Use of wood ash and paper sludge as potting substrate and potential soil amendment for agriculture production on podzols in boreal climate

By

Muhammad M Farhain

A thesis submitted to the School of Graduate Studies

In partial fulfillment of the requirements for the degree of

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Approved:

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Abstract

This study was designed to investigate the use of wood ash (WA), paper sludge (PS) (wastes from paper mill) and biochar (BC) as potting substrates, and potential amendment for podzolic soil. WA and PS were applied by two methods; 1) on volume basis to prepare a suitable potting media (Study-one), and 2) on mass basis to amend the podzolic soil and for assessment of heavy metals leaching behavior (Study-two). Important physicochemical properties were measured in both experiments. In study one, the treatment of 50% PS + 25% BC was noted as the best treatment based on the measured properties as a suitable potential potting media. This treatment had high organic matter (8.33%), field capacity–FC (0.33 $cm^3\ cm^{-3}$) and plant available water-PAW (0.40 $cm^3\ cm^{-3}$) with low bulk density (0.53 $g\ cm^{-3}$). In the study-two, WA alone and with BC did not show significant difference from control to improve the physicochemical properties of amended soil, and PS with combination of BC found as the best treatment having optimum pH (6.5) with the highest total porosity (0.68 $cm^3\ cm^{-3}$), FC (0.36 $cm^3\ cm^{-3}$) and PAW (0.28 $cm^3\ cm^{-3}$) among all treatments. BC addition in leaching column experiment significantly reduced the heavy metals (Arsenic, Cadmium, Cobalt, Copper, Molybdenum and Nickel) concentrations in collected leachates compared to bC unamended treatments. Outcomes of these studies would be useful for farmers to improve the agricultural production in the region and influence the government policy for the application of paper mill wastes in agricultural industry.

General Summary

Poor soil conditions (low pH, less fertility and coarse texture) in Newfoundland and Labrador (NL) are the major constraints limiting agricultural productivity. The Corner Brook Pulp and Paper Ltd. (CBPPL) produces two major waste streams (wood ash–WA and paper sludge– PS) as by products of their paper manufacturing process and can be potential nutrient sources to improve soil quality, thus increase crop production. WA and PS produced from CBPPL, have high pH and calcium carbonate equivalency with low bulk density. Furthermore, PS has a fibrous structure and high water holding capacity. Lab experiments showed that WA and PS alone and in combination with of biochar improved the physicochemical properties of potting media and as well as podzolic soil following application as a soil amendment. Total leached heavy metals concentrations in all treatments evaluated in the leaching experiments were lower than the water quality guidelines developed for irrigation, livestock and human consumption by the Canadian Council and Ministers of Environment-CCME (CCME, 1999). Using WA and PS as potting substrates and potential soil amendments could be a pragmatic approach to integrate waste management and food production to achieve food security and mitigate negative environmental effects in the region.

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Muhammad Mashaallah Farhain

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List of abbreviations

As = Arsenic

BC = Biochar

BD = Bulk Density

CBPPL = Corner Brook Pulp and Paper Ltd.

Cd = Cadmium

CEC = Cation Exchange Capacity

Co = Cobalt

Cr = Chromium

EC = Electrical Conductivity

FC = Field Capacity

GHG = Greenhouse Gas

ICP-MS = Inductively Coupled Plasma Mass Spectrometry

K = Potassium

Mo = Molybdenum

N = Nitrogen

NH_4^+= Ammonia

Ni = Nickel

NO_3^- = Nitrate

OM = Organic Matter

PAW = Plant Available Water

Pb = Lead

PCA = Principal Component Analysis

PMW = Paper Mill Wastes

PS = Paper Sludge

RE = Relative Error

RMSE = Root Mean Square Error

SOM = Soil Organic Matter

SWRC = Soil Water Retention Curve

TC = Total Carbon

TN = Total Nitrogen

TP = Total Porosity

w/w = Weight/Weight

WA = Wood Ash

WHC = Water Holding Capacity

WR = Water Repellency

Chapter One

General introduction

1.1 Overview

Agriculture in Newfoundland and Labrador (NL) is restricted to very small scale, mostly in the Deer Lake (Pasadena) region, Cordoy valley and south of St. John's. In 2020 NL primarily produced potato, carrots, beets, turnips and cabbage, these accounted for 81% of all vegetables or root crop production (www.gov.nl.ca/farm-guide/interesting-facts-about-our-agriculture-industry). The total number of operating agricultural farms in NL has been reduced by 20.2% from 2011 to 2016 representing 407 farms in total, which represents less than 1 % of total farms in Canada (Statistics Canada, 2016). The NL agriculture industry is very small, and to fulfill the basic food requirement, about 90% of the vegetables and fruits are imported from mainland Canada and other countries. The number of vegetable farms have been decreased from 112 in 2011 to 78 in 2018 and the field vegetable production area has declined from 306 to 249 ha from 2014 to 2018 (Statistics Canada, 2019). In general, the farm area producing organic products in NL slightly increased from 1.0% to 1.2% from 2011 to 2016. The land used for greenhouse flower and vegetable production dropped by 17.1% (52305 m^2) from 2011 to 2016 (Statistics Canada, 2017). Greenhouse and nursery style farms were the most common in NL, accounting for 19.4% of all farm types in the province (Statistics Canada, 2017).

Reduced agricultural production is the primary reason for intensification in import of fruits, vegetables, and other agriculture related food products to NL. Some of the foremost reasons of low agricultural productivity which make NL distinctively challenging for agricultural development are short growing season, extreme cold weather conditions, poor soil, high liming and fertilizer cost (Nadeem et al., 2019). The NL has a boreal climate with characteristic of podzolic soils having low pH (Sanborn et al., 2011) and poor fertility. Application of limestone is currently being practiced amending these low pH podzols in the province, which is an additional cost for the farmers. Alternative soures as soil amendments with low cost that give better performance as a liming agent and soil conditioner are required. The application of organic wastes as soil conditioners/ammendment is an ancient but progressively popular way that not only assist to reduce agrochemicals dependence, but also represents an ecologically-sound, economically attractive and socially acceptable alternative to landfill disposal of different wastes (Gómez-Sagasti et al., 2018). The amelioration of poor fertile soil with organic wastes can serve dual purpose and include (1) disposal of wastes from the generation site, and (2) help to improve physical, biological, and chemical properties of soil, in turn foster the improved crop performance (Corti et al., 2012). Moreover, unsuitable, and non-sustainable ways of waste management like open burning or open dumping not only cause environmental pollution, but also affect the urban landscape and human health. Openly disposing the wastes enhance the threat of soil pollution in regions adjoining the disposal sites due to leaching of heavy metals and other toxins. Leaching and surface runoff from these sites cause contamination of ground water and surface water bodies (Sharma et al., 2019). Organic materials, like municipal solid waste, green wastes, paper mill and sewage sludge can be converted into valued resources by composting and subsequent application to agricultural and forest soils (Diacono and Montemurro, 2010; Sharma et al., 2017). Quality and quantity of applied organic matter through repurposing these wastes could have strong effect on soil physicochemical properties; and therefore need to be considered when setting up field applications (Diacono and Montemurro, 2010; Eden et al., 2017). Recent findings showed that application of organic wastes can improve the physicochemical properties of amended soils.

Beneficial effects of organic wastes include the lowering bulk density, increasing the water holding capacity (WHC), water infiltration rate, pH, organic matter, cation exchange capacity (CEC) and improved biological activities (Bouajila and Sanaa, 2011; Zebarth et al., 1999; Eneje and Innocent, 2012; Zema et al., 2019). In addition to the above stated advantages of recycling organic wastes, they are also associated with certain risks. Use of organic waste as soil amendment may pose risks of food chain contamination due to the presence of potentially toxic heavy metals (Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Molybdenum (Mo) and Nickel (Ni)) (Sharma et al., 2018). These risks vary depending on types and source of the organic waste.

1.2 Paper mill wastes

Rashid et al. (2006) reported that the pulp and paper industries globally producing 2.5 million Mg of biosolid wastes annually and this is anticipated to increase to 3.0 million Mg by 2050. Increasing energy costs and improved co-generation technology have directed Canadian pulp and paper mills to generate power through ignition of wood waste (Rashid et al., 2006), which produces huge amounts of wood ash (fly ash and bottom ash) that has been disposed of through landfilling, with an allied cost for both tipping fees and transport charges (Beauchamp et al., 2002). The rising disposal costs of these wastes (from paper mill to disposal sites) also combined with restricted environmental regulations. Corner Brook Pulp and Paper Mills Ltd., (CBPPL) produces approximately 10,000 Mg of wood ash and 50,000 Mg of paper sludge annually (Personal communications). Disposing off at landfilling site is a considerable cost for the CBPPL, which projected to increase in near future due to provincial legislation and transport charges. In different provinces of Canada, pulp and paper mills spread wood ash to soils as a liming and restorative material (Hannam et al., 2016). It is commonly believed that wood ash can be used as a liming material and its application will be a suitable way to recycle nutrients (Naylor and Schmidt, 1989; Maheswaran, 2019) On the other hand, increasing cost of lime and chemical fertilizers have increased the interest of farmers to finding alternative sources of soil amendments for low pH and low fertility soils of Atlantic Canada region (Sharifi et al., 2013).

Wood ash has a great potential as a soil-amending agent in the agricultural and forest lands for reclamation of less productive lands because of wood ash's unique properties. Various studies have shown that application of wood ash increased soil pH and decreased the exchangeable Al content of acidic soils (Naylor and Schmidt, 1989; Maheswaran, 2019). Numerous studies have concluded that wood ash reacts quickly with soils than lime, subsequently a rapid increase in pH (Muse and Mitchell, 1995; Arshad et al., 2012). Water retention properties governs the water flow rate through soils profile and measures the chances of surface run-off. Numerous researchers have reported that wood ash application has positive effects on soil hydraulic properties like increased WHC in coarse textured amended soil (Moragues-Saitua et al., 2017; Stoof et al., 2010; Pathan et al., 2003) in addition to improved water penetration and root growth (Yunusa et al., 2006). Adverse effects have also been detected, e.g. entrapped wood ash has been reported to cause pore clogging (Woods and Balfour, 2010; Pitman, 2006). Studies on effects of wood ash as soil amendment to improve the physical and hydraulic properties are rare and need to investigate its effects on soil quality and plant growth.

The pulp and paper mills produce a huge volume of paper sludge, resulted from clarifying and settling wastewater used in the paper making process. The CBPLL produces a large amount of paper sludge with a higher moisture content of 85-95%, mechanical pressing helps to eliminate the water, but the resultant material still has higher moisture contents. The CBPPL currently uses paper sludge with some other biomass (hog fuel) as fuel for the enery co-generation unit of boiler.

The timber wastes undergo an oxidation process for the duration of treatment and produces the ash as byproduct, however. The paper sludge produced has the essential nutrients to support plant growth. The use of paper sludge in agriculture (horticulture and agronomic crops) and forest lands (either growth media, field or greenhouse) without burning or dumping would be a desirable management strategy. Landfilling and incineration of the paper sludge are very unfavorable means of disposal. Paper sludge contains high organic matter and minerals such as nitrogen (N), carbon (C) and phosphorous (P) and fibrous structure. Due to these beneficial properties, paper sludge can be used as a soil conditioner/amendment or plant nutrient source. Paper sludge used as a soil amendment improved the soil physicochemical and biological properties (Camberato et al., 2006). Paper sludge application at 160 Mg ha^{-1} to loam soil, decreased the bulk density of top soil from 1.21 to 1.01 g cm^{-3} and resulting in increased total porosity and hydraulic conductivity (Chow et al., 2003). Fierro et al. (1999) reported that bulk density of sandy soil decreased from 1.7 to 1.3 g cm^{-3} after 2 years of paper sludge application at 105 Mg ha^{-1}. Paper sludge application of 225 Mg ha^{-1} to a sandy loam soil significantly increased the plant available water (PAW) held between –60 and –1500 kPa by 49% compared to unamended soil (Zibilske et al., 2000). Chrysargyris et al. (2019) evaluated the effect of paper mill wastes to replace the peat as growth media for marigold (*Calendula officinalis* L.), petunia (*Petunia* × *hybrita* L.) and matthiola (*Matthiola longipetala)* and observed paper mill solid waste increased the media pH by 1.73 units and decreased the aeration porosity. Decreasing the irrigation requirement by increasing the WHC is another potential advantage of paper sludge application. Two applications of paper sludge increased the PAW of plain loamy sand soil from 0.07 to 0.09 cm^3 cm^{-3} (Foley and Cooperband, 2002). Legendre et al. (2004) applied the paper sludge as liming material to silt loam soil at 13 and 26 Mg ha^{-1} and observed pH increased in upper 0-15 cm of the soil by 0.4 and 0.8 units, respectively. Besides the above mentioned beneficial aspects of paper mill wastes, the authors also observed heavy metals contamination problems. In CBPPL, pulp and paper process are sustained by steam created from mill boilers which burns a fuel of waste oil, hog fuel and bunker C fuel. The bunker C fuel is known as No.6 fuel oil (residual oil) having high viscosity and some metals (Zhang et al., 2017). During the wood combustion as these metallic elements are volarised, condensed and become a part of the wood ash (mixture of fly ash and bottom ash). Chemical analysis of wood ash and paper sludge showed these amendments have significant amount of heavy metals (based on our preliminary test). In order to reduce the harmful effects of heavy metals from wood ash and paper sludge, it is essential to control the soluble and exchangeable fractions of metals in amended soils. Biochar is a rich source of recalcitrant carbon which can reduce the heavy metals mobility and improve the physicochemical properties of amended soil (Saha et al., 2020; Maheswaran, 2019; Karami et al., 2011). Biochar has significant effect in increainge the pH, electrical conductivity and CEC of podzolic soil (Vermooten et al., 2019; Saha et al., 2020) and its porous structure can increase the WHC of amended soil (Qiao-Hong et al., 2014; Moragues-Saitua et al., 2017). The heavy metals mobility is an important consideration since their higher concentrations can reduce the crop production and result in bio-accumulation risk and bi-magnification in food chain (Beesley et al. 2010). There are also the risk of superficial water and groundwater contamination (Wuana and Okieimen, 2011). Numerous studies have shown that biochar application can lower the mobility of heavy metals in contaminated soils which decrease the risk of plants uptake and ground water contamination. Skjemstad et al. (2002) and Cheng et al. (2006) concluded that biochar derived from bamboo can adsorb the Cr, Ni, Cu, and Hg from both soils and water. Furthermore, Cd and Zn contaminated soil was amended with hardwood-based biochar and its application significantly reduced both metals in pore water (Beesley et al. 2010). Using the same soil for leaching column experiment conducted byBeesley and Marmiroli (2011) noticed that biochar addition significantly reduced the Cd and Zn concentration in pore water. Biochar application can reduce the heavy metals leaching through redox reactions. Choppala et al. (2012) conducted leaching column experiments to evaluate the Cr mobility in sandy soil amended with biochar derived from chicken manure and observed a reduction of the more mobile Cr (VI) species to the less mobile Cr (III) species, thus demonstrating an overall decrease in the leaching of Cr. The decrease in Cr leaching was attributed to Cr (III) adsorption on cation exchange sites (Bolan et al., 2013). Maheswaran (2019) conducted the leaching column experiment to assess the heavy metals mobility in wood ash and biochar amended sandy loam podzolic soil and concluded that biochar addition significantly reduced the Ni, Cr, Co, Cu and Mo concentrations in collected leachates compared to biochar unamended treatment (Control). Numerical simulation of water movement in soil profile is a suitable method to estimate the influence of organic amendments on volumetric moisture contents (VMC) of amended soil at different depths, as well as providing a better understanding about their effects on actual field conditions (Mo'allim et al., 2018). Hydrus-1D software is a valued tool to simulate the hydrological properties for biochar amended soil (Zheng et al., 2017). Hydrus-1D worked on the basis of Richards' equation and precisely can predict the water, heat and solute transport in saturated and unsaturated porous media (Tafteh and Sepaskhah, 2012; Jiménez-Martínez et al., 2009). Pal et al. (2014) and Saha (2020) used the Hydrus-1D model to simulate the VMC in different soil columns (depth 20 – 60 cm) and found that the simulated results were close to the measured values.

The above-mentioned findings showed that wood ash and paper sludge have great potential to improve the physicochemical properties of amended soil, though there is limited information in current scientific literature on how these paper mill wastes (wood ash & paper sludge) can be used as potting media substrate or as potential amendment alone and with combination of biochar for podzolic soils. This information is even more limited when applied to the application of these waste streams as media amendment for agriculture production on podzolic soils in boreal climate. Thus, the aim of this work is to use these paper mill wastes combined with biochar to develop suitable soil based potting media as well as to investigate the suitability of these wastes as soil amendment to improve the physicochemical properties of podzolic soil when used for agriculture cultivation in boreal climate. I also seek to investigate the combination of both waste streams with biochar and assess the effectiveness in reducing heavy metals mobility.

The principal hypotheses of the conducted study were “wood ash, paper sludge and biochar have porous structure, high pH and low bulk density and could be used as potential potting media and valuable amendments to ameliorate the podzolic soils, which can improve the physicochemical properties of podzolic soils and biochar addition can reduce the heavy metals concentration in podzolic soil leachates that will evade the surface and ground water contamination”.

1.3 Objectives

The specific objectives of the study were:

1. To investigate the impact of different ratios (Volume basis) of wood ash, paper sludge and biochar on the physicochemical properties of podzolic soil based horticultural potting media.
2. To optimize the suitable application rates of wood ash, paper sludge and biochar as soil amendment, and assess their effects on the physicochemical properties and simulated VMC of podzolic soil as well as the combination with biochar on heavy metals leaching behavior of podzolic soil.

It is predicted that scientific findings from this study would be helpful to significantly improve the understanding of wood ash, paper sludge and biochar use as a possible potting media and potential soil amendment to improve the physicochemical properties of podzolic soil. Also, the findings could be used as a road map for further scientific investigation of wood ash and paper sludge application in improving agricultural soils. The anticipated results also suggest paper mill wastes not only could be helpful for farmers to increase agricultural productivity and reduce the environmental pollution but will also generate increase revenue for the company. These findings will be valuable for developing guidelines for application of paper mill wastes to amend podzolic soils common in boreal climate in regions such as NL for improving agrinc productivity in the agriculture and forest industry.

1.4 Thesis organization

The thesis is organized in a manuscript style and divided into four chapters. The thesis has a general introduction chapter, two stand-alone chapters (manuscript format) and one as general discussion and conclusion.

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

Chapter two (study one): The title for this chapter is "Potential of developing podzolic soil-based potting media from wood ash, paper sludge and biochar".

Chapter three (study two): The title of the chapter is "Effects of wood ash, paper sludge and biochar amendment on physicochemical properties and heavy metals leaching of boreal podzolic soils".

Chapter four: This chapter present an overall discussion about study findings and conclusion. Also, this chapter provides the recommendations for further studies.

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Co-authorship statement for study one

Chapter 2 (Study One) a manuscript entitled "Potential of developing podzolic soil-based potting media from wood ash, paper sludge and biochar: An environment sustainable approach" has been submitted to Journal of Environmental Management (YJEMA 113811, accepted) [Impact Factor: 6.78] and it is in-press. Muhammad M Farhain, the thesis author was the primary author and collected the samples, prepared the study design, executed the experiment and statstically analyzed the data and drafted the manuscript. Dr. Lakshman Galagedara (supervisor), was the corresponding and the last author. He helped to design the study, data analysis, especially to complete the soil water retention curves from saturation to permanent wilting point, gave expert view on statistical analysis, helped in results interpretation, reviewed and edited the manuscript. Dr. Mumtaz Cheema was the 2nd author, helped in conducting the study, results explanation and reviewed and edited the manuscript. Yeukai Katanda, Dr. Muhammad Nadeem, Bilal Javed helped in data collection, reviewed and edited the manuscript. Dr. Raymond Thomas (Committee member) helped to finalize the methodology, data analysis, edited and reviewed the manuscript. Ratnajit Saha helped in data collection, reviewed and edited the manuscript.

Chapter Two (Study One)

Potential of developing podzolic soil-based potting media from wood ash, paper sludge and biochar

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Highlights

1. Valorization of organic waste is important to improve environment sustainability through recycling of valuable waste.
2. Herein we investigated the potential applications of wood ash and paper sludge as potting media for horticultural crops.
3. Wood ash and paper sludge improved the podzolic soil physicochemical properties.
4. Paper sludge is more effective than wood ash in improving the soil hydrological properties.
5. Furthermore, the incorporation of biochar in the potting media enhanced the water holding capacities.

Abstract

Background and objectives: Organic waste management in environmentally sustainable way is important not only to reduce the negative impacts on ecosystem but also valorizing the valuable waste resources. Herein we evaluated the potential of wood ash (WA) and paper sludge (PS) waste from pulp and paper mill as potting media and their effects on podzolic soil physicochemical properties.

Methods: WA, PS and biochar (BC) were mixed in different combination with sandy loam podzolic soil. Potting media treatments included: T1–Soil (negative control); T2– Promix^{TM} (positive control); T3–50%Soil+50%WA; T4–75%Soil+25%WA; T5–50%Soil+50%PS; T6–75%Soil+25%PS; T7–75%Soil+25%BC; T8–25%Soil+50%WA+25%BC; T9–50%Soil+25%WA+25%BC; T10–25%Soil+50%PS+25%BC; T11–50%Soil+25%PS+25%BC, T12–25%Soil+25%WA+25%PS+25%BC and replicated three times.

Results: Potting media treatments expressed significant (p<0.00) effects on pH, bulk density, porosity, field capacity, plant available water (PAW) and water retention curves. Potting media amended with WA showed high pH (8-12) while PS amendments exhibited pH in range of 6.5-7.5 where most plant nutrients are available. Results depicted significantly lower bulk density and improved porosity and water holding capacity of growth media amended with WA and PS. BC addition further enhanced the water retention properties compared to combinations without BC. T6, T10 and T11 produced high amount of PAW with desired pH compared to T1 and T2.

Conclusion: WA, PS and BC showed high potential to developing the podzolic soil-based potting media but assessing their effects on plant growth and elemental uptake needs to be investigated.

Keywords: Hydrological properties, paper mill wastes, potting media, wood industry by-products, heavy metals, soil amendments

2.1. Introduction

Decreasing fertile lands, water shortage, erratic weather patterns, combined with increasing urbanization, food insecurity and climate change have created serious pressure on the agricultural sector (Gruda, 2019). All stakeholders, including researchers, are highly interested in finding improved or new alternatives to meet the growing needs for food and feed particularly in northern or boreal regions where the soils have sandy texture and low pH (podzolic) (Nadeem et al., 2019). Advancements in agricultural sciences have improved our knowledge in developing plants with enhanced adaptability, superior genetics as well as cropping systems with improved plant protection standards and nutrient management strategies. Organic soil amendments have been explored as a suitable nutrient management strategy to mitigate the negative effects of the changing environment on agriculture production under controlled environmental conditions using greenhouse production systems (Aznar-Sanchez, 2020; Ishii et al., 2016). Thus, greenhouse agriculture has expanded rapidly across the globe including in boreal regions as a strategy to circumvent the food security challenges associated with climate change and increasing population (Aznar-Sanchez, 2020; Fernandez et al., 2018). The greenhouse industry is continuously seeking new approaches such as soil or soilless growth media to promote crop production and reduce the harmful environmental impacts to meet the market requirement (Fernandez et al., 2018; Ghoulem et al., 2019; Shamshiri et al., 2018).

Historically, peat was extensively used as a growing medium for horticultural crop production and forest tree nursery growth. There has been a shift towards finding alternatives or substitutes for peat due to higher price, low supply, variation in quality and environmental constraints associated with peat accessibility (Barrett et al., 2016; Bonn et al., 2014; Gruda, 2011). This has led to a global movement in exploring the use of organic waste materials for application as growth media in the horticultural industry (Perez et al., 2006). To date, several different organic wastes produced by agriculture, livestock, forestry and fisheries sectors have been successfully tested as potting media for horticultural plants (Sayara et al., 2020; Gomah et al., 2020). For example, organic wastes such as sewage sludge (Guerrero et al., 2002; Perez et al., 2006), agriculture wastes such as rice hulls, coir, sawdust (Benito et al., 2005) and paper mill wastes (Arancon et al., 2008; Chrysargyris et al., 2019; Mendez et al., 2015) have been used as a cheaper, nutrient rich and environmentally sustainable media amendment (Sanchez-Monedero et al., 2004) to replace traditional ingredients such as peat moss and manures. Paper mill waste and other biproducts from the paper industry are of significant interest as high volume sources of organic waste containing suitable characteristics as alternative media amendment for horticultural crop production. In fact, paper sludge (PS) and wood ash (WA) are prime wastes produced in large volume by the pulp and paper mill industry (Cherian and Siddiqua, 2019; Rashid et al., 2006). Rashid et al. (2006) reported annual global production of bioslolids waste from pulp and paper industries were exected to increase from 2.5 million Mg of biosolid wastes annually and this is anticipated to increase to 3.0 million Mg by 2050. Canadian pulp and paper mills produce more than 1 million Mg of WA annually (Cherian and Siddiqua, 2019). Locally, Corner Brook Pulp and Paper Limited, (CBPPL), Newfoundland and Labrador (NL), Canada produces 5,000 Mg of PS and 10,000 Mg of WA annually as waste materials (Churchill and Kirby, 2010; Maheswaran, 2019). Chemical analysis of the wood waste produced by CBPPL revealed high heavy metal content that can cause soil and water contamination (Churchill and Kirby, 2010; Maheswaran, 2019). Furthermore, Jaria et al. (2017) reported that to dispose-off such wastes, the pulp and paper industry bears significant energy cost, transport fees as well as has to obey environmental legislation for safe disposal. Thus, mills such as CBPPL are interested in alternative approach, that could simultaneously allow remediation and applications in different sectors as effective ways to handle such wastes (Sanchez-Monedero et al., 2004). Reports published in the scientific literature suggest PS and WA can be used effectively as a liming agent in agricultural and forest soils owing to their high pH (Adekayode and Olojugba, 2010; Rashid et al., 2006). Furthermore, Rashid et al., (2006) and Sharifi et al. (2013) concluded that soil amended with PS and WA have improved physicochemical properties including pH, electrical conductivity (EC), organic matter (OM) and plant available water (PAW). Generally, PS and WA application to the soil as an amendment is believed to be a convenient way to improve the soil health by recycling the essential nutrients (Adekayode and Olojugba, 2010; Chow et al., 2003). In fact, Zhang et al. (1993) observed that application of PS to soil increased the water holding capacity (WHC) and moisture content by 20% and 74% at -33 kPa and -1500 kPa, respectively compared to unamended soil. Physicochemical properties of growth media play vital role in seedling establishment, crop growth and yield attributes. The physical or hydrological properties i.e. bulk density, porosity, WHC, water repellency (WR) and their drying pattern are foremost important to decide the eminence of potting media (Benito et al., 2005; Mendez et al., 2015; Kim et al., 2017).

