capacity (CEC). As a result, the biochar retarded vertical movement of NH_4^+ at the bottom of the leaching column which is a deeper layer of soil, and less NH_4^+ would be found in the leachate (Yao et al., 2012). Also, biochar could increase NO_3^- and NH_4^+ adsorption in the coarse-textured soil (Dil et al., 2014; Sika and Hardie, 2014). Han et al. (2016) mentioned that biochar has a greater effect on reducing NH_4^+ leaching only 0 – 40 cm as topsoil is generally situated in this layer. After that, it has a limitation of reducing NH_4^+ leaching. Usually, E-horizon (sandy soil) exists after topsoil (clay), where the amount of NH_4^+ leaching is a little bit higher. The study findings also confirmed that the leaching column which consists of top & E-horizon soil released a higher amount of NH_4^+ compared to topsoil and mixed soil.

Studies reported that biochar reduced a significant amount of NO_3^- (34%) and NH_4^+(14%), and the percentage of leaching of ions was not uniform that varies based on types of biochar (Yao et al., 2012; Qiao-Hong et al., 2014). In this study, CEC of both applied powder and granular biochar was high and power biochar possessed hydrophilic properties and granular biochar showed hydrophobic properties (Saha et al., 2020). That could be one of the reasons why powder biochar treated soil was more likely to increase adsorption of NO_3^-. Sika and Hardie (2014) found that the cumulative amount of NO_3^- leaching reduced by 26 – 96% and the amount of NH_4^+ leaching reduced by 12 – 86% with the biochar treatment rate 0.5 – 10.0% compared to control soil. Liu et al. (2017) found that a 2 – 4% biochar amendment reduced NO_3^- leaching by 28.65 – 29.19% in a loamy soil. Also, Sun et al. (2017) reported that biochar reduced NO_3^- (34.0%) and NH_4^+ (34.7%) compared to the control sandy soil. In this study, biochar amended soil reduced NO_3^- leaching by 36% - the findings on the percentage of N ion retention is almost same as the previous study findings. The experimental results indicated that a higher rate of biochar application could reduce a higher percentage of NO_3^- and NH_4^+ leaching – the results also match with the results of Sika and Hardie (2014) study.

N leaching from agricultural fields is considered a non-point source contaminant, which deteriorates groundwater quality (Elmi et al., 2012). Biochar amendment reduces N leaching from the soil and improves N use efficiency (positively) in sandy soil (Oladele et al., 2019; Liu et al., 2017; Qiao-Hong et al., 2014). As biochar can reduce N leaching, plants will get more nutrients in the root zone. However, some studies mentioned that NH_4^+ leaching from soil would not be a major problem as it is absorbed by the clay minerals, which are negatively charged. This is a reason why the magnitude of NO_3^- leaching is greater than NH_4^+ leaching in the biochar amended soil (Xu et al., 2016). The leachate analysis revealed that the amount of NH_4^+ (0.18 – 2.02 mgL^{-1}) was low compared to NO_3^- (4.96 – 12.04 mgL^{-1}). As biochar can retain more nutrients (in the form of N), biochar has a positive impact on the soil (Widowati et al., 2014).

In this study, biochar influenced hydraulic conductivity that could alter soil porosity, pore shape and pore size distribution. The effect would be varied according to the type and rate of biochar and soil texture (Li et al., 2018). The simulated results of hydraulic properties indicated that the biochar effect on the hydrological process was highly variable. In 2019, Altdorff et al. found high variability in the simulated hydrological process of biochar amended podzolic soil, such as significantly decreasing flux values with the increasing rate of biochar. Jiménez-Martínez et al. (2009) mentioned that simulated soil moisture dynamics and field measurements were almost accurate. The simulated values were effective in sustaining soil moisture dynamics in the crop root zone. Mo'allim et al. (2018) confirmed that simulated values of Hydrous 1D found reasonable and effective for solute transportation. Also, Iqbal et al. (2020) mentioned that Hydrous 1D found an effective tool to simulate VSMC in rainfed conditions.

