

**CHARACTERISATION OF POTATO WASTE BIOCHARS AND
EFFECT ON CARBON DIOXIDE EMISSION, LIMING POTENTIAL
AND AVAILABILITY OF PRIMARY MACRO-NUTRIENTS OF TWO
AMENDED CONTRASTING SOILS**

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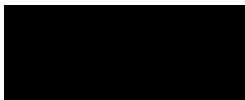
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DECLARATION

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Dr N.N Dube

ABSTRACT

About 30% of food produced across the world goes to waste that ends up in landfills and present disposal challenges as it undergoes a series of bioconversion into biogas. The production of biochar from these wastes could minimize the waste stockpiles while recycling nutrients and adding carbon to agricultural soils with limited negative effects. Despite the abundance of potato waste in South Africa, there is no published research that could be accessed in literature on the characteristics, carbon sequestration potential and nutrient release pattern of biochar from this waste. Pine bark is a major waste of the timber industry in South Africa and has been widely published. The aim of this study was to determine the effect of feedstock and pyrolysis temperature on the characteristics, carbon dioxide emission, liming ability and nutrient release (NPK) of biochars produced from potato waste. The biochars were produced from potato peels (PP); cull potatoes (CP) and pine bark (PB) feedstocks at 350 and 650 °C under minimal oxygen. Both the biochars and feedstocks were characterized for physico-chemical, proximate and ultimate analysis, surface functional groups and external morphology. Biochars were added to two contrasting soils Bonheim and Clovelly (i.e. Luvisol and Ferralsol) collected at 0-20 cm to study liming ability, carbon dioxide emission and selected soil properties in three separate incubation studies. The first incubation study investigated acid neutralizing ability of biochars applied based on CaCO_3 rates. It was applied at different rates for Ukulinga (0 t ha⁻¹, 5 t ha⁻¹, and 2.5 t ha⁻¹) and Bulwer (0 t ha⁻¹, 30 t ha⁻¹ and 15 t ha⁻¹). The samples were analysed for pH after 10 days. The second incubation study involved using the soils amended with only CP and PB biochar at equivalent rates of 0 and 10 t C/ha for 140 days and were analysed of mineral-N, P, extractable K and pH. The same experiment was repeated for CO₂-C emission but incubated for 84 days. Potato waste biochars had higher ash content, volatile matter, and lower fixed carbon, pH, calcium carbonate equivalence (CCE), K content and P compared to pine bark. The yield, volatile matter, total C, N H, O decreased with increasing pyrolysis temperature, while ash, pH, CCE increased. Surface functional groups varied with feedstock and pyrolysis temperature. The acid neutralising ability was higher for potato biochar than pine bark. Cull potato biochars increased available P, K and soil pH compared to pine bark biochars while none of the biochars affected ammonium and nitrate-N when compared to the control for both soils. Application of biochar in Luvisol increased CO₂-C emission, while in Ferralsol compressed CO₂-C emission was observed. Biochar characteristics and soil type affect the effectiveness of biochars for carbon sequestration. The findings imply that characteristics of

potato waste and pine bark biochar are different and application of cull potato waste biochar increases fertility of soils by increasing soil pH, P and K availability.

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1. CHAPTER ONE: GENERAL INTRODUCTION

1.1. Background and Justification

Globally, potato is the fourth produced essential crop following rice, wheat and maize (Gebrechristos and Chen 2018). South Africa produces 1.09 million tons of potato waste annually (Potato South Africa, 2010), of these potato peels are commonly discarded at landfill, cull potatoes in dumpsite, or other disposal sites, while other portions are converted into livestock feed and compost (Meister and Thompson, 1976). Solid waste from the potato industry, including potato processing waste and cull potatoes, is between 40 – 50 % (Charmley *et al.*, 2006). The potato peel waste is derived from the manufacturing of potato-based food products, while cull potatoes are whole potatoes of low market value, which are generally rotten (Olsen *et al.*, 2001). The potato processing industry has increased globally, and future projections indicate a further increase due to greater demand (Pandey *et al.*, 2009). The potato wastes are commonly disposed of at landfill sites with negative impact on the environment. Dumping of organic waste at the landfills results in ground water contamination due to nutrient leaching and contributes negatively to atmospheric pollution through release of ammonia, methane, CO₂ and N₂O (Matsakas *et al.*, 2017). While burial, use as livestock feed, direct land application and composting (Olsen *et al.*, 2001) may be alternative management strategies, most of them overlook minimizing environmental effects and maximizing beneficial use (Bastian, 2005).

Burial results in nutrient leaching to ground and surface water from the stockpiles, through subsurface water flow (Olsen *et al.*, 2001), which causes major loss of nutrients and pollution. The use of potato waste as livestock feed has a positive effects on reducing environmental pollution, however, the volume of waste produced can be massive for this approach to be an alternative (Larney and Angers, 2012). Field application of cull potatoes, as a way of recycling nutrients, has been reported to produce good growing media for grain and forage production (Larney and Angers, 2012), possibly due to the high concentrations of potassium (K) (Camire *et al.*, 2009), nitrogen (N) and to some extent phosphorus (P) (Larney and Angers, 2012; Liang *et al.*, 2015). Larney and Angers (2012) reported that cull potatoes contain 2.14% N, 0.29% P, and 2.40% K, while potato peels were reported to contain 2.73% N, 1.8% P and 3.09% K (Toma *et al.*, 1979). However, the direct application of these wastes may result in crop diseases

in potato fields (Olsen *et al.*, 2001). Olsen *et al.* (2001) reported increase in nematodes, powdery scab, weed seeds and soil-borne diseases from the direct land application of potato wastes. Attributed by potato wastes being a good host for diseases, hence soils amended with potatoes are susceptible to pests and soil-borne diseases from the direct land application of potato wastes. While composting could be a good alternative for waste management, the high levels of moisture in potatoes makes the compost conditions anaerobic, with foul smell, thus contributing negatively to air pollution (Cooperband, 2000). Furthermore, while production of biogas and extraction of lactic and phenolic acids and alkaloids from potato peels has been effective, the high costs limit their practical use (Wu, 2016). There is need for simple and cost-effective alternative waste management methods of disposal of potato peels and cull potato to limit negative environmental effects while positively contributing to agricultural productivity through recycling nutrients. Production of biochar from these wastes could be important, with the view of improving carbon sequestration and nutrient cycling in agriculture.

Biochar, a carbon-rich material produced by pyrolysis of organic wastes, under limited oxygen, has shown promising environmental effects including immobilization of heavy metals in soil (Qambrani *et al.*, 2017), reduction in greenhouse gas emissions to mitigate climate change, improvement of soil quality and agronomic productivity (Steinbeiss *et al.*, 2009; Spokas *et al.*, 2012). These effects are dependent on the physical and chemical properties of biochar mainly influenced by feedstock type and pyrolysis condition (Sohi *et al.*, 2010; Spokas *et al.*, 2012; Singh *et al.*, 2014). The feedstocks that have been used for production of biochar vary in the chemical composition, including content of cellulose, hemicellulose and lignin content (Mimmo *et al.*, 2014). In addition, pyrolysis conditions, particularly temperature, also alter biochar characteristics with low temperature producing biochar with similar composition to the raw feedstock while at higher temperatures the biochar properties are closer to those of graphite (Butnan *et al.*, 2015). Biochars have been produced from a variety of feedstocks, including wood chips and wood pellets, tree bark; crop residues including straw, nut shells, rice hulls, switch grass, organic wastes including paper sludge, sugarcane bagasse, distillers grain, olive waste; chicken litter, dairy manure and sewage sludge (Sohi *et al.* 2010; Spokas *et al.* 2012). Biochar has been advocated for as a stable organic soil amendment with dual ability for carbon sequestration and increasing soil fertility (Uzoma *et al.*, 2011).

Acidic soils are known to be susceptible to Al toxicity, P fixation, and low base status (Delgado *et al.*, 2016; Magalhaeus *et al.*, 2018). Biochar has been shown to be alkaline and its addition

could lime the soil and remediate these challenges, including increasing availability of macronutrients in acidic soil (Lehmann and Rondon, 2006). (Lehmann and Rondon, 2006). Liu *et al.* (2014) reported that P and K contents in biochar increase while total N decreases with increase in pyrolysis temperature. The aromatic functional groups in biochar increase its resistance to degradation when compared with the raw feedstock, with some authors suggesting that it can last for decades within the soil, with positive effects to carbon sequestration (Nzediegwu *et al.*, 2019). The porous structure, high surface area, and prevalent oxygen functional groups contribute to the immobilisation of pollutants and retention of nutrients in the soil (Qambrani *et al.*, 2017). The contribution of potato waste biochar to soil productivity is not clearly understood. While pyrolysis of potato peel waste has also been tested for production of bio-oil and extracting ethanol (Önal *et al.*, 2011; Liang *et al.*, 2015), and resulted in higher biochar yield relative to bio-oil (Liang *et al.*, 2015), the characteristics of that biochar and that of cull potato have not been studied. Moreover, the impacts of potato waste biochar on carbon dioxide emission, soil fertility and nutrient release need to be clearly understood. The use of potato waste biochar could improve soil quality, supply large quantities of the primary nutrients while minimizing disposal challenges. To date, there is a paucity of comprehensive studies on nutrient release pattern from cull and potato peels biochar in different soil types.

The low water-soluble carbohydrates in potato waste have been reported to restrict microbial activity at the waste surfaces thus limiting the composting process (Charmley *et al.*, 2006). Pyrolysis of the potato waste could produce biochar that is high in nutrients, alkaline pH with surface properties that enhance carbon sequestration and can be used as a soil amendment. Most studies on the characteristics of biochars and their value as soil amendment have been done with woody organic materials, including pine bark. Pine bark is therefore a good reference material to test potato waste biochars.

Data on quantities of pine bark production in South Africa could not be found in the literature but an estimate annual production of softwood bark was about 1.5 million m³ in 1985 (Smith, 1985). As such, pine bark is a major waste of the timber industry in South Africa and contains high carbon content. The characteristics of biochar produced from pine bark has been widely published (Singh *et al.*, 2014). Conversely, the characteristics of potato peel biochar are limited (Liang *et al.*, 2015), while no published research could be accessed in the literature on the characteristics of cull potato biochar. The study by Liang *et al.* (2015) showed that the potato

peel biochar had 56.3% fixed C and 4.10% N. The comparative characteristics of biochar from cull potato and potato peel waste relative to pine bark, its effects on nutrient release, carbon sequestration and acid neutralizing ability also remain a gap that needs to be studied, considering the large quantities of potato wastes and the environmental pollution they cause when disposed of improperly. Studies that focus on application of biochar from potato waste and pine bark biochars on soil fertility are equally non-existent.

1.2. Objectives

The aim of this study was to characterise the biochar produced at increasing temperatures of pyrolysis of cull potato, potato peel waste relative to pine bark and its effect on the release of carbon dioxide and macro-nutrients in soil. The findings from this study will motivate the further research and uses of potato waste as feedstocks and its biochar for their value in carbon sequestration and soil fertility. The specific objectives of this study are to determine the effects of:

- Pyrolysis temperature and feedstock on characteristics of biochar from potato wastes relative to pine bark.
- Application of potato and pine bark biochar on soil acidity.
- Pyrolysis temperature and feedstock on carbon dioxide emission, and release of macro-nutrients from soil amended with biochar from potato and pine bark.

CHAPTER TWO: EFFECTS OF BIOCHAR APPLICATION ON SELECTED SOIL PROPERTIES, CARBON DIOXIDE EMISSION AND AVAILABILITY OF PRIMARY MACRONUTRIENTS IN AMENDED SOILS: A REVIEW

2.1 Introduction

Biochar application as a soil amendment has been the center of attention, for reasons such as liming potential (acid neutralising power) in acidic soil, sequestering C and reducing greenhouse gas emissions (Shetty and Prakash 2020). Biochar is a product of thermal degradation of biomass under minimal oxygen conditions (Kloss *et al.*, 2012) and the product qualifies as biochar if it has carbon content > 40% (Bista *et al.*, 2019). The potential of biochar to ameliorate the soil depends on biochar characteristics, which are influenced by feedstock and pyrolysis conditions (Lehmann and Joseph, 2012). Feedstock compositions vary in proportions of cellulose, hemicellulose and lignin, which gives variation in the physico-chemical properties of the product (Enders *et al.*, 2012). Pyrolysis of biomass results in biochar with aromatic C which increases the stability of biochar-C thus promoting carbon sequestration in amended soils (Lehmann and Joseph, 2012). High pyrolysis temperature has been reported to produce more stable biochar-C which sequester more C compared to low pyrolysis temperature biochar (Spokas *et al.*, 2012). Results from Chapter 3 (Meta-analysis) showed that with increasing temperature the carbon content increases and the O/C and H/C decreases signifying aromaticity and stability of the biochar (Spokas *et al.*, 2012). In addition to producing more recalcitrant product, based on aromaticity parameters, increasing pyrolysis temperature also results in alkaline biochar, as depicted by the results in Chapter 3. Biochar addition could therefore have a liming effect when applied to acidic soils and therefore, enhance nutrient availability.

Application of peanut shell biochar to highly acidic red soil was reported to increase soil pH and nutrient availability and resulted to improved cabbage growth. This is achieved by the

increase in microbial biomass and activity increasing the rate of decomposition of SOM releasing N and P and increasing the CO₂-C emission (Hossain *et al.*, 2017). However, the increase in microbial activity could also result to immobilisation of N and P where these nutrients are low. The addition of biochar increases C in the soil and provide essential nutrient (N, P and K) to soils. The release of CO₂-C, mineral N, P, and available K in amended soils could depend on the composition of the biochar and the characteristics of the soil, among other factors. Biochar tends to have higher C/N ratio than the feedstock, which may result in N immobilisation. The release of P depends on the P concentration in the biochar feedstock and may become more available in soils due to increased concentrations following pyrolysis and liming effect of the biochar. Potassium is highly mobile within all levels of plants (Marschner, 2002) and not structurally bounded, hence, it is readily available (Wyn Jones *et al.*, 1979). Upon addition of biochar, the K is expected to be immediately released to the soil and becomes available. Most of the studies on CO₂-C evolution and nutrient availability, have been done with biochar from woody materials, with some studies done with crop waste biochar. There is a need to understand the effect of crop waste biochar on carbon sequestration potential, mineral N, P and K in soils. Therefore, the objective of the literature was to review the available literature on the effect of crop waste biochar on their liming ability, carbon sequestration potential and mineral N, P and K in soils.

2.2 Biochar stability

While biochar is considered biologically and chemically stable (Skjemstad *et al.*, 2002), there is evidence that biochar can decompose biotically or abiotically (Jiang *et al.*, 2016). There are some contradictory results that have been reported in the literature where decomposition of biochar reported to be rapid and while for others the process is slow (Lehmann *et al.*, 2006). The decomposition rate of biochar varies significantly with feedstock, pyrolysis temperature at which the biochar is produced (Jiang *et al.*, 2016) and soil characteristics (Kloss *et al.*, 2012), particularly soil clay content. The variation in resistance to degradation of biochars depends on differences on the chemical composition of the original feedstock (Wang *et al.*, 2016). Recent research shows that biochar derived from wood have higher stability than crop residue biochar, while grass biochar are comparable to crop derived biochar (Wang *et al.*, 2016; El-Naggar *et al.*, 2019). The high lignin content in wood feedstock, induces greater C stability when subjected to pyrolysis temperature (Bird *et al.*, 1999). In addition to stability due to the

chemical composition of the feedstock, the level of pyrolysis temperature makes a significant contribution to the stability of biochar.

Biochar pyrolysis temperature highly contributes to biochar stability with higher pyrolysis temperature yielding higher stability (Novak *et al.*, 2009b). When biochar is produced at high pyrolysis temperature, its carbon (C) are dominated by polycyclic aromatic C (Spokas *et al.*, 2012), which are characterised by low O/C (< 0.2) and they provide resistance to microbial and physical breakdown, hence, making them persist in soil (Glaser *et al.*, 2002). In the literature, biochar produced at low pyrolysis temperature are regarded as being least stable owing to high O/C (between 0.4 – 0.6), which indicates lower aromatic C and high proportion of aliphatic C (Spokas *et al.*, 2012). The latter means that the biochar produced at low temperature is easily degradable by microorganisms. Tomczyk *et al.* (2020) reported that biochar produced at low pyrolysis temperature (200°C) increased microbial communities while those produced at high pyrolysis temperature (500°C) suppressed the microbial communities in the soil. Luo *et al.* (2011) reported high C mineralisation for low pyrolysis temperature miscanthus biochar as compared to high pyrolysis temperature biochar for low and high pH soil pH on a clay loam soil. Biochar produced from wheat straw reported high CO₂-C from low pyrolysis temperature applied in a sandy loam soil of low and high pH as compared to high pyrolysis temperature (Bruun *et al.*, 2012). This behaviour was associated with the high volatile matter and high O/C (lower structural stable C) in the low pyrolysis biochar, which supplies the micro-organisms with labile carbon making the biochar not stable in the soil.

Soil type and predominantly clay content could affect biochar stability (Bruun *et al.*, 2014). Bruun *et al.* (2014) observed that biochar interacts with minerals in the soil, including intercalation with clay minerals and surface hydrophilic and hydrophobic interaction. The biochar-C can be protected by aggregates protecting it from microbial decomposition (Purakayastha *et al.*, 2015). The experimental duration after biochar incorporation is also found to impact the stability of the biochar owing to decrease in decomposition with increase in incubation time (Wang *et al.*, 2016). The addition of barley derived biochar decreased its biochar-C mineralisation with increasing clay content (11.2, 16.8 and 23%) in three Danish soils (Bruun *et al.*, 2014). Zhang *et al.* (2019) reported an increase in CO₂-C in smectite and kaolinite and a decrease in goethite dominated soils. This is due to the involvement of ligand exchange reaction between biochar-C and goethite surfaces.

The fact that high-pyrolysis biochar is resistant to breakdown and merits its use for carbon sequestration, its application in soil could hamper the release of nutrients from the biochar and the soil, and thus using it for plant growth may not be ideal, except for its liming effects. Low pyrolysis biochars are reported to favour microbial decomposition and release nutrients, for plant growth, with less C being sequestered (Laird *et al.*, 2009). In the literature, high clay content (40-70%) has been shown to decrease the decomposition of biochar (Wang *et al.*, 2016), and biochar addition is of merit in soil containing Fe oxides (Zhang *et al.*, 2019). There is a trade-off between producing biochar for carbon sequestration or for improving crop growth.

2.3 Carbon sequestration in soils treated with biochar

Biochar application to soil has been advocated for as an effective way for long-term carbon storage (Cheng *et al.*, 2008; Wang *et al.*, 2016). The effect of biochar on carbon sequestration is, however, variable due to different interactions and processes that occur when biochar is applied in the soil (Sohi *et al.*, 2009). This involves biochar particles coating with minerals, rapid association of biochar surfaces with Al and interaction of biochar with positive charge or variable charge oxides by ligand exchange and anion exchange (Bruun *et al.*, 2014). The latter hinders C availability for decomposition hence lowering CO₂-C emission. Mekuria and Noble (2013) reported that 40% of C is lost during pyrolysis, 10 % is lost due mineralisation and the remaining 50% is stable in the soil for millennia. Mathews (2008) reported a minimal loss of carbon during a long-term test and modelling in biochars, while Zimmerman (2010) observed sugarcane bagasse biochar produced at 650°C as having a half-life of 102 to 1000 years. Sugarcane bagasse produced at low temperature (250- 400°C) biochar increased CO₂-C during incubation while biochar produced at 650°C suppressed CO₂-C by its interaction with soil during early and late stages of incubation, as was grass biochar at 400 °C during late stage of incubation when applied in three different soils (Mollisol, Entisol, and Alfisol) (Zimmerman *et al.*, 2011). Biochar produced from corn stover application in a silt loam and loamy sand was reported to suppress CO₂-C emission due to improved stabilisation (Spokas and Reicosky, 2009). The reduction is possibly due to low available carbon for micro-organisms.

The ability of biochar to sequester carbon is significantly affected by pyrolysis temperature, and mainly soil type. Wheat straw biochar produced at 600°C showed significant CO₂-C

emission in ultisol, while in Mollisol no CO₂-C was emitted (Purakayastha *et al.*, 2016). This is related to the quality of soil organic carbon, ultisol had lower C:N indicating that the native SOM decomposes rapidly than that of the Mollisol. The corn stover biochar (600°C) was able to sequester carbon in Mollisol, but switch grass biochar produced at 400°C and 600°C had no significant effect (Purakayastha *et al.*, 2016). This could be explained by the wider C:N ratio of the biochar. In addition to C sequestration, amendment with biochar may also affect soil pH.

While biochar ought to be stable in the soil, numerous studies have reported a flush of CO₂-C following biochar incorporation (Bertrand *et al.*, 2007; Jones *et al.*, 2011; Bruun *et al.*, 2014), possibly due to the re-wetting of soil, which has been reported to increase activity of microorganisms, hence decomposing the labile carbon (Iovieno and Bååth, 2008). Some of the released CO₂-C is anticipated to be derived from the carbonates of the biochar (Brunn *et al.*, 2014). This is believed to be primarily an abiotic process and it occurs for a short period of time more especially for high pyrolysis temperatures attributed to high CaCO₃ content. Carbonates are usually inherited from the feedstock and during pyrolysis they become concentrated resulting in high carbonates in biochar. Following application to the soil the carbonates may be released as CO₂-C depending on soil pH (Jones *et al.*, 2011). In an incubation study where plant biochar was incorporated in calcareous soil, the emission from carbonates were relatively large (Bertrand *et al.*, 2007). The CO₂-C released during a short-term incubation should not be linked to decomposition of biochar as this would lead to an over estimation of biochar carbon mineralisation. During pyrolysis CO₂-C may be sorbed onto the surface of biochar (Radosz *et al.*, 2008). Hence, there are some possibilities that the CO₂-C emitted might have originated from that sorbed on biochar surfaces. However, Bruun *et al.* (2014), reported biotic mineralisation as being highly responsible for the CO₂-C emission in studies as biochar has the potential of liming the soil and increases microbial activity. The CO₂-C released after incorporation of biochar to soils could be a combined effect of C from carbonates in the ash, CO₂ sorbed of surfaces of the biochar and mineralization from biochar due to higher microbial activity following the liming effect of biochar.

2.4 Liming effects of biochars

Biochar pH varies from slightly acidic (4) to alkaline range (8 – 13) (Uras *et al.*, 2012). Studies by Shetty and Prakash (2020) reported that biochar addition decreases soil acidity through its liming ability. The knowledge of initial pH of soil and biochar is of paramount important for soil amendment using biochar (Sohi *et al.*, 2009). Application of biochar on acidic soils increases pH towards neutral pH and in alkaline soils it reaches highly alkaline, possibly due to high pH and the presence of carbonates or alkaline metals oxides, which tend to increase with pyrolysis temperature (Singh *et al.*, 2010). The carbonates react with H^+ and Al^{3+} , hence, increasing soil pH (Novak *et al.* 2009b). However, the presence of carbonates varies with the feedstock used for the biochar, and the higher the quantity of carbonates the more effective it is on counteracting soil acidity.

According to Tomczyk *et al.* (2020) and Laird *et al.* (2010), the alkalinity of biochar is controlled by the presence of oxygen containing functional groups ($-COO^-$ and $-O^-$) and the carbonates. Crop residue biochars has higher alkalinity than wood biochars (Fidel *et al.*, 2017). (Yuan *et al.*, 2011c) observed that incorporation of crop-residue biochars increased soil pH due to their high liming effect. Research conducted by Wang *et al.* (2014a) on an acidic soil revealed that crop residue biochars significantly increased soil pH, which was attributed to high alkalinity and calcium carbonates. This indicated higher solubility of salts and the idea that pH and carbonates content should be considered before conclusion on the ability of biochar's liming potential. Inherent pH of biochar decreases after its application to acidic soil (Jones *et al.*, 2012), this raises concern of long-term application of biochar.

Biochar has been a novel strategy to remediate acidic soils, however, the benefit is short-lived due to lessening of alkalinity and neutralisation associated with biochar aging (Jones *et al.*, 2012). The possible reasons for the decrease in soil pH over time following biochar incorporation could be surface functional groups oxidation, losses of carbonyl and carboxyl groups which are associated with alkaline metals (Cheng *et al.*, 2006; Jones *et al.*, 2012). Another possible reason could be rapid mineralisation and decomposition of biochars that provide labile C, hence, enhancing nitrification leading to a reduction in soil pH (Shetty and Prakash, 2020). Increasing soil pH increases microbial activity, which in turn increases organic matter decomposition resulting in CO_2 -C emission and nutrient mineralisation and availability in soils (Sohi *et al.*, 2009).