Biochar (BC) is another source of organic waste that can be considered as an alternative media amendment similar to PS and WA from the paper mill industry for horticulture crop production. The use of BC with other waste streams such as WA and PS has ability in sequestering contaminants such as heavy metals in these waste streams preventing their entry into sensitive ecosystems. The BC is a carbon rich material produced by pyrolysis of organic biomass at high temperature 450-1000 °C in the absence of oxygen (Lehmann et al., 2006; Kim et al., 2017). The chemical and physical characteristics of BC have been observed to varies depending on biomass source and pyrolysis conditions. This have contributed to varied results, some being very promising when used as a soil media amendment in different agriculture production systems and climates (Vaughn et al., 2013). Consistent with this observation, our group have reported that BC incorporation in podzolic soils common in boreal climate improved the soil physicochemical properties (pH, EC, OM and PAW) and structure (Saha et al., 2020; Vermooten et al., 2019; Wanniarachchi et al., 2019). Similarly, other researchers reported on the potential applications of BC in the immobilization of several different heavy metals when applied to contaminated soil thereby reducing their phyto-availability (Beesley et al., 2010; Cao et al., 2009; Maheswaran, 2019).

Although the literature is replete with reports of the use of PS, and WA in improving crop production in the horticultural industry. However, remains a paucity of information on the potential of these organic waste streams in amending acidic soils such as podzolic as a suitable potting media for horticulture crop production in boreal regions. We hypothesized that WA, PS and BC in different combinations could provide a suitable platform to develop podzolic soil-based potting media with enhanced physicochemical properties. Overall, this study was formulated to 1) investigate the effects of WA, PS and BC different combinations (volume basis) on soil physicochemical properties, 2) to find the suitable ratio for WA, PS and BC combination to prepare the potting media and dynamics of soil water retention curve.

2.2. Material and Methods

2.2.1. Potting media amendments and their sources

For current study, the soil was collected in September 2019 from 0-15 cm top soil deth from a potato-harvested field situated in Wooddale Centre for Agriculture & Forestry Development, Grand Falls (49° 01' 30'' N and 55° 33' 30'' W), NL. The Soil was air dried and sieved using a 2mm mesh at Boreal Ecosystem Research Facility, Grenfell Campus, Memorial University of NL, Canada. Samples were air-dried and sieved using a 2 mm mesh. Two potting media amendments including WA and PS were collected from CBPPL, NL, Canada and composite samples were prepared separately using 30 individual samples collected over a period of 15 days. Composite samples were air-dried at room temperature and the PS sample was ground using a Wiley Mill (Arthur Thomas Co, USA) and sieved using a 2 mm mesh. The third potting media amendment was BC and purchased from Air Terra Inc. (Alberta, Canada). BC was prepared using slow pyrolysis of yellow pine wood at 500 °C for 30 min. Promix^{TM} was used as a positive control in this study and is a commercially available growth media (Premier Tech Home and Garden, Quebec, Canada) containing Canadian sphagnum peat, peat humus. It was purchased from a local store.

2.2.2. Physicochemical properties of soil, wood ash, paper sludge and biochar

The physicochemical properties of amendments used in the media composition are given in Table 2.1. Calcium carbonate equivalent (CCE) and some other basic physicochemical properties of WA, PS and soil were determined. For this, the samples were sent to the Agriculture and Food Laboratory at University of Guelph, Guelph, ON, Canada, where USEPA Method 3052 microwave assisted acid digestion (Kingston and Jassie, 1988) was used to measure the heavy metals and CO_2 loss method was used to measure the CCE (Black, 1965) of WA and PS. According to the USDA soil classification system, soil having a sandy loam texture with following proportions: sand = 55.8% (±2.04), clay = 27.52% (±2.00) and silt = 16.72% (±2.36).

The heavy metals concentrations in WA and PS composite samples were compared with the Canadian Council of Ministers of the Environment (CCME) biosolids limit and the CCME compost category A and B guidelines are given in Table 2.2. We assessed the heavy metal contamination risks in developing the potting media using WA and PS in different combinations with BC (Table 2). We observed that the heavy metal concentrations in WA and PS are below the CCME guidelines for compost category B (CCME, 2005) and biosolids limit (CCME, 2012) (Table 2). Considering the lower concentrations of heavy metals, WA and PS could be used as a suitable alternative to peat to develop potting media with improved soil physicochemical properties (Table 2.1 & 2.2).

Table 2.1: Physicochemical properties of podzolic soils, wood ash, paper sludge and biochar used in developing potting media.

Parameter	Unit	Wood ash	Paper sludge	Biochar	Soil
CCE	% dry	10.4	12.9	-	
pH		12.6	8.2	9.4	5.9
EC	dS m^{-1}	9.52	0.32	0.43	0.02
TC	%	5.09	40.1	88.6	0.43
TN	%	0.03	1.04	-	-
NH_4^+-N	mg kg^{-1}	0.74	876	-	4.02
NO_3^--N	mg kg^{-1}	5.09	2.00	-	1.42
OC	% dry	3.45	39.9	88.6	0.42
BD	g cm^{-3}	1.16	0.12	0.14	1.44
WR	S	2.49	3.67	1.90	0.65
DM	%	97.79	68.12	84.8	97.94

Abbreviations: CCE: calcium carbonate equivalency; EC: electrical conductivity; TC: total carbon; TN: total nitrogen; NH_4^+-N: ammonium nitrogen; NO_3^--N: nitrate nitrogen; OC: organic carbon; BD: bulk density; WR: water repellency; DM: dry matter.

Table 2.2: Assessment of the heavy metal content of the substrates used in the formulation of podzolic soil-based potting media

Heavy metal	Soil (mg kg^{-1})	Wood ash (mg kg^{-1})	Paper sludge (mg kg^{-1})	Compost limit (mg kg^{-1})	Biosolids limit (mg kg^{-1})

				A	B	
Arsenic	9.3	2.5	2.1	13	75	41
Cadmium	0.059	1.3	3.1	3	20	15
Chromium	32	130	55	210	1016	1000
Cobalt	11	14	5.1	34	150	150
Copper	16	190	94	400	757	1500
Lead	7	20	35	150	500	300
Mercury	0.04	0.041	0.20	0.8	5	4
Molybdenum	0.31	16	6.3	5	20	20
Nickel	22	88	42	62	180	180
Selenium	0.17	0.17	0.44	2	14	25

Source: Canadian Council of Ministers of the Environment (CCME, 2005; CCME, 2012)

2.2.3. Potting media preparation and experimental treatments

After assessing the physicochemical properties and heavy metals risk assessments, different combinations of WA, PS and BC were prepared on the volume basis using established protocols (Kim et al., 2017). There were a totals twelve experimental treatments including ten different combinations of WA, PS, WA and soil plus two controls (100% soil and 100% Promix^{TM} -positive control) as shown in Table 2.3.

Table 2.3: Potting media amendments and their ratios used in current study to evaluate the recycling potential of wood ash, paper sludge and biochar.

Treatment number	Treatment name
T1	100% Soil
T2	100% Promix^{TM}
T3	50%Soil + 50%WA
T4	75%Soil + 25%WA

T5	50%Soil + 50%PS
T6	75%Soil + 25%PS
T7	75%Soil + 25%BC
T8	25%Soil + 50%WA + 25%BC
T9	50%Soil + 25%WA + 25%BC
T10	25%Soil + 50%PS + 25%BC
T11	50%Soil + 25% PS + 25%BC
T12	25%Soil + 25%WA + 25%PS + 25%BC

Abbreviations: WA- Wood ash; PS- Paper sludge: BC- Biochar

All the treatment mixtures were prepared by thoroughly mixing the respective paper mill waste with BC and soil. After determining the moisture factor, sub samples from the prepared media for each combination were used to measure the different physicochemical properties.

2.2.4. Analyses of physicochemical properties of developed potting media

2.2.4.1. Bulk density

Disturbed dry bulk density was measured for each developed media using standard soil sampling cores with 5 cm height and 4.75 cm diameter. Briefly, the sampling cores were filled with each potting media treatment to approximately 1/3 of the core height at a time. After each fill, cores were tapped 3-4 times on a flat table to uniformly packed the particles and remove the excess void spaces. The bulk density was calculated by dividing the dry mass of the sample by the core volume (88.6 cm^3) (Kim et al., 2017) and dry mass of samles were calculated by using moisture fector for each treatment.

2.2.4.2 Water repellency

After measuring the bulk density, the same soil cores were used to measure the WR following the water drop penetration time (WDPT) test. The WDPT was measured at air-dry conditions and field capacity (FC). The bottom of each soil core was covered with a geotextile cloth to hold the sample. One drop of deionized water was placed on the sample surface from a 10 mm height by using a 50-µL volume burette, and the WDPT was recorded using a stopwatch. The WR was categorized as non-repellent (WDPT ≤ 1 s), slightly repellent (WDPT = 1-60 s), strongly repellent (WDPT = 60 – 600 s), severely repellent (WDPT = 600-3600 s) or extremely repellent (WDPT ≥ 3600 s) according to the method of Leelamanie et al. (2008).

2.2.4.3 pH and electrical conductivity

We used a portable pH/EC/TDS/Temperature meter (HANNA—HI9813–6 with CAL Check, ON, Canada) to measure the pH and EC in all the potting media treatments using 1:2 ratio of soil to deionized water (15 g air-dried sample:30 mL deionized water) as determined by Brady and Weil (2008). Polypropylene tubes (VWR, Mississauga, ON, Canada) containing potting media were stirred for 1 h at 120 RPM and allowed to settle for 30 min, then readings were recorded (Saha et al., 2020; Brady and Weil, 2008).

2.2.4.4 Organic matter

The developed potting media samples were sent out to the Soil, Plant and Feed Laboratory, Government of NL, St. John's, Canada for OM. Where, Lab used the function of loss on ignition method to measure the OM, where they ash the sample at 450 °C for one hour in muffle furnace (Donald and Harnish, 1993).

2.2.5. Soil water retention curve

2.2.5.1. Total porosity

A sandbox apparatus (Acc. To ISO 11274, art no. 0801, Eijkelkamp, Giesbeek, Netherland) was used to develop the wet end (0 to -10 kPa) of the soil water retention curve (SWRC). For this, the metallic cores used for bulk density and WR measurement were refilled with media samples. We initially saturated the sandbox and maintained a 0.5 cm of water layer on the sand surface. After setting and leveling the sandbox, samples were randomly placed on the sand surface and left for 1 h. Samples were saturated by increasing the water level up to 1 cm below the top edge of the sampling cores and leaving on the sand surface for three days in open air while ensuring that all the pore spaces were filled with water. The nine data points were recorded by increasing the suction level from 10 cm (1 kPa) to 90 cm (9 kPa), following the same procedure. The total porosity was calculated as saturation weight by using Equation 1 at 0 kPa (Saha et al., 2020).

$$Total\ Porosity\ (P) = \frac{W_s - W_0}{V_t} \qquad (1)$$

Where, W_s is saturated sample weight, W_0 is dried sample weight and V_t is the total sample volume.

2.2.5.2. Field capacity

Pressure plate extractors (0700CG23F1 Manifold and 0505V# Compressor, model 1600-500 kPa ceramic plate extractor and model 1500 F2 1500 kPa ceramic plate extractor, Soil Moisture Equipment Corp., Goleta, CA, USA) were used to record the data from FC of -10 kPa to -700 kPa. Soil and all potting media samples were packed in small plastic rings with a volume of 21.53 cm^3 to their respective disturbed bulk density. The saturated samples were placed in a 500 kPa pressure extractor and the initial pressure of 10 kPa was applied. When the water discharge stopped from outlet valves of the extractor and the samples reached a constant weight at the set pressure, their weights were recorded. Then, the samples were placed back in the chamber and increased the pressure up to 20 kPa. The same procedure was followed to record data subsequently for 30, 40, 50, 70, 100, 300, 400, 500, 600, and 700 kPa pressure. Data for pressure at 500, 600 and 700 kPa were collected using the 1500 F2 1500 kPa ceramic plate extractor. The FC was calculated at -10 kPa by using Equation 2 (Glab et al., 2016; Saha et al., 2020).

$$\mathrm{FC} = \frac{W_d - W_0}{V_t} \times 100 \qquad (2)$$

Where, FC is field capacity, W_d is drained sample weight at 10 kPa, W_o is dried sample weight and V_t is the total volume

2.2.5.3. Plant available water

Volumetric moisture contents (VMC: θ) from 0 kPa to 700 kPa and pressure (ψ) were fitted to the van Genuchten model (Equation 3) (van Genuchten, 1980). The best fit van Genuchten parameters (α and n) were obtained by using MS excel solver function and validated by using the measured VMC data. Then, VMC values from 800 kPa to permanent wilting point (PWP) at 1500 kPa were estimated by using the van Genuchten equation. The best fit parameters were those obtained from 0 kPa to 700 kPa. The PAW was calculated as the difference between VMC at FC and PWP as given in Equation 4 (Glab et al., 2016; Saha et al., 2020).

$$\theta(\psi) = \left[\frac{\theta_s - \theta_r}{[1+\alpha(\psi)^n]^m}\right] + \theta_r \qquad (3)$$

where, $\theta(\psi)$ is volumetric moisture content ($cm^3\ cm^{-3}$), ψ is pressure applied (cm of water), θ_s is saturated moisture contents (porosity: $cm^3\ cm^{-3}$), θ_r is residual moisture contents (< PWP) ($cm^3\ cm^{-3}$), α and n are the shape parameters, and m = 1 – 1/n

$$\mathrm{PAW} = \theta_{FC} - \theta_{PWP} \qquad (4)$$

Where, PAW is plant available water, θ_{Fc} is VMC at field capacity and θ_{PWP} the VMC at permanent wilting point.

2.6. Statistical analysis

To quantify the effects of developed potting media treatments on podzolic soil physicochemical properties, the analysis of variance (ANOVA) was performed. Where the treatments were significantly different, the Fisher's least significant difference (LSD) was used to compare the treatments means at alpha = 0.05. Statistics 10.0 (Analytical software, Tallahassee, FL, USA) was used for statistical analyses, and graphical visualization was done through Sigma Plot (Version 14.5, Systat Software, San Jose, CA) and MS Excel 2016. Coefficient of determination (R^2) and the root mean square error (RMSE) were computed to check the accuracy of the van Genuchten model predicted values. Principal component analysis (PCA) was performed to explore relationships among treatments and the measured properties by using XLSTAT (Premium 1060, Version 2020, Addinsoft, NY, USA). Furthermore, Pearson's correlation was carried out using the XLSTAT (version 2021.3.1) program.

2.3. Results

2.3.1. Bulk density

The developed potting media treatments had significant effects on disturbed bulk density (Figure 2.1a). Podzolic soil (control) expressed a significantly high bulk density whereas the lowest density was recorded in Promix^{TM} (0.21 g cm^{-3}) as shown in Figure 2.1a. Paper mill waste and BC treatments positively reduced bulk density compared to the negative control (Figure 2.1a). The treatment T10 had the lowest bulk density of 0.53 g cm^{-3} among paper mill waste amended potting media but was significantly higher than T10 (Figure 2.1 a).

2.3.2. Total porosity

The developed potting media treatments had significant effects on total porosity (Figure 2.1b). All treatment combinations significantly increased the total porosity compared to negative control (soil). Treatment T2 (positive control) has the highest porosity and was statistically at par with treatment T8. Both WA treatments (T3 and T4) and PS treatments (T5 and T6) significantly increased the total porosity in comparison to T1 (control). However, no significant difference was observed between WA and PS at 50% and 25% ratios, respectively. We also observed that T3 is similar to T5, while T4 is most similar to T6. The results showed that when we mixed WA and PS with 25% BC it significantly increased the total porosity (Fig. 1b) in the following order T8 (72%) > T10 (69%) > T9 (65%) > T12 (63%) > T11 (56%).

2.3.3. Water repellency

The prepared combinations had significant ($p<0.05$) effects on WR at air-dry and FC conditions (Figure 2.1c). WDPT slightly increased with the application of WA, PS and BC as compared to the control (1.39 s) at air-dried conditions, while T10 had the highest WDPT value (6.37 s). We observed that WDPT significantly decreased with increasing moisture contents at FC among all treatments. This same trend was also observed in air-dry conditions, where WDPT increased along with the increasing volume of WA and PS. All treatments tested in this study were classified as "slightly repellent" based on the classification of Leelamanie et al. (2008), because they showed WDPT<60 s at air-dry condition, as well at FC level (Figure 2.1c).

2.3.4. Organic matter

The developed potting media treatments had significant effects on the OM contents of the growth media (Figure 2.1d). Treatment T2 has the highest OM contents among all treatments. WA treatments alone at 25% did not show a significant difference from soil, though treatment T3 (50% WA) had higher OM than soil. However, when BC was mixed with WA, it significantly increased the OM content compared to the control. PS treatments alone (T3 and T4) and in combination with BC (T9 and T10) significantly increased the OM content. We observed the trend for the change in

OM content for the PS treatments are as follows: T10 (8.53 %) > T12 (5.01 %) > T5 (5.01 %) > T11 (4.47%) (Figure 2.1d).

2.3.5. pH

Different ratios of WA, PS and BC had significant effects on the pH across all media combinations. Both soil (pH = 5.4) and Promix™ (pH = 5.0) have low pH compared to WA, PS and BC treatments. WA treatments alone (T3 and T4), and in combination with BC (T8 and T9), showed very high pH (9.9-11.5). On the other hand, PS treatments alone (T5 and T6), and with combination of BC (T10 and T11), showed pH variations of 6.3-7.3, which can be considered as the optimal range for several horticultural crops and ornamental plants (Figure 2.1e).

2.3.6. Electrical conductivity

The prepared combinations had significant effects on the EC of the growth media (Figure 2.1f). Sandy loam soil (podzolic), when used as the base soil in the media mixtures, has very low EC (0.02 dS m^{-1}), whereas all the other combinations tested have EC in range of 0.02-2.50 dS m^{-1}. WA treatments showed higher EC compared to PS treatments and control, where T8 showed the highest value (2.44 dS m^{-1}). PS alone in T5 and T6 increased the EC (0.37 dS m^{-1} and 0.16 dS m^{-1} respectively) and with combinations of BC in T10 and T11 (0.92 dS m^{-1} and 0.86 dS m^{-1} respectively) compared to the control, but these values were lower than the EC value in T2 (1.90 dS m^{-1}). The EC value in T6 was similar to that of T7 while T9 is similar to that of T11 (Figure 2.1f).

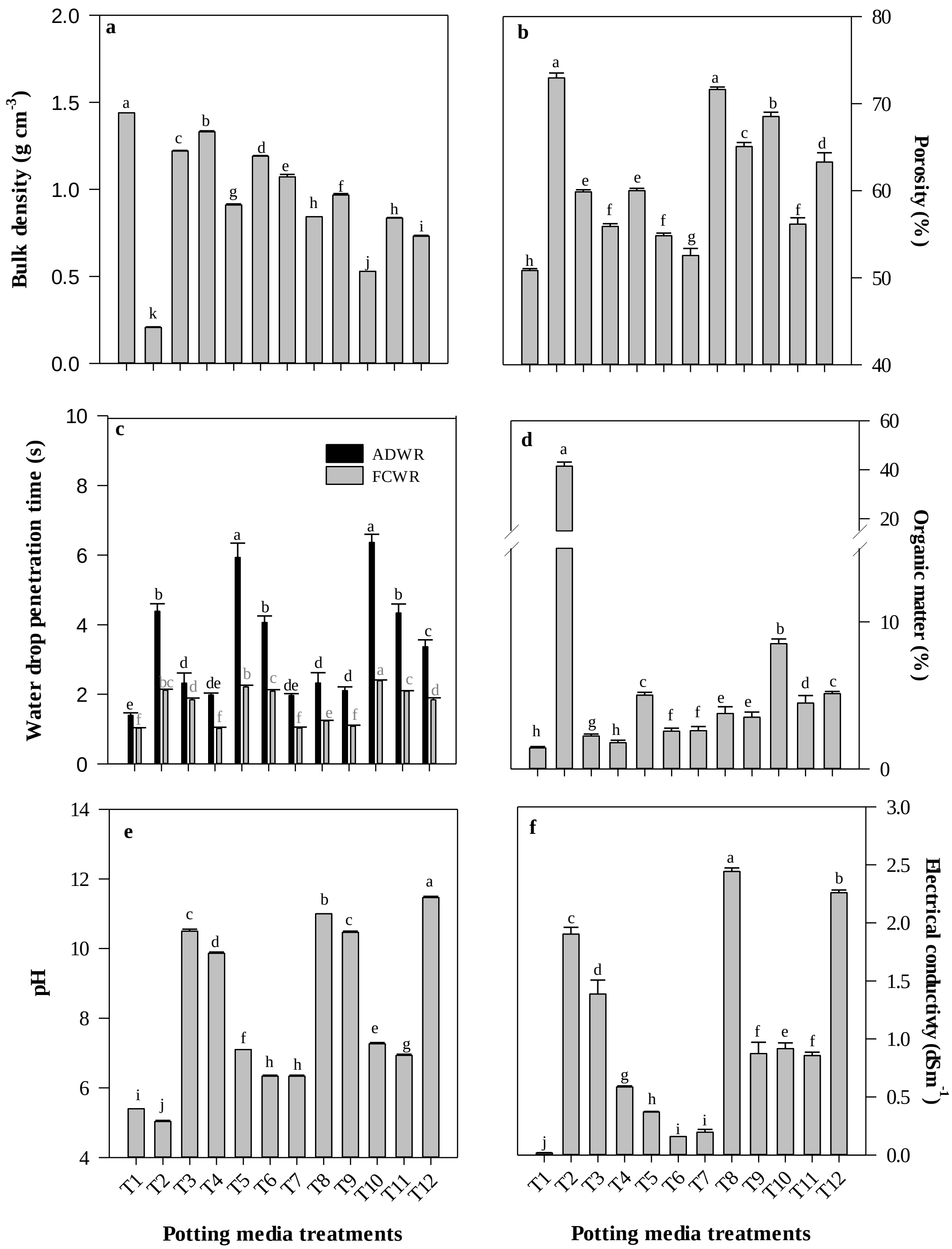
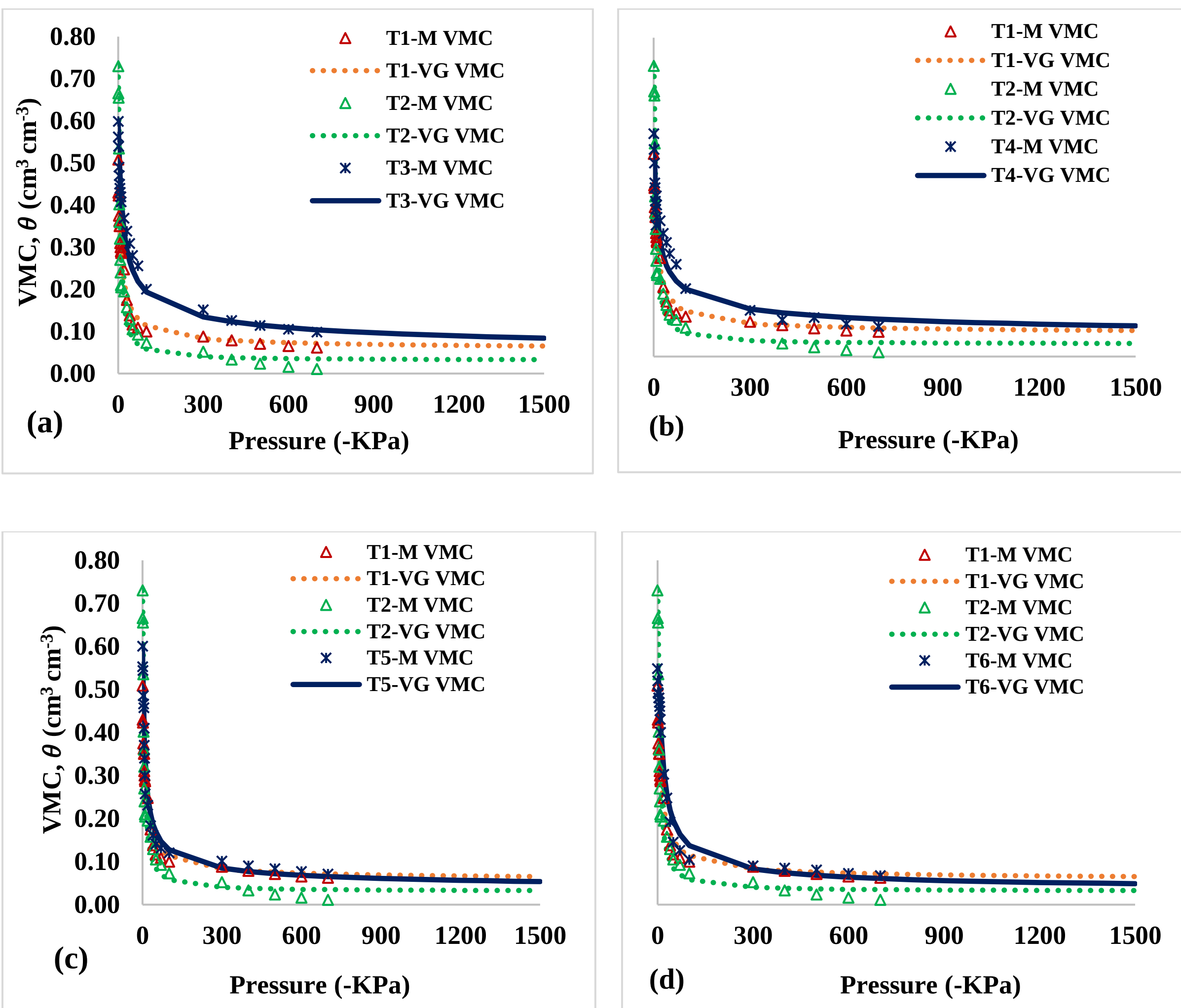
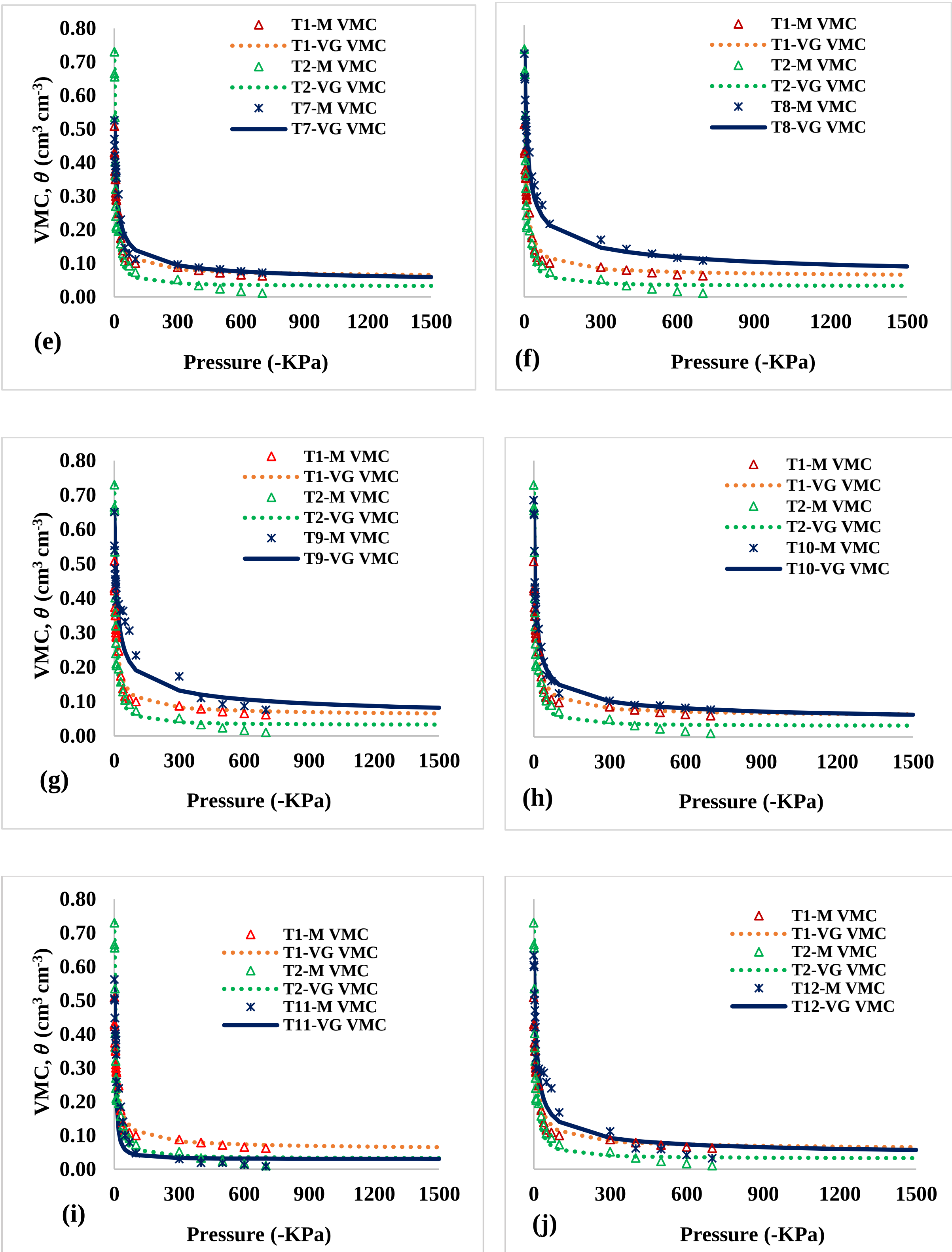