Experimental vs simulated values of time to leach was compared in this study. A high coefficient of determination (R^2), low RMSE and low RE were found between experimental and simulated values. Pal et al. (2014) and Negm et al. (2017) validated the experimental vs simulated values and found very little error on those values. When we simulate soil hydraulic properties for a particular seasonal crop, we need to consider soil pressure head distribution on that specific agricultural field and crop growing season (Tan et al., 2014). The values of simulated hydraulic properties (like soil moisture content and hydraulic conductivity) will help to understand how harmful substances (like NO_3^-, etc.) are leaching and the amount and rate of leaching of those substance from the agricultural field. Many studies have been conducted on SMC simulation with different types of soil, climate condition, and a wide variety of vegetation coverage using the Hydrous 1D model. It would be better if a detailed *in situ* experimental plan executes with important hydraulic properties and calibrates and validates the model at that site (Tafteh and Sepaskhah, 2012). A long–term study design and simulation exercises using Hydrous 1D at laboratory and field will give a comprehensive output on biochar functionality of podzolic soil in boreal ecosystem.

The study findings suggested that a 2% powder biochar application rate can reduce a greater amount of NO_3^- leaching from the soil. That could be an effective information for farmers to optimize agricultural soil management practices, especially on podzolic (acidic) soil in boreal ecosystem and protect groundwater contamination by reducing NO_3^- leaching (Hagemann et al., 2017; Šimanský et al., 2018). As biochar types influence nutrient sorption, biochar's sorption properties should get the top priority of investigation before biochar applied in agricultural soil (Yao et al., 2012). Understanding the mechanism of biochar and N interaction and the best possible biochar– soil combination to get the optimum amount of N retention in podzolic soil could provide farmers a vital information for agricultural practices. Optimum application of biochar on podzolic soil could improve ecological functioning and that will ensure a sustainable ecosystem.

The way forward:

- For further investigation, long-term field experiments would give a comprehensive knowledge of appropriate biochar applications to improve the nutrient status and minimize environmental risks due to NO_3^- leaching.

- For further simulation in Hydrous 1D, the optimum thickness of the biochar treated soil related to the soil moisture content and runoff information would help to protect environmental contamination.

- As applied biochar persist long-time in the agricultural field, evaluation of biochar's phytotoxicity would be essential to know the negative environmental impacts of biochar.

- An experiment on how microbial communities influence N retention in the biochar amended soil could give essential information on the microscopic level and protect nutrient leaching from the soil.

- The microscopic mechanism on the effect of biochar on soil properties and the nutrient movement in the soil-plants system need to be investigated.

- A further experiment on the chemical form of immobilized N in the biochar amended soil would be important to know the mechanism on how and when the immobilized N will be released into the soil.

4.5 Conclusion

The study findings indicated that biochar application on the podzolic soil significantly reduces N leaching from the leaching zone and improves hydraulic properties. The Hydrous 1D model was used to simulate water movement in the leaching column. Simulation indicated that the biochar amendment increased VSMC by 6.97% in topsoil and 8.56% in mixed soil. In the leaching column experiment, the application of granular biochar increased leachate volume by 29%, while the powder biochar amendment reduced leachate volume by 46%. Also, in the powder biochar amended soil, NO_3^- leaching was reduced by 36% compared to control soil. Notably, a higher percentage of NO_3^- reduced by the application of powder biochar in the mixed soil compared to other treatments. In the experiment, the amount of NH_4^+ leaching (from 0.18 to 2.02 mgL^{-1}) was found low compared to NO_3^- (from 4.96 to 12.03 mgL^{-1}) leaching from the leaching column. A positive correlation was observed between the amount of NO_3^- and the volume of leachate. A 2% biochar amendment in the podzolic soil showed a greater impact on improving VSMC and reducing significant amounts of NO_3^- and NH_4^+ leaching and decreasing the volume of leachate. Based on the findings, the application of biochar on mixed soil could be recommended to improve hydraulic properties and retain more N in the crop root zone – as a result plants will get more nutrients. For further investigation, the microscopic mechanism on biochar's effect on nutrient movement in the soil-plant system would be needed to increase soil nutrient level. Also, evaluation of biochar's phytotoxicity in the agricultural field would be essential to know the negative impact of biochar on podzolic soil in boreal ecosystem.