2.5 Biochar application and availability of primary macro-nutrients

Biochar has been the center of attention for its promising and cost-effective benefits to soil fertility improvement (El-Naggar *et al.*, 2019), through increase in organic carbon (El-Naggar *et al.*, 2018), microbial activity (Igalavithana *et al.*, 2018), nutrient availability and retention (El-Naggar *et al.*, 2019) and remediation of acidic soils (Yuan *et al.*, 2011b). These benefits have been reported following incorporation of crop residue biochars as reviewed by Sohi *et al.* (2009). Liu *et al.* (2012) reported rice straw biochar as a tool for enhancing soil fertility, due to its ability to increase soil C and N retention and being nutrient rich. However, the nutrient release capacity following biochar application vary due to biochar composition, which is a function of feedstock type and pyrolysis condition (Mukherjee and Zimmerman, 2013). The pH of the soil is also an important factor affecting nutrient availability (Silber *et al.*, 2010). Contrasting effects of biochar on soil fertility have been reported including negative, positive and neutral effect (Igalavithana *et al.*, 2018). El-Naggar *et al.* (2018) reported that rice straw biochar increased N, available P and exchangeable cations when compared to wood and grass biochars during incubation in a sandy soil. Albuquerque *et al.* (2014) reported that the effect is strongly dependent on the biochar type in a greenhouse experiment, wheat straw increased P availability and olive tree pruning increased soil pH due to high CaCO₃. The nutrient release may be suppressed by the reduction in soil C mineralisation (Ippolito *et al.*, 2012) linked to biochar stability. Kuppusamy *et al.* (2016) observed that biochar produced at temperatures greater than 600°C adsorbed the nutrients, hence reducing nutrient availability, than those produced at low pyrolysis temperature, which have high volatile matter, labile C and increase microbial communities, mineralising nutrients in the soil. The release of nutrients into the soil solution is highly correlated with volatile matter content and acid functional groups and the sorption affinity (Mukherjee and Zimmerman, 2013). Low pyrolysis temperature and pH may increase the availability of N and P, while pyrolysis temperature increases the availability of K (Ding *et al.*, 2016).

2.6 Nitrogen mineralization and immobilization process in soils

Soil nitrogen mineralisation is found to be affected by biochar incorporation to the soil (Gaskin *et al.*, 2008). Addition of rice husk biochar to the paddy soil resulted in slower mineralisation

(Dempster *et al.*, 2012; Knoblauch *et al.*, 2011) while wheat biochar increased N mineralisation (Castaldi *et al.*, 2011) and switch grass biochar (250-500°C) had no effect on N mineralisation when applied in loamy sand (Schomberg *et al.*, 2012). Knicker and Skjemstad (2000) reported that plant derived biochar has low N availability due to the presence of heterocyclic N structure. Crop residue biochars are recognised for enhancing NH_4^+ while reducing recovery of NO_3^- (Nelson *et al.*, 2011). The biochar may contain bioavailable N forms, but its mineralisation and release will be dependent on how recalcitrant the biochar and soil N and C pools are on the soil and biochar C:N ratio (Clough *et al.*, 2013). The N mineralisation might be decreased due to adsorption of NH_4^+ or NO_3^- onto the biochar surfaces attributed to enhanced cation exchange capacity and anion exchange capacity (Ameloot *et al.*, 2015). Conversely, ammonia sorption by reacting with surface oxygen functional groups enriches biochar with N, and that N is bioavailable due to its ability to dissolve and dissociate (Spokas *et al.*, 2012). The latter occurs in a reversible manner for low pyrolysis temperature biochars. High C/N ratio in biochar leads to N immobilisation when being prone to microbial decomposition (Bruun *et al.*, 2012). In an incubation study, Curtin *et al.* (1998) reported that pH plays a fundamental role in stimulating N mineralising micro-organisms. This implies that the liming potential of biochar is an important factor for enhancing N mineralisation by stimulating soil microbial biomass. In conclusion, soil pH, CEC and acidic functional groups are the key fundamental factors regulation the N cycle. These soil parameters also affect availability of other nutrients including soil P and K.

2.7 Phosphorus and potassium availability as affected by biochar application

Phosphorous availability is significantly limited by various soil factors that include pH, acidity and Al and Fe compounds (Murphy and Stevens 2010). Lehmann *et al.* (2003) reported that biochar contains high P content and is believed to act as slow-release P fertilisers (Glaser and Lehr, 2019). Crop residue biochars have shown a positive response to P availability in amended soils, while wood derived biochars are not ideal as P fertilisers (Glaser and Lehr, 2019). This effect could be attributed to biochar decomposition followed by the mineralisation of organic P (Chan *et al.*, 2007), or could be the interference of biochar with soil pH leading to the release of bounded P to the soil system in acidic soils (Jin-Hua *et al.*, 2011). Previous studies (Masto *et al.*, 2013; Cui *et al.*, 2011) showed that amended soils with crop residue biochar increased P

availability in deficient and acidic soils due to biochar liming effect and subsequent release of P from Fe and Al compounds (Singh *et al.*, 2010). Xu *et al.* (2014) reported a view for an acidic sandy soil amended with straw biochar where P decreased due to precipitation of Al and Fe bound P. It may be necessary to use alkaline biochars to acidic soils and acidic biochars to alkaline soils for increasing available P in soils (Glaser and Lehr, 2019). The reason is that pH changes affects P sorption and desorption. Biochar produced at pyrolysis temperature below 450°C increases P availability in soils, while with increasing pyrolysis temperature the effect of biochar on P availability decreases (Zheng *et al.*, 2013). This can be explained by the presence of inorganic P (tricalcium) at high pyrolysis temperature (Glaser and Lehr, 2019), or due to P volatilisation at high pyrolysis temperature (Wang *et al.*, 2012). In addition to modification of P and its dynamics in soils, biochars also add other nutrients, like K.

The increase in K content following biochar application has been advocated in previous research (El-Naggar *et al.*, 2019). Joško *et al.* (2013) reported significant increase in K content in a crop residue biochar (300- 500°C) amended soil. The increase could be due to inherent higher amount of K content in crop residue feedstock (Singh *et al.*, 2010). Masto *et al.* (2013) observed sorption of K on biochar surfaces thus increases release once applied to the soil. Wang *et al.* (2014c), reported an increase in K content from 42 to 324 mg kg⁻¹ following rice husk biochar application in an acidic soil. The release of K is not pH-dependent (Zheng *et al.*, 2013), and high K is observed with high pyrolysis temperature (Singh *et al.*, 2014).

2.8 Conclusion

The use of biochar increases soil pH in acidic soils and increases availability of phosphorous and potassium. For enhance P availability biochar prepared at medium pyrolysis temperature are ideal. Biochar affects the N cycle in soils and the results vary with type of biochar used for amending the soil. However, there are trends that biochar can adsorb ammonium and mineralisation can occur. The ability of biochar to sequester C, lime acidic soils, increase nutrient availability depends on the pyrolysis temperature and the type of the feedstock used and the soil typed used. High pyrolysis temperature sequesters more carbon in the soil, low pyrolysis temperature biochar enhances nutrient availability and sequesters relatively low C in the soil. While there is vast literature on crop biochar effects on soil C sequestration and

emission, N, P and K dynamics in soil, these effects are known to vary with type of feedstock, pyrolysis temperature and soil properties. The common crop wastes that could be used for production of biochar which can then be applied to soil vary from crop residues of cereals, legumes, tubers (e.g., potatoes) and other, together with wastes produced through the whole supply chain. Instead of disposing of the wastes at landfill sites, they can be pyrolysed into biochar for soil application. Although they are all crop wastes, the differences in their characteristics suggest that the biochar characteristics and their effectiveness for C sequestration, and nutrient dynamics could also vary. Before biochar from a particular crop waste can be recommended for soil application, it needs to be characterised and tested in the soil to determine its effects

3. CHAPTER THREE: LITERATURE REVIEW

CHAPTER 3. EFFECTS OF CROP RESIDUE FEEDSTOCKS AND PYROLYSIS TEMPERATURE ON BIOCHAR PHYSICO-CHEMICAL PROPERTIES: RESULTS FROM META-ANALYSIS

3.1 Introduction

Large amounts of agricultural and forestry residues and other biomass are burned or left to decompose on site or at landfills, worldwide, thereby releasing carbon dioxide (CO₂) and/or methane (CH₄) into the atmosphere and leaching nutrients, like nitrates to ground water (Woolf *et al.*, 2010; Spokas *et al.*, 2012; Sohi *et al.*, 2010). Collectively, agricultural activities account for carbon-equivalent emissions equal to those of transport (Sohi *et al.*, 2010). The emission contributes negatively to the atmosphere and results to climate change (Matsakas *et al.*, 2017). Solutions that will address these challenges are urgently required. Thermal stabilisation is a promising approach since it sequesters C hence mitigating climate change. The potential to sequester carbon as thermally stabilized biomass using existing organic resource is estimated to be at least 1 Gt yr⁻¹ (Lehmann, 2007). A study by Woolf *et al.* (2010) estimated the potential to mitigate climate change and nutrient leaching by utilising available biomass feedstock that can be converted to biochar.

Biochar is the product of thermal decomposition of biomass feedstocks produced under limited supply of oxygen and at temperatures of less than 700°C (Spokas *et al.*, 2012; Sohi *et al.*, 2010). The physical and chemical properties of biochar are mainly influenced by feedstock type, and pyrolysis conditions (Sohi *et al.*, 2010; Spokas *et al.*, 2012; Singh *et al.*, 2010). Characteristics of the raw feedstock biomass confer specific properties, such as ash content, elemental constituents, and hardness of the biochar. Biomass with high elemental contents usually produces biochar with even higher elemental concentration, particularly in the ash portion. Biochars from grass, maize

stover and manure feedstocks contain higher amounts of ash than those from other biomass sources (Spokas *et al.*, 2012).

Ash content provides a measure of the relative inorganic composition of biochar, including metals which may serve as nutrients for plants, fungi and bacteria (Mitchell *et al.*, 2013). During pyrolysis, a series of cleavage and polymerization reactions occurs, resulting in the formation of fixed carbon (aromatic) structures (Spokas *et al.*, 2012). The carbon of biochar produced at pyrolysis temperatures of 400–700°C is distributed in more poly-condensed aromatic structures that have low O/C ratios and are resistant to microbial degradation and thus are suited for long-term soil carbon sequestration (Spokas *et al.*, 2012; Mitchell *et al.*, 2013). The ranges of pyrolysis temperatures determine the extent of volatilization and therefore the final volatile composition of the resulting biochar. The volatile matter fraction of biochar may be utilized as an energy source by microbes to stimulate growth. However, this fraction of biochar is more labile and its decomposition by microbes may contribute to the net release of carbon dioxide through microbial respiration (Lehmann *et al.*, 2011). The carbon content of biochar increases with increasing pyrolysis temperature and is inversely related to biochar yield. Beyond a certain temperature threshold, biochar yield may continue to decrease with no further increase in the concentration of carbon within it. However, since ash is broadly conserved, the ash content of biochar increases with temperature (Sohi *et al.*, 2010).

Biochar pH varies widely depending on the nature of the feedstock in addition to pyrolysis conditions (Mitchell *et al.*, 2013). The neutral to basic pH of many reported biochars may be used to neutralize excess soil acidity. Cation exchange capacity (CEC) provide an indication of the ability of biochar to retain cations on the particle surface which are vital for plant growth and good soil structure (Sohi *et al.*, 2010). The CEC of biochar increases with pyrolysis temperature through the formation of micropores and the abundance of carboxyl groups on those surfaces (Sohi *et al.*, 2010). Elemental ratios can provide insight into biochar structure and stability. For example, the ratio of hydrogen to carbon decreases as the biochar structure becomes increasingly dominated by aromatic structures whereas the oxygen to carbon ratio can provide information about the level of oxidation in the biochar. In addition, the ratio of carbon to nitrogen has been used to estimate the likelihood of nitrogen immobilization or mineralization due to biochar addition to soil (Mitchell *et al.*, 2013). Moreover, the O/C and H/C have been found to provide a reliable measure of both

the extent of pyrolysis and the level of stability of biochar in the soil (Sohi *et al.*, 2010). All these biochar characteristics depend on the feedstocks used.

Biochars have been produced from a variety of feedstocks, including wood chip and pellets, tree bark, switch grass, paper sludge, sugarcane bagasse, distillers grain, olive waste; chicken litter, dairy manure, sewage sludge and crop residues such as straw, nut shells, and rice hulls (Sohi *et al.*, 2010; Spokas *et al.*, 2012). Studies on biochars produced from different feedstocks under a range of pyrolysis conditions remain an important area of research for selection of biochars with specific characteristics for specific benefits (Sohi *et al.*, 2010; Spokas *et al.*, 2012). Considering the large quantities and diversity of crop residues produced in agriculture, biochars derived from a range of residues have been intensively studied in recent years. These include cassava residues, corncobs, rice husk, rice straw, coffee husk, maize residue, maize straw, wheat straw, corn stover, rape stalk, cotton stalk, switchgrass, coconut husk, coconut shell, sugarcane bagasse, among others (Ashworth *et al.*, 2014; Windeatt *et al.*, 2014; Domingues *et al.*, 2017; Liu *et al.*, 2018; Mohan *et al.*, 2018; Nyambo *et al.*, 2018; Billa *et al.*, 2019). There is need for a clear global understanding of the effects of groups of crop residues, as feedstock, and pyrolysis temperature on physico-chemical properties of biochars, which will have implications on carbon sequestration potential and nutrient dynamics when used as soil amendments. The main question is “Are there major differences in biochar characteristics that affect carbon sequestration and nutrient dynamics between residues of cereals, legumes and other crop wastes?” The objective of this chapter was to review the available literature on the effects of different groups of crop residue feedstocks and pyrolysis temperature on physico-chemical properties of biochar.

3.2 Methods and Material

3.2.1 Database compilation

The global synthesis of the characteristics of biochar from groups of crop residues (as feedstocks) was performed on peer reviewed articles from different journals. The extensive literature search was performed using Google scholar, Science direct and Researchgate, to collect information using keywords such as “biochar characterisation”, “crop residue biochar”, “agricultural residue biochar” and “pyrolysis of crop residues”. Only papers that studied crop residue biochar characterisation and had detailed information on production temperature, feedstock and the physico-chemical characteristics were considered. The database consisted of 42 peer reviewed articles starting from 2007 to 2019, based on studies from 18 countries (Spain, China, USA, Ghana, Australia, India, Pakistan, Sri Lanka, Iran, Sierra Leone, Indonesia, Korea, Ethiopia, Brazil, Cameroon, South Africa, England and Italy) as depicted in Figure 3.1. China had the highest number of peer reviewed articles (n = 13) followed by USA (n = 5). Where the GPS coordinates were not provided or considered, the Google Earth Pro was used.



Figure 3.1 Global distribution of the sites where data used in the analysis was generated.

3.2.2 Data categorization

The data were grouped into feedstock and pyrolysis temperature classes to aim for homogenisation in the data. The feedstocks were categorised into cereal, legume and green waste. Any feedstock that did not qualify to be a cereal or legume was grouped as green waste. The crop residues which aligned with these categories are depicted in Table 3.1. The pyrolysis temperatures were categorised into low (<400 °C), medium (400–550 °C) and high (>550 °C).

Table 3.1 Factors describing the crop residue feedstocks utilised and pyrolysis temperatures used for analysis.

Factors	Group	Class range
Feedstocks	Cereals	Rice husk, wheat straw, corn cobs, rice straw, corn straw, corn stover
	Legumes	Peanut hulls, canola straw, soybean straw, pea straw, white clover, coffee husk
	Green waste	Switch grass, green waste, sugarcane bagasse, amur silver grass, orange peels
Pyrolysis temperature	Low	< 400°C
	Medium	400 - 550°C
	High	>550°

3.2.3 Data Analysis

The data obtained were subjected to analysis using different types of software. Genstat Ed. 18 was used for summary statistics, Sigma plot was used for plotting box plot and for statistical difference any outliers were removed, while spearman's correlation analysis was done using Statistica 10.0 (Jambu, 1991) (Table 3.3). The means of the treatments were significant at 95% interval. Different descriptive stats were analysed (mean, maximum, minimum, quartile 1 and 3 indicating 25th and 75th quartile, respectively, standard error mean (SEM), skewness (Skew), kurtosis (Kurt) and coefficient of variation (CV%) for all the studied parameters in the database (Table 3.2).

3.3 Results

3.3.1 Summary statistics

The yield (mean = 37.7 ± 1.52 %) varied (CV = 31.4%) from 18.3% for cereal biochar produced at high pyrolysis temperature in Spain (Jindo *et al.*, 2014) to 75% for those from green waste and cereal at low pyrolysis temperature in China (Liu *et al.*, 2018). Volatile matter (mean = 23.9 ± 2.03 %; CV=71%) varied from 3.17 % for cereal biochar produced at high pyrolysis temperature in Spain (Jindo *et al.*, 2014) to 74.4% for green waste produced at low pyrolysis temperature in USA (Novak *et al.*, 2009a). Mean fixed carbon was 56.1 ± 2.5 % with values ranging from 21.1% for cereal biochar produced at low pyrolysis temperature in China (Liu *et al.*, 2018) to 91.9% for that from green waste at high pyrolysis temperature in England (Windeatt *et al.*, 2014). Ash content exhibited high variation (CV=68.6%) with a mean of 17.7 ± 1.34 % and ranging from 1.9% in green waste biochar produced at low pyrolysis temperature in Brazil (Domingues *et al.*, 2017) to 56.2% in that from green waste feedstock at medium pyrolysis temperature in Australia (Smider and Singh, 2014). The carbon content exhibited low variation (CV = 25.7%) with a mean of 60.6 ± 1.49 % ranging from 18.7% for cereal biochar produced at low pyrolysis temperature in Indonesia (Nurhidayati and Mariati, 2014) to 93.9% for that from green waste at high pyrolysis temperature in England (Windeatt *et al.*, 2014).

The lowest nitrogen was 0.11% for legume biochar produced at high pyrolysis temperature in Cameroon (Billa *et al.*, 2019) and highest (4.8%) for that from green waste at high pyrolysis

temperature in England (Windeatt *et al.*, 2014), with a mean of $1.21 \pm 0.0865\%$. Hydrogen in the biochars exhibited high variation (mean = $3.03 \pm 0.202\%$; CV = 55.7%) from 0.25% for cereal biochar produced at high pyrolysis temperature in Spain (Jindo *et al.*, 2014) to 10.3% for legume biochar produced at high pyrolysis temperature in USA (Novak *et al.*, 2009). Oxygen varied widely (mean = $13.9 \pm 0.947\%$; CV = 56 %) from 1.6% for legume biochar produced at high pyrolysis temperature in USA (Novak *et al.*, 2009b) to 35.6% for green waste biochar produced at low pyrolysis temperature in USA (Novak *et al.*, 2009a). The C/N ratio with a mean of 86 ± 7.76 varied widely (CV = 89.8%), ranging from 12 for green waste biochar produced at medium temperature in Australia (Smider and Singh., 2014) to 536 for legume biochar produced at high pyrolysis temperature in Cameroon (Billa *et al.*, 2019). The H/C ratio (CV = 67.3%) with a mean of 0.523 ± 0.0424 ranged from 0.0468 for green waste biochar produced at low pyrolysis temperature in Austria (Colantoni *et al.* 2016) to 1.62 for cereal biochar produced at low pyrolysis temperature in China (Liu *et al.*, 2018). The O/C ratio varied widely (mean = 0.187 ± 0.0147 ; CV = 64.7%) from 0.01 for legume biochar produced at low pyrolysis temperature in USA (Novak *et al.*, 2009a) to 0.51 for green waste biochar produced at low pyrolysis temperature in China (Liu *et al.*, 2018).

Biochar pH_(H2O) showed the least variation (CV = 14.8 %) with a mean of 9.02 ± 0.143 ranging from 5.4 for green waste biochar prepared at low pyrolysis temperature in USA (Novak *et al.*, 2009a) to 12.1 for green waste biochar prepared at medium pyrolysis temperature in Australia (Smider and Singh, 2014). Biochar Ca (mean = 30.2 ± 5.34 cmol_c/kg) varied widely (CV = 93.8%) ranging from 0.0013 cmol_c/kg for cereal biochar produced at medium pyrolysis temperature in South Africa (Nyambo *et al.*, 2018) to 96.3 cmol_c/kg for legume biochar produced at low pyrolysis temperature in China (Yuan and Xu, 2011). Biochar Mg with a mean of 13.2 ± 2.78 cmol_c/kg ranged from 0.0014 cmol_c/kg for cereal biochar produced at medium pyrolysis temperature in South Africa (Nyambo *et al.*, 2018) to 47.7 cmol_c/kg for cereal biochar produced at low pyrolysis temperature in China (Wang *et al.*, 2014a). Biochar K (22.9 ± 6.02 cmol_c/kg) varied widely (CV = 184%) ranging from 0.0012 cmol_c/kg for cereal biochar produced at medium pyrolysis temperature in South Africa (Nyambo *et al.*, 2018) to 188 cmol_c/kg for cereal biochar produced at low pyrolysis temperature in China (Yuan and Xu, 2011).

The Na with a mean of 7.64 ± 2.76 cmol_c/kg varied widely (CV = 191%) ranging from 0.6 cmol_c/kg for cereal biochar produced at low pyrolysis temperature in China (Wang *et al.*, 2014a) to 64.4 cmol_c/kg for legume biochar produced at low pyrolysis temperature in China (Yuan and Xu, 2011). Biochar CEC with a mean 45 ± 7.07 cmol_c/kg varied widely (CV = 94.3%) ranging from 2 cmol_c/kg for green waste biochar produced at high pyrolysis temperature in Brazil (Domingues *et al.*, 2017) to 180 cmol_c/kg for cereal biochar produced at low pyrolysis temperature in China (Yuan *et al.*, 2011a). Biochar phosphorous also varied widely (CV = 137%) with a mean 212 ± 70.8 mg/kg and ranging from 8.5 mg/kg for cereal biochar produced at low pyrolysis temperature in Ethiopia (Dume *et al.*, 2015) to 763 mg/kg for cereal biochar produced at medium pyrolysis temperature in China (Dume *et al.*, 2015). Electrical conductivity with a mean of 4.04 ± 0.471 d S m⁻¹ varied widely (CV = 79%) ranging from 0.17 d S m⁻¹ for green waste biochar produced at medium pyrolysis temperature in South Africa (Uras *et al.*, 2012) to 12.8 d S m⁻¹ for legume biochar produced at high pyrolysis temperature in Brazil (Domingues *et al.*, 2017).

Table 3.0 Summary statistics for variables used in the meta-analysis.

Variables	n	Mean	Median	Min	Max	Qt 1	Qt 3	SD	SEM	% CV	Skew	Kurt
Yield (%)	61	37.7	36.2	18.3	75	31.3	41	11.8	1.52	31.4	1.51	2.83
VM (%)	70	23.9	19.5	3.17	74.4	13.1	30.1	17	2.03	71.2	1.3	1.09
FC (%)	45	56.1	55.3	21.1	91.9	45.9	65.9	17.2	2.56	30.6	0.0092	-0.325
Ash (%)	79	17.7	16.3	1.9	56	8.21	23.4	12.2	1.37	68.6	1.03	0.865
C (%)	109	60.6	60.3	18.7	93.9	50	71.4	15.6	1.49	25.7	-0.0204	-0.394
H (%)	70	3.03	2.8	0.25	10.3	1.94	3.69	1.69	0.202	55.7	1.31	3.62
O (%)	68	13.9	12.5	1.6	35.6	8.37	17.9	7.81	0.947	56.1	0.77	0.193
N (%)	104	1.21	1.01	0.11	4.8	0.565	1.65	0.882	0.0865	72.7	1.46	2.51
C/N	99	86	64.5	12	536	36.3	109	77.3	7.76	89.8	2.82	11.5
H/C	69	0.523	0.48	0.0468	1.62	0.29	0.68	0.352	0.0424	67.3	1.04	1.08
O/C	68	0.187	0.165	0.01	0.51	0.1	0.25	0.121	0.0147	64.7	0.74	-0.139
pH _(H2O)	87	9.02	9.2	5.4	12.1	8.22	9.95	1.34	0.143	14.8	-0.397	0.0137
Exch.Ca (cmolc/kg)	28	30.2	20.7	0.0013	96.3	6.69	47.9	28.3	5.34	93.8	0.868	-0.27
Exch.Mg (cmolc/kg)	28	13.2	7.41	0.0014	47.7	5.18	12.2	14.7	2.78	111	1.54	0.815
Exch.Na (cmolc/kg)	28	7.64	2.62	0.6	64.4	1.5	5.08	14.6	2.76	191	2.91	7.48
Exch.K (cmolc/kg)	49	22.9	4.2	0.0012	188	2.8	21.1	42.1	6.02	184	2.66	6.73
CEC (cmolc/kg)	36	45	24.1	2	180	16.9	64.9	42.4	7.07	94.3	1.54	1.89
Extract. P (mg/kg)	17	212	17.6	8.55	762	11.3	410	291	70.8	137	1.02	-0.599
EC (dSm ⁻¹)	46	4.04	3.6	0.17	12.8	1	5.8	3.19	0.471	79	0.707	-0.173

VM = volatile matter; FC = Fixed carbon; C = carbon; N = nitrogen; H = hydrogen; O = oxygen; Exch. = exchangeable cations (calcium, magnesium, sodium and potassium; respectively); CEC = cation exchange capacity; extract. P = extractable Phosphorous; EC = electrical conductivity. Descriptive statistics (min: minimum, max: maximum, Qt1 and Qt3: quartile 1 and quartile 3, respectively, SEM: standard error of mean, skew: skewness, kurt: kurtosis, CV%: coefficient of variation) of biochar characteristics.