Figure 2.1: The effects of different amendments on the bulk density (a), porosity (b), water drop penetration time (c), organic matter (d), pH (e) and electrical conductivity (f) of podzolic based potting media developed. **Abbreviations:** ADWR-air-dry water repellency; FCWR-field capacity water repellency. Data represents mean ± SE (n = 3). Different letters on the bars indicate significant difference according to Fisher's LSD test (p < 0.05)

2.3.7. Soil water retention curves

The SWRC's development explains the important hydrological parameters (porosity, FC, drainable water-DW, PAW, PWP) of the different media combinations tested and the comparisons between measured and predicted values (Figure 2.2 (a-j)). All media combinations have very high R^2 values and very low RMSE values, which strongly suggest that the values predicted by the van Genuchten model closely matched with the measured values (Table 4). We observed that different ratios of WA and PS alone, and in combination with BC, significantly increased the soil water retention characteristics compared to the control treatments (T1 and T2).





(e)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T7-M VMC
T7-VG VMC
VMC, θ (cm3 cm-3)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
300
600
900
1200
1500
Pressure (-KPa)
(f)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T8-M VMC
T8-VG VMC
Pressure (-KPa)
(g)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T9-M VMC
T9-VG VMC
VMC, θ (cm3 cm-3)
Pressure (-KPa)
(h)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T10-M VMC
T10-VG VMC
Pressure (-KPa)
(i)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T11-M VMC
T11-VG VMC
VMC, θ (cm3 cm-3)
Pressure (-KPa)
(j)
T1-M VMC
T1-VG VMC
T2-M VMC
T2-VG VMC
T12-M VMC
T12-VG VMC
Pressure (-KPa)

Figure 2.2: Assessment of wood ash, paper sludge and biochar effect on measured volumetric moisture contents (M VMC) from 0 kPa to 700 kPa vs. van Genuchten volumetric moisture contents (VG VMC) from 0 kPa to 1500 kPa of SWRC. Each sub-figure compares a treatment mixture with T1–Soil (control) and T2– Promix™ (Positive control): T3–50%Soil+50%WA (a); T4–75%Soil+25%WA (b); T5–50%Soil+50%PS (c); T6–75%Soil+25%PS (d); T7–75%Soil+25%BC (e); T8–25%Soil+50%WA+25%BC (f); T9–50%Soil+25%WA+25%BC (g); T10–25%Soil+50%PS+25%BC (h); T11–50%Soil+25%PS+25%BC (i) and T12–25%Soil+25% WA+25%PS+25%BC (j).

Table 2.4: Assessment of wood ash, paper sludge and biochar effect on measured and predicted volumetric moisture contents at saturation, residual moisture contents and van Genuchten model parameters from 0 kPa to 700 kPa and respective statistical parameters

Treatment	θs ($cm^3\ cm^{-3}$)		θr ($cm^3\ cm^{-3}$)	α	n	R^2	RMSE ($cm^3\ cm^{-3}$)
	a	b					
T1	0.51	0.51	0.05	2.00	1.67	0.98	0.0404
T2	0.73	0.73	0.03	2.55	2.00	0.95	0.0428
T3	0.60	0.60	0.03	2.02	1.41	0.97	0.0530
T4	0.56	0.56	0.03	2.78	1.40	0.94	0.0523
T5	0.60	0.60	0.03	2.85	1.52	0.98	0.0373
T6	0.55	0.55	0.03	1.12	1.64	0.98	0.0328
T7	0.53	0.53	0.03	2.20	1.48	0.97	0.0392
T8	0.72	0.72	0.03	2.56	1.41	0.98	0.0561
T9	0.65	0.65	0.03	2.45	1.42	0.91	0.0559
T10	0.69	0.69	0.03	3.01	1.46	0.97	0.0509
T11	0.56	0.56	0.03	2.01	1.81	0.97	0.0301
T12	0.63	0.63	0.03	2.01	1.56	0.94	0.0491

θs–saturated moisture contents (at 0 kPa); a–measured values of saturated moisture contents; b–predicted values of saturated moisture contents; θr–is residual moisture contents (always less than PWP); α and n are shape parameters of the van Genuchten (1980) model. R^2–is the coefficient of determination; RMSE–root mean square error between measured and predicted values.

2.3.8. Field capacity

The treatment T8 had the highest VMC (0.47 cm3 cm-3) and that T2 had the lowest VMC (0.28 cm3 cm-3) at FC level. WA treatments, i.e. T3 increased the FC by 35.48% compared to T1 (soil-control) and by 50 % compared to T2, T4 increased the FC by 16.13% compared to T1 (soil-control) and by 28% compared to T2. Similarly, an increase in FC with PS treatments were observed. For example, in treatment T5 and T6, FC increased by 9.68% and by 32.26%, respectively compared to T1, and FC increased in T5 by 21.43% and in T6 by 46.43% compared to T2 (Figure 2.3).

BC alone (T7) was found to be effective in increasing the FC by 9.8% and by 21.43% compared to T1 and T2, respectively. When WA was mixed with BC, the FC increased by 51.61% in T8 and by 35.48% in T9 compared to T1 and we observed FC increased by 67.86% in T8 and by 50% in T9 compared to T2. Treatment with 50% PS in combination with 25% of BC (T10) increased the FC by 29.03% and by 42.86% compared to T1 and T2, respectively. In contrast, T11 decreased the FC by 6.45% compared to T1, but increased by 3.57% compared to T2. The combinations of WA, PS and BC (T12) increased the FC by 25.81% compared to T1 and by 39.29% compared to T2 (Figure 2.3). These findings showed that WA and PS alone and in combination with BC have the potential to increase the WHC at FC level in the podzolic soil-based potting media developed in this study.

2.3.9. Plant available water

WA, PS and BC treatments increased the PAW compared to soil and Promix™. We observed T8 had the highest PAW across all the treatments. WA treatments, T3 and T4 was found to increase the PAW by 41.67% and by 16.67% compared to T1, but increased the PAW by 36% and 12% compared to T2, respectively. PS treatments i.e. T5 and T6 increased the PAW by 20.83% and by 50% compared to T1 respectively and PAW increased by 16% in T5 and by 44% in T6 compared to T2. BC combination (T7) increased the PAW by 16.67% compared to T1 and by 12% compared to T2. WA with combination of BC i.e. T8 and T9 increased the PAW by 58.33% and by 41.67% compared to T1 and PAW increased by 52% in T8 and by 36% in T9 compared to T2. We observed in PS and BC combination T10 PAW increased by 37.50% compared to T1 and increased by 8.33% compared to T2. Similarly, in combination T11 PAW increased by 32% compared to T1 and by 4% compared to T2. The combined treatment (T12) where all amendments were mixed at 25% volume, showed PAW increased by 41.67% compared to T1 and by 36% compared to T2 (Figure 2.3).

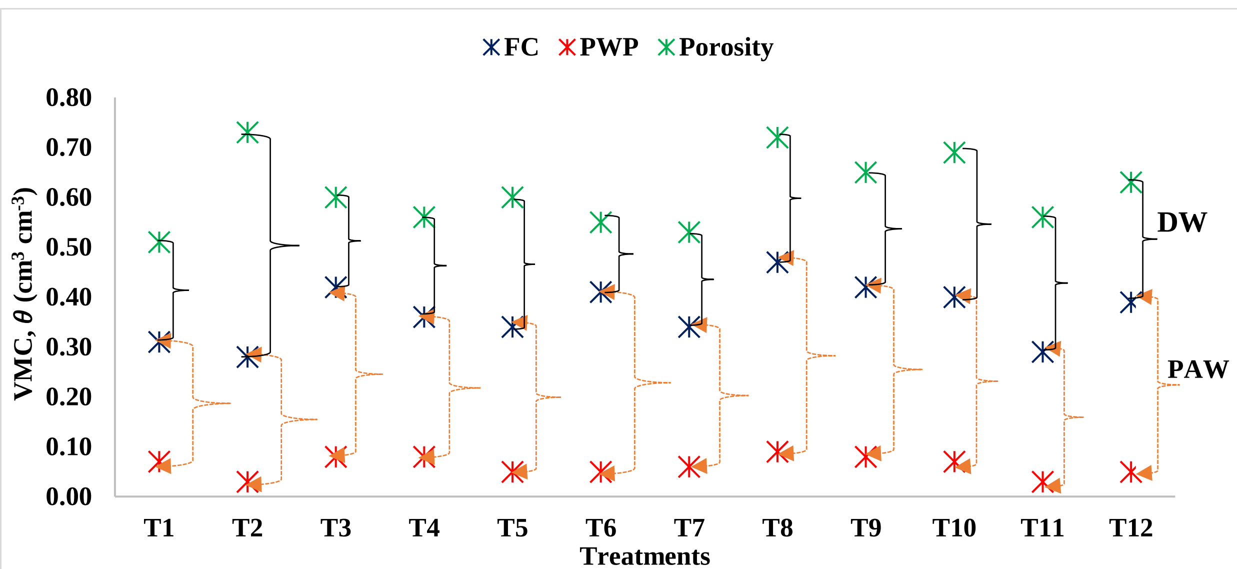


Figure 2.3: Effect of wood ash (WA), paper sludge (PS) and biochar (BC) on porosity, field capacity (FC), drainable water (DW), permanent wilting point (PWP) and plant available water

(PAW). Symbol "}" solid line shows the DW (porosity-FC). Symbol "}" with yellow dotted line shows the PAW (FC-PWP).

2.3.10. Relationship between soil physicochemical properties and the media substrates

Principle component analysis (PCA) was used to show the relationships between the substrates used in the media formulations and their contributions to the measured physicochemical properties of the resultant media combinations (Figure 2.4). The PCA output explained 75.94% of the overall variability in the dataset with component-1 explaining 44.37% and component-2 explaining 31.58% of the variability. We observed different physicochemical properties clustered in different quadrants of the PCA biplot clearly showing the impacts of WA, PS and BC application on the properties of the growth media. We observed that hydrological properties such as FC, PWP and PAW formed a cluster in 1st quadrant of PCA with media combinations T2, T10 and T12 (Figure 2.4), where T9, T8 and T3 showed clear separation with PAW, FC, PWP and pH along PC2 axis by forming a cluster (Figure 2.4). Formulated media treatments T7, T6, T4 and T1 are highly associated with bulk density in the 4th quadrant. Where it showed clear separation from other physicochemical properties (pH, EC, FC, PAW and OM). We observed bulk density decreased and pH, EC, porosity, FC, and PAW increased with application of different amendments.

A positive association between developed substrates combinations and measured physicochemical properties was observed (Figure 2.4). Further relationship was confirmed by Pearson correlation analysis between different physicochemical properties (Table 2.5). We observed different hydrological and chemical properties have significant correlation. Where pH has positive correlation with EC, FC, PAW and PWP, and negative correlation with OM of prepared media substrates. The pH is positively corelated with EC of developed potting media, which indicates that increase in WA and PS volume significantly increase the oxides, carbonates, hydroxides and salts concentration. Application of WA, PS and BC significantly decreased the bulk density, which has negative correlation with porosity, air-dry WR and DW. Decrease in bulk density significantly increased the void spaces (macro and micro porosity), which ultimately enhanced the WHC of potting media compared to soil and Promix^{TM}. Bulk density and OM showed significantly negative correlation with each other, increase in volume of WA and PS increase the OM of media while decreasing the bulk density. In tested combinations, VMC at FC has highly positive correlation with PAW and PWP, nevertheless negatively correlated with DW (Table 2.5).

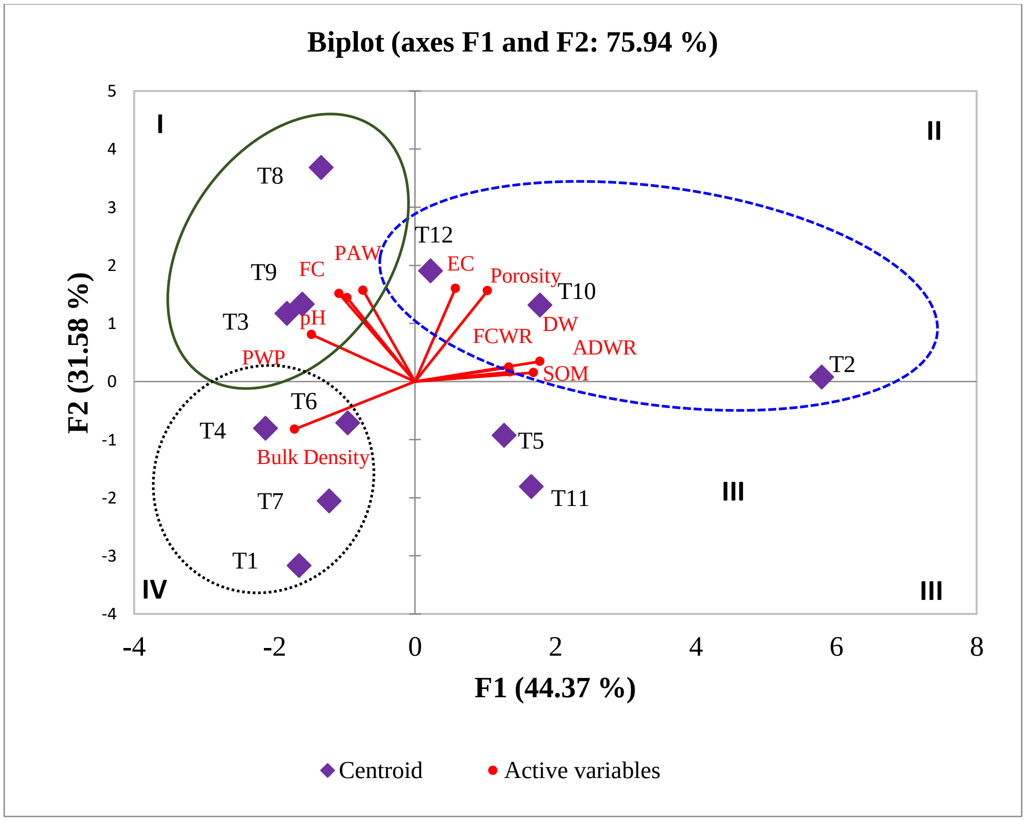


Figure 2.4: Principal component analysis (PCA); biplot showing the effect of different growth media combinations (Centroids) on their physicochemical properties (Active variables).

Table 2.5: Pearson's correlation coefficients (r) showing the relationship between different physicochemical properties of developed media.

Variables	pH	EC	OM	BD	Porosity	FC	DW	PWP	PAW	ADWR
EC	0.56***									
OM	-0.41*	0.38*								
BD	0.13^{Ns}	-0.59***	-0.76***							
Porosity	0.28^{Ns}	0.78***	0.59***	-0.80***						
FC	0.42*	0.20^{Ns}	-0.26^{Ns}	0.09^{Ns}	0.19^{Ns}					
DW	-0.17^{Ns}	0.27^{Ns}	0.50**	-0.51**	0.41*	-0.44**				
PWP	0.34*	0.048^{Ns}	-0.30^{Ns}	0.28^{Ns}	0.04^{Ns}	0.72***	-0.48**			
PAW	0.39*	0.28^{Ns}	-0.20^{Ns}	0.01^{Ns}	0.22^{Ns}	0.95***	-0.36*	0.49**		
ADWR	-0.20^{Ns}	0.01^{Ns}	0.19^{Ns}	-0.36*	0.21^{Ns}	-0.16^{Ns}	0.46**	-0.52**	0.01^{Ns}	
FCWR	-0.16^{Ns}	0.07^{Ns}	0.21^{Ns}	-0.33^{Ns}	0.19^{Ns}	-0.14^{Ns}	0.40*	-0.60***	0.08^{Ns}	0.90***

Abbreviations: EC: electrical conductivity; OM: Organic matter; BD: Bulk density; FC: Field capacity; DW: Drainable water; PWP: Permanent wilting point; PAW: Plant available water; ADWR: Air-dry water repellency; FCWR: Field capacity water repellency. (All the bold values showing significant relation, *** Significant at $p < 0.001$, ** Significant at $p < 0.1$, *Significant at $p < 0.05$, N_S= Non-Significant,)

2.4. Discussion

The overall results of this study indicate that WA and PS, alone and in combination with BC had a significant effect on the physicochemical properties of podzolic soil-based potting media evaluated in this study. WA, PS and BC combinations significantly reduced the bulk density and improved the porosity, while WA, PS and BC combinations significantly increased the VMC at FC and PAW compared to soil and Promix^{TM}. The combinations containing WA had the high pH (9.9-11.5) and EC (0.59-2.44 dS m^{-1}), whereas media amended with PS exhibited pH in the optimum range for plant growth (6.3 - 7.3) with an EC range of 0.16-0.86 dS m^{-1}.

Both WA and PS from CBPPL have high CCE and high pH which significantly increased the pH of media exhibiting WA and PS. The pH of the media increased when WA and PS was mixed with soil alone and in combination with BC, due to high $CaCO_3$ content and their higher volume in the mixture compared to liming needs (Mokolobate and Haynes, 2002). Similar results were found when forest soil (Richard et al., 2018) and luvisolic soil (Patterson, 2001) were amended with WA. The particle size of liming material has a strong influence on its reactivity and efficiency (Patterson, 2001). The WA that we used in our experiments has the particle size < 2.00 mm; due to this fineness of WA, it can quickly react with the soil to increase the pH as compared to PS and BC. Chrysargyris et al. (2019) used paper mill waste at different ratios as a peat substitute in fertigation system for some ornamental plants (*Tagetes erecta* (Marigold), *Petunia exserta* (Petunia) *Petunia exsrta* and *Matthiola incana* (Matthiola)), and concluded that paper mill waste increased the pH and EC for all media combinations. The media pH is one of the most important property as it strongly influences the availability of elemental plant nutrients, like the phosphorus and magnesium availability decreases by decrease in the media pH (Robbins, 2005) Therefore, most crop plants grow and produce the higher desirable harvest at optimum pH (6.5-7.5) (Pausas and Austin, 2001; Soti et al., 2015). Miyabei maple-*Acer miyabei*, Red horsechestnut-*Aesculus carnea*, Katsura tree-*Cercidiphyllum japonicum* and Redbud-*Cercis canadensis* are horticultural plants which can grow better in alkaline conditions (pH 7.5-8.2) (Bassuk, 2003; Jett, 2005; Cregg, 2014). The several horticultural crops e.g., *Beta vulgaris* L., Spinach-*Basella alba* and Apium graveolens L. were found to be highly adaptive species to neutral alkaline conditions (having pH 7.0-8.0) (Cox and Koenig, 2010). Some tolerant lentil species (Singh et al., 2018) and finger millet-*Eleusine coracana* L. (Krishnamurthy et al., 2014) also showed great potential under alkaline conditions having the pH above 7. Some plant species like Junipers, Geranium, and Arborvitae can grow better at the pH above 7.0 (Robbins, 2005). The media combinations with higher pH, above 8.0, can be used as a potting media, by mixing with low pH (3.5-4.5) sphagnum peat, (Mofidpoor, 2007) or mixing with elemental sulfur or fertilization with ammonium sulfate (Jett, 2005).

All the media combinations had EC below the critical value of 3.5 dS m^{-1}. Without any fertilizer, the typical range of EC for horticultural growth media is 0.5-3.0 dS m^{-1} (Robbins, 2005). Chen and Li (2006) tested coal ash to grow ornamental plants and concluded that EC > 3.5 dS m^{-1} was not suitable for plant production. In our research, WA combinations have higher EC compared to PS and BC combinations, because of higher minerals concentration. Different ratios of paper mill waste, olive mill waste, sewage sludge, and tree bark have been tested as growth media. Often their amounts exceeding 50% and sometimes may be up to 100%. This high level could potentially increase the pH and EC to toxic levels, but could be managed after several rounds of irrigation as salts can be leached out quickly to bring pH and EC within the optimal range (Manios, 2004). Dumroese et al. (2011) reported the first use of pelletized BC in soilless culture, and observed that pelletized BC treatment performed well and improved the physicochemical (0.90-3 dS m^{-1})

properties when it substituted the peat at 25% (V/V). Maheswaran (2019) conducted lab experiments using sandy loam soil amended with fly ash and BC, and concluded that granular BC had a significant effect in reducing the bioavailability of heavy metals and improved the chemical properties (pH and EC) of amended soil compared to control (without BC). Vaughn et al. (2013) observed similar results from two BC types derived from wood pellets and wheat straw and concluded that peat substitution with BC at different ratios (5%, 10% and 15% V/V) increased the pH, EC and OM of potting media under greenhouse conditions. PS treatments alone and in combination with BC in our experiment significantly (p=0.000) increased the OM percentage compared to control (soil). Similarly, Cline and Chong (1991) found OM increased when they incorporated 50 Mg ha^{-1} PS into sandy soil. PS has a higher amount of OM in the form of ligo cellulosic wood fiber (Cline and Chong, 1991).