Acknowledgment

Authors acknowledge members of Hydrology & Agrophysics Group, Grenfell Campus – Memorial University of Newfoundland for their help and constructive comments during the study. Authors gratefully acknowledge Dr. Tao Yuan, Lab Coordinator of the Boreal Ecosystem and Research Facility, Grenfell Campus, Memorial University of Newfoundland for his valuable contribution in conducting analysis, especially on Ion Analyzer (LACHATE), and overall coordinating activities in the lab. Authors are thankful to Dr. Yeukai Katanda and Dr. Muhammad Nadeem – postdoctoral Fellow, School of Science and the Environment, Grenfell Campus, Memorial University of Newfoundland for providing support during study design and executing experiments. This research was financially supported by the School of Science and the Environment, Grenfell Campus, Memorial University of Newfoundland, Canada.

Conflicts of interest

"The authors declare no conflict of interest" in this experiment-based study. A comprehensive study design was prepared and executed without having any influences. The findings presented in this article were obtained from the experiments. The findings also compared with the published peer-reviewed journal articles' findings.

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Chapter Five

Conclusion

5.1 General discussion and conclusion

The studies presented in this thesis aimed to assess the influence of biochar type and rates on the physicochemical properties and N transport of podzolic soils used for agriculture production in boreal ecosystem. A total of 210 most relevant published articles related to the impacts and limitations of biochar applications were reviewed. A metadata analysis (study location, goal, and outcome) of the studies were done. Ten physicochemical parameters {bulk density (BD), porosity, field capacity (FC), plant available water (PAW), water repellency (WR), electrical conductivity (EC), pH, cation exchange capacity (CEC), total carbon (TC), and nitrogen (N)} were investigated through a total of 72 experimental units. Biochar morphological structure and pore size distribution were examined using a scanning electron microscope, whereas specific surface area was assessed by the Brunauer−Emmett−Teller method. In addition, laboratory-based experiments were conducted to assess some of the gaps indicated in the review-based study to better understand biochar application as an amendment in boreal ecosystem. Leaching column experiments were conducted at the laboratory and the amount of nitrate (NO_3^-) and ammonia (NH_4^+) in the leachate were analyzed by Ion Analyzer (LACHAT Instruments). The Hydrous 1D model was used to simulate leaching column soil hydraulic properties (moisture content, hydraulic conductivity, and water flux). A total of 270 experimental units were executed to get accurate results from the leaching column experiment and simulation.

The critical review of the published articles indicated that most of the studies were conducted in tropical ecosystems, with only a few studies done at high latitude areas, especially in podzolic soils under boreal climates. According to the comparative and critical review, biochar has been applied in a wide variety of areas with a positive-impacts ascertained on the physicochemical properties of soil, reduced nitrogen leaching from soils, enhanced plant growth, increased carbon sequestration and may serve as a potential strategy for mitigating greenhouse gases; facilitated organic matter degradation; reduced wastes toxicity, volume, and density during composting; can be used for wastewater purification as well as effectively removed heavy metals (Cd, Cu, Pb, and Zn) from contaminated soil and accelerates the biodegradation of Polycyclic Aromatic Hydrocarbons in the petroleum-polluted soils. The review-based study suggested that there is lack of knowledge on the threshold amounts of biochar applications for positive agronomic effects and environmental sustainability in different ecosystem. The focus of biochar research on podzolic soils would be very useful under the potential northward shift of agriculture mainly due to climate change.

The experiment on the effect of biochar on the physicochemical properties of soil provided strong evidence that supports the positive impact of the biochar amendment in podzolic soil. Biochar application increased pH (especially in the E-horizon soil), EC, CEC, and TC: N ratio in podzolic soil while reducing bulk density. In this study, WR was found to be slightly increased with the different rates of biochar treatment, but the treatment combinations were still classified as slightly-repellent. Biochar doses on podzolic soil showed a temporal effect on pH and EC from day 1 to day 7. The biochar amendment showed great ability in improving soil water retention. Both types of biochar amendments increased porosity in the treatment combination. However, the FC and

PAW increased more in the powder biochar amended soil than the granular biochar amended soil. Granular biochar was determined to be slightly hydrophobic, and powder biochar was determined to exhibit hydrophilic characteristics. The study results suggested that the application of 2% biochar could have a beneficial influence on the physicochemical properties of podzolic soil. The application of biochar in the mixed soil showed better improvement in physicochemical properties with increasing biochar rates, compared to the improvements found in its application to topsoil and E-horizon soil.