3.3.3 Effects of different crop residues and pyrolysis temperature on biochar yield and proximate analysis (volatile matter, fixed carbon and ash content).

There was no significant difference in biochar yield, volatile matter and fixed carbon between biochar from different crop residue groups (Figure 3.2). Cereal biochar has significantly higher ash content than green waste and legumes, which were similar. Increase in pyrolysis temperature led to a significant decrease in volatile matter and yield while it increased fixed carbon and ash content (Figure 3.3). The yield decreased in order low (50.2%) > medium (35.8%) > high (38.7%) pyrolysis temperature. The trend of fixed carbon was high (67.1%) > medium (55.9%) > low (43.2%) pyrolysis temperature. Low pyrolysis temperature resulted in biochar with higher volatile matter than medium and high, temperatures. Volatile matter in low pyrolysis temperature was >100% higher than medium and high pyrolysis temperature. The medium (19.6%) and high (18.9%) pyrolysis temperature had similar ash content, which was significantly higher than low (14.0%) pyrolysis temperature.

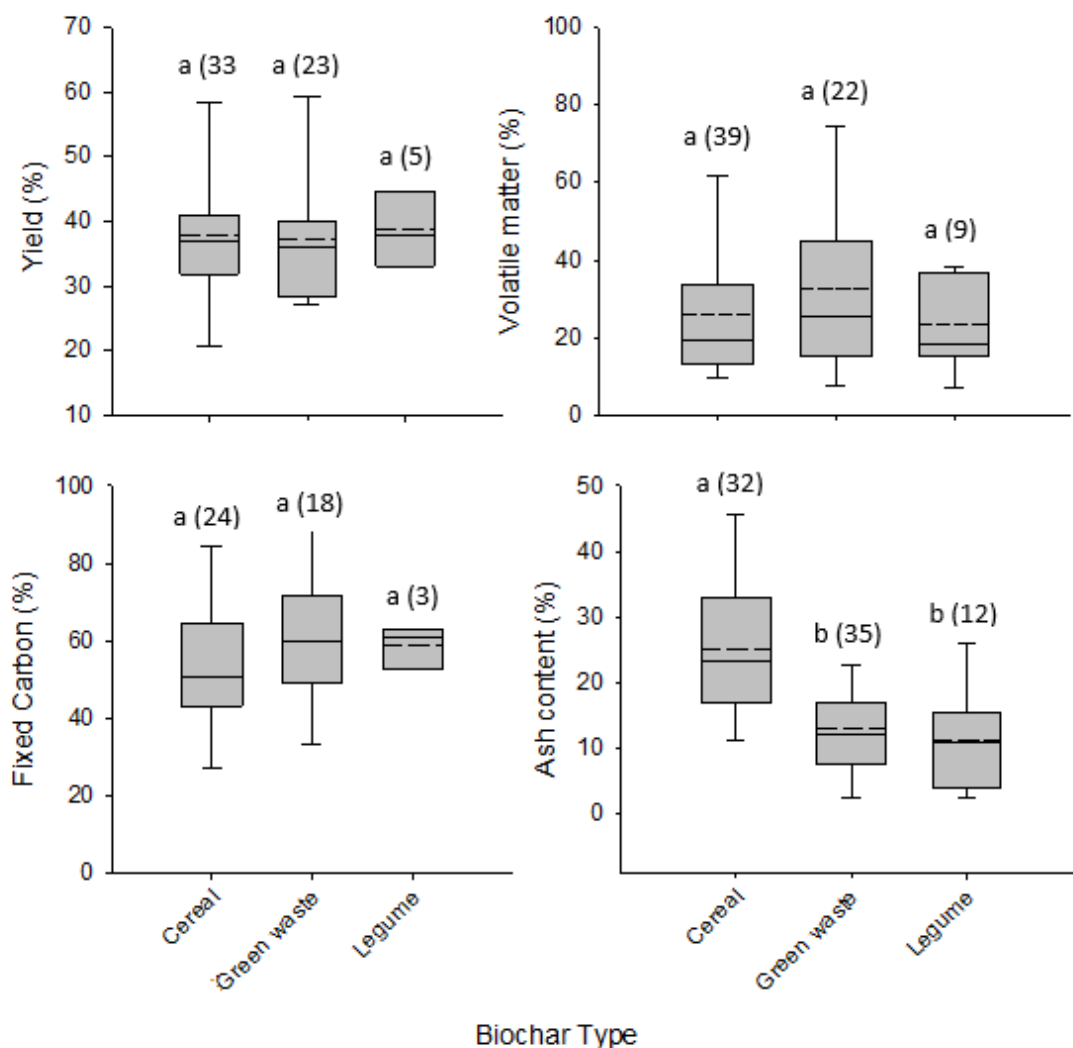


Figure 3.2 Effects of different crop residue feedstocks on biochar yield and proximate analysis (Volatile matter, Fixed Carbon and Ash content). Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

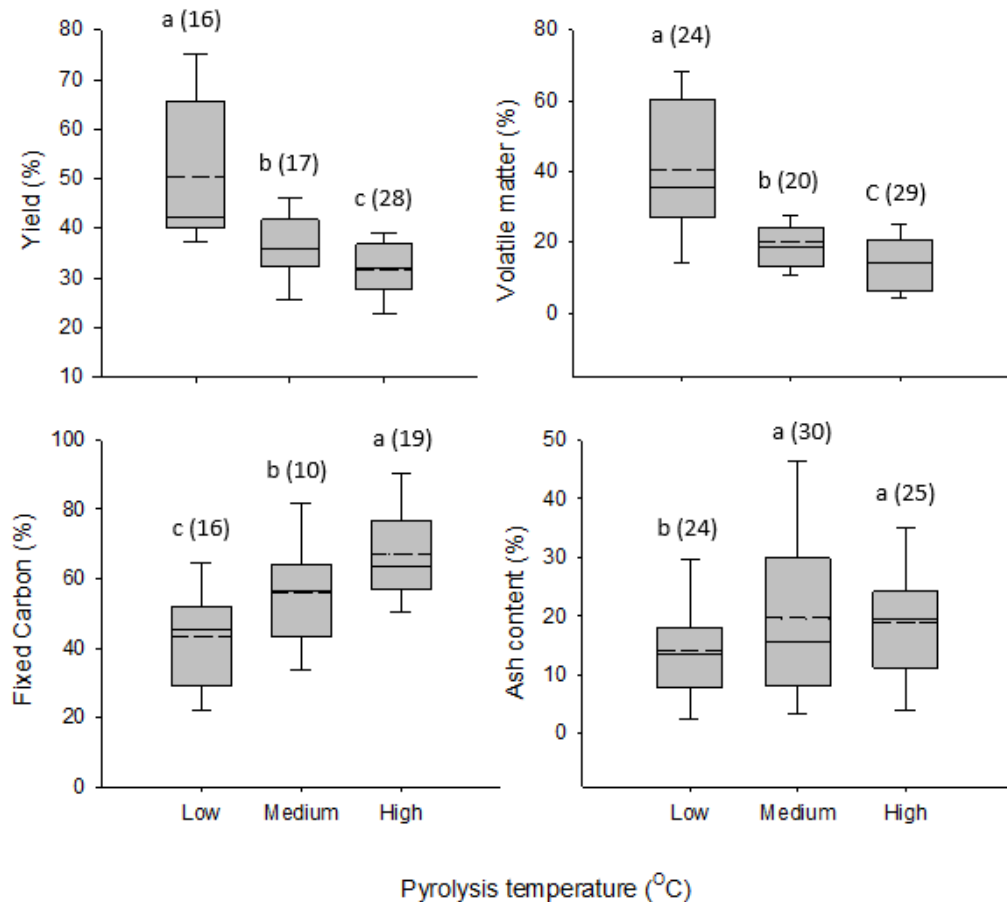


Figure 3.3 Effects of pyrolysis temperature on crop residue biochar yield and proximate analysis (volatile matter, fixed carbon and Ash content). Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.4 Effects of different crop residues and pyrolysis temperature on biochar total carbon, nitrogen and C/N ratio.

Legume (67%) and green waste (68%) had significantly higher total carbon than cereal (53%) (Figure 3.4). Total nitrogen from cereal (1.04%) and green waste (1.16%) were significantly lower than legume (1.85%) biochar. There was no significant difference in C/N between crop residue biochars. However, pyrolysis temperature showed significant effect in these parameters (Figure

3.5). Total C was significantly increased with pyrolysis temperature in the order of low (55%) < medium (61%) < high (90) while total nitrogen decreased in the order of low (1.45%) > medium (1.14%) > high (0.998%). Biochar from low (65) and medium (79) pyrolysis temperature had significantly lower C/N than the high (127) pyrolysis temperature.

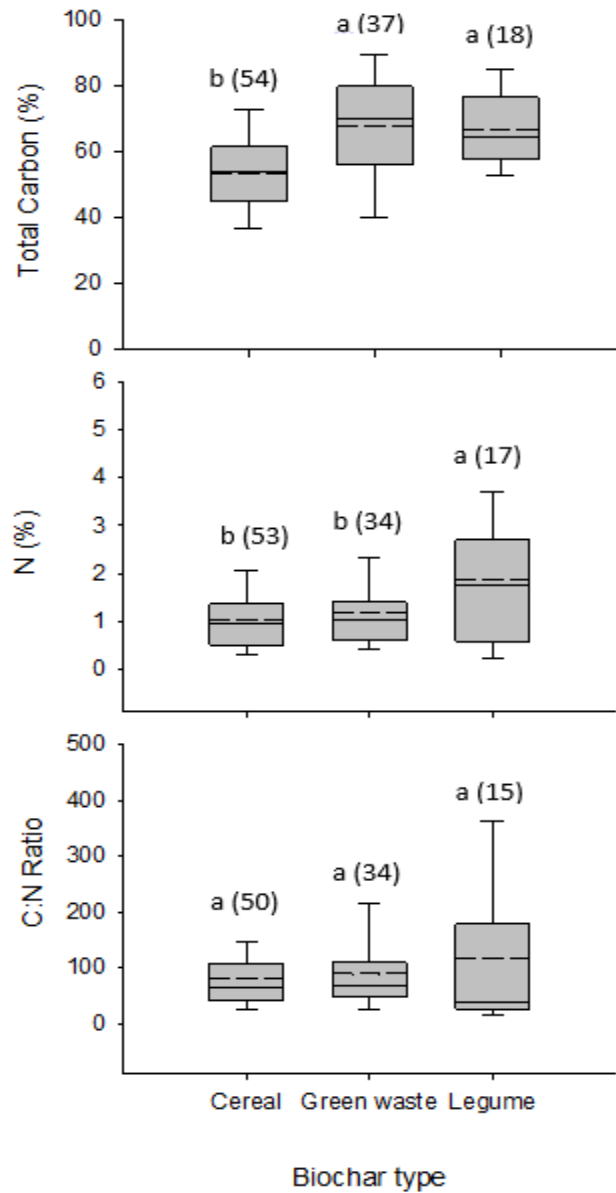


Figure 3.4 Effects of different crop residue feedstocks on biochar Total carbon, nitrogen and C/N. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

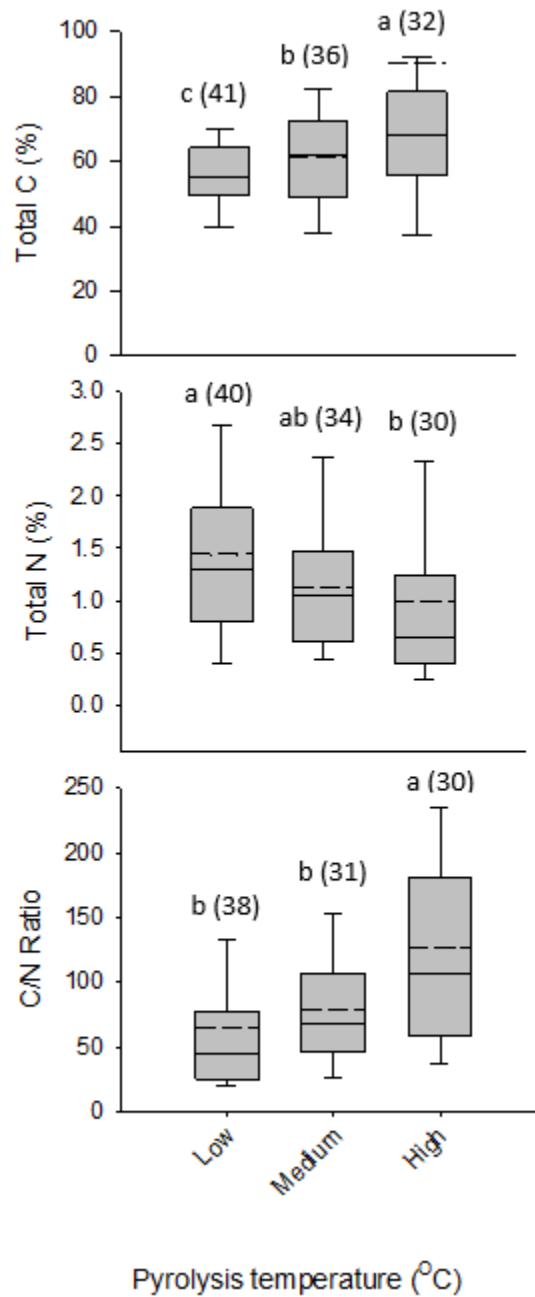


Figure 3.5 Effects of pyrolysis temperature on crop residue biochar total carbon, nitrogen and C/N. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.5 Effects of different crop residues and pyrolysis temperature on biochar total H, O and O/C and H/C ratio.

Different crop residue biochar had similar total H, O, H/C and O/C (Figure 3.6). However, pyrolysis temperature led to a significant decrease in the parameters (Figure 3.7). High pyrolysis temperature had significantly lower total H and O than low and medium pyrolysis temperatures, which were similar. The low and medium pyrolysis temperature were 95% and >100% higher than the high pyrolysis temperature; respectively (Figure 3.7). Total O in the low and medium pyrolysis temperature was >100% and 47% higher than the higher pyrolysis temperature. Biochar H/C and O/C showed a significant decreasing trend with increasing pyrolysis temperature. The H/C and O/C at each pyrolysis temperature was at low (0.80; 0.27), medium (0.45; 0.18) and at high (0.32; 0.11) pyrolysis temperature.

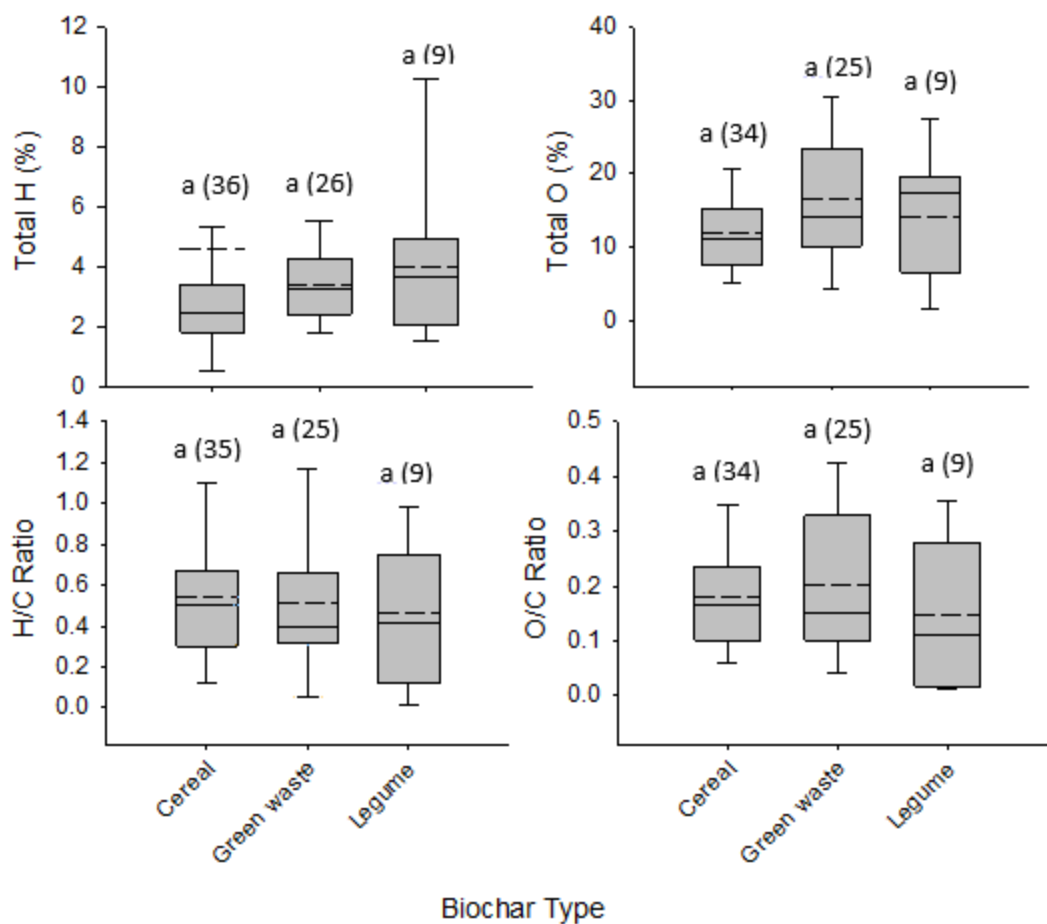


Figure 3.6 Effects of different crop residue feedstocks on biochar total H, O and H/C and O/C. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

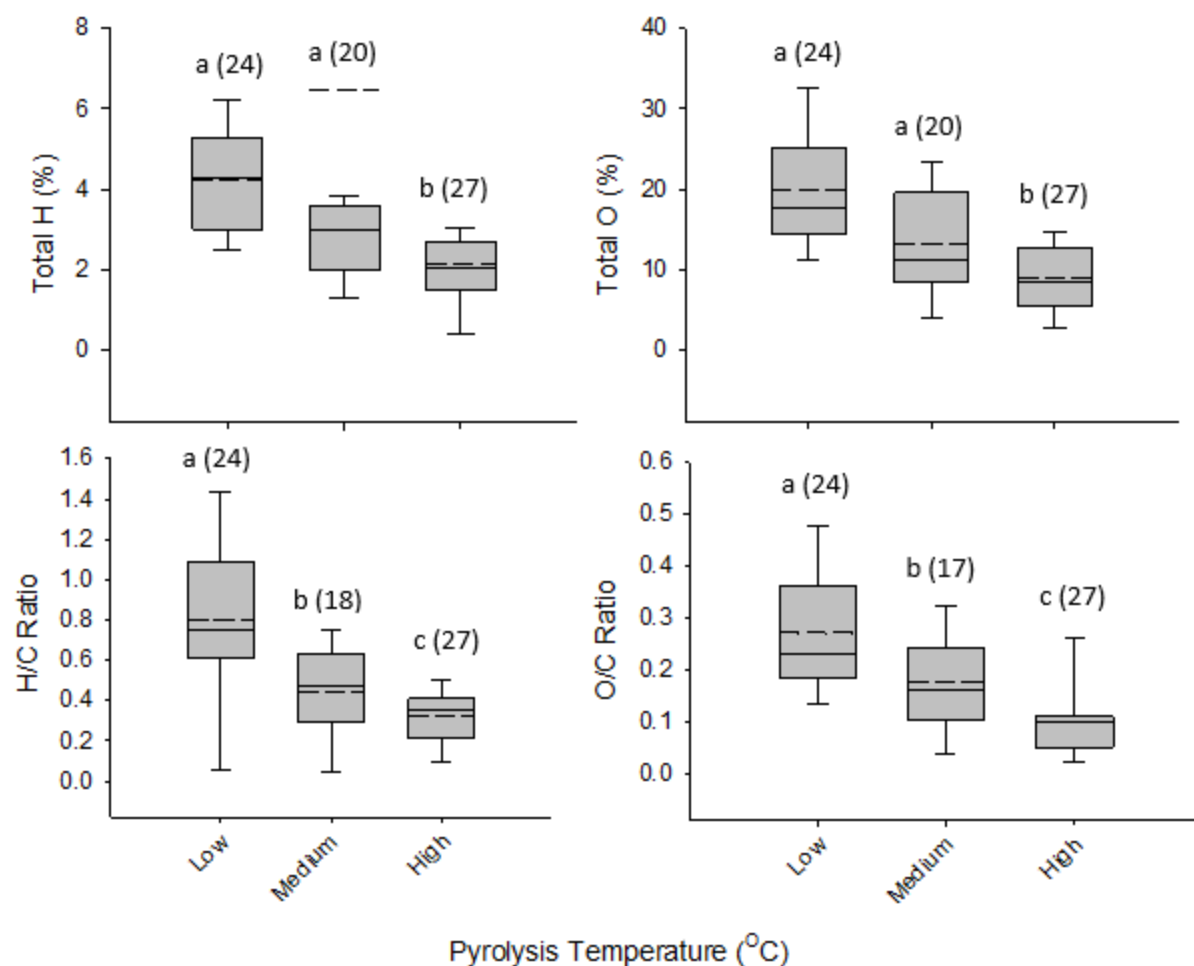


Figure 3.7 Effects of pyrolysis temperature on crop residue biochar total H, O and O/C and H/C ratio. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.6 Effects of different crop residues and pyrolysis temperature on biochar pH.

There was no significant difference in crop residue biochar $\text{pH}_{(\text{H}_2\text{O})}$ (Figure 3.8). Increasing pyrolysis temperature significantly increased biochar pH (Figure 3.9). The pH ranges around 7.42 to 9.87.