WA and PS obtained from our industry partners site (CBPPL) have some heavy metals. There are no specific limitations developed by the CCME and the Canadian Food Inspection Agency (CFIA) to use organic waste material as growth media. However, the CCME developed A and B compost categories and the biosolids limit for waste application in the agriculture industry. Category A compost can be used in agricultural lands, potting media industry, local gardens, forest sites and other businesses (Maheswaran, 2019; Hannam et al., 2016). Category B compost has some restrictions due to the higher level of trace elements, but materials having trace elements concentration up to B category can be used in the agriculture sector. Materials that do not meet either category A or B must be disposed with extra precautions (CCME, 2005). WA and PS used in this study have lower concentrations of heavy metals than the compost category A and B and the biosolids application limit, which make these amendments suitable for the agriculture industry with extra precautions when deemed necessary by the province.

Organic amendments influence soil hydrological properties, and consequently plant growth and development (Saha et al., 2020). WA, PS and BC helped to improve the physical properties of growth medium by changing the structure (pore spaces) and increasing the OM. WA and PS significantly reduced the bulk density and improved the porosity compared to control (soil). WA, PS and BC used in all experiments have a very low bulk density (0.91 g cm^{-3}, 0.12 g cm^{-3} and 0.14 g cm^{-3}, respectively) which makes them suitable to be used as a potting media substrate. However, all media combinations have a significantly higher bulk density than Promix^{TM}, because of the higher bulk density (1.44 g cm^{-3}) of sandy loam soil. Lower bulk density facilitates the plant growth with air and water distribution to sustain the root functions. Different commercially available soil-less media cultures have a range of bulk densities, i.e. peat (0.10-0.15 g cm^{-3}), vermiculite (0.90-0.15 g cm^{-3}) and expanded clay (0.60-0.90 g cm^{-3}), though the ideal range for soilless culture is 0.19-0.70 g cm^{-3} with 50-85% of total porosity (Pardossi et al., 2011). WA and PS volume have an inverse relationship with bulk density, as expected, thus increasing their volume in the mixture resulted the significant decrease in bulk density. PS with the combination of BC showed the lowest bulk density (0.53 g cm^{-3}) in the ideal range for soilless culture, because of its light weight, high porosity and fibrous structure. Chantigny et al. (2000) and Gallardo et al. (2012) reported that PS is not only beneficial to improving the soil physicochemical properties. WA and BC mixture (T8) showed the maximum total porosity that is similar to Promix^{TM}. Mostly the paper mills WA has <1.00 mm size particles (Etiegni and Campbell, 1991), which increases the microporosity in media mixtures. PS, alone and in combination with BC, improved the total porosity by increasing the macropores through wood fibers and because of the large particle size of BC, as these combinations have high relative percentage of DW compared to WA combinations. Saha et al. (2020) supported these findings, as they observed granular BC to be effective in increasing macro porosity due to its non-uniform shape and porous structure within soil particles. Outer surface and physical structure (pore size, surface area) of BC particles can mediate its behavior as well as change the physicochemical properties of growth media. Large particle size of 0.5 to 500 µm can improve the total pore volume by increasing the macropores (Saha et al., 2020; Hardie et al., 2014). Camberato et al. (2006) found that land application of PS reduced the bulk density and improved particles aggregation, porosity, and WHC of the amended soil compared to control. WA and PS ratios are directly associated with WDPT. However, all the combinations have WDPT < 60s, thus all the combinations are categorized as slightly repellent, according to Leelamanie et al. (2008). Moisture contents have an inverse relationship with WR, as also found by Saha et al. (2020). At the FC level, WDPT of all combinations decreased compared to air-dry conditions, similar to the findings of Hermansen et al. (2019), Regalado et al. (2008) and Saha et al. (2020).

The amount of OM has a significant positive correlation with WR, findings supported by Kawamoto et al. (2007) and Regalado et al. (2008). PS combinations showed higher WDPT values compared to WA and BC combinations. Variation in moisture contents alter the alignment of amphiphilic molecules of OM. Amphiphilic molecules are comprised of the hydrophilic functional group at the end of the hydrocarbon chain. In high moisture contents, the hydrophilic end opened to make the covalent bond with water molecules, while at low moisture contents, the hydrophilic end turned inward, therefore exposing the non-polar end rendering the WR and increasing the hydrophobic characteristic (Roy and McGill, 2000). If the material is slightly hydrophobic it will not have much effect on water retention (Saha et al., 2020).

Different horticultural substrates have unique properties, as growth media used in the horticultural industry are mostly from organic sources. Although there are no universal standards for physical properties of growth media, there are ranges in which most growth medium is utilized in large-scale production of horticultural crops. These include total porosity values ranging from 50 to 85%, aeration porosity from 10 to 30% and bulk densities from 0.19 to 0.70 g cm^{-3} (Yeager et al., 1997). Robbins (2005) suggested that 10-20% aeration porosity and 50-70% total porosity is favorable to develop a good quality growth medium. WA and PS was found to be very effective in increasing the VMC at FC and PAW. Developed SWRCs showed the ability of WA, PS and BC to increase the water retention capacity of growth media and ultimately this will support good plant growth. WA at 50% volume with the combination of 25% BC (T8) has the maximum FC (0.47 cm^3 cm^{-3}) and PAW (0.38 cm^3 cm^{-3}). WA used in this experiment has fine particles and these particles have the porous structure and can swell after contact with water molecules, and thus could increase the water retention capacity of the mixture. These results agree with Etiegni and Campbell's (1991) findings, in which the authors concluded that fine WA with smaller particles (80% <1 mm) is more effective for increasing microporosity and the WHC of amended sandy soil. PS of 25% alone (T6) also has higher FC (0.41 cm^3 cm^{-3}) and PAW (0.33 cm^3 cm^{-3}) but has low aeration porosity potentially due to more macrospace between sludge and soil particles. These results are supported by Zibilske et al. (2000), who observed that PS application at 225 Mg ha^{-1} increased PAW (between -60 kPa and -1500 kPa pressure) by increasing the total porosity and aggregation in sandy loam soil. In our study, we observed that all media combinations had higher FC than control (soil and Promix™), which is attributed to the increase in DW due to macroporosity. BC was found to be effective in increasing the PAW consistent with the findings of Kim et al. (2017), in which authors successfully ameliorate horticultural growth media using rice hull mixed with BC (pyrolyzed temp. = 550 °C) to grow Kale under controlled environmental conditions. The authors observed that water volume increased compared to control at 1 kPa and 5 kPa tension levels. The WHC of any substrate is related to pore connectivity and their distribution pattern, which primarily depended on particle size (texture) and its arrangement with structural properties (aggregation) (Verheijen et al., 2010). Changes in soil structure primarily change the slope of SWRC (Saha et al., 2020). The OM fractionation and microscopic studies showed that PS wood fibers promptly could make the aggregates with mineral particles and act as a central core of water-stable macroaggregates (Bipfubusa et al., 2008). The OM percentage is well known to improve the physicochemical properties of growth media substrates (Etiegni and Campbell 1991; Kim et al., 2017), which play an important role as a binding material to increase the aggregation. These aggregates have a vital role in the microporosity development, which can increase the WHC of amended soil (Saha et al., 2020; Igalavithana et al., 2017). The WHC of PS was recorded to be 0.36 $cm^3\ cm^{-3}$ and 0.26 $cm^3\ cm^{-3}$ at FC level (-33 kPa) and PWP (-1500 kPa), respectively; yet, these values were greater than mineral soil (Bellamy et al., 1995). Thus, in our experiment, PS combinations showed an increase in WHC as compared to the control. Zhang et al. (1993) reported that higher application of PS at 246 Mg ha^{-1} increase WHC by 20% at FC and 74% at PWP. Increase in total PAW is a very influential factor for modulating the plant growth, development and yield as well as in irrigation scheduling, mw compared to WHC (Igalavithana et al., 2017).

Based on the findings of this study, the following points need to be further evaluated in future research studies:

- Effect of these media combinations on plant growth and elemental uptake and nutritional quality.
- Long-term assessment of physicochemical properties to check the recycling capacity of media (e.g. assessing the changes in structural properties).

- Structural analyses are required to measure the pore space changes, specific surface area and media structure along functional groups attached on their surfaces.
- Risk assessment of heavy metals present in WA and PS application in horticulture industry on human health and environment. Generation of this information is necessary to develop the provincial application guidelines for these amendments to ensure safe use of paper mill wastes in boreal agriculture.
- Preparation of potting media by mixing these amendments with other available market growth media (Promix^{TM}, compost, perlite, vermiculite) and further evaluation of their physicochemical properties and evaluation of the effects on plant growth.

2.5. Conclusions

The experiment results concluded that wood ash (WA) and paper sludge (PS) alone, and in combination with biochar (BC) significantly improved the physicochemical properties of podzolic soil-based potting media. WA combinations showed very high pH compared to PS and BC combinations. Both WA and PS improved the porosity, whereas WA showed higher porosity than PS and BC. Among WA treatments, T8 had the highest porosity and the maximum water holding capacity among WA and PS combinations, but it is not suitable for plant growth due to a very high pH of 11. Although WA at 50% and 25% (V/V) also improved the hydrological properties, it would not be suitable for potting media development due to the same issue of high pH. On the other hand, PS combinations, having the pH in the range of 6.3 to 7.3, were found to be in the desired range for most vegetables and ornamental plants. PS at 50% and 25%, alone and with the combination of BC had increased the lant available water relative to control, and overall the treatment T10 (25%Soil+50%PS+25%BC) found as a best combination to prepare the podzolic soil-based potting media having high PAW within the desired range of porosity and drainable water. These findings suggest that PS is a suitable substrate to prepare the potting media with combination of podzolic soil and BC for the horticultural industry.

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Co-authorship statement for study-two

A manuscript based on chapter 3 (Study-two) entitled "Effects of wood ash, paper sludge and biochar amendment on physicochemical properties and heavy metals leaching of boreal podzolic soils" will be submitted to Nature Communications [Nature Publisher]. Muhammad M Farhain, the thesis author was the main author, designed the study, conducted all experiments and collected the leachate samples, analyzed the heavy metals concentration, statistically analyzed the data, drafted and edited the manuscript. Dr. Lakshman Galagedara (supervisor), was the corresponding and the last author, design the study, helped especially to complete the soil water retention curves and to run the Hydrus-1D profiles, gave expert opinion on statistical analysis, helped in results interpretation, reviewed and edited the manuscript. Dr. Mumtaz Cheema (co-supervisor) and Dr. Thomas (committee member) were second and third authors, respectively and helped to finalize the methodology, data analysis, edited and reviewed the manuscript. Dr. Muhammad Nadeem, Yeukai Katanda, Bilal Javed and Irfan Mushtaq helped in data collection, statistical analysis, reviewed and edited the manuscript.

Chapter Three (Study-Two)

Effects of wood ash, paper sludge and biochar amendment on physicochemical properties and heavy metals leaching of boreal podzolic soils

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Highlights

1. Wood ash and paper sludge are important wastes from pulp and paper industry.
2. Research is required to assess wood ash and paper sludge effects on podzolic soil properties and heavy metal risk assessment.
3. Wood ash and paper sludge improved podzolic soil physiocochemical properties.
4. Biochar addition with wood ash and paper sludge further reduced heavy metal leaching risks.
5. Hydrus-1D was an effective tool to predict the hydrological properties of podzolic soil.

Abstract

The use of industrial wastes as soil amendment could pose risks of heavy metal contamination to both the media formulated and the crops grown in the media. Wood ash (WA) and paper sludge (PS) are two important potential amendments from the pulp and paper industry that could be used to improve the soil quality. However, heavy metal contamination may pose serious challenges to the applications of wood ash and paper sludge as soil media amendment. Herein, this research will evaluate the effect of WA, PS and biochar (BC) on physicochemical properties and the potential of biochar on reducing heavy metal leaching in WA and PS amended podzolic soils. Treatments were control (limestone), WA, PS, WA + PS, control + BC, WA + BC, PS + BC and WA + PS + BC. WA at 17.25 Mg ha^{-1}, PS at 55 Mg ha^{-1}, WA + PS at 14 Mg ha^{-1} + 11 Mg ha^{-1} and BC at 20 Mg ha^{-1} were applied in their repective treatments. Hydrus-1D model was used to simulate the water movement in WA, PS and BC amended soil. The leaching column experiment was a completely randomized design with 4 x 2 factorial settings and replicated three times. Results showed strong agreements between Hydrus-1D simulated and measured leaching time, and saturation level. WA, PS and BC had significant ($p<0.05$) effects on bulk density, total porosity, field capacity (FC), plant available water (PAW), pH, electrical conductivity (EC), soil organic matter (SOM), cation exchange capacity (CEC) and heavy metals (Arsenic, Cadmium, Cromium, Cobalt, Lead and Nickel) retention. WA, PS and BC significantly improved the pH of amended soil compared to control with all treatments having a pH of 6-6.5. Wood ash alone did not show significant ($p<0.05$) effect on bulk density and total porosity compared to control, but PS and PS + BC significantly decreased bulk density and increased the total porosity. BC significantly reduced the heavy metals levels in leachate, PS + BC was found to be the most effective treatment to retain the heavy metals with maximum PAW and FC. BC has potential to retain heavy metals when applied with WA and PS. Further field experiment to assess the effect of WA, PS and BC on heavy metals is recommended.

Key Words: Podzolic soil, Hydrus-1D, Wood ash, Paper sludge, Biochar, Leachate, Heavy metals.

3.1 Introduction

Some of the major reasons for limited crop growth and lower food production in Newfoundland and Labrador (NL), Canada are short growing season, extreme climate and poor soil conditions (Nadeem et al., 2019). Most soils in boreal regions, including NL, Canada are podzols (acidic) with sandy texture and subjected to heavy nutrient leaching under natural conditions (Maheswaran, 2019). These acidic soils need constant application of liming material to achieve the target pH to enhance nutrients uptake and crop production (Atlantic Soil Fertility Committee, 1970), but leads to a higher cost of production. These problems can be solved by improving soil quality with application of different organic wastes from agricultural (Benito et al., 2005), fisheries (Laos et al., 1998), sewage treatment (Gubišová et al., 2020) and paper mill industries (Foley and Cooperband, 2002). Recycling of these wastes will not only improve the soil physicochemical properties, but also can reduce their hazardous impacts on landfilling sites. Considering the current growing demand to protect the natural resources and energy, recycling of these waste for alternative uses is of foremost importance (Ayilara et al., 2020).

Wood ash (WA) and paper sludge (PS) are the prime wastes from the pulp and paper mills and contain significant levels of soil nutrients with high pH and could be suitable to ameliorate poor soils including podzolic soils common in boreal climate (Demeyer et al., 2001; Rashid et al., 2006). Both WA and PS are frequently treated as waste materials having toxic heavy metals like Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Molybdenum (Mo) and Nickel (Ni) (Maheswaran, 2019; Camberato et al., 2006). WA contains important mineral nutrients except nitrogen and has high liming capacity owing to its higher content of metal oxides and hydroxides (Demeyer et al., 2001). WA is highly reactive in soil and can alter the physicochemical properties of amended soils (Cherian and Siddiqua, 2019). Application of WA to agricultural or forest lands may be beneficial to improve soil's physical properties. total porosity and water retention, hence significant improved crop yield (Rautaray et al., 2003). Sahu et al. (2018) revealed that WA application to sandy soil can alter the soil texture permanently, increase the total porosity and water holding capacity (WHC). Addition of WA at 0, 5, 10 and 15% by weight to clay soil effectively decreased the bulk density and improved the soil structure, which altered the total porosity, root penetration and WHC of soil (Korcak, 1995). The calcium contents in WA can readily exchange with sodium at exchange sites and thus improve the flocculation of soil clay particles, which helps to maintain friable soil thus to improving the water infiltration (Jala and Goyal, 2006). Results from several research experiments concluded that WA is more reactive than limestone to increase the pH of acidic soils and effective to lower the exchangeable Al contents of soil (Jala and Goyal, 2006; Maheswaran, 2019). Bang-Andreasen et al. (2017) conducted an incubation experiment to measure the liming effect of WA on acidic soil and concluded that WA application rate has positive correlation with pH and electrical conductivity (EC). Their findings were similar to previously reported results of increase in pH (Demeyer et al., 2001) and EC (Arvidsson and Lundkvist, 2003). PS has high level of nitrogen and other essential nutrients (C, N and P) as well as some heavy metals (As, Cd, Cr, Cu and Ni), which always depended on fiber source and the treatment process (Camberato et al., 2006). Several other studies have reported that PS enhanced the soil quality by increasing soil organic matter (SOM) and by improving the physical, chemical and biological properties of degraded soils (Amini and Naeini, 2013; Foley and Cooperband, 2002). Baziramakenga et al. (2001) reported the water contents of silt loam at field capacity (FC) significantly increased after 2 months when PS compost was applied at 14-42 Mg ha$^{-1.}$ Fierro et al. (1999) observed that PS application at a higher rate of 105 Mg ha^{-1} has supreme effect to increase the plant available water (PAW) in sandy soils by 42, 27 and 72% at 4, 359 and 743 days after incorporation, respectively.

Corner Brook Pulp and Paper Ltd (CBPPL), NL, Canada, produced high amounts of WA (10,000 Mg year^{-1}) and PS (5,000 Mg year^{-1}) as a by-product, WA is generally disposing at local landfill site and dewatering the PS for burning which is costly for mill. CBPPL spends a large amount of money annually for these wastes disposal which can cause land, water and air pollution (Maheswaran, 2019). It is well accepted in the literature that these wastes have high liming effect and can be used as liming agent for acidic soils. However, their application as a liming agent can also be associated with heavy metals contamination which is a serious health and environment concern (Maheswaran, 2019; Churchill and Kirby, 2010). CBPPL wastes have some heavy metals, which are non-degradable (Pitman, 2006) and can affect the food web and aquatic ecosystems long-term (Singh et al., 2011). In order to reduce the harmful effects that can accrue from heavy metal contamination, it is essential to control the soluble and exchangeable fractions of metals in soils amended with WA and PS.

Biochar (BC) is a carbonaceous material which can improve the soil quality by improving the physicochemical properties (Saha et al., 2020; Moragues-Saitua et al., 2017; Jien and Wang., 2013) limiting the mobility and bioavailability of heavy metals (Karami et al., 2011), and thus can reduce the uptake of heavy metals by plants. Some recent studies showed that BC has great potential to remediate the contaminated soils (Uchimiya et al., 2010a; Karami et al., 2011; Park et al., 2011). BC has porous structure (Saha et al., 2020), active functional groups (Zhang et al., 2017), high pH (Saha et al., 2020; Vermooten et al., 2019) and cation exchange capacity (CEC) (Zhang et al., 2017; Park et al., 2011) which increase its affinity for heavy metals adsorption. Maheswaran (2019) conducted leaching column experiments and concluded that BC is a suitable soil amendment to reduce heavy in leachate of CBPPL WA amended sandy loam soil. These studies revealed that by amending the soil with WA, PS and BC could be a sustainable and environment friendly approach to improve soil quality and associated crop productivity.

Numerical simulation of hydraulic properties (especially water movement) is a valuable way to assess the effect of different organic amendments on soil quality by simulating the different scenarios to improve our knowledge how these amendments alter the hydraulic properties under practical field conditions (Saha, 2020; Tan et al., 2014; Iqbal et al., 2020). Hydrological models can predict the variability of the water fluxes effortlessly with acceptable level of accuracy when input data have higher accuracy (Saha, 2020; Kaushal et al., 2009). Hydrus-1D software package is a public domain hydrological model for simulating water, heat, and solute movement of one-dimensional variability in unsaturated, partially saturated, and fully saturated soil profiles (Šimůnek and van Genuchten, 2016). Hydrus-1D model was demonstrated to accurately predict moisture contents using soil columns (30-60 cm depth) and the predicted results were closely matched to the actual measured values (Pal et al., 2014). Furthermore, Mo'allim et al. (2018) used the Hydrus-1D model to precisely predict solute transportation at various soil depths.

Based on the literature and our understanding, it appears that less attention has been given to the use of WA, PS alone and in combination with BC to improve the physicochemical properties of boreal podzolic soil. Thus, strong scientific investigation or validation on water movement and heavy metals movement and leaching ability is critical for sustainable use of these waste materials and agricultural production in boreal ecosystem. The principal hypothesis of this study was the application of WA, PS and BC to podzolic soil will improve its physicochemical properties when applied as an organic amendment. Furthermore, combination of these byproducts with BC could be an effective approach to sequester the heavy metals present in their composition thereby preventing their leaching into other ecosystems.

To test this hypothesis, the experiments focused on answering the following research questions: (i) Can WA, PS and BC be used as a suitable amendment for improving the physicochemical properties of podzolic soil? (ii) What will be the optimum rate of WA and PS alone and their combination as soil amendment for podzolic soil? (iii) What will be the effect of these amendments on soil water retention curve (SWRC)? (iv) What will be the effect of BC on heavy metals retention from WA and PS amended soil? (v) Can we use Hydrus-1D to predict the water flow in podzolic soil amended with WA, PS and BC? It is anticipated that the findings of this study could provide guidelines for the use of WA, PS and BC as suitable organic amendments to improve the physicochemical properties of podzolic soil during field crop production in boreal climate. Use of these PMW in agriculture industry will generate revenue and reduce landfill costs for the paper mill and reduce the environmental pollution at the disposal site.

3.2 Materials and Methods

3.2.1 Basic properties of soil, wood ash, and paper sludge

Basic chemical properties (CCE**,** macronutrients, micronutrients, heavy metals, total carbon and total nitrogen, mineral nitrogen) of soil, WA, and PS were measured by sending samples to Agriculture and Food Laboratory, University of Guelph, Guelph, ON, Canada.

3.2.2 CBPPL wastes sampling

Thirty samples of WA and PS were collected intermittently (twice daily over a 15-d period) from CBPPL to prepare separate composite samples of both wastes. WA contained a mixture of fly ash (20%) and bottom ash (80%) obtained from the furnace after the burning process (source from paper mill). PS resulted from the mechanical pressing of secondary sludge, which was obtained from clarifying and settling processes during aerobic wastewater treatment in pulp and paper manufacturing was used for all experiments. Each composite was air dried at room temperature and sieved with 2 mm mesh before mixing with soil. The PS was ground by using a Wiley Mill have a 2mm sieve size (Arthur H. Thomas Co, USA) before sieving.

3.2.3 Biochar and lime

BC for this experiment was purchased from Air Terra Inc. (Alberta, Canada), prepared from yellow pine wood using slow pyrolysis (500 °C, 30 min). Some properties of the BC are given in Table 3.1. Powder limestone used in this study was purchased from NCL Contractors Ltd (Cormack, NL, Canada).

3.2.4 Soil sampling

Bulk soil was collected at 0-15 cm depth from a newly converted agricultural field near the Wooddale Centre for Agriculture & Forestry Development (WCAFD), Grand Falls (49° 01' 30" N and 55° 33' 30" W), NL, Canada managed by the Department of Fisheries, Forestry and Agriculture of the Government of NL. Bulk soil was air dried at room temperature and 2 mm sieved in a greenhouse at WCAFD and brought to the Boreal Ecosystems Research Facility (BERF) of Grenfell Campus, Memorial University for subsequent use.

3.2.5 Application rates of limestone, wood ash, paper sludge and biochar

Lime requirement was 7.1 Mg ha^{-1} suggested by the Soil, Plant and Feed Laboratory of the Government of NL, St. John's, NL, Canada to bring the soil pH within optimum range (6.0-6.5) for several cole crops (kale cabbage, cauliflower, broccoli) lettuce and annual ryegrass. The pH of amended soil at different WA and PS application rates was tested to find the suitable application rates to bring the soil pH in the desired range (Table 3.1). WA and PS were applied at 17.30 Mg ha^{-1} and 55 Mg ha^{-1}, respectively. As for the combination treatments, application rates were 14 Mg ha^{-1} (WA) + 11 Mg ha^{-1} (PS). BC was applied at 20 Mg ha^{-1} rate since it has been reported as the best application rate by Moragues-Saitua et al. (2017) to improve the hydraulic properties of amended soil with combination of WA.

Table 3.1: CBPPL wastes application rates and amended soil pH

CBPPL Waste	Application rate (Mg ha^{-1})	Soil pH
WA	69	7.4±0.05
	34.5	6.8±0.09
	17.30	6.5±0.03
PS	85	7.3±0.05
	70	6.9±0.03
	55	6.2±0.04
WA + PS	20 + 15	6.9±0.02
	15+15	6.6±0.06
	14+11	6.3±0.03

Soil pH showed as mean value value ± standard deviation (n=3±SD), CBPPL-Corner Brook Pulp and Paper Ltd. **Abbreviations: WA-**Wood ash; PS-Paper sludge

3.2.6 Experimental design and treatments

This research study comprised of eight treatment combinations with two factors. Factor one was Paper mill wastes (PMW) at four levels (lime (No PMW), WA, PS, WA + PS) and the second factor was BC at two levels (0 Mg ha^{-1} and 20 Mg ha^{-1}). The experimental design was completely randomized design (CRD) in factorial arrangement with three replicates. The application rates of lime, WA, PS and BC in the different treatment combinations are given in Table 3.2.

Table 3.2: Treatments with application rates of lime, wood ash, paper sludge and biochar

Treatments	**Application rate (Mg ha^{-1})**	
	Paper mill wastes/Lime	**Biochar**
Lime (control)	7.1	0
WA	17.3	0
PS	55	0
WA + PS	14+11	0
Lime + BC	7.1	20
WA + BC	17.3	20
PS + BC	55	20
WA + PS + BC	14+11	20

Abbreviations: WA-Wood ash; PS-Paper sludge

All the treatment mixtures were prepared by adding the soil with their respective amendments and thoroughly mixed. Moisture factor for each treatment mixture was estimated by oven drying three samples from each treatment. All the mixed treatments were stored in plastic polyethylene bags to keep the moisture contents constant throughout the study period at the BERF of Grenfell Campus, Memorial University before use to conduct the different lab experiments. Sub samples were obtained from these stored mixtures when measuring physicochemical properties and carrying out the leaching column experiment.