The leaching column experiment results showed that the application of granular biochar increased the volume of leachate (up to 29%), while powder biochar reduced leachate volume (up to 46%) from the leaching column. The findings also confirmed that granular biochar showed hydrophobic characteristics and powder biochar possess hydrophilic characteristics. In the leachate, NH_4^+ concentration (from 0.18 to 2.02 mgL^{-1}) was low compared to NO_3^- concentration (from 4.96 to 12.03 mgL^{-1}). Both types of biochar reduced NO_3^- leaching up to 36% compared to control soil. Notably, a higher percentage of NO_3^- leaching was reduced by the application of powder biochar in the mixed soil. Hydrous 1D simulation indicated that biochar amendment increased volumetric soil moisture content in the topsoil and mixed soil. The application of 2% biochar had a greater impact on improving volumetric soil moisture content and reduced significant amounts of NO_3^- and NH_4^+ as well as the volume of the leachate from podzolic soil. Overall experimental findings indicated that biochar application in the mixed soil (a combination of topsoil and E-horizon soil) can be recommended to retain more N and improve hydraulic properties of podzolic soil in boreal ecosystem.

5.2 Significance of findings for agricultural production on podzolic soil in boreal ecosystem

The study findings would be a road map for further scientific exploration of biochar application. The results could be helpful to better understand the use of biochar for improving the physicochemical properties and retain more N (as nutrients) within the root zone of podzolic soil in boreal ecosystem. Overall, the outcome of the study would be applicable for farmers, enhance agricultural productivity as well as influence government policy for agricultural practices.

5.3 Recommendations

Further studies need to be focused on:

- A comprehensive assessment of ecosystem functioning on the impact of biochar in different regions across the world would be essential for the sustainability of agricultural practices and the environment.

- Chemical and structural analyses are needed to accurately calculate the percentage of pore space changed through biochar application.

- A deep investigation into the physicochemical properties of the biochar (morphological structure, pore size, surface area, surface chemistry) to the N transport and amendment abilities of the char.

- Further research is needed to evaluate effectiveness of biochar in long-term field studies.

- The long-term ecotoxicological effects of biochar need to be examined to ensure ecological sustainability in the future.

Appendices

Manuscript one

Title: Effects of biochar on agricultural and environmental sustainability: A review

Authors: Ratnajit Saha, Lakshman Galagedara, Raymond Thomas, and Kelly Hawboldt

Journal: *Journal of Cleaner Production* [Elsevier publisher]

Status: Submitted and under peer-review; Ms. Ref. No.: JCLEPRO-D-20-17314

Manuscript two

Title: Investigating the influence of biochar amendment on the physicochemical properties of podzolic soil

Authors: Ratnajit Saha, Lakshman Galagedara, Raymond Thomas, Muhammad Nadeem, and Kelly Hawboldt

Journal: *Agriculture* (ISSN 2077-0472) (Impact Factor: 2.072) [MDPI publisher]

Status: The research article has been published in *Agriculture* journal.

Reference: Saha, R.; Galagedara, L.; Thomas, R.; Nadeem, M.; Hawboldt, K. Investigating the Influence of Biochar Amendment on the Physicochemical Properties of Podzolic Soil. *Agriculture* **2020**, *10*, 471. https://doi.org/10.3390/agriculture10100471

Manuscript three

Title: Effect of biochar on nitrogen transport and hydraulic properties of podzolic soil in boreal ecosystem

Authors: Ratnajit Saha, Lakshman Galagedara, Raymond Thomas, and Kelly Hawboldt

Journal: *Journal of Soil Science and Plant Nutrition* [Springer publisher]

Status: Manuscript in the process of submission

Manuscript four

Title: Biochar application in the boreal podzolic soil suitable for ecosystem sustainability

Authors: Ratnajit Saha, Lakshman Galagedara, Raymond Thomas, and Kelly Hawboldt

Journal: *Nature Communications* [Nature publisher]

Status: Manuscript in progress

Conference (poster presentation)

Title: Assessing the temporal effects of biochar amendment on pH and EC in podzolic soil

Authors: Ratnajit Saha, Lakshman Galagedara, Muhammad Nadeem, Raymond Thomas, and Kelly Hawboldt

Conference: 5th CIGR International Conference (Integrating Agriculture and Society through Engineering), Québec City, Canada, May 10-14, 2021

Status: Accepted (Contribution ID: 297; https://cigr2020.ca/en/)