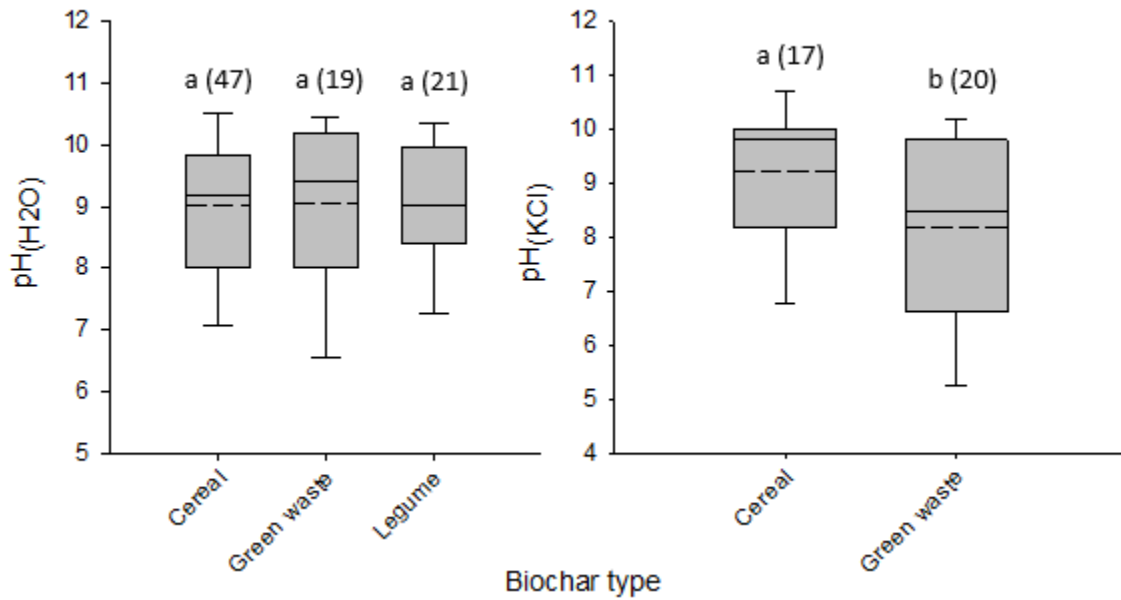


Figure 3.8 Effects of different crop residue feedstocks on biochar pH. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

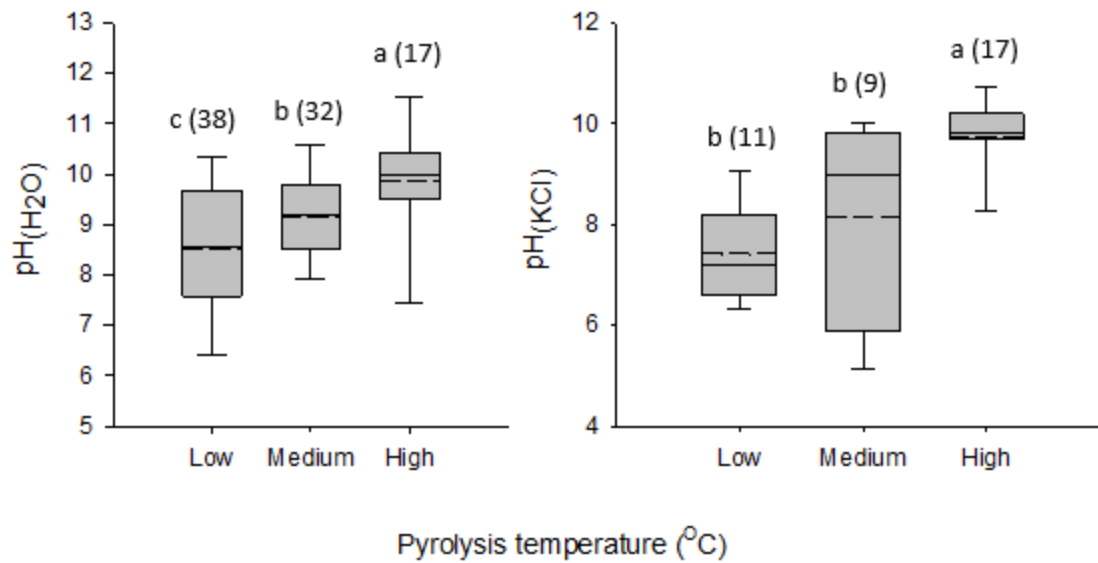


Figure 3.9 Effects of pyrolysis temperature on crop residue biochar pH. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.7 Effects of different crop residues and pyrolysis temperature on biochar exchangeable cations.

Exchangeable cations within crop residue biochar followed a similar trend (legume > cereal > green waste) except for Na, where cereal and legume were similar and higher than green waste biochar (Figure 3.10). Increasing pyrolysis temperature decreased exchangeable cations (Figure 3.11). However, medium and high pyrolysis temperature were similar but lower than low pyrolysis temperature. Exchangeable Na was not significantly affected by pyrolysis temperature.

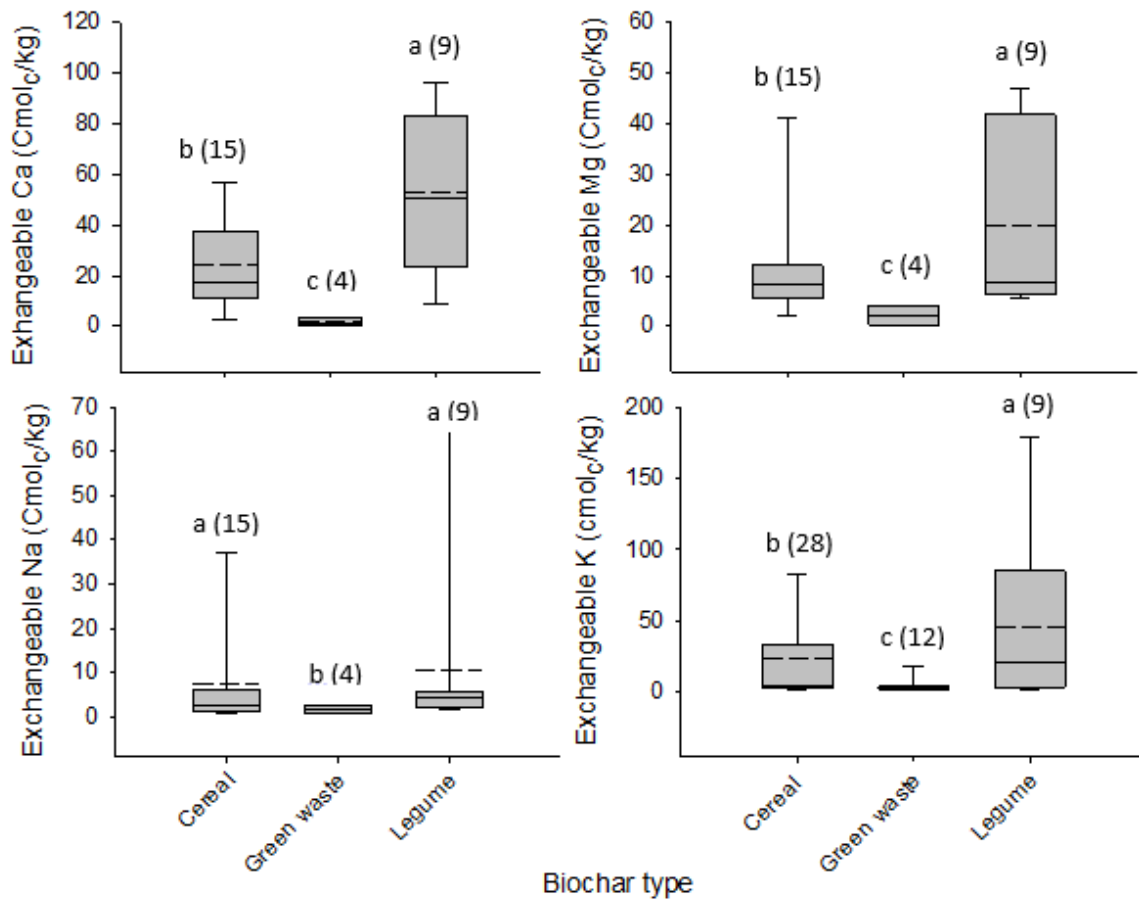


Figure 3.10 Effects of different crop residue feedstocks on biochar exchangeable cations. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

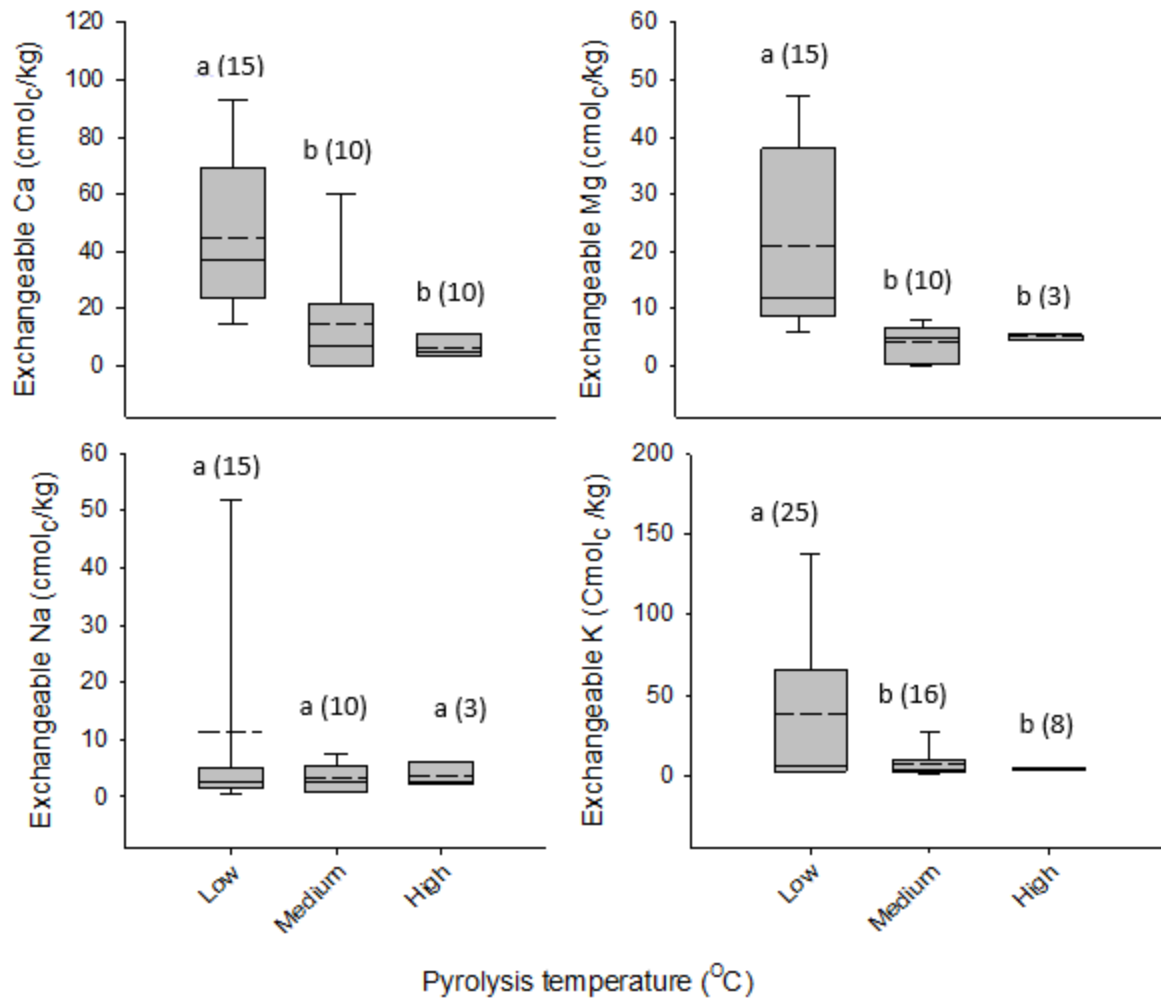


Figure 3.11 Effects of pyrolysis temperature on crop residue biochar exchangeable cations. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.8 Effects of different crop residues and pyrolysis temperature on biochar cation exchange capacity (CEC).

Legume biochar (59 cmol_c/kg) had significantly higher CEC than green waste (28.5 cmol_c/kg) (Figure 3.12). The CEC in cereal was not statistically different from green waste and legume biochar. High pyrolysis temperature (15 cmol_c/kg) had significantly lower CEC than low (61 cmol_c/kg) and medium (42 cmol_c/kg) pyrolysis temperature, which were not significantly different (Figure 3.13).

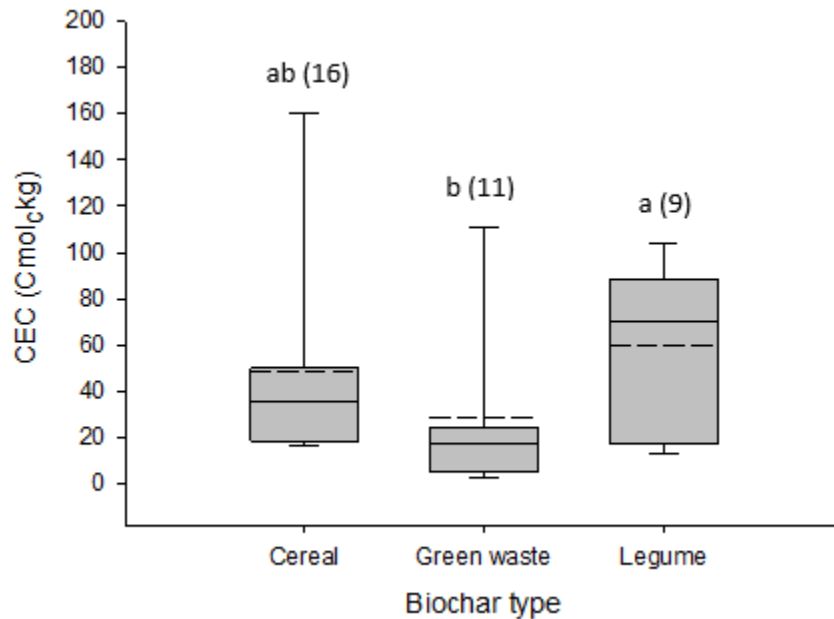


Figure 3.12 Effects of different crop residue feedstocks on biochar cation exchange capacity (CEC). Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

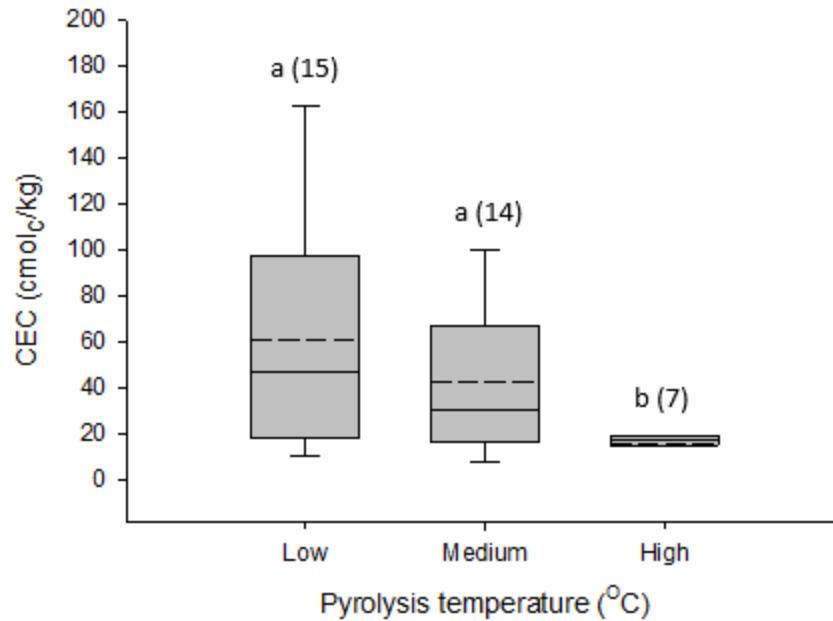


Figure 3.13 Effects of pyrolysis temperature on crop residue biochar cation exchange capacity. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.9 Effects of different crop residue and pyrolysis temperature on biochar extractable phosphorous.

The cereal (264 mg/kg) and green waste (242 mg/kg) biochar resulted in higher ($p < 0.05$) extractable P than legume which was 100 mg/kg (Figure 3.14). Medium pyrolysis temperature (400-550 °C) resulted in significantly higher extractable P than low (<400°C) and high (>550°C) pyrolysis temperature (Figure 3.15). The extractable P from medium pyrolysis temperature was >100 % than low and high pyrolysis temperature.

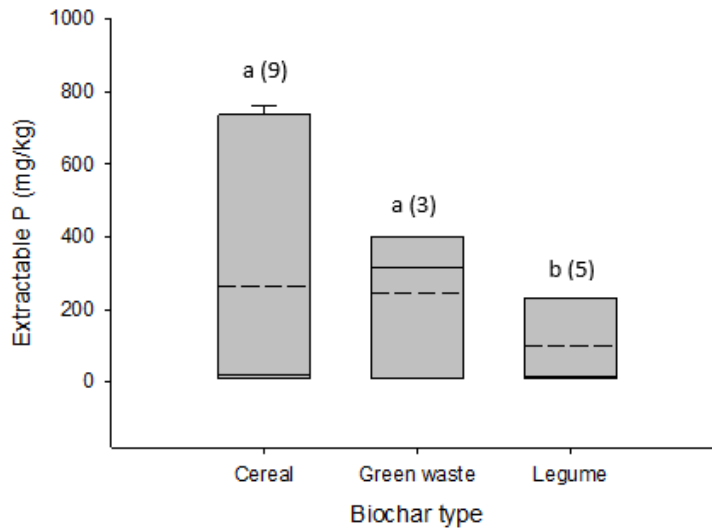


Figure 3.14 Effects of different crop residue feedstocks on biochar extractable phosphorous. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

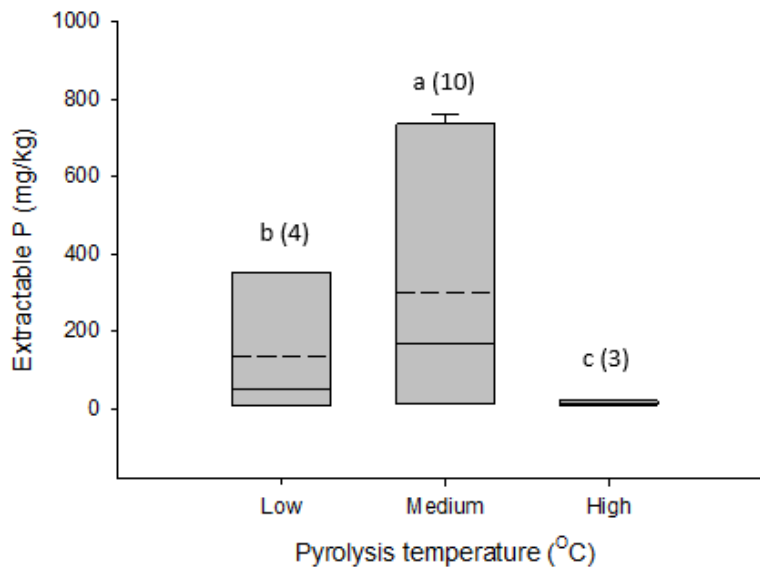


Figure 3.15 Effects of pyrolysis temperature on crop residue biochar extractable phosphorous. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.10 Effects of different crop residues and pyrolysis temperature on biochar electrical conductivity (EC)

The legume biochar had significantly higher electrical conductivity (EC) than green waste and cereal, which were not significantly different (Figure 3.16). The biochar was >100% and 98% higher than green waste and cereal; respectively. Low pyrolysis temperature had significantly higher EC than medium pyrolysis temperature (Figure 3.17). However, high pyrolysis temperature was not statistically different from low and medium pyrolysis temperature.

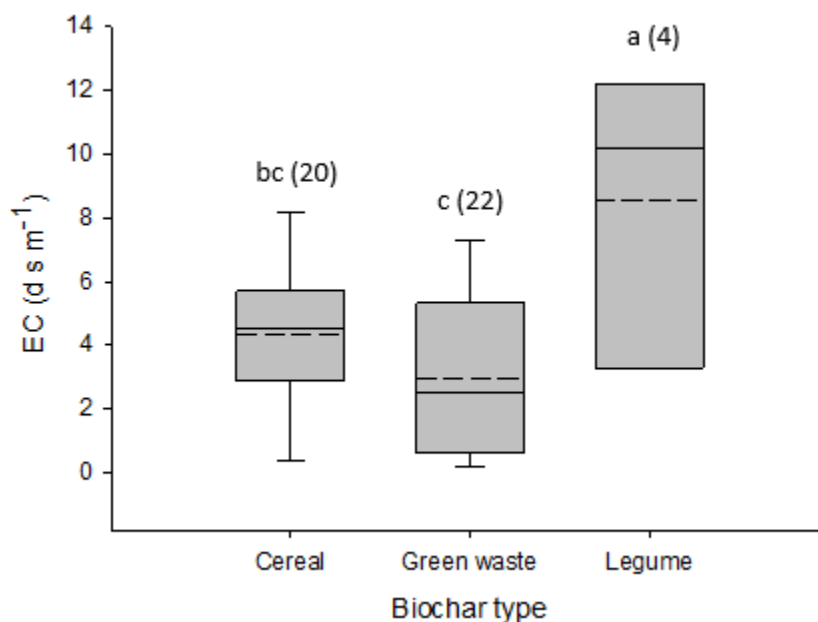


Figure 3.16 Effects of different crop residue feedstocks on biochar electrical conductivity. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

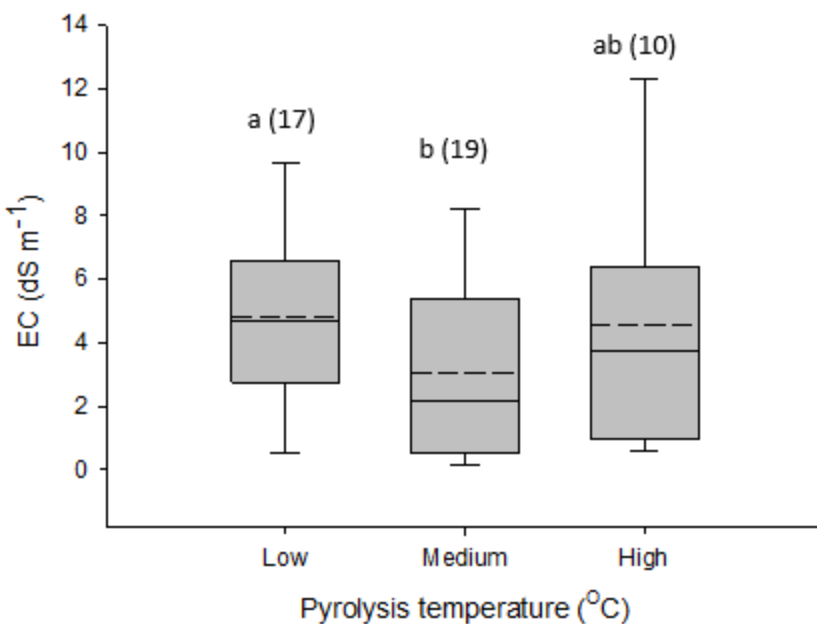


Figure 3.17 Effects of pyrolysis temperature on crop residue biochar electrical conductivity. Each plot indicates minimum, maximum, quartile 1 (25%) and quartile 3 (75%). Dotted line indicates means and solid lines indicate median. Similar letters in a box plot indicates no significant difference at $p < 0.05$. Numbers between brackets are the sample sizes.

3.3.2 Correlation matrix for pyrolysis temperature and biochar characteristics

Pyrolysis temperature was negatively correlated to yield ($r = -0.669$), volatile matter ($r = -0.67$), nitrogen ($r = -0.316$), hydrogen ($r = -0.723$), oxygen ($r = -0.676$), H/C ($r = -0.67$), O/C ($r = -0.598$), Ca ($r = -0.545$), Mg ($r = -0.7690$), and CEC ($r = -0.388$) and positively correlated to fixed carbon ($r = 0.6$), carbon ($r = 0.296$), C/N ($r = 0.395$) and pH (H₂O) ($r = 0.399$). Yield was negatively correlated to fixed carbon ($r = -0.836$), carbon ($r = -0.408$), C/N ($r = -0.369$), pH (H₂O) ($r = -0.679$) and positively correlated to nitrogen ($r = 0.301$), hydrogen ($r = 0.58$), oxygen ($r = 0.425$), H/C ($r = 0.707$), O/C ($r = 0.435$) and Mg ($r = 0.9$). For volatile matter, it was negatively correlated to ash content ($r = -0.329$), fixed carbon ($r = -0.583$), C/N ($r = -0.551$), pH (H₂O) ($r = -0.56$) and positively correlated to nitrogen ($r = 0.582$), hydrogen ($r = 0.817$), oxygen ($r = 0.715$), H/C ($r = 0.833$) and O/C ($r = 0.423$). Ash content was positively correlated to pH (H₂O) ($r = 0.385$), EC ($r = 0.438$),

and negatively correlated to C ($r = -0.52$), H ($r = -0.409$) and O/C ($r = -0.392$). Fixed carbon was negatively correlated to H ($r = -0.395$), O ($r = -0.514$), H/C ($r = -0.615$), O/C ($r = -0.681$) but positively correlated to C ($r = 0.828$), C/N ($r = 0.383$) and K ($r = 0.52$).

Carbon was positively correlated to C/N ($r = 0.208$), but negatively correlated to O/C ($r = -0.472$), CEC ($r = -0.465$) and P ($r = -0.769$). Nitrogen was positively correlated to H ($r = 0.453$), H/C ($r = 0.268$), Ca ($r = 0.532$), CEC ($r = 0.49$) and negatively correlated to C/N ($r = -0.946$). The C/N ratio was negatively correlated to H ($r = -0.378$), O ($r = -0.28$) and H/C ($r = -0.301$). The H was positively correlated to O ($r = 0.665$), H/C ($r = 0.659$), O/C ($r = 0.418$) and negatively correlated to pH (H₂O) ($r = -0.456$). The O was positively correlated H/C ($r = 0.372$), O/C ($r = 0.892$), CEC ($r = 0.762$) and negatively correlated to K ($r = -0.63$). For H/C, it was negatively correlated to K ($r = -0.443$), and OC was also negatively correlated to K ($r = -0.5$) but positively correlated to CEC ($r = 0.85$). For Ca, it was positively correlated to Mg ($r = 0.747$). For K, it was positively correlated to Ca ($r = 0.38$), Mg ($r = 0.557$), P ($r = 0.588$) and EC ($r = 0.435$).

Table 3.2 Spearman’s rank correlation of pyrolysis temperature and biochar characteristics.