3.2.7 Analyses of physicochemical properties of amended soil

Soil particle size analysis

Soil texture with sand, silt and clay percentage was measured by using the hydrometer method (Bouyoucos, 1962).

pH and electrical conductivity

A portable pH/EC/TDS/Temperature meter (HANNA–HI9813–6 with CAL Check, ON, Canada) was used to measure pH and EC for all treatments using a ratio of 1:2 soil to deionized water ratios (15 g air dried sample: 30 mL deionized water) according to Brady and Weil (2008). Polypropylene tubes (VWR, Mississauga, ON, Canada) containing sample and water were stirred for one hour at 120 RPM and allowed to settle for 30 min and readings were recorded (Saha et al., 2020; Brady and Weil, 2008).

Cation exchange capacity and soil organic matter

For CEC and SOM measurement, all treatments samples were sent to the Soil, Plant and Feed Laboratory of the Government of NL, St. John's, NL, Canada, where rapid method of exchangeable bases used for CEC measurement (Hajek et al., 1972) and loss on ignition (LOI) method was used to measure the SOM (Donald and Harnish, 1993).

Bulk density

Disturbed dry bulk density was measured by dividing the dry mass of the sample over the stainless-steel core (5 cm diameter x 5 cm height) volume (88.6 cm^3) (Kim et al., 2017). Each core was filled by 1/3 of core height at a time and tapped 3-4 time to fill the whole core for reducing the extra void spaces.

3.2.8 Soil water retention curve

Total porosity

A sandbox apparatus (Acc. To ISO 11274, art no. 0801, Eijkelkamp, Giesbeek, Netherland) was used to record the porosity (0 kPa) of all treatments by the saturation method. Stainless steel cores used for bulk density measurement were refilled with soil samples and saturated in sand box for three days. The total porosity was calculated as saturation weight by using Equation 1 at 0 kPa (Saha et al., 2020).

$$\textbf{Total Porosity}\ (\boldsymbol{P}) = \frac{\boldsymbol{W_s - W_0}}{\boldsymbol{V_t}} \qquad \textbf{(1)}$$

Where, W_s is saturated sample weight, W_0 is dried sample weight and V_t is the total sample volume.

Field capacity

Pressure plate extractors (0700CG23F1 Manifold and 0505V# Compressor, model 1600-500 kPa ceramic plate extractor and model 1500 F2 1500 kPa ceramic plate extractor, Soil Moisture Equipment Corp., Goleta, CA, USA) were used to record the data from 10 kPa to 700 kPa. Samples were packed in small plastic rings having volume of 21.53 cm^3 on their respective bulk density (similar to bulk density of sand box samples). All samples were saturated in a plastic tub, fully saturated samples were placed in the pressure plate extractor and 10 kPa pressure was applied. When the water discharge stopped from the outlet tube, the samples were weighed and the gravimetric moisture content was calculated. The same procedure was followed to record data subsequently for 30, 40, 50, 100, 200, 300, 400, 500, 600, and 700 kPa pressure levels. The FC was calculated at 30 kPa by using Equation 2 (Glab et al., 2016; Saha et al., 2020).

$$\mathbf{FC} = \frac{\boldsymbol{W_d - W_0}}{\boldsymbol{V_t}} \times \mathbf{100} \qquad \textbf{(2)}$$

Where, FC is field capacity, W_d is drained sample weight at 10 kPa, W_o is dried sample weight and V_t is the total sample volume.

Plant available water (PAW)

Calculated gravimetric moisture contents were converted to volumetric moisture contents (VMC: θ) multiplying by the respective bulk density. The estimated VMC from 0 kPa to 700 kPa and pressure (ψ) were fitted to the van Genuchten model (Equation 3) (van Genuchten, 1980). The best fit van Genuchten parameters (α and n) were obtained by using MS excel solver function. Then, VMC values from 800 kPa to permanent wilting point (PWP) at 1500 kPa were estimated using the van Genuchten equation and best fit parameters (0 kPa to 700 kPa). The PAW was calculated as the difference between VMC at FC and PWP as given in Equation 4 (Glab et al., 2016; Saha et al., 2020).

$$\boldsymbol{\theta(\psi) = \left[\frac{\theta_s - \theta_r}{[1+\alpha(\psi)^n]^m}\right] + \theta_r} \qquad \textbf{(3)}$$

Where, $\theta(\psi)$ is volumetric moisture content (cm^3 cm^{-3}), ψ is pressure applied (cm of water), θ_s is saturated moisture contents (porosity: cm^3 cm^{-3}), θ_r is residual moisture contents (< PWP) (cm^3 cm^{-3}), α and n are the shape parameters, and m = 1 – 1/n

$$\mathbf{PAW = \theta_{FC} - \theta_{PWP}} \qquad \textbf{(4)}$$

Where, PAW is plant available water, θ_{Fc} is VMC at field capacity and θ_{PWP} VMC at permanent wilting point.

3.2.9 Leaching experiment

A leaching column experiment was conducted to evaluate the mobility and leaching potential of the heavy metals from WA, PS and BC amended soil. This experiment was organized under laboratory conditions at room temperature at the BERF, Grenfell Campus, Memorial University of Newfoundland. The above-mentioned treatments (Table 3.2) with three replications were arranged under CRD design in a custom-built leaching column setup (Figure 3.1). Transparent polymethyl methacrylate pipes (Osprey Scientific Inc. AB, Canada) having the length of 30 cm and radius of 2.25 cm were used. Treatment mixtures were filled up to 25 cm depth and a 5 cm head space was kept for water addition (Figure 3.1a). The soil columns for each treatment were filled with amended soil at their respective bulk density by making different layers to ensure a uniform density as much as possible in the entire column up to 25 cm depth, each column was taped down (3-4 times) on ground and 1/3 filled for each round. A total of 24 leaching columns were prepared (8 treatments * 3 replication). Four leaching events were carried out and a one-week interval was maintained between each leaching event. Each column was flushed with 255 mL of deionized water for one leaching event with total amount of 1016 mL deionized water for 4 leaching events (equivalent to 586.19 mm rainfall), which corresponds to the average total rainfall during the growing season (May-Nov) in the study area calculated using 30 years of rainfall data (https://climate.weather.gc.ca). In the leaching column experiment, the flux rate 3.66 cm h^{-1} was maintained by adding 63.55 mL of deionized water per 15 min intervals.

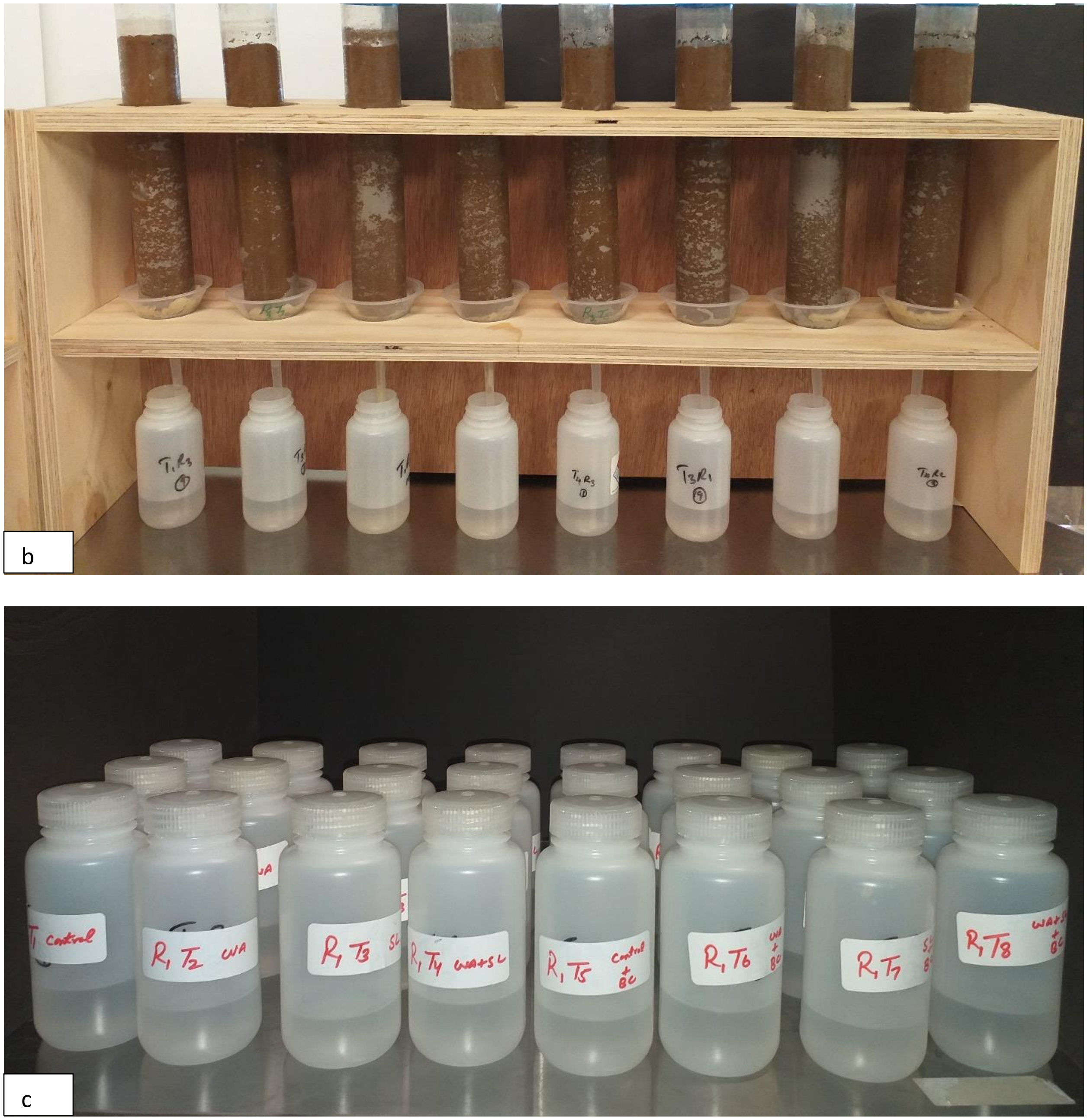


Figure 3.1 (a-c): Leaching column experiment setup with collected leachate.

3.2.10 Heavy metals measurement in leachate

After each leaching event, the leachates were collected in plastic bottles (Figure. 1c) and concentrated HNO_3 **(**Catalog No. A509P212, Fisher Scientific, Ottawa, Ontario, Canada) was added to bring the leachate pH to 2, and to facilitate mineral digestion for elemental or heavy metal analysis. All the leachate samples were analyzed for AS, Cd, Cr, Cu, Pb, Mo and Ni using

Inductively Coupled Plasma Mass Spectrometry (Thermo Scientific CAP Q ICP-MS) according to established methods in our research program (Zaeem et al., 2021). The amount of each heavy metal leached out during each leaching event was calculated by using the leachate volume of that leaching event.

3.2.11 Simulation study of the leaching column experiment

The Hydrus-1D model was used for the simulation of VMC from 0-4 h by keeping the leaching column depth of 25 cm and a flux rate -3.66 cm h^{-1} ("–" sign represents downward movement of water in Hydrus-1D), as used in heavy metals leaching experiment for all treatments. In simulated leaching columns, the VMC for different treatments were predicted on the basis of water movement from surface to bottom as described by modified Richard's equation (Equation 5) (Iqbal et al., 2020; Saha, 2020; Zheng et al., 2017).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[k\left(\frac{\partial h}{\partial x} + 1\right)\right] - S\,(z, t) \quad (5)$$

Where, h-Water pressure head (cm), θ -Volumetric water content (cm^3 cm^{-3}), t-Time (hours), z-maximum soil depth (cm), x-Spatial coordinate (cm), k-Unsaturated hydraulic conductivity (cm day^{-1}), S-Source/Sink term of the flow equation. The Hydrus-1D model results from time to start leachate was compared with actual time to start leachate from respective leaching column experiment.

3.2.12 Statistical analysis

To quantify the effects of PMW and biochar different combinations on physicochemical properties and heavy metals leaching ability from amended podzolic soil, analyses of variance (ANOVA) were performed, and the Fisher's least significant difference (LSD) was used to compare the treatments means at alpha = 0.05. Statistic 10.0 version (Analytical software, Tallahassee FL

32317, USA) was used for statistical analysis and graphical visualization was done through MS excel 2016. Computation of the coefficient of determination (R^2) and root mean square error (RMSE) (Equation 6) to check accuracy of the van Genuchten model predicted values for SWRC and RMSE and relative error (RE) (Equation 7), were used to evaluate the precision of Hydrus-1D predicted values by using measured values quantitatively. Principal component analysis (PCA) was performed to explore relationships among treatments, measured properties and heavy metals leached out by using XLSTAT (Premium 1060, Version 2020.5.1, Addinsoft, New York, NY, USA).

$$\mathbf{RMSE} = \sqrt{\Sigma \frac{(Si-Ei)^2}{n}} \qquad \mathbf{(6)}$$

$$\mathbf{RE\ (\%)} = \frac{1}{n}\sum_{i=0}^{n} \frac{Si-Ei}{Ei} \times 100 \qquad \mathbf{(7)}$$

Where, Ei shows the experimental value at the time i, Si shows the simulated value at the same time, and n = number of observations.

3.3 Results

3.3.1 Properties of soil, wood ash, paper sludge and biochar used in experiments

The basic properties of soil, WA, PS, and BC are given in Table 3.3

Table 3.3: Physicochemical properties of soil, wood ash, paper sludge and biochar used for the soil amendment rates and leaching experiments

Parameter	Unit	Wood ash	Paper Sludge	Biochar	Soil
CCE	% dry	10.4	12.9	-	-

pH		12.6	8.2	9.4	5.7
EC	dSm^{-1}	9.52	0.32	0.43	0.04
TC	%	5.09	40.1	88.6	1.31
NH_4^+-N	$mgkg^{-1}$	0.74	876	-	4.79
NO_3^--N	$mgkg^{-1}$	5.09	2.00	-	0.61
OC	%	3.45	39.9	88.6	1.29
Field BD	gcm^{-3}	1.16	0.12	0.14	1.18
DM	%	97.79	68.12	84.8	95.79

Abbreviations: CCE–Calcium carbonate equivalency; EC–Electrical conductivity, TC–Total carbon; TN–Total nitrogen; NH_4^+-N–Ammonium nitrogen; NO_3^--N–Nitrate nitrogen; OC–Organic carbon; BD–Bulk density; DM–Dry matter

3.3.2 Particle size distribution.

According to the USDA soil classification system, soil is classified as loam texture with sand = 50 (±2), clay = 17.38% (±1.15) and silt = 32.62% (±1.15).

3.3.3 Heavy metals

Heavy metals concentration in WA and PS composite samples and their comparison with Canadian Council and Ministers of Environment (CCME-2005 and CCME-2012) compost category A and B guidelines and biosolids limits are given in Table 3.4.

The measured heavy metals concentrations in both WA and PS are below the compost category A except for Mo and Cd for only PS and below the limits developed for the biosolids application and compost category B (Table 3.4), therefore WA and PS can be used in agriculture soils under these two categories (compost category B and biosolids limit) with extra precautions when deemed necessary by the province or other geography of end use location.

Table 3.4: Comparison of heavy metals in wood ash, paper sludge and soil with different application guidelines.

Heavy metal	Soil ($mg\ kg^{-1}$)	Wood ash ($mg\ kg^{-1}$)	Paper sludge ($mg\ kg^{-1}$)	Compost limit[#] ($mg\ kg^{-1}$)		Biosolids limit[#] ($mg\ kg^{-1}$)
				A	B	
Arsenic	8.8	2.5	2.1	13	75	41
Cadmium	0.08	1.3	3.1	3	20	15
Chromium	36	130	55	210	1016	1000
Cobalt	8.2	14	5.1	34	150	150
Copper	13	190	94	400	757	1500
Lead	7.9	20	35	150	500	300
Molybdenum	0.42	16	6.3	5	20	20
Nickel	19	88	42	62	180	180

[#]Canadian Council of Ministers of the Environment (CCME, 2005, 2012)

3.3.4 Physicochemical properties

pH

The PMW and BC application significantly ($p<0.001$ & $p<0.05$, respectively) increased the pH of amended soil compared to untreated soil, but their interaction (co-application of PMW and BC) did not show significant ($p=0.207$) effect regarding to increase the pH compared to (Table 3.5 a). All the treatments had a pH in the desired range (6.0-6.5), where WA was found to be the most responsive to increasing the pH. As such the highest pH was observed in WA + PS (6.5 and the lowest (6.0) in control (lime) treatment (Table 3.5 b).

Electrical conductivity

The PMW and BC application significantly ($p<0.001$ & $p<0.001$, respectively) increased the EC of amended soil compared to untreated soil, but their interaction (co-application) did not show significant ($p=0.815$) effect to increase the EC of amended soil (Table 3.5 a). WA amended treatments showed higher EC in comparison to PS treatments. The treatment WA + BC showed the highest EC (0.23 dS m^{-1}) followed by the lowest of 0.05 dS m^{-1} for control (lime) among all treatments (Table 3.5 b).

Cation exchange capacity

The PMW individually showed significant effect ($p<0.001$) in increasing the CEC of amended soil, but BC addition as a factor reduced the CEC of amended soil compared to BC untreated treatments, and its effect was not significant ($p=0.619$). The interaction (co-application) effect was not significant ($p=0.815$) to change the CEC of amended soil compared to lime amended soil (Table 3.5 a). The treatments comprising WA have higher CEC compared to PS treatments similar to the effects on EC. The CEC increased in WA treatment by 84.2% compared to control (lime), which was the highest among all treatments and the lowest was found in control (lime) that is found to be statistically at par with PS treatment (Table 3.5 b).

Soil organic matter

The PMW and BC showed significant ($p<0.001$ & $p<0.05$) effect to increase the SOM of amended soil, where S application showed the highest increase of 46.38% compared to the control (limestone treatment), while BC addition increased the SOM by 9.30% compared to the nonamended BC treatments. The PMW and BC interaction (co-application) did not show significant ($p=0.849$) effect on SOM contents (Table 3.5 a). PS amended treatments showed higher SOM contents compared to WA combinations as expected. Highest SOM contents was observed in PS + BC (3.55%) among all combinations where, it increased by 57.1 % compared to control (lime), which showed the lowest increased percentage of 2.26 (Table 3.5 b).

Bulk density

The PMW and BC showed significant ($p<0.001$ & $p<0.001$) effect to reduce the bulk density of amended soil. BC addition significantly reduced the bulk density by 6.45% compared to treatments without BC. The PMW and BC interaction (co-application) effect was non-significant ($p=0.068$) on the bulk density (Table 3.5 a). Overall, PS treatments have significantly lowered bulk densities compared to WA and control treatments potentially to due fibrous and porous nature of PS. Control (lime) treatment has the highest bulk density (1.29 g cm^{-3}) and PS with combination of BC (PS + BC) had the lowest bulk density (1.07 g cm^{-3}) which was 17.1% lower than the control (lime) (Table 3.5 b).

Total porosity

The PMW and BC showed significant ($p<0.001$ & $p<0.001$) effect on total porosity of amended soil and their interaction (co-application) did not show any significant ($p=0.3524$) effect on changing the total porosity (Table 3.5 a). Although PS treatment alone and with combination of BC showed higher total porosity compared to WA and lime treatments. The PS and BC combination (PS + BC) showed the highest total porosity (0.68 cm^3 cm^{-3}), which increased by 25.9% compared to control and the lowest total porosity (0.54 cm^3 cm^{-3}) was observed in lime (Table 3.5 b).

Field capacity

The FC level of soil amended with PMW and PS was significantly ($p<0.001$ & $p<0.01$, respectively) increased. PS amended treatments increased the FC by 10.34% compared to lime, and BC application increased the FC by 14.28% compared to unamended BC treatments. The PMW and BC interaction ($p<0.05$) effect (co-application) was significant and showed an increase in the FC level (Table 3.5 a). The maximum FC was recorded in PS + BC treatment (0.36 cm^3 cm^{-3}), which was 24.1% greater than control (lime) (Figure 3.3). The FC in WA treatment significantly decreased by 3.4% compared to lime, which was found to be statistically at par with WA + BC and PS (Table 3.5 b).

Plant available water

The PMW and BC both significantly ($p<0.001$ & $p<0.01$, respectively) increased the PAW of the amended soil. PS had the highest effect and increased the PAW by 14.28% compared lime. BC amended treatments have 15% greater PAW than treatments without BC. The PMW and BC interaction (co-application) showed significant ($p<0.05$) effect on PAW of the amended soil (Table 3.5 a). The PS and BC combination (PS + BC) significantly increased the PAW by 33% compared to control treatment (lime). The lowest PAW (0.20 cm^3 cm^{-3}) was noted in control (lime) (Figure 3.3), which was found to be statistically at par with lime + BC, WA, WA + PS (Table 3.5 b).

Table 3.5 a: Individual effect of paper mill wastes (PMW) and biochar on the physicochemical properties of podzolic soil

Parameter	p-value			Mean					
				PMW				Biochar Mg ha^{-1}	
	PMW	Biochar	PMW * Biochar	LS	WA	PS	WAPS	0	20
pH	<0.001	<0.05	0.207	6.0c	6.4a	6.2b	6.4a	6.2b	6.3a
EC	<0.001	<0.001	0.815	0.06c	0.22a	0.13b	0.21a	0.15b	0.16a
CEC	<0.001	0.619	0.599	7.01b	12.21a	8.20b	10.74a	9.73	9.35
SOM	<0.001	<0.05	0.849	2.35b	2.35b	3.44a	2.65b	2.58b	2.82a

BD	<0.001	<0.001	0.068	1.25a	1.24a	1.12c	1.20b	1.24a	1.16b
Porosity	<0.001	<0.001	0.3524	0.55c	0.57c	0.65a	0.61b	0.57b	0.62a
FC	<0.001	<0.001	<0.05	0.29b	0.28c	0.32a	0.31b	0.28b	0.32a
PAW	<0.001	<0.001	<0.05	0.21bc	0.20c	0.24a	0.22b	0.20b	0.23a

Mean ± SE sharing different letters have significant differences at alpha 0.05. ($p < 0.001$= highly significant, $p < 0.05$ = significant, $p > 0.05$ = Non–Significant). PMW *Biochar represents the interaction effect of both factors

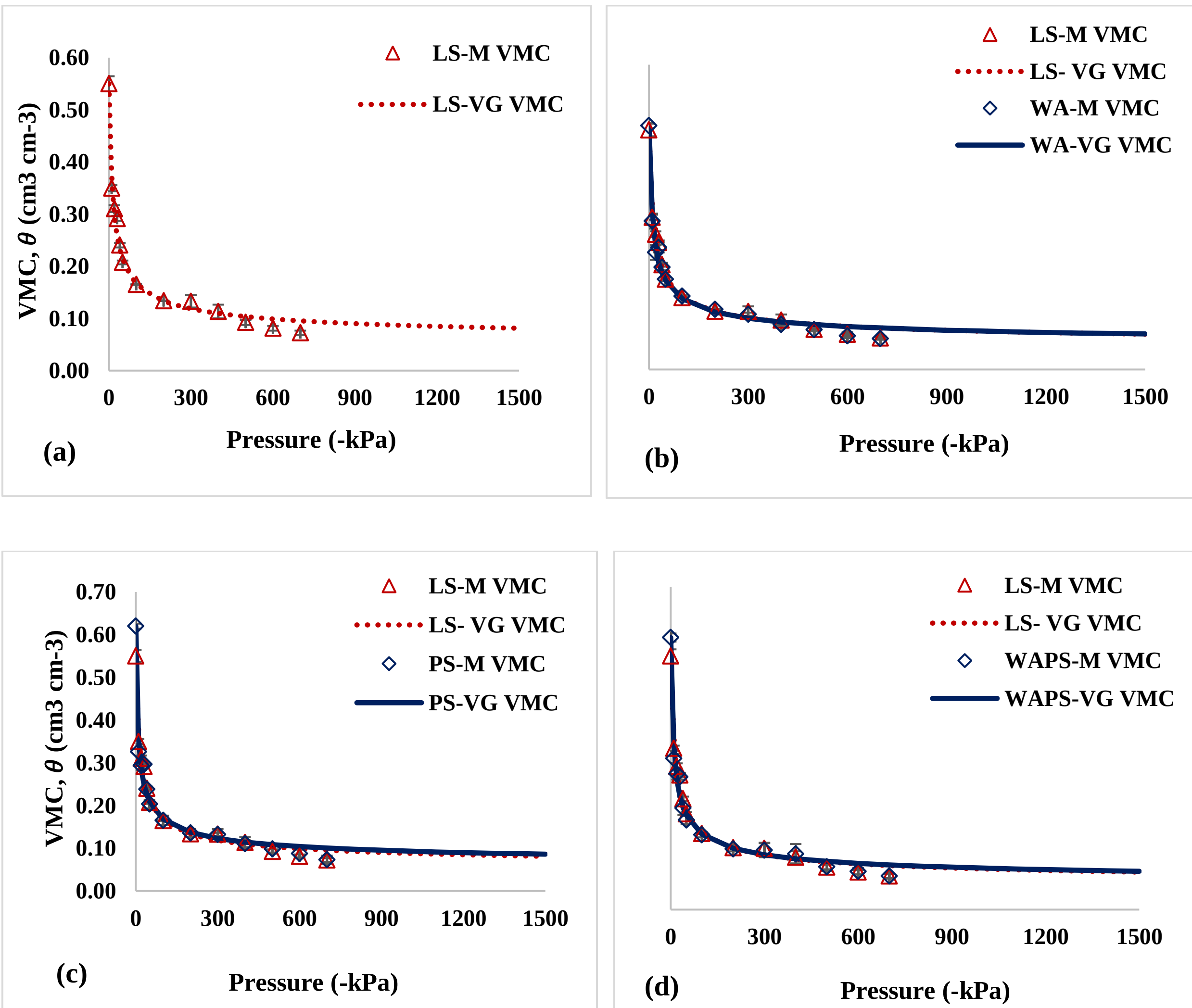
Table 3.5 b: The interacion effects of paper mill wastes combined with biochar on the physicochemical properties of podzolic soil

Properties	LS	WA	PS	WAPS	LSBC	WABC	PSBC	WAPSBC
pH	6±0.05	6.5±0.03	6.2±0.00	6.3±0.03	6.1±0.03	6.5±0.00	6.2±0.03	6.5±0.05
EC	0.05±0.00	0.22±0.00	0.12±0.00	0.20±0.00	0.06±0.00	0.23±0.00	0.14±0.00	0.22±0.00
CEC	6.72±0.99	12.38±0.74	9.22±1.39	10.58±1.25	7.3±1.13	12.04±1.12	7.17±0.44	10.91±0.94
SOM	2.26±0.11	2.27±0.11	3.34±0.12	2.45±0.13	2.45±0.13	2.44±0.17	3.55±0.19	2.84±0.12
BD	1.29±0.01	1.28±0.00	1.18±0.01	1.23±0.00	1.21±0.00	1.21±0.01	1.07±0.01	1.18±0.00
Porosity	0.54±0.01	0.56±0.00	0.62±0.00	0.58±0.00	0.57±0.00	0.59±0.01	0.68±0.00	0.64±0.00
FC	0.29cd±0.00	0.28d±0.01	0.30cd±0.00	0.29cd±0.00	0.31c±0.00	0.28d±0.00	0.36a±0.01	0.33b±0.00
PAW	0.21cd±0.00	0.20d±0.01	0.21cd±0.00	0.21cd±0.00	0.22bc±0.00	0.21cd±0.00	0.28a±0.01	0.24b±0.00

Abbreviations: PMW–Paper mill wastes; LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar; EC–Electrical conductivity (dS m^{-1}); CEC–Cation exchange capacity (Cmol kg^{-1}); SOM–Soil organic matter (%); BD–Bulk density (g cm^{-3}); FC–Field capacity (cm^3 cm^{-3}); PAW–Plant available water (cm^3 cm^{-3}). Mean values ± SE sharing different letters have significant differences at alpha 0.05.