	Temp	Yield	VM	Ash	FC	C	N	C/N	H	O	H/C	O/C	pH (H ₂ O)	pH (KCl)	K	Ca	Mg	Na	CEC	P	EC	
Temp	1																					
Yield	-0.669	1																				
VM	-0.67	0.576	1																			
Ash	0.194	-0.046	-0.329	1																		
FC	0.6	-0.836	-0.583	-0.229	1																	
C	0.296	-0.408	0.046	-0.52	0.828	1																
N	-0.316	0.301	0.582	0.0169	-0.162	0.086	1															
C/N	0.395	-0.369	-0.551	-0.151	0.383	0.208	-0.946	1														
H	-0.723	0.58	0.817	-0.409	-0.395	0.214	0.453	-0.378	1													
O	-0.676	0.425	0.715	-0.392	-0.514	-0.14	0.243	-0.28	0.665	1												
H/C	-0.67	0.707	0.833	-0.005	-0.615	-0.143	0.268	-0.301	0.659	0.372	1											
O/C	-0.598	0.435	0.423	-0.188	-0.681	-0.472	0.024	-0.163	0.418	0.892	0.196	1										
pH (H ₂ O)	0.399	-0.679	-0.56	0.385	0.249	-0.096	0.057	-0.068	-0.456	-0.15	-0.308	-0.1	1									
pH (KCl)	0.745	-0.602	-0.738	0.569	0.577	0.348	-0.055	0.127	-0.604	-0.71	-0.667	-0.7	1	1								
K	-0.19	-0.451	-0.274	0.262	0.52	-0.048	-0.19	0.142	-0.35	-0.63	-0.443	-0.5	-0.155	0.642	1							
Ca	-0.545	0.6	0.214	0.0061		0.018	0.532	-0.31	-0.5	-1	-1	-0.5	0.04		0.38	1						
Mg	-0.769	0.9	0.286	-0.164		0.004	0.464	-0.363	-0.5	-1	-1	-0.5	-0.245		0.557	0.747	1					
Na	0.031	0.6	0.036	0.188		0.143	0.198	-0.064	1	0.5	0.5	-0.5	0.175		0.236	0.168	0.118	1				
CEC	-0.388	0.0066	0.13	0.294	-0.455	-0.465	0.49	-0.4	0.161	0.762	0.531	0.85	0.058	-0.1	-0.42	0.121	-0.06	-0.396	1			
P	0.049	0.6	0.6	0.517		-0.769	-0.275	-0.418	-0.4	-1	-1	-0.5	-0.367		0.588	-0.398	-0.248	0.226	-0.105	1		
EC	-0.056	-0.187	-0.319	0.438	0.179	-0.201	0.018	-0.099	0.085	-0.3	0.0049	-0.2	0.274	0.349	0.435	-0.4	-0.4	1	0.024	0.5	1	

Highlighted correlations are significant at $p < 0.05$. Temp = pyrolysis temperature, VM = Volatile matter, FC = fixed carbon, C = carbon, N = nitrogen, O = oxygen, H = Hydrogen, CEC = cation exchange capacity, K = Potassium, Ca = Calcium, Mg = Magnesium, Na = Sodium P = phosphorous, EC = electrical conductivity.

3.4 Discussion

Feedstock composition and pyrolysis temperature are determining factors for crop residue biochar yield and its physical and chemical characteristics (Singh *et al.*, 2010). The crop residues are mostly composed of cellulose and hemicellulose (Enders *et al.*, 2012). Similar proximate analysis and yield could be explained by similar composition of the studied crop residues (Figure 3.2). The findings showed that yield, volatile matter and fixed carbon of biochar from legumes, cereals and other crop wastes were not affected by feedstock (Figure 2.2) but by pyrolysis temperatures (Figure 3.3). Similar to Peng *et al.* (2011) and Lehmann and Joseph (2012) observed characteristics of crop residue biochars were significantly affected by pyrolysis temperature. The lower yield observed at high temperature is due to extensive decomposition of organic material at higher temperature releasing volatile materials (Crombie *et al.*, 2013). This largely includes to the high degree of decomposition of cellulose, hemicellulose and lignin (Demirbaş and Arin, 2002). Cellulose and hemicellulose decompose completely at temperatures between 300 – 400 °C (Singh *et al.*, 2010) which could explain the huge mass loss from low to medium pyrolysis temperature (Figure 3.3). Pyrolysis temperature results in losses of carbon, hydrogen and thermal decomposition of hemicellulose, cellulose and lignin while concentrating the salts concentration and simultaneously increasing stable C content (Kloss *et al.*, 2012). Hence, the increase in pyrolysis temperature promotes carbonization or aromaticity (Chun *et al.*, 2004). The increase in aromatic carbon can be associated with the loss of H and O containing functional groups (Figure 3.7) which are aliphatic functional groups with increasing pyrolysis temperature.

The cereal residues result in biochar with higher ash content than the legumes and other green wastes. This was the result of differences in the chemical composition of the crop residues with cereals residues being rich in silica content as reported in the literature (Crombie *et al.*, 2013; Mukome *et al.*, 2013). The increase in salts concentration with pyrolysis temperature increases ash content (Figure 3.3). Pyrolysis temperature results to increase in ash due to volatilization, lowering the yield and leaving the ash content in the final products. The ash content of crop residue biochars is higher than wood derived biochar and lower than sewage sludge derived biochars (Kloss *et al.*, 2012; Singh *et al.*, 2010; Koetlisi and Muchaonyerwa, 2018). The higher the ash content in biochar the lower the carbon content of the biochar (Enders *et al.*, 2012; Windeatt *et al.*, 2014). The highest carbon content was highest in the legume (67%) and green waste (68%) and lowest in the cereal (53%). This corresponds with the ash content, with cereal

biochar having high ash content and legume with green waste having low ash content. This corroborates with Enders *et al.* (2012) suggestion that ash content hinders organic compound degradation and formation of aromatic structures thus biochars with high ash produces biochar with low fixed carbon content.

The high total nitrogen for legume relative to green waste and cereal (Figure 3.4) is plausibly due to the ability of legumes to fix nitrogen (Carlsson and Huss-Danell, 2003) making them N rich feedstocks. The results here confirm the discussion by Kookana *et al.* (2011) that N rich feedstocks results to N rich biochars. The similarity in C/N is because while legumes have higher C than cereal biochars, they also have higher N, suggesting that the C/N may not affect decomposition of biochars from crop residues. The C/N for crop residue tested is lower as compared with those of woody-derived biochar and higher as compared with those of sewage sludge (Singh *et al.*, 2010; Koetlisi and Muchaonyerwa, 2018). This implies that sewage sludge biochar will be decomposed more rapidly, while woody biochar will be resistance or stable to degradation, hence will remain in the soil for a long period of time as compared to the crop residue biochars.

High pyrolysis temperature showed the highest total carbon content (Figure 3.5) due to dehydration and decarboxylation of weak bonds (aliphatic compounds) released as volatile matter (Lehmann and Joseph, 2012; Crombie *et al.*, 2013; Domingues *et al.*, 2017) revealing the high aromatic carbon content. Similar results were reported by Jindo *et al.* (2014) and Mimmo *et al.* (2014). Total N decreased with increase in pyrolysis temperature due to N volatilisation at high temperature (Wu *et al.*, 2012). This means that at higher temperature the volatile matter consists of low C but concentrate C as aromatic materials in the final product. The increase in C/N was due to increased concentration of C and decreased concentrations of N.

The findings showed that total H, O, H/C and O/C of biochar from legumes, cereals and other crop wastes are not affected by feedstock but by pyrolysis temperatures. This was similar to biochar yield, volatile matter and fixed C. These parameters are lower than wood derived biochars and higher than sewage sludge derived biochars. Coherent with results from Spokas *et al.* (2012), the increase in pyrolysis temperature resulted in a decrease in H and O content. This is due to loss of volatile hydrocarbons and oxygenated hydrocarbons while increasing aromatic carbon and stability and decreasing cation exchange capacity (CEC) (Windeatt *et al.*, 2014). This align well with Singh *et al.* (2010) discussion that formation of aromatic carbon is

formed by continuous dehydration and decarboxylation which leads to higher degree of aromaticity and stability. The O/C ratio obtained are within the ranges of those reported by Spokas *et al.* (2012) 0.2 – 0.6 which indicates a residence time of 100 – 1000 years when incorporated into the soil. The woody derived biochars has higher elemental ratios while sewage sludge biochar has lower as compared to the crop residue biochars. This signifies that the woody derived biochar will be recalcitrant and will remain in the soil for years while the sewage sludge biochar will decompose easily.

The pH of biochar increased with increasing pyrolysis temperature (Figure 3.8). Such results have been previously reported by Zhao *et al.* (2013) and the increase was linked to enrichment of ash with increasing pyrolysis temperature (Butnan *et al.*, 2015) and hydrolysis of salts as pyrolysis temperature increases (Gaskin *et al.*, 2008). According to Lehmann and Joseph (2012) alkali and ash content are directly correlated to biochar pH. In literature, biochar pH has been reported to be between 4 to 12 (Singh *et al.*, 2010). This compares well with biochar pH values obtained since they were within the range found in literature. These results imply that crop residues biochars could be used as lime to neutralise acidity, hence, increase nutrient availability in acidic soils.

The crop residue feedstock had different cations (Figure 3.10). The concentration varies between feedstocks (Enders *et al.*, 2012) and different biochar (Windeatt *et al.*, 2014). This maybe plausibly due to differences in elemental composition (Singh *et al.*, 2010). Despite having high ash content, cereal residues had low basic cations as a result of high Si content relative to basic cations (Crombie *et al.*, 2013). An increase in pyrolysis temperature (>400°C) led to a decrease in exchangeable cation (Figure 2.11) due to the decrease in surface charge densities through loss of volatiles (Kloss *et al.*, 2012). Similar results were reported by Wu *et al.* (2012) on the decrease in cations with increasing pyrolysis temperature (> 400°C). The decrease in surface charged densities reduces the cations retained on the biochar surfaces.

Legume biochar had higher CEC (Figure 3.12), despite having similar C, H, O as the crop residue feedstocks. Higher N in biochar from legume biochar could suggest that the N containing functional groups make a major contribution to the biochar CEC. The decreased in CEC with increase in pyrolysis temperature (Figure 3.12) can be associated with the decrease in O and H and consequent decline in the oxygenated functional groups which are responsible for negative charges on biochar surfaces (Conz *et al.*, 2017; Domingues *et al.*, 2017). The CEC of biochar are higher due to enrichment of oxidised functional groups (carboxylic groups) on

its surface through pyrolysis (Liang *et al.*, 2006). The decline is also associated with the improvement of aromatic nature of biochar, lowering the surface charge.

The P-rich feedstocks provides higher amount of available P compared to P-poor feedstock (Glaser and Lehr, 2019). which explains the higher extractable P for cereal (Figure 3.14). The wood derived biochars has lower extractable P and the manure derived biochars has higher extractable P as compared to the crop residues tested (Glaser and Lehr, 2019). The enhanced P availability with medium pyrolysis temperature (Figure 3.15) was in line with (Nwajiaku *et al.* (2018), who reported increase in available P with increasing pyrolysis temperature. Pyrolysis temperature causes disproportionate volatilisation of carbon which leads to cleavage of organic P bonds and thus results to increased P availability in biochar (Nwajiaku *et al.*, 2018). However, a further increase in temperature (>550 °C) resulted to a decrease in P availability (Figure 3.15), due to disappearance of organic P in favour of inorganic P compound such as tricalcium phosphate (Glaser and Lehr, 2019). Another explanation is likely the volatilization of P which occurs at temperatures >700 °C (Wang *et al.*, 2014b) could also be due to decrease in cations availability (Wu *et al.*, 2012). Application of the crop residue biochar (produced at low to medium temperatures) to soils will increase P availability, due to the biochar richness in P concentration and the biochar liming effect will increase P availability. Legume had high electrical conductivity (Figure 3.16) possibly due to high salt concentration within the original feedstock (Singh *et al.*, 2010). This is supported by high exchangeable cation in Figure 3.10.

3.5 Conclusion

Crop residue biochars had similar proximate analysis, yield, and elemental composition of H and O and ratios with C (H/C and O/C). Cereal biochar had higher ash content, while legume and green waste biochar, had higher total carbon. Legume biochar had higher total nitrogen, exchangeable cations, cation exchange capacity and electrical conductivity, and lower extractable phosphorous than those from other feedstocks. Increasing pyrolysis temperature resulted in higher fixed carbon and ash content and lower yield, volatile matter, total N, H, O, H/C and O/C. High pyrolysis temperature therefore resulted in biochar with high stability. Exchangeable cations, cation exchange capacity and electrical conductivity decreased with pyrolysis temperature and extractable P was high at medium pyrolysis temperature. The biochars had alkaline pH, which increased with pyrolysis temperature. The use of these crop

residue biochars could sequester C and have liming effects in acidic soils, hence, enhancing availability of nutrients. The recommended pyrolysis temperature for sequestering C and liming acidic soils is high pyrolysis temperature. While medium pyrolysis temperature could be used for producing biochar for recycling nutrients.

CHAPTER FOUR: CHARACTERISATION OF BIOCHAR FROM POTATO WASTES FOR YIELD AND PHYSICO-CHEMICAL PROPERTIES AND IMPLICATIONS FOR LIMING OF ACIDIC SOILS

4.1 Introduction

To date, about 30% of food produced across the world goes to wastes (Mak *et al.*, 2020) of approximately 1.3 billion tonnes (Raak *et al.*, 2017). These food wastes end up in landfills and present disposal challenges since they undergo a series of bioconversions into biogas (Melikoglu *et al.*, 2013). The nutrients and carbon in these wastes can pollute ground water from leaching at landfills while the ammonia, methane, CO₂ and N₂O and odours contribute negatively to air quality and increase concentration of greenhouse gases in the atmosphere (Matsakas *et al.*, 2017). Over 3 billion tonnes of CO₂-C is released which is about 8% of total anthropogenic greenhouse gas emission (Mak *et al.*, 2020). Potato wastes are among the major food wastes globally.

A total of 35.5, 3.84 and 1.09 million tons of potato waste are produced globally in Africa and in South Africa, respectively (FAO, 2014). This waste is disposed at landfill sites and only a portion is used as animal feed (Wu, 2016). These waste materials have little economic value but when disposed they may have negative consequences on the environment due to odours during anaerobic decomposition and nutrient leaching to groundwater (Olsen *et al.*, 2001). Wu (2016) reviewed literature on alternative uses of potato peels and concluded that production of biogas and extraction of lactic acids, phenolic acids and alkaloids could contribute to food and pharmaceutical industries. The author, however, reported that the high costs of such industrial uses limit the practical benefits from the potato wastes. Waste management strategies that return these food wastes to agricultural soils could be a cheaper option to enrich soils and maintain or even improve crop productivity. Returning the wastes to agricultural soils could be a cheaper option.

Potato tubers contain high nitrogen (N) (Mateus-Rodríguez *et al.* 2012), and potassium (K) (Fritsch *et al.*, 2017). Hence, addition of potato wastes to soils could improve crop productivity in the long-term (Olsen *et al.*, 2001). The elemental composition of potato peel wastes reported by Toma *et al.* (1979) showed that potato peels contained 40% C, 1.4% N, 3.09% K, 0.3% P, 0.156% Ca,

0.150% Mg and 0.041% Na. Olsen *et al.* (2001) reported that cull potato contained 2.14% N, 2.40% K, 0.29% P, 0.074% Ca, 0.148% Mg and 0.0029% Na. Although the wastes may have been produced under different conditions in different parts of the world, the two studies suggest differences in elemental composition between cull potatoes and potato peels, and that both wastes may have high concentrations of macronutrients, particularly N and K. Elemental composition of potato culls and peels and its effect on biochar characteristics has not been thoroughly studied. This knowledge is vital for deciding between the direct uses of potato feedstocks or further processing into biochar as strategies for recycling of nutrients and storing carbon in the soil. Conversion of waste biomass to biochar has been a promising approach to lessen waste disposal challenges (Van Zwieten *et al.*, 2010) and improve nutrient recycling (Oni *et al.*, 2019).

Conversion of plant-based materials to biochar has been prominent in the literature, particularly rice husk, straw, maize, and pine bark. These plants derived biochar have been found to contain high aromatic C assignable to their lignin and cellulose content (Bird *et al.*, 1999). The latter prompts high resistance to microbial decomposition. The high C content can give biochar the ability to sequester carbon in the soil which could have been emitted to the atmosphere as CO₂-C. In South Africa, pine bark is a readily available plant-based waste material in the forestry industry. The characteristics of biochar derived from pine bark have been shown in numerous reports. However, there is a lack of information on the characteristics of biochar derived from potato waste. The differences in the chemical composition of these two plant materials may influence their biochar characteristics. This poses a need to understand how characteristics of potato wastes biochar compare with that from wood, one of the most used materials. Volatile matter (VM), ash content, and fixed carbon (FC) are among the most important parameters used for characterisation of biochar. Biomass materials with high nutrient concentration can produce biochar with high ash content and liming ability (Deenik *et al.*, 2010). Hence, biochar can be used to remediate acidic soils. The ash and FC have the ability of predicting biochar behaviour in terms of nutrient supply, liming potential and nutrient retention (Butnan *et al.*, 2015). Biochar produced at low temperature has been found to have higher VM and lower FC than those produced at high temperature (Jindo *et al.*, 2014). On the other hand, high temperature pyrolysis reduces yield and VM, and increases surface area, porosity and aromatic C content, which in turn increases the adsorption capacity and recalcitrance of biochar (Kloss *et al.*, 2012; Jindo *et al.*, 2014; Rehrah *et al.*, 2014; Zhang *et al.*, 2015). While numerous studies have been conducted on other waste products in terms of their

composition and the effect of their pyrolysis biochar characteristics, there is currently a scientific gap on characteristics such as biochar yield, VM, fixed C, aromatic C content, surface functional groups, physical structure, and nutrient composition, following pyrolysis of potato wastes. Understanding the chemical changes that occur during biochar production from potato waste due to pyrolysis temperature is of relevance to understand the potential contribution of the biochar in sequestering C (stabilisation), providing nutrients and retaining nutrients when the biochar is added to agricultural soils. Therefore, the objective of this study was to determine the effect of feedstock and pyrolysis temperature on the characteristics of biochar produced from potato peels (PP), cull potatoes (CP) and pine bark (PB) and its liming potential.

4.2 Materials and Methods

4.2.1 Potato and pine bark wastes

The biochar used in this study was produced from potato peels (PP), cull Potatoes (CP) and pine bark (PB). The PP were collected at the Pietermaritzburg CBD from shops that use potatoes for chips and hawkers. The PP were collected into black plastic bags, air-dried, and then stored in plastic bags. The CP were collected from the Pietermaritzburg Fresh Produce Market located in Mkondeni, Pietermaritzburg. The CP consist of whole potatoes of low market value as these are generally rotten. The CP were collected into black dustbins, chopped using a slasher and air-dried for four days, then stored in plastic bags. The PB was collected from a private forestry by-product factory located at Cramond, Pietermaritzburg air dried and stored in plastic bags. The PP, CP and PB samples were ground to < 2 mm particles using a grinding mill machine, Retsch KG 5657 HAAN, West Germany model, and stored in white plastic bags. The particles were then oven-dried at 80 °C for 24 hours.

4.2.2 Biochar production

The milled samples were pyrolysed at a muffle furnace (Enders *et al.*, 2012). The furnace temperature was raised to set levels of 350°C and 650°C at a rate of 10°C /min. The feedstocks were carbonized for 2 hours per pyrolysis temperature (Koetlisi and Muchaonyerwa, 2018). The biochars were cooled and weighed to determine the yield and stored in sealed plastic containers for further analysis. For convenience, the non-carbonised feedstocks (original feedstocks) were referred to as “0°C pyrolysis temperature”.

4.2.3 Volatile matter, ash content, moisture content and fixed carbon

Proximate analysis of the materials was done following the American Society for Testing and Materials (ASTM) standard 1762-84 protocol (Wu *et al.*, 2012). Moisture content was determined by oven-drying the milled samples at 105°C for 2 hours, while the volatile matter was based on weight loss at 950°C for 6 min. Ash was determined by weight loss after combustion at 750°C for 6 hours and fixed C was calculated using Equation 1 (Domingues *et al.*, 2017).

$$\text{Fixed C (\%)} = 100 - \text{volatile matter (\%)} - \text{ash (\%)} \quad \text{Equation 1}$$

4.2.4 Selected physico-chemical properties of the biochar types

The pH was determined in water and KCl at a ratio of 1:10 (Enders *et al.*, 2012). The EC was determined on the supernatant of pH_(H₂O) using an EC meter (Ohaus starter 3100C). Total carbon (C) and nitrogen (N) were analysed on a 0.2 g ground soil (< 250 µm), by dry combustion using the Leco Trumac (CNS) autoanalyser instrument (Leco Corporation, 2012). Total H was analysed using the CHN elemental analyser. Total O was calculated using equation 2 (Enders *et al.*, 2012). Extractable P was determined calorimetrically following AMBIC – 2 extractions as described by Non-Affiliated Soil Analysis Working Committee (1990). For each sample, 2.5 g was transferred into individual centrifuge tubes and then 25 mL of Ammonium Bicarbonate (AMBIC-2) solution added. The suspension was shaken at 180 cycles per minutes for 15 minutes on a reciprocal shaker (Model E5850 Thomas Scientific, Swedesboro, NJ, USA) at 6000 rpm. The mixture was filtered

using whatman No.1 filter papers into storage bottle. A volume of 2 ml of the extract was diluted with 8 ml of distilled water followed by addition of 10 ml colour reagent while slowly swirling. The mixture was allowed to stand for 45 to allow for the blue colour development prior to analysis using the UV/VIS spectrophotometer at a wavelength of 670 nm (Murphy and Riley, 1962). The cation exchange capacity (CEC) and exchangeable bases were determined using the 1M ammonium acetate (NH₄OAC) method (Ross and Kettering, 2011). The concentration of NH₄⁺ was determined using the Thermo Scientific Gallery Discrete Auto-analyser, following some leaching using ethanol. The solution was also analysed for all basic cations using Atomic absorption spectrometry (Ca²⁺ and Mg²⁺) and Atomic flame spectrometry (K⁺). For K analysis, Caesium (1200 mg/L) solution was added (5 ml) to the extract as an ionisation suppressant to reduce interference from other elements, as for Ca and Mg, Strontium (2500 mg/L) was added (1 ml). The biochar liming potential or calcium carbonate equivalent was evaluated following the method by Singh *et al.* (2017). For each biochar sample, 0.5 g was transferred into a centrifuge tube and then treated with 10 ml of 1M HCl. The solution was shaken at 180 cycles per minutes for 2 hours on a reciprocal shaker (Model E5850 Thomas Scientific, Swedesboro, NJ, USA) at 6000 rpm and left to stand overnight (16 hours). It was titrated against 0.5M NaOH to reach a pH value of approximately 7 and the volume used was recorded. The results were used to calculate the calcium carbonates equivalents following equation 3.

$$\text{Total O (\%)} = 100 - (\text{C} + \text{H} + \text{N} + \text{ASH}) \quad \text{Equation 2}$$

$$\text{CaCO}_3 \text{ equivalent (\%)} = \frac{M \times (b - a) \times 10^{(-3)} \times 100.09 \times 100}{2 \times W} \quad \text{Equation 3}$$

Where:

“M” is the molarity of NaOH (mol L⁻¹), “b” is the NaOH volume (ml) used by the blank, and “a” is the volume (ml) of NaOH used by the biochar sample. The “W” is the mass (g) of biochar used.

4.2.5 Surface functional groups

Fourier Transformed Infrared (FTIR) spectrometry was used to analyse the chemical functional groups of the feedstock and biochar as explained by Koetlisi and Muchaonyerwa (2018). Infrared spectrum in the region of 400-4000 cm^{-1} was obtained by allowing the shining beam containing many frequencies of light at once to pass through the sample and measured absorbance of the beam by the sample. The Chemical functional groups were then assigned to the wave numbers from the FTIR spectrometry.

4.2.6 External morphology and surface characteristics

The surface characteristics of the biochars were analysed by using Scanning Electron Microscope (SEM) (EVO LS15, Carl Zeiss Microscopy, New York, USA). The samples were held onto an adhesive carbon tape on an aluminum stub. They were sputtered with gold coating for 6 runs prior to viewing using a gold sputtering machine (Quorum Q150R ES, Quorum Technologies, East Sussex, UK). The analyses through using SEM involved a beam of electrons generated in a vacuum, which is collimated by electromagnetic condenser lenses and scanned across the sample surface by a coil. Secondary electrons were then made to fall on the surface of a photosensitive plate in a photomultiplier tube. Amplified electrons are sent to phosphorescent screen which provided magnified image of sample surface.