3.3.5 Soil water retention curves

The developed SWRC explained important hydrological parameters (total porosity, FC, PAW, PWP) of WA, PS and BC amended treatments and comparison between measured and predicted values for all treatments from saturation to 700 kPa (Figure 3.2 (a-j)). It was observed that WA, PS and BC applications significantly increased the water retention characteristics of amended soil. The predicted values obtained using the van-Genuchten model from 0 kPa to 700 kPa were very close to the measured values with high R^2 and very low RMSE values (Table 3.6).



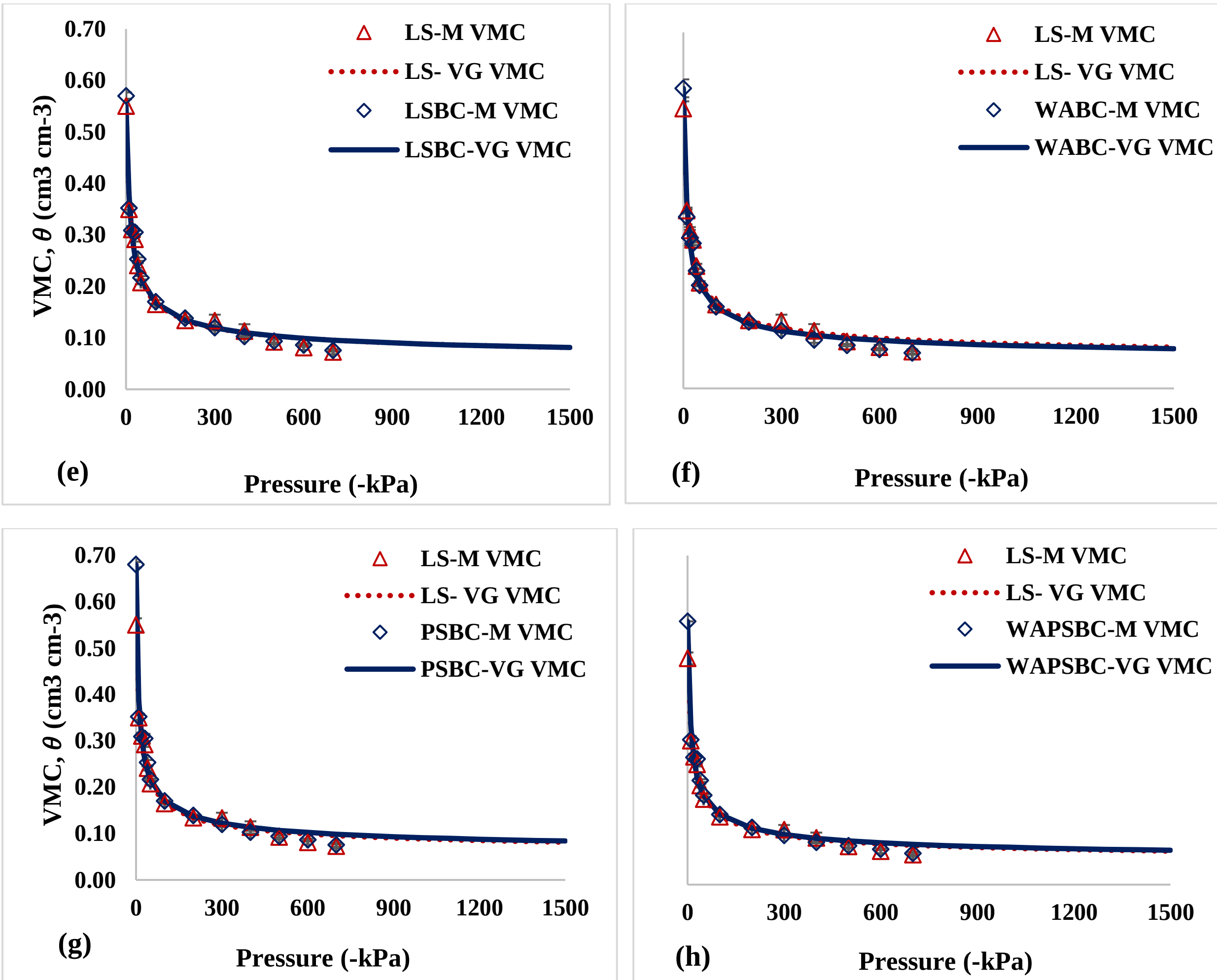


Figure 3.2: Soil water retention curve (SWRC) of measured volumetric moisture contents (M VMC) from 0 kPa to 700 kPa vs. van-Genuchten volumetric moisture contents (VG VMC) determined from 0 kPa to 1500 kPa. Sub-figure a–only for lime and sub-figures from b to h–compares a treatment mixture with lime (control). **Abbreviations:** LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar.

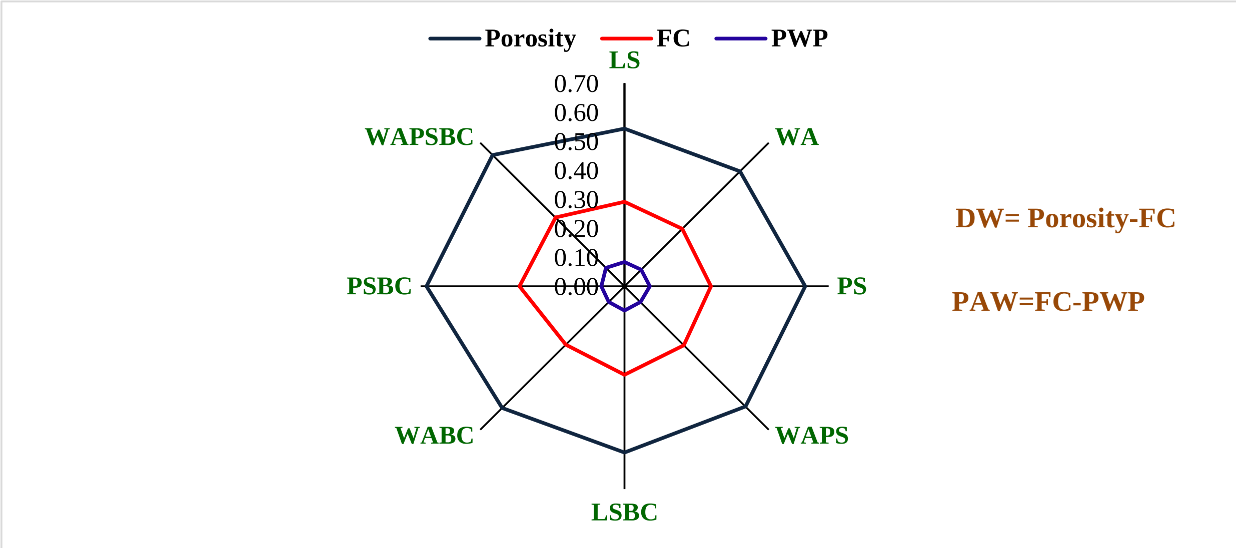


Figure 3.3: Effect of wood ash, paper sludge and biochar on porosity (cm^3 cm^{-3}), FC–Field capacity (cm^3 cm^{-3}), DW–drainable water (cm^3 cm^{-3}), PWP–Permanent wilting point (cm^3 cm^{-3}) and PAW–Plant available water (cm^3 cm^{-3}); LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar

Table 3.6: Measured (a) and predicted (b) water content at saturation (θs), residual water content (θr) and van-Genuchten model parameters (α, n) from 0 kPa to 700 kPa

Treatment	**θs (cm^3cm^{-3})**		**θr (cm^3cm^{-3})**	**α**	**n**	**R^2**	**RMSE (cm^3cm^{-3})**
	a	b					
LS	0.55	0.55	0.05	1.83±0.12	1.49±0.02	0.981±0.00	0.017±0.00
WA	0.56	0.56	0.05	2.43±0.56	1.46±0.01	0.977±0.00	0.021±0.00
PS	0.62	0.62	0.05	3.54±0.00	1.43±0.01	0.977±0.00	0.021±0.00

WAPS	0.59	0.59	0.05	3.00±0.35	1.45±0.03	0.972±0.00	0.023±0.00
LSBC	0.57	0.57	0.05	1.92±0.13	1.49±0.01	0.978±0.00	0.018±0.00
WABC	0.59	0.59	0.05	2.37±0.59	1.50±0.02	0.983±0.00	0.017±0.00
PSBC	0.68	0.68	0.05	2.95±0.15	1.47±0.00	0.956±0.00	0.032±0.00
WAPSBC	0.64	0.64	0.05	2.78±0.23	1.47±0.00	0.976±0.00	0.022±0.00

Abbreviations: θs (a)–measured saturated VMC; and θs (b)–predicted saturated VMC; θr–residual VMC; α, n–are shape parameters; LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Bioch*ar* Values are given for *α*, n, R^2 and RMSE are mean ± SE

3.3.6 Heavy metals concentration in leachate

The PMW showed significant effect on Cd, Mo and Ni concentrations but no significant effect was observed for As, Cr, Co, Cu and Pb concentrations in the collected leachates (Table 3.7a). Overall, BC application significantly reduced the concentrations of Cd (by 6.42%), Co (by 10.95%), Cu (by 11.76%), Pb (by 30%) and Ni (by 3.75%) in the collected leachates. BC application also reduced the concentration of As (by 2.83%), Cr (by 2.73%) and Mo (by 0.91%), though these differences were not significant from BC unamended treatments (Table 3.7). The PMW and BC interaction effect (co-application) was significant in reducing the concentration of Pb and Ni but was not significant for the levels of As, Cd, Cr, Co collected in the leachate (Table 3.7a & 3.7b). WA treatment has the highest concentration of Cd and Mo, and PS has the highest concentration of As, Cu and Pb, while WA + PS had the highest concentration of Cr and Co in the collected leachates among all treatments (Table 3.7b). During the 1st leaching event, all heavy metals concentrations were very low in the collected leachate and there was no significant difference between treatments. The 2nd and 3rd leaching events showed that Cd, Cu, Pb and Ni concentration increased with the number of leaching events and a clear difference was observed among the different treatments during the 3rd leaching event (Figure 3.4). The application of water produced a pulse in the leachates during the experiment, then concentrations decreased thereafter. In the leaching experiment, we observed that Mo and Ni concentration significantly increased with each leaching event and needed more time to reach its peak concentration (Figure 3.4)**.**

Table 3.7 a: Effects of paper mill wastes (PMW) and biochar on heavy metal leaching (µg L^{-1}) from podzols

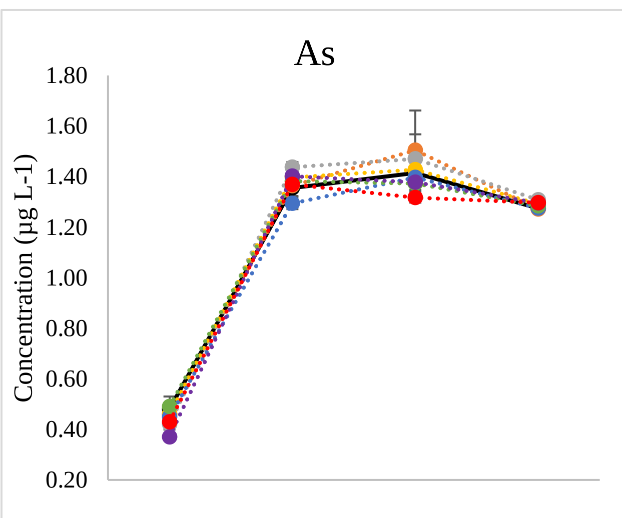
Heavy metals	p-value			Mean					
				PMW				Biochar Mg ha^{-1}	
	PMW	Biochar	PMW * Biochar	LS	WA	PS	WAPS	0	20
As	0.7746	0.0775	0.9111	4.46	4.56	4.53	4.49	4.58	4.45
Cd	<0.05	<0.001	0.3672	3.38b	3.65a	3.44b	3.40b	3.58a	3.35b
Cr	0.2353	0.2753	0.5612	2.06	2.20	2.20	2.18	2.19	2.13
Co	0.7461	<0.05	0.3188	0.66	0.69	0.70	0.71	0.73a	0.65b
Cu	0.3723	<0.05	0.0755	3.09	3.38	3.22	3.24	3.40a	3.00b
Pb	0.2141	<0.001	<0.05	0.69	0.61	0.74	0.67	0.80a	0.56b
Mo	<0.001	0.5525	0.9646	5.23b	5.93a	5.21b	5.42b	5.47	5.42
Ni	<0.05	<0.05	<0.05	6.88b	6.94b	7.30a	7.17a	7.21a	6.94b

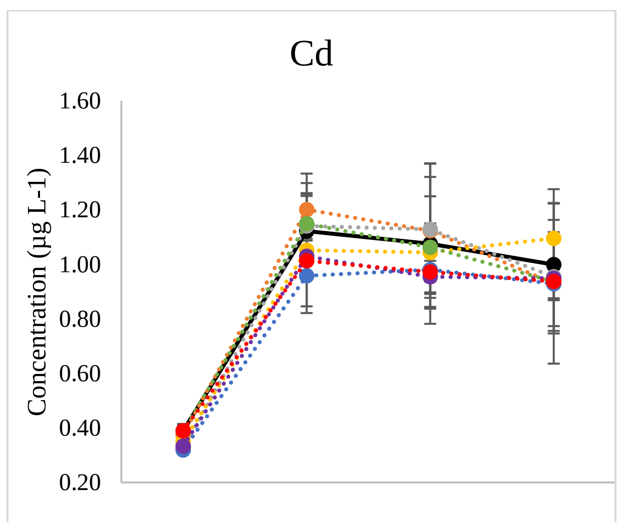
Mean ± SE sharing different letters have significant differences at alpha 0.05. ($p < 0.001$= highly significant, $p < 0.05$ = significant, $p > 0.05$ = Non–Significant). PMW *Biochar represents the interaction effect of both factors

Table 3.7 b: Interaction effects of paper mill wastes (PMW) and biochar on heavy metal leaching (μg L^{-1}) of podzols

Heavy metals	LS	WA	PS	WAPS	LSBC	WABC	PSBC	WAPSBC
As	4.51±0.01	4.59±0.07	4.63±0.12	4.57±0.14	4.41±0.05	4.53±0.02	4.44±0.05	4.41±0.12
Cd	3.55±0.08	3.70±0.07	3.62±0.09	3.45±0.11	3.20±0.25	3.59±0.12	3.26±0.11	3.34±0.11
Cr	2.04±0.14	2.20±0.01	2.25±0.02	2.27±0.05	2.07±0.08	2.19±0.03	2.16±0.11	2.09±0.03
Co	0.71±0.01	0.69±0.03	0.75±0.03	0.78±0.08	0.62±0.01	0.70±0.02	0.65±0.06	0.63±0.04
Cu	2.91±0.24	3.42±0.15	3.68±0.48	3.61±0.13	3.06±0.14	3.34±0.41	2.76±0.39	3.61±0.23
Pb	0.67bcd±0.09	0.69bc±0.13	0.98a±0.11	0.83ab±0.08	0.70bc±0.06	0.53cd±0.05	0.50d±0.12	0.51d±0.20
Mo	5.22±0.18	5.99±0.30	5.23±0.13	5.42±0.12	5.23±0.44	5.86±0.26	5.18±0.15	5.38±0.08
Ni	6.95b±0.20	6.84b±0.10	7.57a±0.33	7.46a±0.13	6.82b±0.07	7.04b±0.12	7.03b±0.23	6.88b±0.20

Abbreviations: PMW–Paper mill wastes; LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar. Mean values ± SE sharing different letters have significant differences at alpha 0.05.





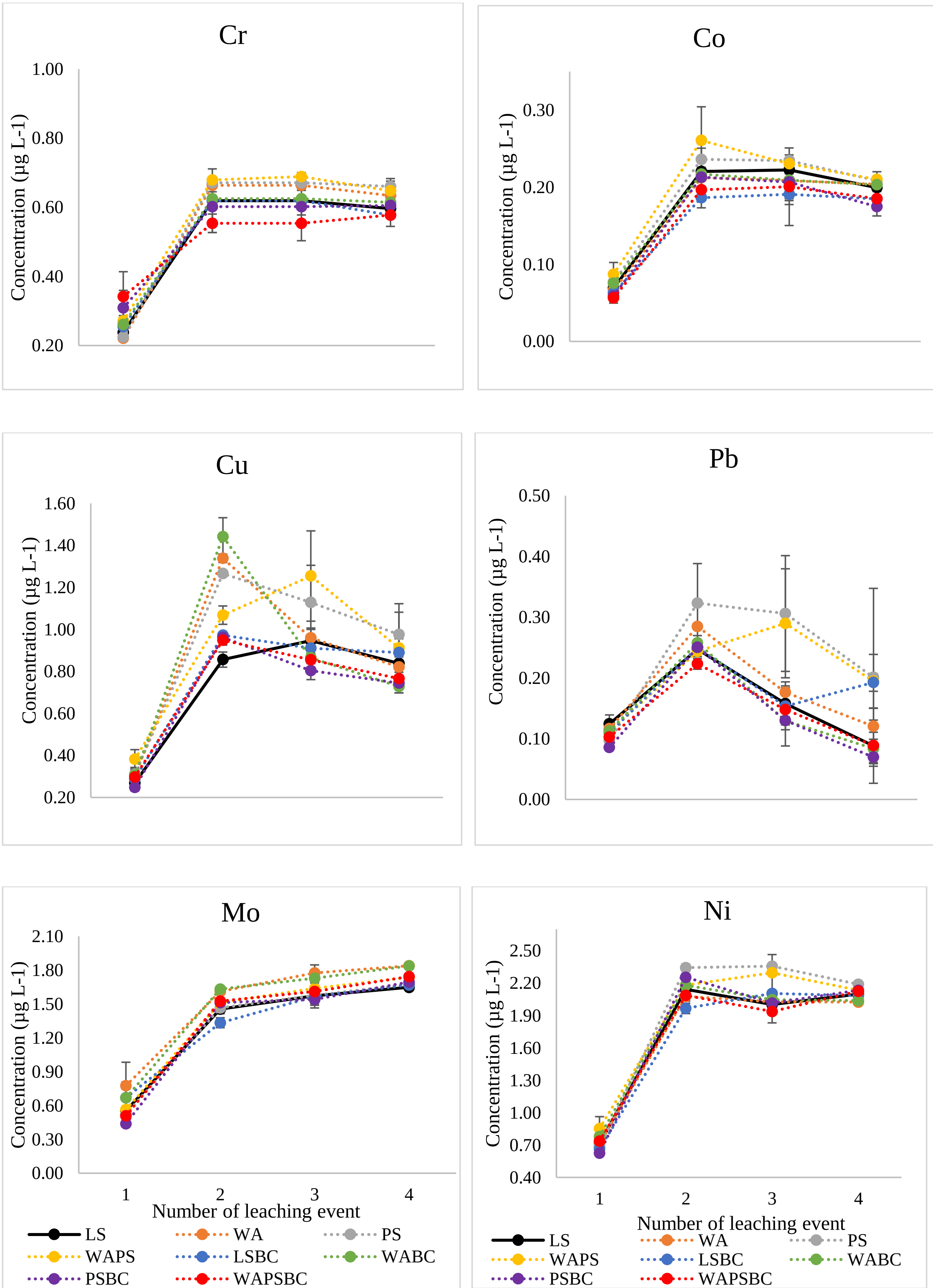

Cr
Concentration (µg L-1)
1.00
0.80
0.60
0.40
0.20
Co
Concentration (µg L-1)
0.30
0.20
0.10
0.00
Cu
Concentration (µg L-1)
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
Pb
Concentration (µg L-1)
0.50
0.40
0.30
0.20
0.10
0.00
Mo
Concentration (µg L-1)
2.10
1.80
1.50
1.20
0.90
0.60
0.30
0.00
1
2
3
4
Number of leaching event
LS
WA
PS
WAPS
LSBC
WABC
PSBC
WAPSBC
Ni
Concentration (µg L-1)
2.50
2.20
1.90
1.60
1.30
1.00
0.70
0.40
1
2
3
4
Number of leaching event
LS
WA
PS
WAPS
LSBC
WABC
PSBC
WAPSBC

Figure 3.4: Variation of heavy metals concentration during different leaching events conducted on podzolic soil. **Abbreviations:** LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar.

3.3.7 Summary of heavy metals in leachate and their comparison with different water quality guidelines

According to the observed results, BC addition enhanced the heavy metals retention within the soil profile during different leaching events. The accumulative concentrations of all heavy metals in the leachate collected from the BC amended treatments were lower than treatments without BC but only Cd, Co, Cu, Pb, and Ni were significantly lower (Table 3.8). The total leached heavy metal concentration was compared with different water quality guidelines developed by CCME e.g., Canadian Drinking Water Quality Guidelines, and Water Quality Guidelines for the Protection of Agriculture (Irrigation and livestock, CCME-1997, accessed on 17-02-2021). In our experiment, the total leached concentration of each heavy metal was recorded below the quality standards for drinking water and quality limits for the protection of agriculture production (Table 3.8), thereby suggesting that heavy metals leaching from the WA and PS amended soil used in this study is unlikely to cause contamination to ground water.

Table 3.8: Total concentration of leached heavy metals in the leachates of the treatments evaluated in this study in comparison with different water quality guidelines developed by CCME-1997

Treatment	Heavy metals concentration (μg L^{-1})							
	As	**Cd**	**Cr**	**Co**	**Cu**	**Pb**	**Mo**	**Ni**
LS	4.51	3.55	2.04	0.71	2.91	0.67	5.22	6.95
WA	4.59	3.70	2.20	0.69	3.42	0.69	5.99	6.84

PS	4.63	3.62	2.25	0.75	3.68	0.98	5.23	7.57
WAPS	4.57	3.45	2.27	0.78	3.61	0.83	5.42	7.46
LSBC	4.41	3.20	2.07	0.62	3.06	0.70	5.23	6.82
WABC	4.53	3.59	2.19	0.70	3.34	0.53	5.86	7.04
PSBC	4.44	3.26	2.16	0.65	2.75	0.50	5.18	7.03
WAPSBC	4.41	3.34	2.09	0.63	3.61	0.51	5.38	6.88
	Water Quality guidelines (μg L^{-1})							
	As	**Cd**	**Cr**	**Co**	**Cu**	**Pb**	**Mo**	**Ni**
Irrigation	100	5.1	8	50	-	200	-	200
Livestock	25	80	50	1000	-	100	500	1000
Drinking water	10	5	50	-	1000	10	-	-

Abbreviations: LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar

3.3.8 Heavy metals leaching percentage

Overall, the leaching experiment showed that total leached heavy metals concentrations were very low compared to total initial amount of heavy metals in all treatments. It may be due to insignificant leaching of heavy metals from soil columns (Table 3.9). According to the results different heavy metals have varying transformation and immobilization rates. In this experiment it was found that Cd and Mo have higher leaching percentage among all measured heavy metals. Since total concentrations of heavy metals in soils are poor indicators for the risk of ground water pollution, leaching percentage are significant criterions for the assessment of leaching ability of contaminated soils. In leaching column experiments, it was observed that different treatments have varying leached percentage of a heavy metals which mainly depends upon the type of amendment and their application rates (Table 3.9).

Table 3.9: Total heavy metals leaching percentage

Treatment	Matrix	As	Cd	Cr	Co	Cu	Pb	Mo	Ni
	Initial	5.8	0.054	34	7.1	10	7.3	0.22	15
LS	**Leachate**	0.0451±0.01	0.0035±0.08	0.0020±0.14	0.0007±0.01	0.0091±0.24	0.0006±0.09	0.0052±0.18	0.0069±0.20
	Leaching %	0.770	6.480	0.006	0.01	0.091	0.009	2.37	0.04
	Initial	7.0	0.075	34	7.5	12	7.6	0.38	16
WA	**Leachate**	0.0045±0.07	0.0037±0.07	0.0022±0.01	0.0006±0.03	0.0034±0.15	0.0069±0.13	0.0059±0.30	0.0068±0.10
	Leaching %	0.060	4.930	0.006	0.009	0.020	0.090	1.55	0.042
	Initial	7.2	0.14	35	7.3	12	8.1	0.26	16
PS	**Leachate**	0.0046±0.12	0.0036±0.09	0.0022±0.02	0.00075±0.03	0.0036±0.48	0.00098±0.11	0.0052±0.13	0.0075±0.33
	Leaching %	0.063	2.571	0.006	0.102	0.030	0.012	2.00	0.046
	Initial	7.8	0.083	36	7.3	12	7.6	0.26	16
WAPS	**Leachate**	0.0045±0.14	0.0034±0.11	0.0022±0.05	0.0007±0.08	0.0036±0.13	0.0008±0.08	0.0054±0.12	0.0074±0.13
	Leaching %	0.057	4.096	0.006	0.009	0.030	0.010	2.076	0.046
	Initial	6.9	0.071	33	7.5	11	7.4	0.25	16
LSBC	**Leachate**	0.0044±0.05	0.0032±0.25	0.0020±0.08	0.0006±0.01	0.0030±0.14	0.0007±0.06	0.0052±0.44	0.0068±0.07
	Leaching %	0.063	4.507	0.006	0.008	0.027	0.094	2.080	0.0425
	Initial	6.6	0.071	35	7.3	12	7.5	0.29	15
WABC	**Leachate**	0.0045±0.02	0.0035±0.12	0.0021±0.03	0.0007±0.02	0.0033±0.41	0.0005±0.05	0.0058±0.26	0.0070±0.12
	Leaching %	0.068	4.929	0.006	0.001	0.027	0.007	2.00	0.047
	Initial	6.8	0.13	32	7.1	12	7.7	0.38	15
PSBC	**Leachate**	0.0044±0.05	0.0032±0.11	0.0021±0.11	0.00065±0.06	0.0027±0.39	0.0005±0.12	0.0051±0.15	0.0070±0.23
	Leaching %	0.064	2.461	0.006	0.010	0.022	0.065	1.342	0.047
	Initial	7.4	0.10	37	7.4	12	7.7	0.19	16
WAPSBC	**Leachate**	0.0044±0.12	0.0033±0.11	0.0020±0.03	0.0006±0.04	0.0036±0.23	0.0005±0.20	0.0053±0.08	0.0068±0.20
	Leaching %	0.060	3.300	0.005	0.008	0.0003	0.006	2.790	0.042

Abbreviations: LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar. **Note:** Initial (Before experiment) values are given in mg kg^{-1} and leachates in mg L^{-1}. Leachate values are given as Mean±S.E

3.3.9 Simulated hydraulic properties

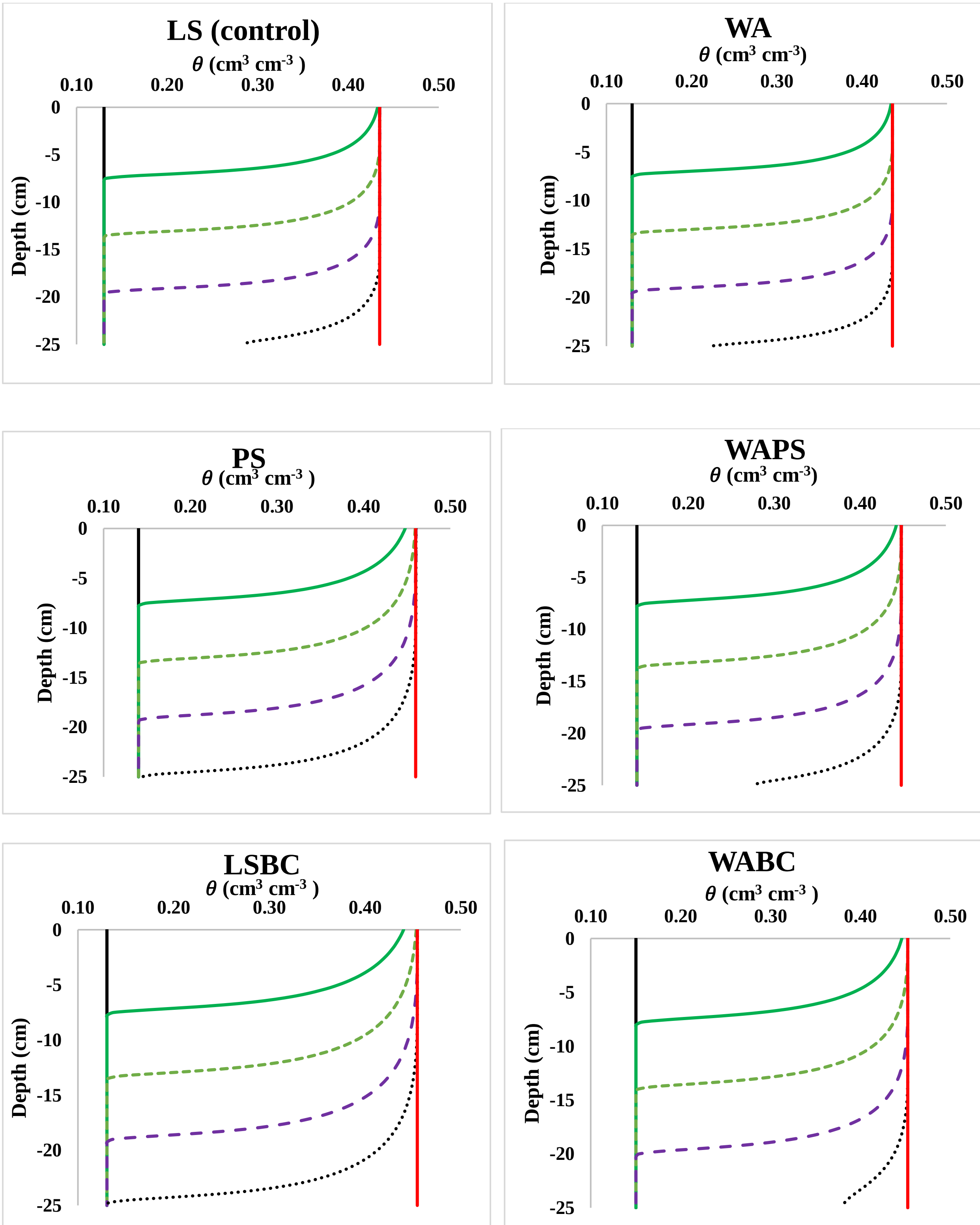
Simulated moisture contents

The Hydrus-1D model used to simulate the VMC for 4 h for leaching columns (25 cm) of different treatments are shown in Figure 3.5. The simulated results showed application of WA, PS and BC to podzolic soil significantly increased the VMC from 0-25 cm depth with a constant flux of 3.66 cm h^{-1}. The maximum simulated VMC observed in PS + BC treatment (0.49 cm^{-3} cm^{-3}), was 14% greater than control (lime) and WA had the lowest simulated VMC which found to be similar with lime (Table 3.10).

Table 3.10: Simulated moisture contents

Treatments	VMC (cm^{-3} cm^{-3})	Saturation time (h)	% Increase in VMC than LS
LS	0.43	2.08	
WA	0.43	2.09	0
PS	0.46	2.20	7
WAPS	0.44	2.10	2
LSBC	0.45	2.22	5
WABC	0.45	2.07	5
PSBC	0.49	2.63	14
WAPSBC	0.46	2.30	7

Abbreviations: VMC–Volumetric moisture contents; LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar.


LS (control)
θ (cm3 cm-3)
0.10
0.20
0.30
0.40
0.50
0
-5
-10
-15
-20
-25
Depth (cm)
WA
θ (cm3 cm-3)
PS
θ (cm3 cm-3)
WAPS
θ (cm3 cm-3)
LSBC
θ (cm3 cm-3)
WABC
θ (cm3 cm-3)

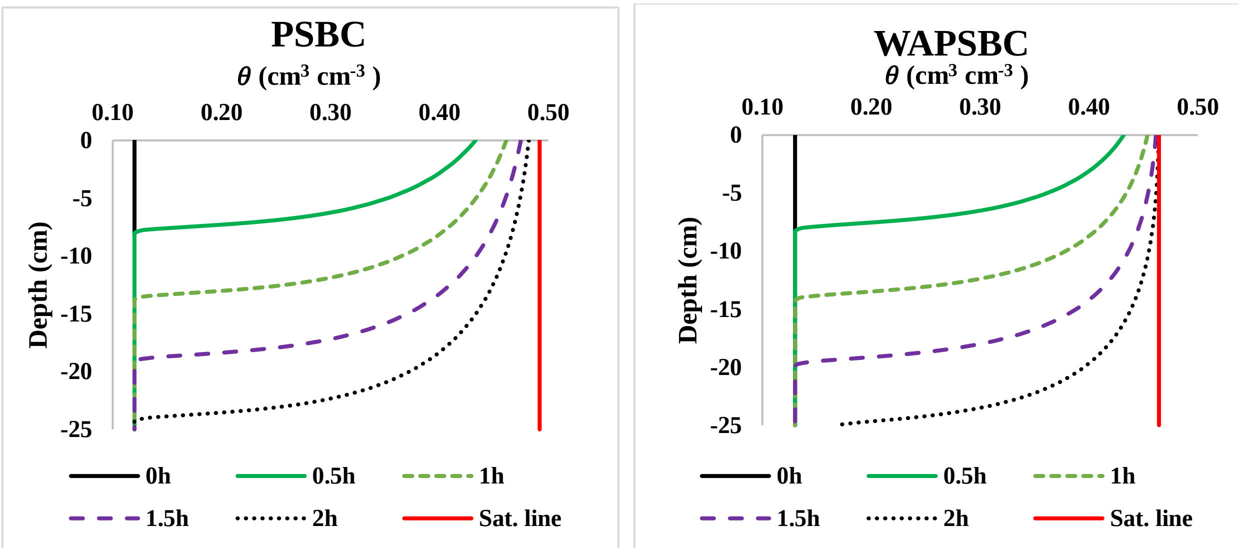


Figure 3.5: Effect of paper mill wastes and biochar on variability of simulated volumetric moisture contents (θ) at different depths within the leaching column at different time intervals. **Abbreviations:** LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar.

Effect of PMW and biochar on time to start leachate and its validation

The PMW effect was significant ($p<0.05$) but BC addition had no effect ($p=0.180$) on time to start leachate from bottom of columns (Figure 3.6). PS from PMW showed highest time to obtain leachate and BC addition increased the leachate collection time compared to treatments without BC. The PMW and BC interaction did not show significant ($p=0.1805$) effect on leaching time (Figure 3.7). The simulated time to start leachate collection and measured time to obtain leachate from the leaching column experiment was almost same. The maximum difference between measured and simulated time to start leachate was observed at 0.2 h in WA + PS treatment. All the treatments have very low RMSE and RE % values which shows higher accuracy of simulated values (Table 3.11)

Table 3.11: Hydrus-1D validation of time to start of leachate

Treatment	RMSE (h)	RE (%)
LS	0.03	-0.7
WA	0.04	-1.0
PS	0.07	-1.9
WAPS	0.07	-1.9
LSBC	0.05	-1.4
WABC	0.04	-1.0
PSBC	0.05	-1.1
WAPSBC	0.05	-1.4

Abbreviations: LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar; RMSE–Root mean square error values; RE–Relative error.

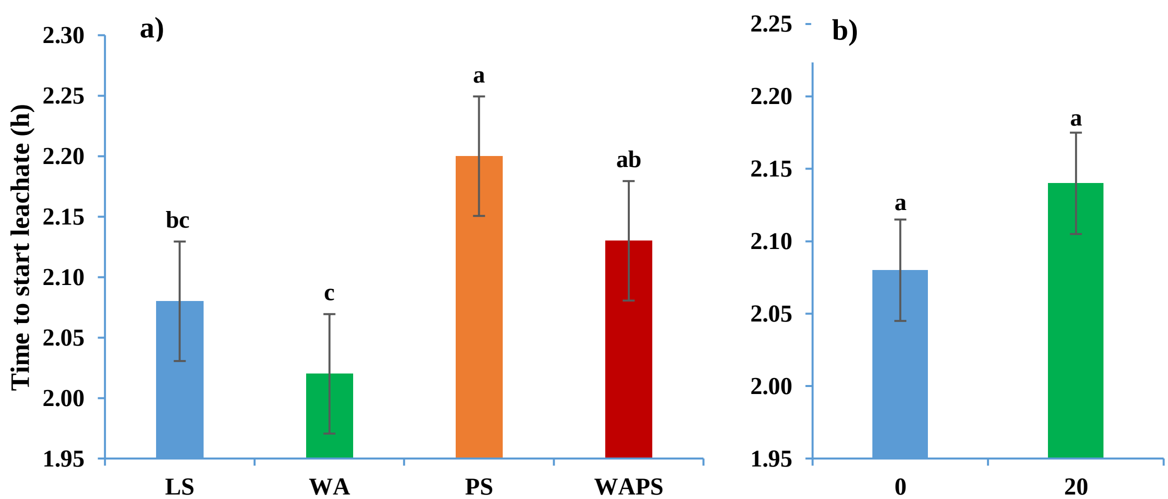


Figure 3.6: Effect of paper mill wastes (a) and biochar (b) on time to start leachate.

Abbreviations: LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge

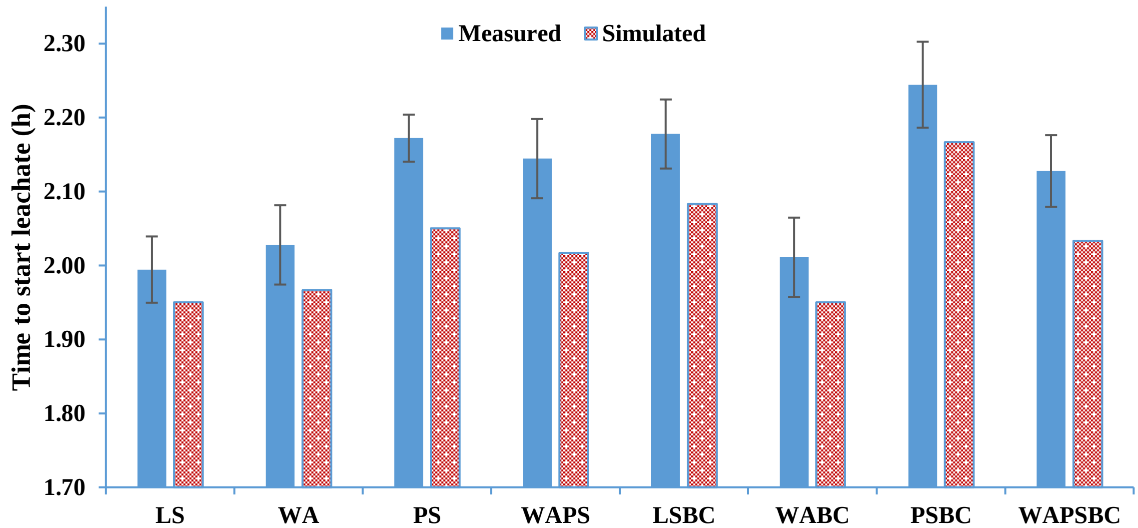
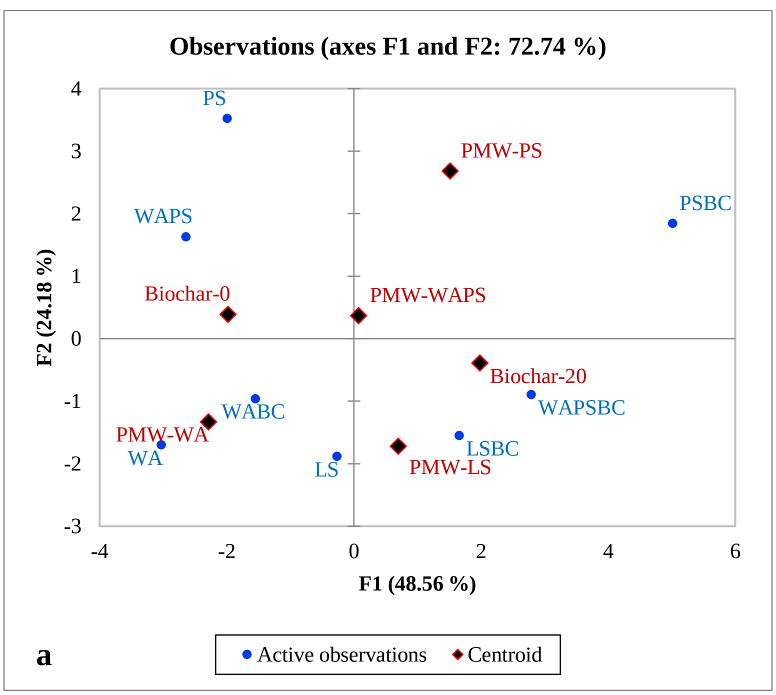


Figure 3.7: Paper mill wastes and biochar interaction effect on time to start leachate. **Abbreviations:** LS–lime; WA–Wood ash; PS–Paper sludge; WAPS–Wood ash + Paper sludge; LSBC–Lime + Biochar; WABC–Wood ash + Biochar; PSBC–Paper sludge + Biochar; WAPSBC–Wood ash + Paper sludge + Biochar

3.3.10 Relationship between measured physicochemical properties and different heavy metals and their association with paper mill wastes (PMW) and biochar

Principal component analysis (PCA) explained the association between PMW, BC physicochemical properties, heavy metals leached from soil columns (Figure 3.8a, b). The PCA explained 72.74% of the overall variability in dataset with component 1 explaining 48.56 % and component 2 explaining 24.18% of the total data variability. In observation graph (Figure 3.8a) centroids showed as factors (PMW and BC) at their different levels along different PCA components. I observed physicochemical properties and heavy metals clustered in different quadrants of the PCA biplot clearly showing the impacts of WA, PS and BC application on heavy metals leaching and measured physicochemical properties of amended podzolic soil. The measured physicochemical properties were highly correlated with PS + BC treatment in the 1st quadrant (Figure 3.8b) with clear separation from other treatments, where it has strong effect on soil hydrological properties (saturation, FC and PAW). The treatments without BC showed a higher concentration of heavy metals in leachate compared to amended treatments. In the 4th quadrant of PCA biplot the PS and WA + PS showed a clear separation from other treatments by forming a cluster with the following heavy metals (As, Ni, Cr, Co, Pb and Cu). It was observed that in the 3rd quadrant lime, WA and WA + BC were highly correlated with bulk density, pH, CEC, Cd and Mo. Application of PMW and BC significantly increased the total porosity, FC and PAW, and decreased the bulk density of amended soil. A positive association of different combinations with measured physicochemical properties and heavy metals were observed (Figure 3.8b). Further relationship was confirmed by Pearson correlation analysis between different physicochemical properties and heavy metals (Table 3.12).



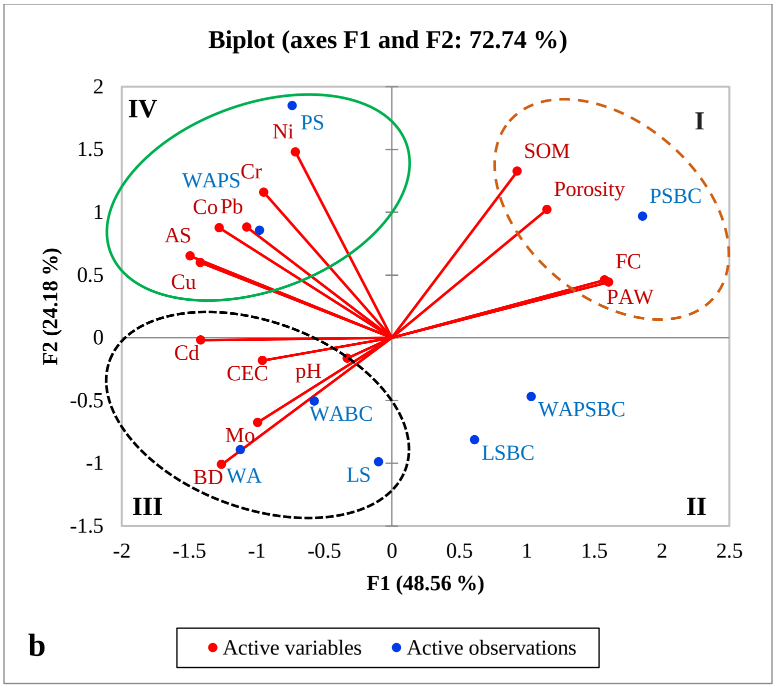


Figure 3.8: Principal component analysis (PCA) showing the segregation of the amendment combinations with the physiochemical properties and heavy metal leached from amended podzolic soil; a–observations and b–biplot showing the association of PMW and biochar with physicochemical properties and heavy metals leached from amended podzolic soil.

3.3.11 Pearson's correlation between different physicochemical properties and heavy metals.

Most of heavy metals had no significant relationship with each other except As, Cr and Ni. Whereas As concentration has positive correlation with Cd, Cr, Co, Cu and Pb, and Cr has positive correlation with Ni, Co and Cu while Ni has positive correlation with Co and Pb (Table 3.12). The FC and PAW of amended soil showed non-significant relationship with measured heavy metals. Total porosity has positive correlation with FC, PAW and SOM, however both were negatively correlated with bulk density. The pH and CEC of the amended soil showed no significant relationship with all heavy metals except Mo, though both were positively correlated with each other (Table 3.12).

Table 3.12: Pearson's correlation coefficients showing the relationship between different physicochemical properties and heavy metals leached from amended podzolic soil

Variables	AS	Cd	Cr	Co	Cu	Pb	Mo	Ni	Porosity	FC	PAW	pH	CEC	SOM
Cd	0.86**													
Cr	0.72*	0.43^{Ns}												
Co	0.85**	0.61^{Ns}	0.71*											
Cu	0.77*	0.50^{Ns}	0.73*	0.67^{Ns}										
Pb	0.72*	0.37^{Ns}	0.50^{Ns}	0.69^{Ns}	0.79*									
Mo	0.38^{Ns}	0.61^{Ns}	0.35^{Ns}	0.11^{Ns}	0.34^{Ns}	-0.17^{Ns}								
Ni	0.65^{Ns}	0.28^{Ns}	0.74*	0.84**	0.62^{Ns}	0.73*	-0.23^{Ns}							
Porosity	-0.36^{Ns}	-0.47^{Ns}	0.18^{Ns}	-0.25^{Ns}	-0.36^{Ns}	-0.31^{Ns}	-0.34^{Ns}	0.18^{Ns}						
FC	-0.70^{Ns}	-0.72*	-0.28^{Ns}	-0.57^{Ns}	-0.72*	-0.52^{Ns}	-0.54^{Ns}	-0.19^{Ns}	0.85*					
PAW	-0.68^{Ns}	-0.72*	-0.21^{Ns}	-0.53^{Ns}	-0.71*	-0.56^{Ns}	-0.48^{Ns}	-0.18^{Ns}	0.85*	0.987***				
pH	0.04^{Ns}	0.185^{Ns}	0.41^{Ns}	-0.03^{Ns}	0.18^{Ns}	-0.32^{Ns}	0.73*	-0.09^{Ns}	0.21^{Ns}	-0.06^{Ns}	-0.03^{Ns}			
CEC	0.39^{Ns}	0.54^{Ns}	0.53^{Ns}	0.24^{Ns}	0.44^{Ns}	-0.04^{Ns}	0.86*	0.05^{Ns}	-0.09^{Ns}	-0.42^{Ns}	-0.40^{Ns}	0.91*		
SOM	-0.12^{Ns}	-0.31^{Ns}	0.23^{Ns}	-0.09^{Ns}	-0.20^{Ns}	0.01^{Ns}	-0.51^{Ns}	0.38^{Ns}	0.89*	0.73*	0.71*	-0.10^{Ns}	-0.29^{Ns}	
BD	0.42^{Ns}	0.59^{Ns}	-0.11^{Ns}	0.32^{Ns}	0.36^{Ns}	0.29^{Ns}	0.45^{Ns}	-0.15^{Ns}	-0.96***	-0.86*	-0.88*	-0.04^{Ns}	0.27^{Ns}	-0.902*

Abbreviations: As–Arsenic; Cd–Cadmium; Cr–Chromium; Co–Cobalt; Cu–Copper; Pb–Molybdenum; Ni–Nickel; FC–Field capacity; PAW–Plant available water; CEC–Cation exchange capacity; SOM–Soil organic matter; BD–Bulk density. **Note:** All the bold values showing significant relation (*** Significant at $p < 0.001$, ** Significant at $p < 0.01$, *Significant at $p < 0.05$, NS= Non–Significant).

3.4 Discussion

This experiment helped to determine the optimum application rates of wood ash, paper sludge and biochar during field application to enhance the physicochemical properties and reduce the heavy metals leaching potential of amended podzolic soil. Wood ash amended treatments showed higher effect to increase the pH and EC followed by paper sludge and then lime. Biochar addition enhanced the pH and EC significantly compared to non-amended biochar treatments. Cherian and Siddiqua (2019) reported that pulp and paper mill wood ash has the potential to increase the pH of amended soil due to its buffering capacity. Higher amounts of calcium carbonates, hydroxides and other calcium comprising minerals were attributed to this effect (Scheepers and Du Toit, 2016; Moilanen and Issakainen, 2000). A significant number of oxides, carbonates, hydroxides and silicates are present in boiler wood ash which is responsible for the induced liming effect on forest land (Moilanen and Issakainen, 2000). These compounds present in wood ash undergo a series of chemical reaction where it reacts with water molecules and segregate to generate OH^-, HCO_3^- Ca^{2+}, K^+ and Na^+ ions. The OH^- or HCO_3^- nutralize the H^+ and increase the OH^- in soil system which increase the soil pH (Cherian and Siddiqua, 2019). These results are in line with the findings of Bang-Andreasen et al., (2017) who conducted experiments with varying wood ash application rates (0-167 Mg ha^{-1}) and concluded that wood ash application increased the pH and EC of amended podzolic soil compared to control.