4.2.7 Incubation Experiment (Liming potential)

The study was conducted at the University of KwaZulu Natal Pietermaritzburg campus (29° 37' 33.9'' S; 30° 24' 14'E) in the province of KwaZulu-Natal in South Africa.

Soils

The two soils used in this study were collected from the University of KwaZulu-Natal Research Farm, Ukulinga (29° 39' 33.9" S; 30° 24' 14"E), and Bulwer (29° 48' 27" S; 29° 45' 35"E). The Ukulinga area receives a mean annual precipitation of 750mm and the soil was under natural

vegetation. The soil from Ukulinga was Bonheim form, with melanic A horizon overlying pedocutanic B horizon (Soil Classification Working Group, 2018). The Bulwer area receives a mean annual precipitation of 877 mm and the soil was used for cultivation of maize. The soil from Bulwer was a Clovelly soil form, with orthic A horizon overlying yellow-brown apedal B horizon (Soil Classification Working Group, 1991). Which was translated to Luvisol and Ferralsol; respectively according to the world classification system (Fey, 2010). The bulk soil samples were collected from the 0–20 cm depth, mixed and homogenized, air-dried and sieved (< 2mm) before analysis.

4.2.8 Incubation experimental set-up

The experiment was a 2×6 in a completely randomized design. The factors were soil types (2 levels); CP and PB feedstock and their biochars at two pyrolysis temperatures (350 and 650°C) (6 levels) triplicated. The biochar application rates were added as lime rates (i) no lime added, (ii) added at the recommended rate and (iii) added at half the normal recommended rate. The lime required to neutralise acidity was calculated (Equation 4) following Manson *et al.* (2012). The recommended lime rate were 5 t ha⁻¹ and 29 t ha⁻¹ for Ukulinga and Bulwer soil; respectively. The soil field capacity moisture content was measured using a pressure plate at -33 kpa. The 100g soil was placed in 500 ml plastic containers with biochar and mixed thoroughly before the soil was moisten. Lime was used as a reference material. The containers were tightly closed with lids and four holes were drilled below the rim to allow gas exchange. The soils were maintained to 100% water holding capacity and the moisture was corrected throughout the incubation based on weight loss. The soils were incubated for 10 days in a constant temperature room at 25°C, as described by Singh *et al.* (2017) and analysed for pH.

$$\text{Lime Requirement (t ha}^{-1}\text{)} = [\text{"Exch. Acidity"} - (\text{"Total cations"} \times \text{PAS}/100)] \times F \quad \text{Equation 4}$$

Where:

PAS is the permissible acid saturation for the crop selected. For this study, the PAS was 5% acid tolerance. F is a factor indicating the amount of lime required to neutralize 1 cmolc/L of exchangeable acidity.

4.2.9. Analysis

Analysis of total C, N, and soil pH

Total carbon (C) and nitrogen (N) were analysed, on a 0.2 g ground soil (< 250 µm), by dry combustion using the Leco Trumac (CNS) autoanalyser instrument (Leco Corporation, 2012). Soil pH was determined in distilled water and in 1M KCl at a ratio of 1:5, where 5 g of soil was suspended in 25 ml of either distilled water or 1M KCl. The samples were stirred with a glass rod and allowed to stand for 30 minutes, before measurement of pH of the supernatant using a pH meter (Ohaus starter 2100).

Analysis of extractable-P, exchangeable bases and acidity

Extractable P was determined calorimetrically following AMBIC – 2 extraction. Soil (2.5 g) was weighed into a 100 cm³ centrifuge tube and 25 ml of AMBIC-2 solution was added, and the suspension was shaken at 180 cycles per minutes for 30 minutes using a reciprocal shaker (Model E5850 Thomas Scientific, Swedesboro, NJ, USA). The supernatant was filtered using a Whatman No. 41 filter paper into storage bottles. An aliquot of the extract (2 ml) was diluted with 8 ml of distilled water, followed by slow addition of the colour reagent (10 ml) while mixing to allow for even distribution. The mixture was allowed to stand for 45 min prior to analysis using the UV/VIS spectrophotometer at a wavelength of 670 nm (Murphy and Riley, 1962).

Soil (5 g) was weighed into a 100 ml centrifuge tube and 50 ml of 1M ammonium acetate (NH₄OAC) (pH 7) was added to determine exchangeable bases. The soil suspension was shaken for 30 minutes and left for 2 minutes before filtration into storage bottles using a Whatman No. 41 filter paper. The extracts were then analysed for Ca, Mg, and K using an atomic absorption (AA) spectrophotometer (Varian AA 240). For K analysis, Caesium (1200 mg/L) solution was added (5

ml) to the extract as an ionisation suppressant to reduce interference from other elements, as for Ca and Mg, Strontium (2500 mg/L) was added (1 ml).

Exchangeable acidity was extracted from 5 g of soil sample with 50 ml of 1M KCl in a 100 ml centrifuge tube. The contents of the centrifuge tube were shaken using a reciprocal shaker at 180 cycles per minute, for 4 minutes, followed by centrifugation at 400 rpm for 2 minutes. The supernatant was filtered using a Whatman No. 41 filter paper into a 100 ml storage bottle. An aliquot of the filtrate (25 ml) was transferred into 100 ml conical flask and 6 drops of phenolphthalein indicator were added, before titration with 0.01M NaOH until a pink endpoint that lasted for at least 30 seconds. The same procedure was followed for a blank which contained 25 ml of 1M KCl (Lourenzi *et al.*, 2011).

Analysis of bulk density and field capacity

Soil bulk density was measured on undisturbed soil cores by the core method (Blake, 1965). The soil cores were sampled, weighed (W2), oven-dried at 105°C for 48 hours, and weighed again (W3). The weight of the core rings and the lids were also recorded (W1). The bulk density was calculated using the oven dry core mass and the volume.

Field capacity was determined using the pressure plate apparatus with the samples at suctions of -33kpa as described by Smith and Mullins (1991). Each soil sample was replicated 3 times for the analysis. The core samples with soil were trimmed to the cylinder volume, saturated with distilled and placed in a pressure plate at -33 kpa and allowed to drain for 24 hours. The core rings were weighed and oven dried over-night and were weighed again.

4.3.0 Statistical analysis

The chemical characteristics, calcium carbonate equivalent, of biochar were analysed using GenStat 18th edition by subjecting them to two-way analysis of variance (ANOVA) to show effects of pyrolysis temperature and feedstock type. The analysis of variance was carried out in the two soils separately for the assessment of acid neutralisation potential of the biochars. Mean separation

was done using least significant difference (LSD) at $p < 0.05$. The Tukey-Kramer test was also used to separate treatment means at $p < 0.05$ and was used in the description of the results.

4.3 Results

4.3.1 Biochar yield and moisture content

Biochar yield decreased with increasing pyrolysis temperature for all the three feedstocks (Table 4.1). Biochar yield varied between feedstocks and was greater for PB, followed by PP and CP, at both 350 °C and 650 °C pyrolysis (Table 4.1). As expected, the biochars had significantly lower ($p < 0.05$) moisture content than the untreated feedstocks (Table 4.1). However, there were no consistent differences in moisture content of the different materials between pyrolysis temperatures (Table 4.1). Potato waste biochars had higher moisture content than that of pine bark biochar at both pyrolysis temperatures. At the pyrolysis temperature of 650 °C, PB had the lowest ($p < 0.05$) moisture content among all treatments.

Table 4.1 Moisture content and yield of biochar prepared from different types of feedstocks.

Pyrolysis temperature (°C)	Feedstock	Yield (%)	Moisture content (%)
0	CP	100 ^g	11.6 ^f
	PP	100 ^g	10.1 ^e
	PB	100 ^g	10.3 ^{ef}
350	CP	30.1 ^c	3.51 ^{cd}
	PP	33.9 ^e	4.15 ^c
	PB	52.2 ^f	2.58 ^{ab}
650	CP	21.8 ^a	6.08 ^d
	PP	24.5 ^b	4.40 ^c
	PB	33 ^d	1.80 ^a

*0°C pyrolysis temperature signifies the original feedstock; values on the same column with different letters indicate significant differences ($p < 0.05$). CP= Cull potato waste; PP= peel potato waste; PB= pine bark waste.

4.3.2 Concentrations of volatile matter, ash and fixed carbon in the materials

The increase in pyrolysis temperature led to a decrease ($p < 0.05$) in volatile matter and to an increase in ash and fixed C for all the feedstocks (Fig. 4.1). The trends of these parameters were in the order: CP > PP > PB for volatile matter PP > CP > PB for ash and PB > CP > PP for fixed C at all pyrolysis temperatures, except at 350 °C, where PB had higher volatile matter than the other two. Ash concentration was considerably higher for the potato biochars compared to pine bark. Differences in fixed C were rather small between biochars at 350 °C, while at 650 °C fixed C was higher for pine bark, and it followed an opposite trend to that of ash for each pyrolysis temperature. The amount of volatile matter ranged 70-78% for feedstocks, 30-41% for biochars at 350 °C and 6-14% for biochars at 650 °C pyrolysis. Ash content ranged 0.4-7.5% for feedstocks, 0.9-19% for biochars at 350 °C and 2-26% for biochars at 650 °C pyrolysis. The content of fixed C ranged 17-30% for feedstocks, 51-58% for biochars at 350 °C and 61-92% for biochars at 650 °C pyrolysis.

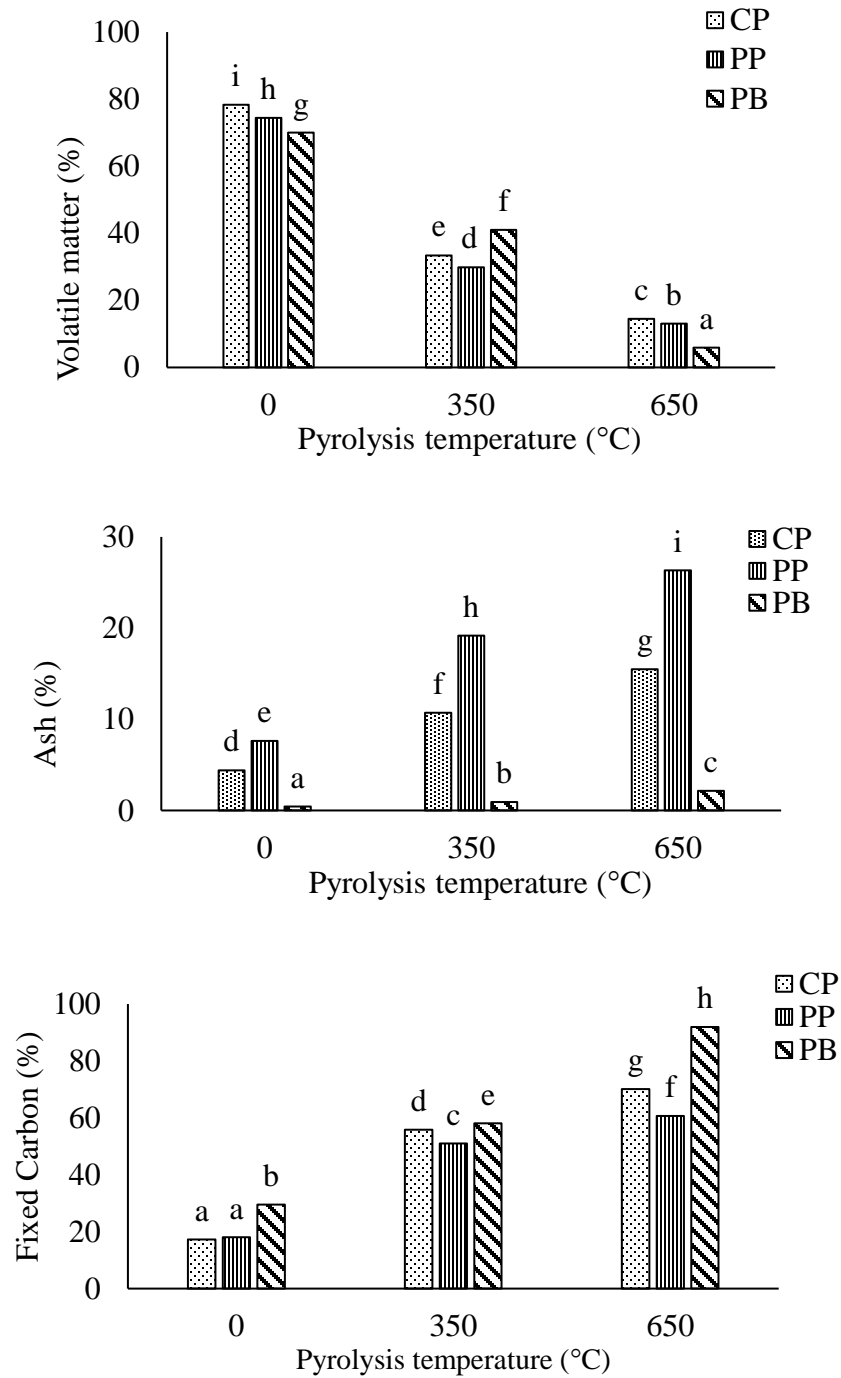
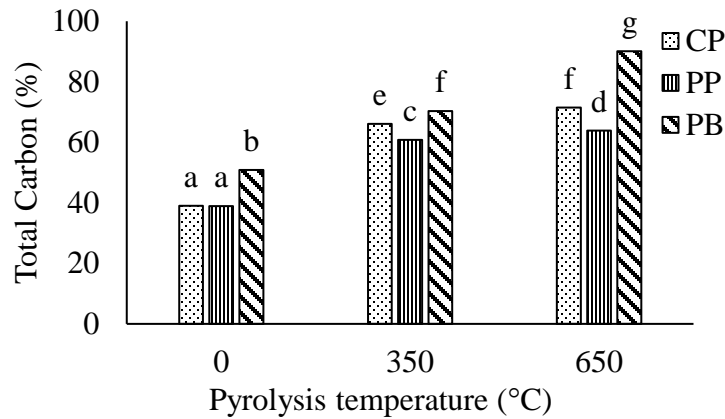


Figure 4.1 Concentrations (%) of volatile matter, ash and fixed carbon for different feedstocks and biochar types pyrolysed at 350 and 650 °C.

4.3.3 Concentrations of carbon, nitrogen, hydrogen and oxygen and their ratios

Total C concentration followed the same trend as that of fixed C for all the materials. Total C increased with increasing pyrolysis temperature across all feedstocks (Fig 4.2). Among feedstocks, PB had greater total C concentration than the potato wastes. This trend was maintained in the biochars after pyrolysis at both temperatures (Fig 4.2). In pine bark, pyrolysis increased total C to 70.3% at 350°C and 90.1% at 650 °C (total C in pine bark feedstock was 50.9%). Pyrolysing CP increased total C from 39% to 66% at 350 °C and to 71% at 650 °C, while for PP total C increased from 39% to 61% at 350°C and to 64% at 650 °C. Total nitrogen (N) content in the feedstocks ranged from 0.249% to 1.468%, being significantly higher for the potato wastes compared to pine bark (Fig. 4.2). Total N content increased significantly ($p<0.05$) after pyrolysis in the potato wastes, but not in PB. However, total N content declined when pyrolysing at 650 °C compared to 350 °C. Pyrolysing CP increased total N from 1.1% to 2.2% at 350 °C and to 1.4% at 650 °C, while for PP total N increased from 1.5% to 2.5% at 350 °C and to 1.8% at 650 °C.



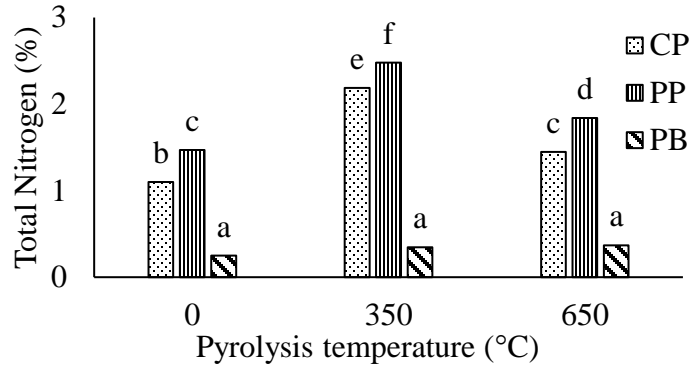


Figure 4.2 Total carbon and nitrogen content (%) of the feedstocks and biochar types pyrolysed at 350 and 650 °C.

Pine bark and its biochar had much higher ($p < 0.05$) C/N than potato wastes at each pyrolysis temperature (Table 4.2). Pyrolysis at 350 °C caused no changes in C/N, whereas at 650 °C it increased C/N across materials. Pyrolysis led to significant decreases in O, O/C, H, and H/C. Increasing pyrolysis temperature from 350 to 650 °C lowered O, H concentration and O/C and H/C ratios significantly ($p < 0.05$). Regarding the feedstocks, PB had lower O, H, O/C and H/C than both potato wastes (Table 4.2). At 350 °C, PB had higher O and O/C than CP and PP, while at 650 °C CP had higher O concentration than PP and PB, and higher O/C than PB. There were no differences in H and H/C between biochars at each temperature.

Table 4.2 The C/N, H/C and O/C ratios of studied biochars and feedstocks.

Pyrolysis Temperature (°C)	Feedstock	C/N	O	O/C	H	H/C
0	CP	35.8 ^{ab}	49.1 ^h	1.26 ^g	6.31 ^d	0.1618 ^d
	PP	26.5 ^a	45.8 ^g	1.18 ^f	6.09 ^d	0.1564 ^d
	PB	205 ^c	43.3 ^f	0.850 ^e	5.15 ^c	0.1013 ^c
350	CP	30.2 ^{ab}	17 ^d	0.257 ^c	4.05 ^b	0.0613 ^b
	PP	24.5 ^a	13.7 ^c	0.225 ^c	3.83 ^b	0.0629 ^b
	PB	203 ^c	24.7 ^e	0.351 ^d	3.78 ^b	0.0538 ^b
650	CP	49.3 ^b	9.74 ^b	0.136 ^b	1.74 ^a	0.0244 ^a
	PP	34.7 ^{ab}	6.24 ^a	0.0977 ^{ab}	1.73 ^a	0.0272 ^a
	PB	245 ^d	5.09 ^a	0.0565 ^a	2.19 ^a	0.0243 ^a

Values on the same column with different letters indicates significant differences ($p < 0.05$).

Selected physico-chemical properties of the biochar types

The pH values, both in KCl and water, significantly increased with increasing pyrolysis temperature. Potato waste biochars (and feedstock) had higher pH than pine bark (Table 4.3). At each pyrolysis temperature, the pH of all the materials were significantly different ($p < 0.05$) from each other and were in the order $PP > CP > PB$. Potato feedstock and biochar types all had alkaline pH values, whereas the pine bark feedstock and biochar produced at 350 °C had acid pH. The pH values in KCl (and in water) ranged 3.0 - 8.3 (4.0-8.6) among feedstocks, 4.8 -10.3 (6.7-11.1) for the 350 °C biochars and 9.1-12.4 (9.1-12.6) for the 650 °C biochars.

Extractable P increased with increasing pyrolysis temperature, except for PB, which was extremely low ($< 15 \text{ mg kg}^{-1}$). Potato wastes and resultant biochars had higher ($p < 0.05$) extractable P than PB, at all pyrolysis temperatures. While there were no differences in extractable P between the two potato waste feedstocks, CP biochar had significantly ($p < 0.05$) higher P at 350 °C and lower at 650 °C pyrolysis temperatures than the PP biochar. Pyrolysis of CP increased extractable P from 82 to 712 mg kg^{-1} (nine-fold) at 350 °C and to 1077 mg kg^{-1} (13-fold) at 650 °C, while for PP, P increased from 44 to 194 mg kg^{-1} (4-fold) at 350 °C and to 1147 mg kg^{-1} (26-fold) at 650 °C. A significant decrease ($p < 0.05$) in ammonium acetate extractable K content occurred as a result of pyrolysis at 350 °C with no further decline at 650 °C for both potato wastes, but not for PB (Table 4.3). Potato wastes and resultant biochars had higher ($p < 0.05$) extractable K than PB at all pyrolysis temperatures. Pyrolysis of CP decreased extractable K from 23 to 16 $\text{cmol}_c \text{ kg}^{-1}$, while for PP the K decreased from 19 to 12 $\text{cmol}_c \text{ kg}^{-1}$ both at 350 °C.

Pyrolysis of PP increased ammonium-acetate Ca from 1.7 to 2.4 $\text{cmol}_c \text{ kg}^{-1}$ at 350 °C and to 3.5 $\text{cmol}_c \text{ kg}^{-1}$ at 650 °C, while for PB the Ca decreased at 350 °C. There were no significant changes in Ca with pyrolysis for CP. Except for PB, ammonium-acetate extractable Mg decreased with pyrolysis temperature. Increasing pyrolysis temperature from 350 to 650 °C led to a further decrease in Mg for PP and CP, while PB was not affected. Pyrolysis decreased CEC for PP and PB, while CP was not affected. The trend of CEC was $CP > PP > PB$ at all pyrolysis temperatures. An increment of 300 °C (350°C to 650 °C) led to a further significant decrease in CEC for PP, with no effect on PB.

Potato waste and resultant biochars had significantly higher EC than PB, at all pyrolysis temperatures. The increase in pyrolysis temperature led to an increase in EC for CP and PP but not for PB. Potato wastes and their biochars had higher CCE ($p < 0.05$) than PB at each pyrolysis temperature. There were no differences in CCE between potato wastes and their resultant biochars for each pyrolysis temperature.

Table 4.0 pH of water and KCl, exchangeable bases, CEC, and EC of feedstocks and biochar types studied.

Pyrolysis temperature (°C)	feedstock	pH		P mg kg ⁻¹	Exchangeable cations cmol _c kg ⁻¹			CEC	CCE %
		KCl	Water		K	Ca	Mg		
0	CP	7.69 ^c	8.12 ^c	81.9 ^b	22.7 ^e	1.11 ^{abc}	6.38 ^c	57.7 ^d	6.97 ^a
	PP	8.29 ^d	8.61 ^d	43.5 ^{ab}	19.2 ^{de}	1.66 ^{cd}	9.67 ^e	57.5 ^d	6.67 ^a
	PB	3.08 ^a	4.00 ^a	14.1 ^a	1.14 ^a	1.24 ^{bcd}	2.29 ^b	12.3 ^b	7.47 ^a
350	CP	10.3 ^f	11.1 ^g	712 ^d	15.9 ^{cd}	1.47 ^{bcd}	7.58 ^d	57.7 ^d	11.5 ^b
	PP	10.1 ^f	10.7 ^f	194 ^c	11.9 ^b	2.39 ^e	7.35 ^{cd}	31.0 ^c	9.43 ^{ab}
	PB	4.78 ^b	6.65 ^b	0.0 ^a	0.92 ^a	0.64 ^a	0.340 ^a	3.25 ^a	8.01 ^a
650	CP	11.6 ^g	12.1 ^h	1077 ^e	13.7 ^{bc}	1.07 ^{ab}	2.95 ^b	56.0 ^d	17.5 ^c
	PP	12.4 ^h	12.6 ⁱ	1147 ^f	10.1 ^b	3.48 ^f	3.24 ^b	10.2 ^b	19.68 ^c
	PB	9.10 ^e	9.14 ^e	0.0 ^a	2.55 ^a	1.71 ^d	0.188 ^a	2.82 ^a	9.43 ^{ab}

Values on the same column with similar letter indicates a non-significant difference ($p < 0.05$) and with different letters indicates a significant difference ($p < 0.05$)
 CEC=cation exchange capacity; EC= electrical conductivity, CCE= calcium carbonate equivalent. CP= cull potato waste; PP= peel potato waste; PB= pine bark waste.

4.3.4 Surface functional groups and physical structures of the materials

The chemical functional groups are shown in Table 4.4. As expected, the CP and PP had similar chemical functional groups. The FTIR of all feedstock samples showed a band at 3200-3570, 1800-21000 and 1550-1650 cm^{-1} which were assigned to the presence of O-H stretching, carbonyl functional group and N-H secondary amine, respectively. The band at 1050-1150 cm^{-1} is due to C-O stretching. The absorption region in-between 2850-2950 cm^{-1} for all feedstocks is associated to C-H stretching. C-H bending (1330-1350 cm^{-1}), O-H bending of phenols (3200-3570 cm^{-1}), phosphate ions (1000-1100 cm^{-1}), and aromatic phosphate (850-995 cm^{-1}) was present for potato waste feedstocks.

Structural alteration occurred due to pyrolysis temperature for the feedstocks. O-H stretching, N-H secondary amine, C-O stretching (potato waste), C-H bending, aromatic phosphate, were demolished. O-H bending of phenols and aliphatic C-H stretching band decreased with pyrolysis temperature (350 and 650 °C). For pine bark C-O stretching band decreased at 350 °C, and 650 °C led to disappearance of the functional group. Carbonyl functional group band increased with pyrolysis temperature for all biochars. Sulfate ions (1080-1130 cm^{-1}) band occurred in potato biochars pyrolysed at 350°C while they disappeared with 300 °C increment in pyrolysis temperature. Pyrolysis temperature (350 °C) led to occurrence of carbonate ions (1410-1490 cm^{-1}) for CP and a further increment (300°C) led to an increase in the band and occurrence for the PP biochar. While for PB pyrolysis temperature (350 °C) led to a decrease in the band and an increment (300°C) led to disappearance of the band. For PP phosphate ions decreased at 350 °C, while for PB it was demolished, and at 650 °C it was demolished for PP and occurred for PB. The C=C-C stretching was present for all biochars and increased with increasing pyrolysis temperature. The O-H stretching of carboxylic acid (2500-3000 cm^{-1}) band occurred for all biochars and increased with increasing pyrolysis temperature, except for PB which demolished with an increment of 300 °C (350 to 650 °C). Heterocyclic amine only existed for potato biochars at 350 °C.

The electron-microscope images indicated that biochar external morphology was highly affected by pyrolysis (Fig. 4.3). For example, the CP feedstock showed an oval shape before pyrolysis.

Increasing pyrolysis temperature led to a considerable increase in pores (micro pores) for the CP and PP biochars.

Table 4.4 FTIR Spectra visible for feedstock and biochars from potato waste and pine bark.

Frequency, Wavenumber (cm ⁻¹)	Functional group	CP			PP			PB		
		0 °C	350 °C	650 °C	0 °C	350°C	650 °C	0 °C	350°C	650 °C
3570-3200	O-H stretching	3265.08			3268.82			3285.59		
3490–3430	Heterocyclic amine		3436.44			3344.11				
3000-2500	O-H stretching of carboxylic acid		2595.38	2649.308		2886.35	2646.22		2659.71	
2950-2850	aliphatic C-H stretch	2922.29	2919.42		2919.34			2917.14	2918.08	
2260-2100	Alkyne	2175.69	2107.99	2111.726	2102.1		2107.128		2106.62	2149.17
2100 - 1800	Metal carbonyl	1876.04	1947.52	2038.011	1871.4	2051.48	2085.918	1881.16		2086.94
2000-1900	C=C-C stretching			1992.611		1906	1993.029		1911.56	1989.9
2000-1750	Aromatic									1797.53
1740-1690	Stretching aldehyde			1720.777			1736.432	1730	1710	
1700-1500	C=C bending of aromatic C	1633.1	1564.06	1544.955		1563.33	1544.968	1557.12	1589.07	1563.74
1650 - 1550	N-H Secondary amine	1556.81			1595.61			1510.98		
1490-1410	Carbonate ions		1424.97	1444.518			1444.314	1440.89	1433.69	
1410-1310	O-H bending of phenol	1403.82	1370.71	1359.074	1364.9	1392.02	1358.763			
1350 - 1330	C-H bending	1336.67			1332.92					
1300 - 1000	ether bonds -C-O-C	1243.02	1250.27		1240.51	1247.56		1263.07		
1150 - 1050	C-O stretch		1147.912		1146.99			1149.98	1148.78	
1130 - 1080	Sulfate ions		1116.03			1111.65				
1100-1000	Phosphate ions	1082.29			1072.29	1012.42		1026.04		1009.71
995 - 850	Aromatic phosphate	961.258			991.31					
900-680	C-H bending of aromatic C	806.492	722.613	840	805.454	756.926	840	811.869	809.035	799.303

CP= cull potato waste; PP= peel potato waste; PB= pine bark

Figure 4.3 shows the morphological structure of the biochars. The external morphology of the biochars is heterogeneous with more pores at pyrolysis temperature of 350 °C.

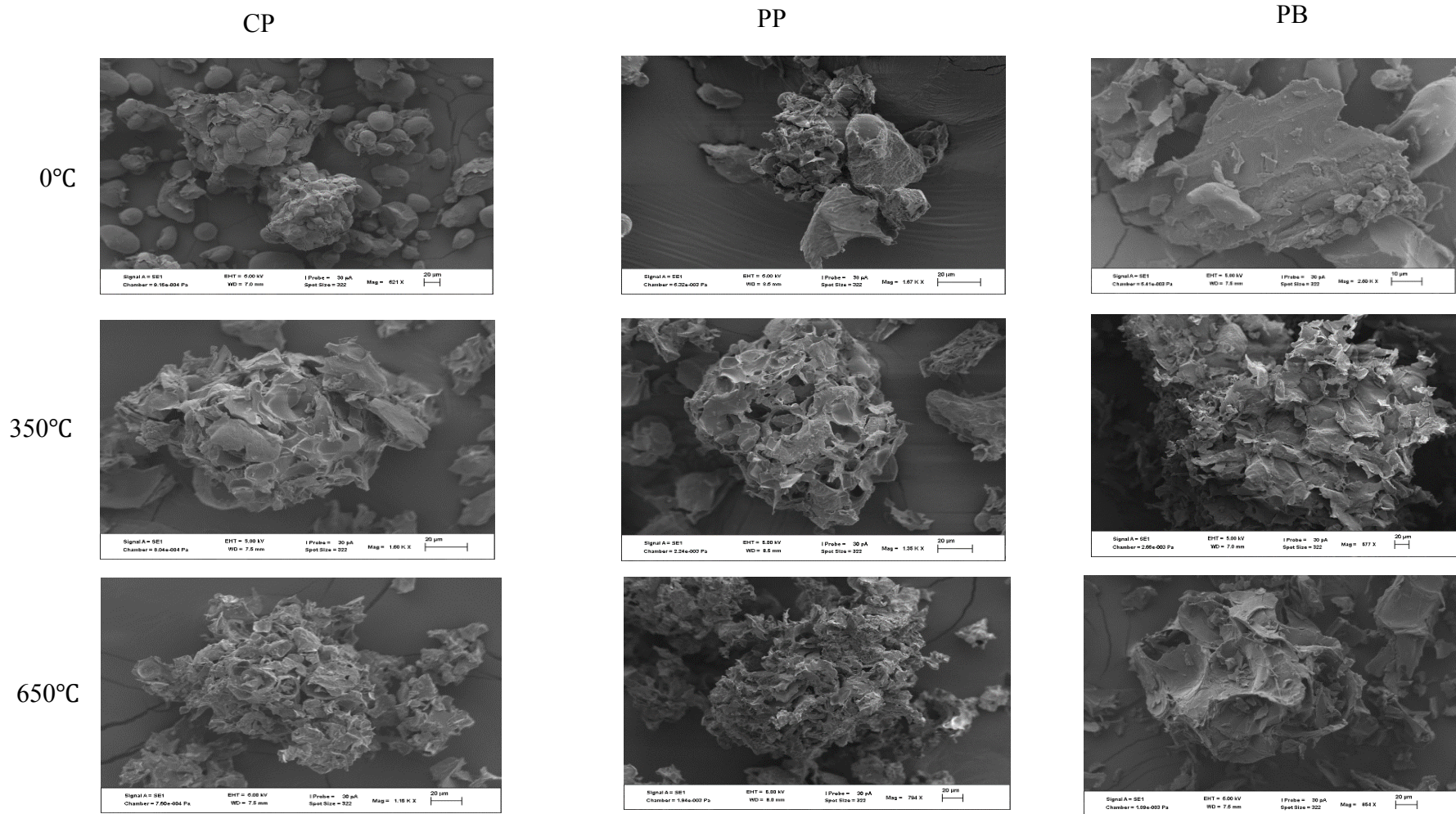


Figure 4.3 Morphological comparison of 6 studied biochars at different pyrolysis temperature using Scanning Electron Microscopy. CP= cull potato waste; PP= Peel potato waste; PB= pine bark.

4.3.5 Soil characteristics

The summary of characteristics of the soils is shown on Table 4.5. The soil from Ukulinga had 39 % clay content, 4.67 $\text{pH}_{(\text{KCl})}$, and a C/N of 16, while that of Bulwer had 23 % clay, 3.97 $\text{pH}_{(\text{KCl})}$, and C/N of 13. The soil from Ukulinga had high Ca and Mg and lower total N, extractable P, exchangeable K and exchangeable acidity compared to that from Bulwer.

4.3.6 Acid neutralisation

Biochar application significantly increased soil pH in comparison to the control, except for PB and its biochars, where PB had significantly lower soil pH values and the biochars showed no effect (Fig 4.4 A and B). However, for the luvisol, all the treatments were significantly lower than the reference material (CaCO_3) at 1%, yet, CP 650 °C at both application rate had similar effect on soil pH as the reference material applied at 0.5%. For the ferralsol, addition of potato waste and their biochars significantly increased soil pH compared to the control but remained much lower than the reference material at both the application rates. Contrary, addition of PB and its biochars led to no significant changes, except CP 650 °C at 1% which significantly increased soil pH by 6 % compared to the control. Biochar from potato waste showed significant liming potential compared to biochars from pine bark.

Table 4.5 Selected physico-chemical properties of the soil used.

Property	Luvisol	Ferralsol
pH_(KCl)	4.67	3.97
pH_(H₂O)	5.87	4.71
Carbon (%)	4.45	5.4
Nitrogen (%)	0.268	0.403
C/N	16	13
Clay (%)	39	23
Bulk density (g cm⁻³)	1.29	1.12
Extractable P (mg/kg)	2.73	18.6
Exchangeable K (cmol_c/kg)	0.0627	0.338
Exchangeable Ca (cmol_c/kg)	2.24	1.02
Exchangeable Mg (cmol_c/kg)	2.24	0.577
Exchangeable acidity (cmol_c/kg)	1.6	8

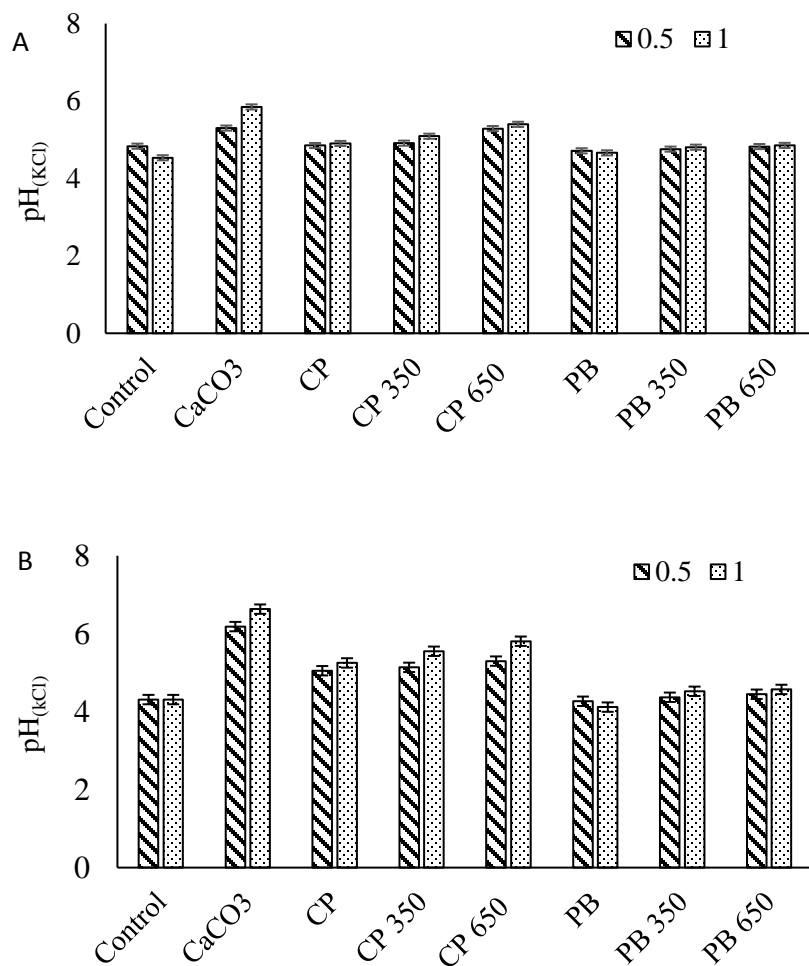


Figure 4.4 pH(KCl) values during a 10 day incubation of soils from (A) Ukulinga and (B) Bulwer amended with CaCO₃ = calcium carbonates and biochars from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. Lime applied at recommended (1) and half (0.5) rate. CP = cull potato; PB= Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

4.4 Discussion

Characterization of biochar provides a clear indication of significant differences in the composition of biochar produced from different feedstocks albeit under same temperatures (Dume *et al.*, 2015). Differences in feedstock determines the composition of biochar produced even when pyrolysis temperature is the same. Pyrolysis temperature led to losses of C, release of water vapour, carbon monoxide and thermal decomposition of lignocellulosic components resulting in the observed decrease in biochar yield. This is consistent with a number of reports on biomass pyrolysis (Kloss *et al.*, 2012; Mimmo *et al.*, 2014; Figueredo *et al.*, 2017) and corresponds to the results of the FTIR which shows losses of functional groups and the restructuring of the C groups (Table 4). Differences in the biochar yield also reflected differences in the feedstock properties. For example, PB biochar produced at both 350 °C and 650 °C showed higher yield than the potato waste biochars due to higher thermal stability as a result of the hard and compact structure of lignin (Walter and Rao, 2015). This is similar to findings of Gani and Naruse (2007); Nanda *et al.*, (2017), who reported high biochar yield from biomass components with high lignin content. In contrast, potato waste had high mass loss due to the high cellulose content in the biomass (Liang *et al.*, 2015). Cellulose in the biomass is accountable for production of volatile products (Sun *et al.*, 2017). The higher yield of the PP biochar relative to CP could be due to presence of inorganic compounds as suggested by the high ash content (Fig 4.1). The decrease in moisture content with pyrolysis temperature is due to dehydration and consequent removal of O-H containing functional groups (Table 4). The higher moisture content ($p < 0.05$) of potato waste biochars compared to PB is a favourable characteristic as biochars with high moisture content could retain water and create a favourable environment for microbial activity and plant growth (Billa *et al.*, 2019).

Increasing pyrolysis temperature led to a reduction in volatile matter (Fig 4.2). (Nguyen *et al.*, 2018) reported similar trend for biochars obtained from corn stover. This was attributed to losses in low molecular functional groups such as aliphatic compounds as pyrolysis temperature increases, prompting aromatisation. Despite this general decrease, potato waste biochars had higher VM than PB owing to its high cellulose content. Differences in VM is attributed to cellulose, hemicellulose and lignin, and their quantity in each biomass (Yang *et al.*, 2017). According to Sun *et al.* (2017) materials with high cellulose content are known to produce high volatile matter.

Volatile matter affects stability of material, its N availability and plant growth (Tomczyk *et al.*, 2020). High VM in potato biochar maybe beneficial as a source for labile C for different microbial communities (Tomczyk *et al.*, 2020) but negative implications for C sequestration due to positive priming effect. Volatile matter could also have detrimental effects in the presence of phenols (Crombie *et al.*, 2013) suppressing the microbial communities through releasing toxic elements.

In contrast to volatile matter, ash content increased with increasing pyrolysis temperature (Fig 4.1) due to accumulation of inorganic compounds (calcium carbonates, potassium silicate, iron and other metals) in the biochar (Nguyen *et al.*, 2018). Ash is the remaining solid after oxidation of all organic elements (C, H, and N) (Domingues *et al.*, 2017). Low ash content of PB biochar compared to that of potatoes is consistent with Domingues *et al.* (2017); Sun *et al.* (2017); Nguyen *et al.* (2018) who compared wood biochar and agricultural biomass. High ash content may be influenced by the nutrient concentration in the biomass (Aller *et al.*, 2017). Potato wastes had high nutrient concentration shown by high CEC (Table 4.3) explaining its high ash content.

Increasing pyrolysis temperature led to an increase in fixed C, which was attributable to losses in volatile matter. Results were consistent with previous biochar studies (Crombie *et al.*, 2013; Figueredo *et al.*, 2017). Pine bark biochars showed high fixed C compared to potato waste biochars, ascribable to high lignin content. Ash content acts as a heat resistant component (Enders *et al.*, 2012) consequently hindering organic compound degradation and formation of aromatic structures. This can explain lower fixed C for potato biochar compared to PB. Similarly, Mimmo *et al.* (2014); Nguyen *et al.* (2018) reported a negative correlation between ash content and fixed carbon.

The increase in C concentration with increasing pyrolysis temperature (Fig 4.2) may be explained by the intensified magnitude of polymerization producing a condensed aromatic carbon structure (Lehmann and Joseph, 2012; Domingues *et al.*, 2017). Similar results were reported for biochars produced from miscanthus (Mimmo *et al.*, 2014) and woody biochars (Jindo *et al.*, 2014). Our findings could also be supported by the loss of oxygenated groups and H (Table 4.2), suggesting breaking down of weak bonds in biochars (Capareda, 2013). Similar to Enders *et al.* (2012) pine bark biochar showed a larger increase in C content relative to other biochars. This may be explained by the aromatic substructure in pine bark. The lower increase in C content of potato

waste biochar suggested the presence of labile carbon. Biochars rich in C being produced at high temperatures can have benefit in carbon sequestration (Nguyen *et al.*, 2018) due to resistance to microbial decomposition (Kookana *et al.*, 2011; Budai *et al.*, 2014). Soils with very low organic material could benefit through the addition of biochar considering their high C content. This approach could benefit smallholder farmers since it could be a convenient way of increasing soil organic carbon. Pine bark biochar produced at 650 °C could be used to sequester carbon considering its high C content applying a recommended rate of 22.46-ton ha⁻¹ of biochar.

Unlike C, nitrogen increased with increasing pyrolysis temperature (350°C) due to heterocyclic compounds (Table 4.4). According to Kazi *et al.* (2011), heterocyclic compounds may be able to increase N content. Pyrolysis temperature of 650 °C decreased N content. Literature indicates that N content usually decreases with temperature ranges of 500 – 800°C (Chatterjee *et al.*, 2020). The decrease could be explained by the volatilization of NH₃ and N containing volatile compounds (Kazi *et al.*, 2011). Pine bark biochar showed no changes in N content which is consistent with results by Koetlisi and Muchaonyerwa (2018). The higher N in potato biochars suggested that potato waste is an N rich feedstock (Kookana *et al.*, 2011). Application rates (kg N ha⁻¹) at 1% of feedstocks CP, PP and PB were calculated as 285, 381, 49; respectively, and their biochars pyrolysed at 350 °C were calculated as 335, 412, 49; respectively and at 650 °C they were 205, 291, and 41; respectively. This was done assuming that all the N will mineralise. It is noteworthy that all the potato wastes and their biochars were above 120kg N ha⁻¹.

The pine bark biochar had higher C/N ratio than potato waste biochars, which was in agreement with previous reports (Sun *et al.*, 2017; Nguyen *et al.*, 2018) . The high C/N ratio could lead to increased N immobilization by microbes in the soil. This may occur due to recalcitrant C or the present of heterocyclic C (Jeffery *et al.*, 2015). The H/C and O/C decreased with the increase in pyrolysis temperature, owing to losses of O, H and polar surface functional groups hence increasing C content (Cantrell *et al.*, 2012). In this study, all the biochars were in the range H/C < 0.6 and O/C < 0.4 appropriate for sequestering carbon (Spokas, 2010). Biochars with O/C range of 0.2 to 0.6 as the ones produced at 350 °C in the current study are believed to have a half-life of 100 – 1000 years, and for O/C < 0.2 as the ones produced at 650 °C in the current study are suggested a half-life greater than 1000 years (Spokas, 2010). The low O/C signifies structural arrangement of the aromatic rings making the biochar more stable (Crombie *et al.*, 2013). The high

O/C for CP at 650 °C indicates the presence of more functional groups in the biochar (Figueredo *et al.*, 2017). The conversion of waste to biochar would be a viable method for carbon sequestration and increasing soil organic carbon that will persist in soils for many years. However, it is important to consider that more feedstock would need to be applied to the soil compared to the biochar, which makes biochar suitable for use looking at the economic benefits.

The rise in pH with increasing pyrolysis temperature (Table 4.3) was in line with Enders *et al.* (2012); Walter and Rao (2015), who reported alkaline biochars with increasing pyrolysis temperature. This is associated with an increase in salts content in ash content, calcium carbonates equivalent (CCE) and loss of acid surface functional groups leaving oxygen functional groups (Butnan *et al.*, 2015). Potato waste biochar showed higher CCE (capacity to neutralise acidity) relative to pine bark and high pH (12) values. Such high pH values have been previously seen in literature ranging from slightly acidic (4) to highly alkaline (13), depending on the feedstock and pyrolysis temperature (Uras *et al.*, 2012; Xie *et al.*, 2015), and are supported by the presence of carbonates in the FTIR (Table 4.4) and consequent high CCE. Similar findings were reported for tomato biochar (Smider and Singh, 2014). Application of potato waste biochars in an acidic soil increased soil pH while PB and its biochars application at similar rates of CCE did not influence the soil pH. The differences in the liming potential of the treatments could be the dissimilarities in the kinetic dissolution of alkaline salts in the ash of the biochars (Singh *et al.*, 2017). Also, the dissolution of some alkaline salts in soils make take longer than 10 days. Another possibility for the increase in soil pH is the presence of the negatively charged functional groups in the potato waste biochars (Table 4.4) which bind H^+ in the soil solution. The increase in soil pH following potato waste biochar addition could be in line with CCE and the inherently high pH, since Ca^{2+} displace the H^+ and Al^{3+} and the H^+ is neutralised in solution (Palansooriya *et al.*, 2019). Similar results were reported for biochars produced from rice hull (Yuan and Xu, 2011) and attributed to high alkalinity.

It is therefore worth noting that remediating acidic soils should not be evaluated solely by pH values, hence liming value which is affected by ash content should also be considered. Smallholders are facing a challenge of remediating acidic soils, due to high lime costs. Thus, using CP 650°C biochar as an alternative could be advantageous to small farmers as it will be more economical than limestone, however, additional lime could still be required due to limited

quantities of biochar. Ameliorating an acidic soil raises pH thus improving nutrient availability, especially P, and microbial activity in the soil. Its application based 10tc/ha results in under-liming in acidic soils.

High extractable P observed for potato waste biochar can be explained by high ash content and consequent increase on soil pH. Moreover, phosphorous is not lost via volatilisation, particularly at pyrolysis temperatures below 700°C (Dume *et al.*, 2015). However, high extractable P does not coincide with the FTIR results (Table 4.4), which shows a lack of phosphate. The available P may be partially bonded to -O- (phytic acid) in the carboxylic group or other functional groups (COO-). The other reason could be P precipitating with Ca^{2+} forming an apatite, commonly observed at high pyrolysis temperature (Bruun *et al.* 2017) owing to biochar being alkaline and having high carbonates ions (Table 4.4). From the agricultural point of view, application of potato waste biochars can increase available P content (mostly in acidic soils), owing to their liming ability, hence they will improve nutrient availability. Application rates (kg P/ha) at 1% application rate were calculated for feedstocks CP, PP and PB (2.12, 1.13, 0.28) and their biochars pyrolysed at 350 °C (10.9, 3.2, and 0) and 650 °C (15.2, 18.2, and 0). This was done assuming that P will not be fixed. Based on this assumption, none of the materials would be sufficient to reach 60-100 Kg P/ha. The use of biochar for available P with additional chemical P fertiliser could be an alternative as compared to feedstocks, since they are slower releaser of nutrients (Wang *et al.*, 2014b). Feedstocks contained lower available P and thus they will require higher application rates compared to their biochars, so conversion of feedstock to biochar is a good alternative.

The higher levels of K and Mg in the potato-based biochars (Table 4.3) compared to pine bark are consistent with Nguyen *et al.* (2018) who reported high K and Mg for plant-based biochars in comparison to wood biochars. Considerably high K content of CP and PP biochars than that of pine bark may be due to high concentration of such elements in the feedstocks (Toma *et al.*, 1979; Olsen *et al.*, 2001). However, CP and PP feedstock had higher K content relative to its biochar suggesting a slow release of K during pyrolysis. Johansen *et al.* (2011) also recorded a decrease in K with pyrolysis temperature. This can be explained by K being bounded to the carbonyl functional groups (Knudsen and Dam-Johansen, 2004) and also forming a stable compound (K_2CO_3) (Van Lith *et al.*, 2008) and cannot be extracted using ammonium acetate method.