In an incubation study, loamy sand soil was amended with wood ash and commercial limestone on CCE basis and results showed that pH of amended soil was higher than the values reported from agricultural lime treatment (Muse and Mitchel, 1995). Wood ash application rate has positive correlation with pH and EC. The change in pH and EC are also responsible for the soil nutrients bioavailability because of pH dependent soil chemical equilibria (Demeyer et al., 2001). Wood ash is highly reactive and have potential to alter several physicochemical properties of forest soils (Karltun et al., 2008; Saarsalmi et al., 2007). Therefore wood ash addition leads to increase in pH, EC and the concentration of different nutrient elements such as K, S, B, Mg, CA, Si and P (Pitman, 2006; Augusto et al., 2008). Biochar addition as a factor improved the pH and EC of amended soil, similar findings for biochar effect was reported by Saha et al., (2020) and Jien & Wang (2013). Paper sludge alone and with combination of biochar increased the pH by 0.4 units and increased the EC by 0.16 units alone and 0.15 unit as combination compared to lime due to its higher CCE, high pH and higher interaction of minerals with soil particles (Table 3.5a). These results are in line with findings of Torkashvand et al. (2010) amended acidic soil with kraft paper mill sludge at 0, 0.5,1, 2 and 4% (weight basis) and conducted several lab experiments on sorghum vulgaris and observed that paper mill sludge increased the pH of the amended soil due to its high CCE (58.4%) and high pH (13.2). Furthermore, the authors reported that the increase in pH was directly proportional to the application rate which accurred concomitant with an increase in the EC compared to the control treatment. Soil amelioration with paper mill sludge was found to be an effective way to utilize this waste to enhance the physicochemical properties of agricultural and forest lands (Torkashvand et al., 2010; Foley and Cooperband, 2002).

The PMW showed the significant effect on CEC of amended soil while biochar addition did not show any significant difference from biochar unamended treatments. Where WA and WAPS have higher CEC values compared to lime and paper sludge because of wood ash has higher ratio of exchangeable bases (Table 3.5a). These results were supported by the findings of Gomez-Rey et al. (2012), who reported that wood ash from eucalyptus bark used in pulp and paper mill have higher exchangeable bases (Ca, Mg and K) which significantly increased the CEC (0.69–1.43 cmol kg^{-1}) compared to unamended topsoil. The CEC of soil is correlated with SOM and texture

(Gomez-Rey et al., 2012). In this experiment wood ash did not show significant difference between control in regard to increasing the SOM, but paper sludge and biochar significantly enhanced the SOM of amended soil compared to lime. Increase in SOM of amended soil depend upon composition and application rate of paper sludge. Higher application rates of paper sludge have a strong effect on SOM while application in smaller amounts may be detectable for years (Camberato et al., 2006). Chantigny et al. (2000) conducted field trials following application of paper sludge and noticed that soil organic matter increased in silty clay loam and loam soil up to 15 cm depth at 100 Mg ha^{-1} and the observed effect was still significant 3 years after of application. In addition, application of paper sludge increased the SOM by 10 g kg^{-1} at 18 Mg ha^{-1} in two years of application. Similarly, increase in SOM was observed at 16 Mg ha^{-1} during the application season of paper sludge (Simard et al., 1998). Wood ash, paper sludge and biochar used in this experiment have bulk density <1 g cm^{-3}. Wood ash did not show significant difference from control (lime). The wood ash application rate was very low, and it has higher bulk density, thus it did not significantly reduce the bulk density. Paper sludge and biochar used in this experiment have light weight and porous structure. Infact, primary sludge applied at 160 Mg ha^{-1} significantly decreased the bulk density of loam soil from 1.21 g cm^{-3} to 1.01 g cm^{-3}, and the improved bulk density was observed to occur committant with improved total porosity and hydraulic conductivity (Chow et al., 2003). The study by Saha et al. (2020) and Wanniarachchi et al. (2019) found when they mixed granular biochar with sandy soil it significantly reduced the bulk density and improved the total porosity. In our study, PMW and biochar significantly increased the total porosity, VMC at FC and total PAW (Table 3.5a). Wood ash did not have any effect on total porosity and PAW in our study, although the FC decreased compared to the control. Paper sludge combined with biochar gave the highest total porosity, FC and PAW. Both factors PMW and biochar significantly changed the shape of SWRCs. The developed SWRCs showed the ability of wood ash, paper sludge and biochar to increase the VMC at FC and PAW. Work done by Moragues-Saitua et al. (2017) on *Pinus radiata* where wood ash applied at 4.5 Mg ha^{-1} revealed that after 15 months there was no significant difference between wood ash amended plots and control with respect to mean pore diameter and total porosity of loamy texture soil. Wood ash decreased the mesoporosity, mean pore diameter and effected the total porosity of amended plots and their SWRCs (Moragues-Saitua et al., 2017). Wood ash after fifteen months led to reduction in slope of SWRC and decreased the WHC of amended soil. Total PAW always depends upon organic matter, pore sizes, soil structure and aggregate stability. In this study paper sludge application increased the VMC at FC and PAW compared to wood ash, lime and biochar. Increase in VMC may be due to decrease in bulk density, because low bulk density often enhances the macro porosity at the cost of micr o porosity (Amini and Naeini 2013). Water retention of paper sludge amended soil increased due to incorporation of paper sludge at high rates and increased total porosity due to paper sludge fibers positioned between soil particles. The organic matter content absorbs and holds high amount of VMC at soil water tension less than 1500 kPa (Amini and Naeini 2013). The study findings here were similar to results reported by Zhang et al. (1993), where they amended sandy texture soil with paper sludge at 246 Mg ha^{-1} and observed increase in VMC by 20 and 74% at -33kPa and -1500 kPa respectively. Trépanier et al. (1996) reported that paper sludge has WHC 0.36 cm^3 cm^{-3} and 0.26 cm^3 cm^{-3} at -33 kPa and -1500 kPa pressure respectively, which was found to be greater than that of most mineral soils. Hence most mineral soils ameliorated with paper sludge have higher WHC. Increase in total PAW has more significant effect FC to influence the crop growth. The magnitude of decrease in bulk density and increase in WHC and soil aggregation in fine sandy loam soil depend upon the rate and frequency or application interval of paper sludge (Zibilske et al., 2000).

In this study, paper sludge treatments significantly increased VMC at FC level but the PWP was similar in lime and wood ash treatments. These results were supported by Foley and Cooperband (2002) findings where, they conducted some vegetable rotation experiment on loamy sand with the application of solid paper mill wastes and observed the VMC increased at -33 kPa and there was no significant effect at 1500 kPa. Though after second application they observed paper mill residue treatments retained VMC 16 to 45% greater than control and the percentage of VMC at -1500 kPa was 2 to 50% greater in amended plots compared to control.

The leaching column study was done to investigate the leaching potential of different heavy metals from podzolic soil amended with wood ash, paper sludge and biochar. The soil was collected from an uncontaminated site a new agricultural converted field, which have naturally significant amount of different heavy metals. The biochar addition significantly reduced the concentration of different heavy metals (Cd, Co, Cu, Pb and Ni) in the leachate. There was no significant difference observed between biochar amended and unamended treatments for As, Cr and Mo, although the concentration of these heavy metals were lower in biochar amended treatments leachates compared to unamended treatments. The immobilization of these heavy metals might be due to rise in pH by enhancement of the metal's retention on the soil surface. The application of biochar with wood ash and paper sludge immobilizes the heavy metals and reduce its concentration in leachates. The As concentration varying in different soils, which is mostly influenced by parent material. In mineral soil, As concentration can range from 5 to 10 mg kg^{-1} (Abbas et al., 2018). Biochar decreased the concentration of As in the leachate, although the difference between biochar unamended treatment was not significant. Biochar have carbonized fractions (CO_3^{2-} and PO_4^{3-}) which can interact with soil contaminants to reduce their bioavailability. Especially, the level of O-containing carboxyl, hydroxyl, and phenolic functional groups in biochar have strong effect to bind the soil contaminants (Uchimiya et al., 2011).

The biochar addition significantly affected the heavy metals concentration in leachates by reducing the total leachate volumes because of increase in water retention in soil columns. Higher WHC of biochar relative to other organic materials correlate with higher surface area and higher micropore volume (Uchimiya et al., 2010b; Ashiq et al. 2020). These numerous characteristics of biochar showed its potential as an environment sorbent for contaminants in soil and water (Maheswaran, 2019). The pH changes have strong effect on immobilization of different heavy metals, as the PMW and biochar has strong liming effect which can promote the mobilization of oxyanions and immobilization of different heavy metals (Almaroai et al., 2013). Li et al, (2016) observed that Cd is a divalent cation, and its sorption behavior is same with Pb, which depends on the types of feedstocks and pyrolysis process. Increasing pH can affect the precipitation of Cd and Pb (Almaroai et al., 2013). The minimum pH ranges is from 8.8-9.8 and 6.1-9.1 for Cd and Pb hydroxides precipitation respectively from soil system (Maheswaran, 2019). However, the pH range for the soil used in leaching experiments was 6.0-6.5 (Table 3.5b). Li et al., (2017) reported that non-electrostatic mechanisms are dominant factor for Pb sorption in soil system. The Cr leaching highly depended on dissolution of Cr carrying oxide and hydroxide. Its solubility highly controlled by Cr_2O_3 and $Cr(OH)_3$ (Komonweeraket et al., 2015). Biochar application to mineral soil can reduce the leaching potential of Cr through redox reaction with metals. Application of biochar prepared from chicken manure and applied to chromate contaminated soil reduced the mobility of Cr (VI) by converting into Cr (III), thus decreased the leaching of Cr from amended soil (Choppala et al., 2015). The decrease in Cr concentration in leachate was attributed to adsorption on cation exchange sites and precipitation in form of $Cr(OH)_3$ in resultant of reduction process of Cr(VI) by releasing the OH^- ion (Choppala et al., 2015). The variation of heavy metals leaching throughout the leaching events are shown in Figure 3.3. Where different heavy metals have different leaching behavior. For most heavy metals, paper sludge + biochar and wood ash + paper sludge + biochar treatments had the lower concentrations of heavy metals among all the amended treatments. The PMW did not show significant difference in Co and Cu concentration in leachate, although biochar addition significantly reduced their concentration during different leaching events. Oxidation-reduction reactions and acid-base properties of the heavy metals always affect their mobility in soil profile. Sometime Cd, Cu and Cr move through the soil pore water (Hayyat et al., 2016). Biochar produced from crop straws have more developed pores compare to wood char, since wood char has more lignin contents (Hayyat et al., 2016). Uchimiya et al., (2010a) conducted some experiments on immobilization of Cu, Cd, Pb and Ni and reported that litter derived biochar significantly adsorbs Cu, Cd, Pb and Ni and deceptive that tendency of the exclusion order was Ni < Cd < Cu < Pb.

A study conducted by Zhou et al. (2013) concluded that Cd and Pb adsorption on biochar was highly influenced by its pore structure, while its functional group was also effective to remove the Cu from contaminated site. During different leaching events the concentration of heavy metals was higher in biochar unamended treatments compared to treatments having biochar. These findings are consistent with the results of Maheswaran (2019), where he conducted the leaching column experiment on paper mill wood ash amended sandy soil and observed biochar had significant effect in reducing the heavy metals concentration in the leachate. Low pH is associated with heavy metals leaching from wood ash, dissolution of metal bearing minerals increased under acidic conditions (Rao et al., 2007). A field experiment was conducted to assess the fertilization effect of wood ash at 1, 2.5 and 5 Mg ha^{-1} on Scots pine (*Pinus sylvestris* L.) and leachates were collected by using the lysimeters at 20 cm depth to measure the leaching concentration of Cd, Cr, Cu and Pb. The leached concentration of Cd, Cr, Cu and Pb for all treatments were below the detection limit of the equipment. Strong increase in pH ensured that these heavy metals were retained in the humus layer in immobilized form, later which can be leached into surface or ground water. In this experiment, it was observed that leached heavy metals concentrations were quite low in comparison to the quality limits developed by CCME for irrigation water, livestock purpose and drinking water.

In this study wood ash, paper sludge and biochar significantly affected simulated VMC at saturation level. Application of PMW significantly influenced the time to leachate and biochar addition further increased the time to leachate but was not significant. The study results showed here strong agreements between Hydrus-1D simulated and measured leaching time. Saha (2020) conducted lab experiments to check nitrogen transport in biochar amended sandy loam podzolic soil and noticed that Hydrus-1D simulated values for time to leachate were close to experimental values. However, variability in hydrological process was observed by Altdorff et al. (2019), where the flux rate significantly decreased with increase in biochar rate. Different researchers have reported that Hydrus-1D simulated values were effective and reasonable to measure the solute transport (Mo'allim et al., 2018). The Hydrus-1D model was found as an effective tool to estimate the water flow for rainfed conditions for different amount of precipitation and evaporation conditions (Iqbal et al., 2020). A high coefficient of determination (R^2) and very low RMSE and RE % was observed between measured and simulated time to leachate consistent with the findings of Pal et al. (2014) and Negm et al. (2017). This suggest simulation of hydrological processes to be accurate and that this model can be used to predict the water flow in various soils amended with different organic amendments (Saha, 2020; Negm et al., 2017). A long-term assessment of hydrological properties and their simulation exercise by Hydrus 1-D will give us more conclusive output about wood ash, paper sludge and biochar use in boreal ecosystem. In general, the study findings suggest that wood ash, paper sludge and biochar have the potential to improve the physicochemical properties of podzolic soil and the biochar application at levels used in this study was effective to improve the physicochrmical properties and in reducing the heavy metals concentration in leachate from podzols. However, the assessment of leaching potential under field condition is needed under natural environmental conditions and different management practices to assess impacts of the utilization of wood ash and paper sludge. To get a complete picture of the role of biochar in reducing the mobilization of heavy metals; there is a need to conduct long-term field experiments with various crops on different soils.

The way forward:

- Need to develop application guidelines for wood ash and paper sludge as soil amendment for agricultural and forest lands under provincial and territorial jurisdiction.
- Need to conduct field trials to check the effect of these amendments on crop growth and development.
- Further simulation of hydrological properties using the Hydrus-1D model would be helpful to develop suitable approach that could protect the environment from heavy metals contamination and other nutrients leaching by finalizing the application rates of different soil amendments.

3.5 Conclusion

The overall study findings indicated that wood ash (WA), paper sludge (PS) and biochar (BC) application to podzolic soil significantly affected the pH, EC, SOM, CEC, BD, total porosity, FC, PAW and heavy metals leaching. All the combinations have optimum pH (6.0s-6.5) for plant growth, where WA and PS had higher effects on increasing the pH and EC compared to lime. PS had higher effect on increasing hydrological properties compared to W and lime WA due to its fibrous structure and very low bulk density. BC addition significantly improved the physicochemical properties of amended soil. The treatment PS combined with BC was found to be the most effective treatment to improve the pH, EC, SOM, total porosity, FC and PAW with minimum bulk density among all treatments evaluated in this study. BC application has significant effect on reducing the concentration of Cd, Co, Cu, Pb and Ni in leachate from podzols. It also reduced the concentration of As, Cr and Mo in the leachate, but its effect was noted as not significant. A significant and positive correlation was observed between most of the hydrological properties and leached out heavy metals. For further investigation, microscopic studies need to be done with WA, PS and BCS effect on their structural properties and functional groups which have prominent role on heavy metals and nutrients adsorption and their mobilization in soil system.

Author Contributions

M.M.F.: Conceptualization, methodology, experiment, formal analysis, writing – original draft, writing – review and editing; M.C.: Funding, project administration, supervision, writing – review and editing; R.T.: Funding, writing – review and editing; M.N.: experiment, data analysis, writing – review and editing; Y.K.: experiment, writing – review and editing; B.J.: Data collection, writing – review and editing; I.M.: Data collection, writing – review and editing; L.G.: Supervision, conceptualization, methodology, writing – review and editing, funding.

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Chapter Four

General conclusions and recommendations

4.1 General discussion and conclusions

The objectives of the present study were:

I. to evaluate the effects of wood ash, paper sludge and biochar on the physicochemical properties of podzolic soil based potting media.

II. to find the suitable application rates for wood ash, paper sludge and biochar alone and their combinations, and to measure their effects as potential soil amendments on the physicochemical properties of podzolic soil.

III. to investigate the effects of biochar on heavy metals concentration of podzolic soil leachates and simulation of volumetric moisture contents (VMC) within the soil profile amended with wood ash, paper sludge and biochar using Hydrus-1D.

The above-mentioned objectives were achieved in two different experiments as detailed in chapter 2–study one (*The potential of developing soil-based potting media from wood ash, paper sludge and biochar*) and in chapter 3–study two (*Effects of wood ash, paper sludge and biochar amendment on physicochemical properties and heavy metals leaching of boreal podzolic soils*). Both experiments provided strong evidence, that wood ash, paper sludge and biochar can be used as potting media and potential soil amendment with extra precautions.

In study one different combinations of wood ash, paper sludge and biochar were prepared and add to podzolic soil (volume basis) and important physicochemical properties were tested to find the suitable combination as soil based potting media. In general, the results of study one provided strong evidence that wood ash and paper sludge alone and in combination with biochar had a significant effect on the physicochemical properties of podzolic soil-based potting media. Specifically, wood ash, paper sludge and biochar applications significantly increased the pH and electrical conductivity (EC) of the potting media. The growth media formulations amended with wood ash showed high pH (9.9 - 11.5) and EC (0.59 - 2.44 dS m^{-1}), though potting media amended with paper sludge alone and combined with biochar exhibited pH in the optimum range for plant growth (6.3 - 7.3) with an EC range of 0.16 - 0.86 dS m^{-1}. Wood ash quickly reacted with the soil and increased the media pH and EC due to its higher calcium carbonate equivalency (CCE) (10.4% dry), high pH (12.6) and EC (9.52). The combination of 25% wood ash + 75% soil did not show any significant effect on the organic matter (OM) percentage, though the addition of biochar to this treatment significantly increased the OM percentage compared to the control. Paper sludge alone and in combination with biochar significantly increased the OM of the potting media, where 50% of paper sludge + 25% biochar treatment showed the highest OM among all media treatments tested. The combination of wood ash and paper sludge alone and with biochar showed high total porosity, high VMC at field capacity (FC) and plant available water (PAW) with reduced bulk density compared to soil (control). Paper sludge at 50% volume with 25% biochar had higher FC (0.33 cm^3 cm^{-3}), PAW (0.40 cm^3 cm^{-3}) with the least bulk density (0.53 g cm^{-3}) and the optimum pH (7.2) and EC (0.92 dS m^{-1}). Of the tested combinations, this treatment is the best combination to prepare soil-based growth media. Both wood ash and paper sludge confirmed water repellent characteristics, where water drop penetration time was increased by increasing the volume of wood ash and paper sludge in tested combinations. However, all combinations were categorized as slightly water repellent due to lower water drop penetration time (1-60 s).

In study two, paper mill wastes (wood ash and paper sludge) and biochar were applied as soil amendment, and their effects were measured to determine improvements of the physicochemical properties of podzolic soil. A leaching column experiment was conducted to measure the effect of biochar on leaching potential of different heavy metals {Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Cobalt (Co) and Nickel (Ni)} in Newfoundland and Labrador (NL) amended podzolic soil. The experiment measured the effects of wood ash, paper sludge and biochar on one dimensional water flow in amended podzolic soil and predicted the VMC from a depth of 0-25cm using the Hydrus-1D model. We observed all the treatments exhibited pH in optimum range (6.0-6.5), though wood ash amended treatments showed higher pH and EC followed by paper sludge and lime because of its higher pH, CCE and EC. Biochar addition significantly enhanced the pH (by 1.61%) and EC (by 6.66%) of amended podzolic soil compared to treatments without biochar. Paper sludge showed great potential for increasing the physicochemical properties of amended podzolic soil because of its high pH (8.2), fibrous structure, high OM (39.90%) and lower bulk density (0.12 g cm^{-3}). The paper sludge + biochar treatment attained the highest total porosity (0.68 cm^3 cm^{-3}), the highest VMC at FC (0.36 cm^3 cm^{-3}) and PAW (0.28 cm^3 cm^{-3}) with the lowest bulk density (1.07 g cm^{-3}) among all treatments. Biochar addition showed a significant effect in reducing the concentrations of Cd (by 1.95%), Co (by 10.95%), Cu (by 11.76%), Pb (by 30%) and Ni (by 3.75%) in the collected leachates. Besides that, biochar also decreased the concentration of As (by 2.83%), Cr (by 2.73%) and Mo (by 0.91%), but the difference was not significant compared to treatments without biochar. The paper mill waste and biochar interaction effect were significant in reducing the concentrations of Pb and Ni but not significant for As, Cd, Cr and Co in the collected leachate. Wood ash treatment showed the highest concentration of Cd and Mo, while paper sludge had the highest concentration of As, Cu and Pb, while wood ash + paper sludge had the highest concentration of Cr and Co in their collected leachates among all treatments. Total leached heavy metal concentrations for all treatments were lower than the water quality guidelines developed for irrigation, livestock and drinking by Canadian Council and Ministers of Environment (2005). These results, based on the laboratory leaching columns experiments, suggested that the heavy metals leaching from the wood ash and paper sludge-amended podzolic soil used in this study are unlikely to cause contamination in surface and ground water supplies Paper mill wastes had a significant effect on leaching time, where wood ash application decreased the leaching time, paper sludge and wood ash + paper sludge increased the leaching time, and biochar addition did not show any significant effect on leaching time. The leaching column experiment showed that paper sludge combined with biochar had the highest leaching time among all treatments as a result of higher water holding capacity (WHC). According to the Hydrus-1D simulation model, wood ash did not show a significant effect on VMC compared to lime, though paper sludge and biochar applications significantly increased the VMC of amended podzolic soil. The simulated values for time to start the leachate were close to experimental values with very low root mean square error and relative error percentage. This showed the precision of the Hydrus-1D to predict the hydrological properties of amended podzolic soil.

4.2 Significance of study findings

These findings could be useful in facilitating better understanding of the role of wood ash, paper sludge and biochar in improving the physicochemical properties and heavy metals immobilization within the root zone of podzolic soils in boreal environment. The information generated from the leaching column experiment could be helpful in determining application guidelines to facilitate the appropriate use of wood ash and paper sludge as soil amendments. Simulation of hydrological properties using the Hydrus-1D model, together with detailed laboratory or field studies, would be helpful in further understanding these processes under different treatment combinations. This information is necessary to protect the environment from heavy metal contamination and other nutrient leaching by deciding the application rates of different soil amendments. Moreover, the findings could also be useful as a decision-making tool in developing government policy for the application of paper mill wastes in agricultural practices. The use of these paper mill wastes in agriculture is not only advantageous for reducing its disposal at landfill sites, but it will also generate some revenue for the paper mills. These findings can provide a road map for further scientific investigation of wood ash, paper sludge and biochar effects on soil quality and subsequent crop growth under greenhouse and field conditions.

4.3 Recommendations

It needs to be pointed out that due to the limited scope of lab study, the conclusion might not be comprehensive and conclusive particularly when applied to field conditions in different climates. Therefore, there needs to be further investigation along with the underlying mechanisms.

Further studies must focus on:

- Comprehensive, multilocational field experiments on the effects of wood ash, paper sludge and biochar on the physicochemical properties of podzolic soil. This would help to analyse the sustainability of agricultural practices and the environment.
- Structural and particle size analyses are necessary to precisely compute the percentage of pore space altered through the application of wood ash, paper sludge and biochar.
- A comprehensive study on the morphological structure, surface area, functional groups, surface chemistry, and exchange sites for cations of the wood ash, paper sludge and biochar and heavy metals mobility under field conditions~~.~~
- The long-term ecotoxicological effects of wood ash, paper sludge and biochar (heavy metals, toxic polycyclic aromatic hydrocarbons and dioxins effects) need to be observed to confirm the ecological sustainability and long term soil health.

- The development of application guidelines for wood ash and paper sludge in the agriculture and forest industries in NL.
- A detailed simulation using the Hydrus modeling approach will help researchers understand further leaching processes at a field scale.

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Appendices

Publications and Presentations:

Abstracts:

Farhain, M., Cheema, M., Katanda, Y., Nadeem, M., Javed, B., Thomas, R., Galagedara, L. **(2021)**. Assessment of hydrological properties of soil-based growth media using wood ash, paper sludge and biochar. 5th CIGR International Conference 2021 on "Integrating Agriculture and Society through Engineering", May 11-14, 2021, Quebec, Canada – Virtual (Oral).

Farhain, M., Cheema, M., Katanda, Y., Nadeem, M., Javed, B., Mushtaq, I., Thomas, R., Galagedara, L. **(2021)**. Heavy metals leaching potential and water flow simulation of NL podzolic soil amended with wood ash, paper sludge and biochar in boreal ecosystem. 5th CIGR International Conference **2021** on "Integrating Agriculture and Society through Engineering", May 11-14, 2021, Quebec, Canada – Virtual (Oral).

Farhain, M.M.; Cheema, M.; Katanda, Y.; Nadeem, M.; Javed, B.; Thomas, R.; Galagedara, L. "Assessment of physicochemical properties of growth media based on wood ash and sludge in combination with biochar".: CSBE/SCGAB webinar series **2020 (Oral).**

Research articles:

Farhain, M.M.; Cheema, M.; Katanda, Y.; Nadeem, M.; Javed, B.; Thomas, R.; Saha, R.; Galagedara, L. "Potential of developing soil-based potting media from paper sludge, wood ash and biochar". **2021.** Journal of Environmental Management (Status: Acceted, In-press).

Farhain, M.M.; Cheema, M.; Katanda, Y.; Nadeem, M.; Javed, B.; Mushtaq, I.; Thomas, R.; Galagedara, L. “Effects of wood ash, paper sludge and biochar amendment on physicochemical properties and heavy metals leaching of boreal podzolic soils”. **2021.** Nature Communications (Status: In-progress)