Nonetheless, the high available K content in the feedstock doesn't make it a suitable K supplement, since organic wastes are susceptible to nutrient leaching when applied directly to the soil (Igalavithana *et al.*, 2018). Henceforth, CP and PP biochars could be a great substrate to add on soil as a source of K and could replace conventional sources of K. Biochar from non-woody material shows higher CEC values compared to wood (Nguyen *et al.*, 2018). This trend was observed in the current study, with pine bark having lower CEC compared to potato waste biochar. Increase in pyrolysis temperature decreased CEC, possibly due to degradation in volatile organic compounds and acidic functional groups (-COO- and -O-) which have been associated to the negative surface charge biochar (Conz *et al.*, 2017).

Differences in infrared spectra reflected water loss, organic matter combustion, and concentration of mineral components that resulted from the heat (Cao and Harris 2010). The removal of functional groups from the feedstock is linked to pyrolysis temperature removing water and phenolic groups. The bands assigned to C-H stretching markedly decreased due to degradation and dehydration of cellulosic and ligneous components. The loss of band 1300-1000 cm^{-1} at high pyrolysis temperature indicated loss of polysaccharides during pyrolysis which led to increase of aromatic structures (Keiluweit *et al.*, 2010). Low pyrolysis led to the increase in the intensity of carboxylic group while carbonyl group increased with increase in pyrolysis temperature, owing to decomposition of carbohydrates (Kloss *et al.*, 2012). This enhanced condensation of biochar organic compounds. The findings were in line with that of Jindo *et al.* (2014). For PB most of the functional groups were lost due to pyrolysis temperature while potato waste retained more of the functional groups because of ash content. Potato waste biochars produced at 650 °C still contain weak functional groups, which might suggest that when applied to the soil it will increase microbial activity attributable to labile C added by the biochars. The CP feedstock showed oval shape, which according to Abdullah *et al.* (2018) shows the presence of starch. The increase in pores at low pyrolysis temperature might be associated with the decrease of carbohydrates.

4.4 Conclusion

Potato waste biochars had low yield and fixed carbon, high ash content and volatile matter compared to pine bark. The nutrient content of potato waste was higher relative to pine bark biochar. Potato waste biochars showed an increase in pH, CCE, and P with increasing pyrolysis temperature and high K content. The incorporation of potato waste biochar (CP) at 650 °C increased soil pH, this could benefit acidic soils and increase availability of P. Pine bark biochars had high C/N, FC, C, and low O/C, H/C and nitrogen with increasing pyrolysis temperature. Pine bark biochars especially produced at 650 °C thus has the ability to sequester carbon in the soil due to increased stability and aromaticity. The FTIR results showed persistence of weak functional groups with increasing pyrolysis temperature, for potato waste biochars which acts as labile carbon. Feedstock acts as primary factor constraining biochar characteristics, while pyrolysis temperature acts as a modifier, influencing the physico-chemical properties and increases the aromatic character of the biochars. Potato waste biochars have high agronomic value and should be tested for their ability to supply K and increase P availability in soils knowing their liming potential. Moreover, understanding the effects of adding these biochars in near neutral and acidic soils on pH, CO₂ emission, mineral N, available P, and available K is recommended.

CHAPTER 5: CARBON DIOXIDE EMISSION AND NUTRIENT RELEASE IN CONTRASTING SOILS AMENDED WITH BIOCHAR FROM CULL POTATO RELATIVE TO PINEBARK

5.1 Introduction

The large amount of organic carbon (Sharma *et al.*, 2019) and nutrients (Baldock and Nelson, 2000) in organic waste materials suggest their potential value in soil fertility improvement. Potato wastes, such as cull potato and potato peels, are among the most abundant organic wastes that often present disposal challenges and contain up to 2.14% N (Larney and Angers, 2012), 3.09 % K and 1.8% P (Toma *et al.*, 1979). The nutrient and carbon composition suggests that application of potato wastes to soil could have significant organic fertilizer value. The benefits as an organic fertiliser may, however, be short-lived due to rapid decomposition in soil (Ghosh *et al.*, 2015), which consequently, increases CO₂-C emission (Igalavithana *et al.*, 2016), and nitrate leaching to groundwater (Ghosh *et al.*, 2015). Pyrolysis of these potato wastes to biochar may reduce these negative effects.

Recently, biochar has been advocated for stable organic soil amendment with dual ability for carbon sequestration and increasing soil fertility, coupled with reduction in nutrient leaching (Uzoma *et al.*, 2011). Biochar is considered to be recalcitrant to decomposition relative to the feedstock has high capacity of nutrient retention and may slowly release the nutrients (El-Naggar *et al.*, 2018). Biochar is characterised by different forms of carbon based functional groups with aromatic C forming a larger proportion (Tomczyk *et al.*, 2020). The recalcitrant nature of biochar makes it to be resistant to microbial attack thus decreasing emission of CO₂-C and contributing to climate change mitigation (Liu *et al.*, 2012). However, the recalcitrance does not indicate complete biological inertness because the presence of labile aliphatic C that promotes decomposition (Jones *et al.*, 2012). Some authors suggest that the application of biochar to soil can decrease or increase overall organic matter decomposition through its interaction with resident soil organic matter through the priming effect (Keith *et al.*, 2011). The priming effect is a short-term increase or decrease in decomposition of soil organic matter as influenced by soil treatment (Kuzyakov *et al.*, 2000), which usually affects the mineralisation of nutrients and CO₂. Igalavithana *et al.* (2016)

concluded that high temperature biochars have a negative priming effect whilst low temperature biochar has a positive priming effect. As such, high temperature biochars can be used for C sequestration due to high stable C whereas low temperature biochars can be used for improving nutrient availability due to presence of high labile carbon (Zornoza *et al.*, 2016). Smith *et al.* (2010) reported that young (newly produced) biochar provides labile C which is available for microbes for a short period of time. Consequently, this could mean that application of biochar irrespective of pyrolysis temperature could lead to carbon dioxide emission. Preliminary experiments (Chapter 3) have shown that potato waste biochar has high pH, which could lime the soil and increase rate of organic matter decomposition especially in acidic soils, where low pH limits microbial activity. Conversely, the recalcitrant nature could limit the decomposition of the biochar.

There is evidence, in literature, that application of biochar to the soil improves soil quality characteristics (Sohi *et al.*, 2010) as it contains organic matter and nutrients (Rawat *et al.*, 2019) and its addition has been associated with increases in pH, EC, organic carbon, available phosphorous, nitrogen, and CEC (Dume *et al.*, 2015). These benefits of biochar compared to unamended soil have been observed by numerous authors (Glaser *et al.*, 2000; Smider and Singh, 2014; Wang *et al.*, 2014a). Shafie *et al.* (2012) observed an increase in K and a decrease in P with increasing pyrolysis temperature for empty fruit bunch biochars from a 15 day incubation in a sandy soil. Conversely, Han *et al.* (2019) found higher P and Na in soybean straw biochars produced at high temperatures. The persistence of these beneficial effects could depend on the stability of the biochar which is dependent on feedstock and pyrolysis conditions. Angst and Sohi (2013) reported that decomposition of biochar depends on soil condition, with faster rates in alkaline than acidic soils. Preliminary experiments (Chapter 3) showed that potato waste biochar has high C, N, P and K and are highly alkaline (up to pH 12), especially when pyrolysed at high temperatures. There is limited information on the decomposition and CO₂ emissions from soil amended with potato waste biochar produced at different pyrolysis temperatures. In addition to C sequestration potential, there is need to understand the nutrient release from the potato waste biochar, especially nitrogen, phosphorus and potassium, and their potential to lime acidic soils.

Acidic soils have low concentration of bases and fix P, and addition of the alkaline potato waste biochar is expected to lime the soil (as reported in chapter 3), increase organic matter decomposition, mineral N, available P, and add large amounts of available K. Currently, no

published research could be accessed in the literature on the carbon sequestration potential and nutrient release pattern of potato waste biochar. Some studies have been conducted on behavior of biochars from other wastes including pine bark, which is locally abundant, on carbon dioxide emission and nutrient release when applied to the soil. There is a need to assess the ability to sequester carbon and release nutrients of potato waste biochar relative to pine bark biochar when applied to contrasting soils. This information will be valuable in using potato waste and potato waste derived biochars for managing soil fertility as a beneficial waste management strategy. The objective of this study was to determine the effects of potato waste and pyrolysis temperature on CO₂-C, mineralisation of N and P and availability of potassium in contrasting soils amended with biochar from cull potato waste relative to pine bark.

5.2 Method and Materials

5.2.1 Soils

The two soils used in this study were collected from the University of KwaZulu-Natal Research Farm, Ukulinga (29° 39' 33.9" S; 30° 24' 14"E), and Bulwer (29° 48' 27" S; 29° 45' 35"E). The site characteristics and soil classification for this study was the same as that described previously in section 4.2.7 of Chapter 4. The physico-chemical properties were analysed as in section 4.2.9 of Chapter 4.

5.2.2 Biochar and feedstock characterisation

The biochar used in this study was produced from cull potatoes (CP) and pine bark (PB). Cull potato waste was selected for this study, instead of potato peels, based on the assumption that more cull potato wastes is generated from the farms (non-marketable quality), market and homesteads. For convenience, the non-carbonised feedstocks (original feedstocks) were referred to as

“pyrolysed at 0 °C temperature”. The methods for biochar and feedstock characterisation are as described in chapter 4, sub-section 4.2.1-4.2.6.

5.2.3 Evolution of CO₂-C from soils amended with the different biochars

The experiment was a 2× 6 factorial in a completely randomized design with two soil types and six organic materials (PP and PB, and their biochars pyrolysed at 350 and 650°C). The treatments were mixed with 100 g of soil at rates equivalent to 10 t C/ha in both soils and were replicated three times. The treatments were no amendment was added (0 t C/ha) was included for both soils as the control. The soils were maintained to 100% water holding capacity. Carbon dioxide emission from the soils was trapped in NaOH in sealable plastic jars. In each plastic container (jar), two vials (one with 100 g moist soil and another with 50 ml of 1M NaOH) were placed, sealed using cling film and incubated in a constant temperature room 25°C for 84 days. Moisture correction was done at every sampling day after determining weight loss. The jars were opened for removal of NaOH for analysis of CO₂-C and replenish O₂ after 3, 7, 14, 21, 28, 42, 56, and 84 days. The initial CO₂ at the time of setting up the experiment was assumed to be zero (0). The NaOH was then treated with 2 ml of 1M BaCl₂ and 3 drops of phenolphthalein indicator, before titrating the mixture with 0.5M HCl from pink to a colourless end point. The volume of 0.5M HCl used was recorded for calculations. The CO₂-C emission was calculated as the mass of C in mg kg⁻¹ soil following the equation depicted below. The cumulative CO₂-C was calculated by adding CO₂-C emitted per sampling day until day 84.

$$\text{Moles (NaOH reacted with CO}_2\text{)} (x) = \text{total moles of NaOH} - \text{Moles of HCl added} \quad (1)$$

$$\text{Mass of CO}_2 = \frac{x}{2} * 44 \quad (2)$$

$$\text{Mass of CO}_2 \text{ in mg kg}^{-1} \text{ soil} = \frac{\text{mass of CO}_2}{10000} \quad (3)$$

$$\text{Mass of C in mg kg}^{-1} \text{ soil} = \frac{\text{Mass of CO}_2 \text{ in mg/kg soil} \times 12}{44} \quad (4)$$

The “x” signifies the moles of NaOH that reacted with CO₂. The 12 and 44 indicates the molar mass of carbon and that of carbon dioxide; respectively.

5.2.4 Changes in mineral nitrogen, phosphorus and potassium in soils amended with the biochars

The incubation experiment set-up was the same as described for CO₂, in terms of treatments and management, except that there were enough replicates to allow for destructive sampling at each period and that the jars used were not sealable in order to allow for continuous replenishment of oxygen. The soil-biochar mixtures were placed in 500 ml plastic containers, which were tightly closed with lids and had four holes drilled below the rim to allow gas exchange. The soils were maintained to 100% water holding capacity and the moisture was corrected weekly throughout the incubation based on weight loss. The soils were incubated for 140 days in a constant temperature room at 25°C with destructive sampling at days 0, 7, 14, 21, 28, 42, 56, 84, 112 and 140. The samples were analysed for pH, extractable P as described in Chapter 3 section 3.2.9. They were also analysed for mineral nitrogen (NH₄⁺-N and NO₃-N) (Rayment and Lyons, 2011), and exchangeable K per sampling day following Non-Affiliated Soil Analysis Working Committee (1990).

5.2.5 Analysis

Ammonium- and nitrate- N were determined using the Gallery Discrete Auto-analyser (Rayment and Lyons 2011) after extraction with 2 M KCl solution. For this, soil (2 g) suspended in 20 ml of 2 M KCl solution, was shaken using a reciprocal shaker (Model E5850 Thomas Scientific, Swedesboro, NJ, USA) at 180 cycles per minutes for 30 minutes, followed by filtration using Whatman No.1 filter paper into storage bottles, before analysis. Extractable- K was analysed from the supernatant of AMBIC-2 following Non-Affiliated Soil Analysis Working Committee (1990). A volume of 1 ml of the extract used for P analysis was mixed with 5ml of Cesium Chloride (1200 mg/l) solution as an ionisation suppressant. The solution was analysed for K using the atomic adsorption spectrophotometry Varian AA 280- fast Sequential Atomic Absorption (FS-AA)

5.2.6 Statistical analysis

The results of CO₂-C evolution and nutrient release were analysed using GenStat 18th edition by subjecting them to the analysis of variance (ANOVA). The results were analysed separately for different incubation times and for soils. Mean separation was done using least significant difference (LSD) at $p < 0.05$, which were used on the graphs. The Tukey-Kramer test was also used to separate treatment means at $p < 0.05$ and was used in the description of the results.

5.3 Results

5.3.1 Soil characterization

The summary of characteristics of the soils is shown on Table 4.4. The soil from Ukulinga (Luvisol) had 39 % clay content, 4.67 pH_(KCl), and a C/N of 16, while that of Bulwer (Ferralsol) had 23 % clay, 3.97 pH_(KCl), and C/N of 13. The Luvisol had high Ca and Mg and lower total N, extractable P, exchangeable K and lower exchangeable acidity than the Ferralsol.

5.3.2 Carbon dioxide emissions (CO₂-C)

There were significant differences in CO₂-C emission among treatments at the different sampling days for the two soils (Figure 5.1 A and B). The CO₂-C emissions had two peaks for the Luvisol (Figure 5.1 A) and three peaks for the Ferralsol (Figure 5.1 B), with the CP treatment following the same trend as the unamended control. The CO₂-C emission increased from day 0 to 3 for all treatments for both soils (Figure 5.1 A and B). At days 7 and 14, higher CO₂-C emission was observed for PB and PB-derived biochar, with PB increasing up to day 21 for Luvisol. The CO₂ emission sharply decreased between days 14 and 28 in the CP, CP 350 and control treatments, and between days 21 and 28 for CP 650, PB, and PB-based biochars. Thereafter, there was a sharp increase in CO₂-C emission from day 28-42, followed by a sharp decrease for all treatments up to

day 84. At day 42, all treatments were significantly lower than the control (823 mg CO₂-C kg⁻¹) and CP (849 mg CO₂-C kg⁻¹) treatment (Figure 5.1 B). The CP continued to follow a similar trend as that of an unamended soil, which was higher than the biochars. After day 42, there was a sharp decrease to day 56 and 84 where CO₂-C was below detection for all treatments.

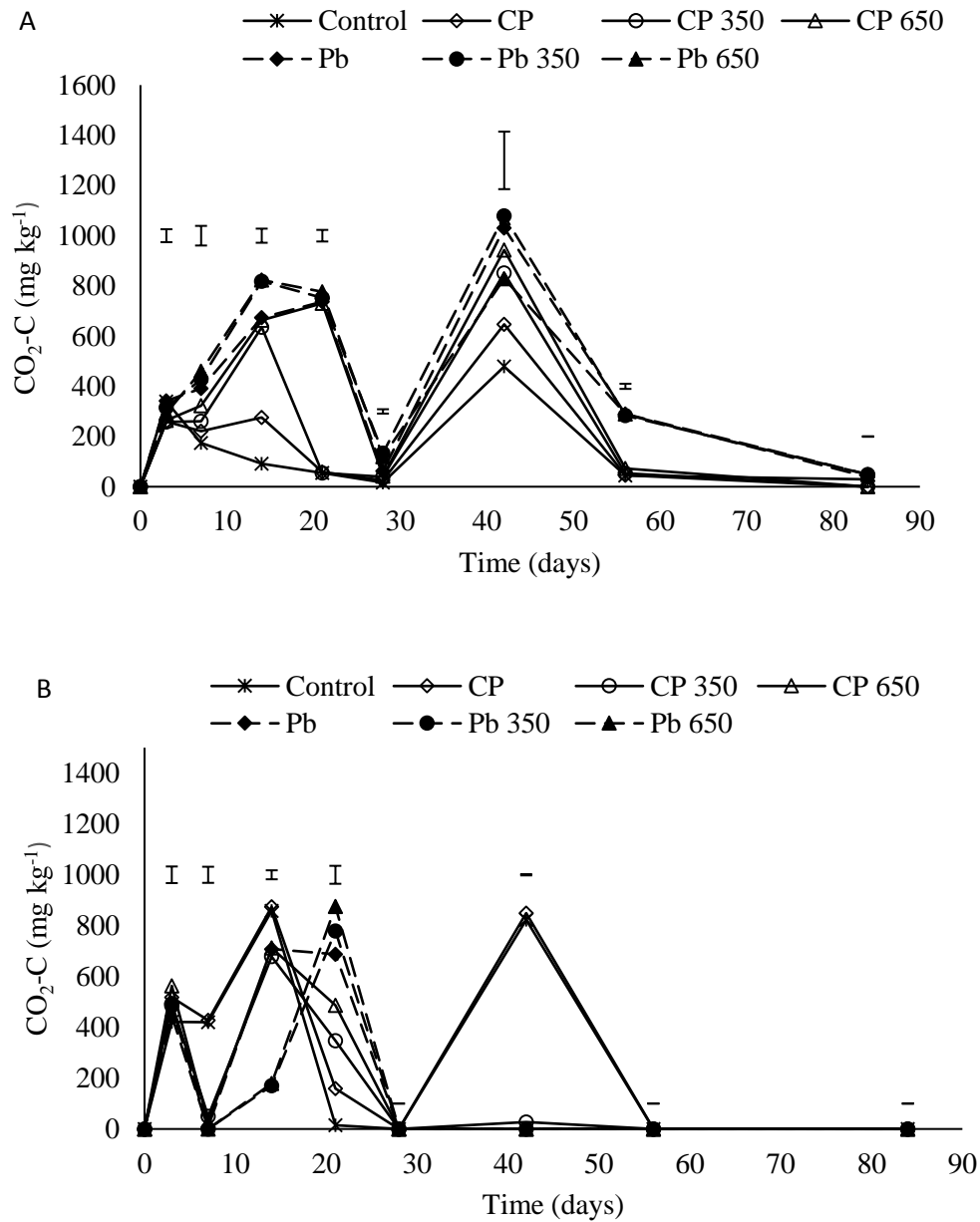


Figure 5.1 Carbon dioxide (CO₂-C) emission during incubation of soils from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.3.3 Cumulative carbon dioxide emissions (CO_2-C)

Cumulative CO_2-C emission was significantly different among treatments (Figure 5.2 A and B). The cumulative CO_2-C in the Luvisol soil was generally higher than in the Ferralsol. The PB 350 treatment showed the highest CO_2-C relative to the control throughout the incubation period reaching a maximum value of 3811 mg CO_2-C kg^{-1} (Figure 5.2 A). For the Luvisol, carbon dioxide emission was in order PB350 (3811 mg CO_2-C kg^{-1}) > PB650 (3600 mg CO_2-C kg^{-1}) > PB (3482 mg CO_2-C kg^{-1}) > CP650 (3044 mg CO_2-C kg^{-1}) > CP350 (2137 mg CO_2-C kg^{-1}) > CP (1422 mg CO_2-C kg^{-1}) > control (1933 mg CO_2-C kg^{-1}). All treatments emitted >100% more CO_2-C compared to the control, except for the CP which was only 35.9% higher than the control (Figure 5.2 A). For both CP and PB treatment, the biochars resulted in higher cumulative CO_2-C emission than the feedstocks. In the Ferralsol, CP followed a similar trend to the control and were both higher than PB biochars (Figure 5.2 B). Addition of biochar decreased cumulative CO_2-C emission shown by higher CO_2-C in the control than all treatments, except the CP, which had higher (Figure 5.2 B). For Ferralsol, CO_2-C emission decreased in order CP (2828 mg CO_2-C kg^{-1}) > control (2533 mg CO_2-C kg^{-1}) > PB (1895 mg CO_2-C kg^{-1}) > CP650 (1778 mg CO_2-C kg^{-1}) > CP350 (1585 mg CO_2-C kg^{-1}) > PB350 (1434 mg CO_2-C kg^{-1}) > PB650 (1414 mg CO_2-C kg^{-1}).

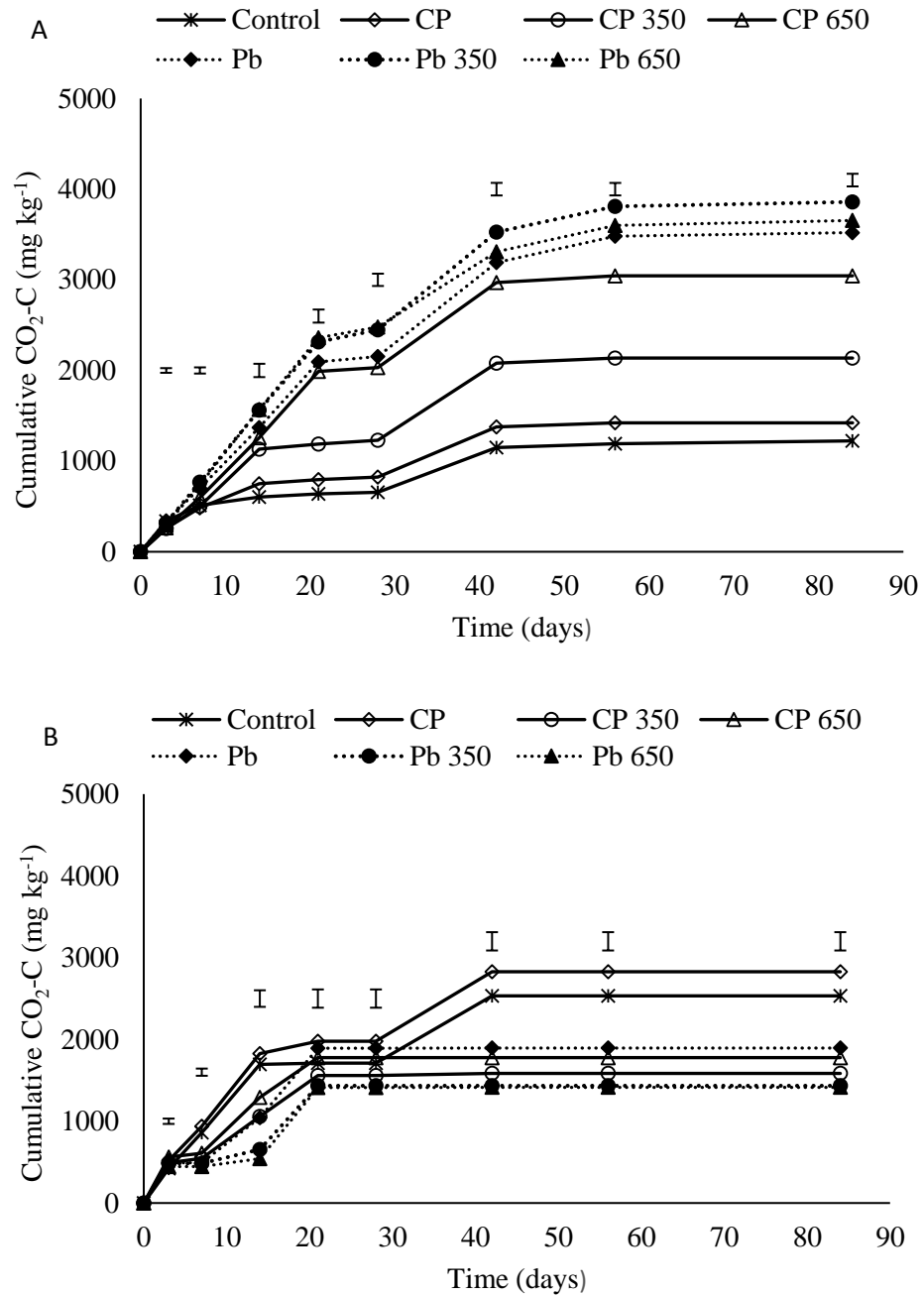


Figure 5.2 Cumulative CO₂-C during incubation from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark produced at varying pyrolysis temperatures. CP = cull potato; PB = Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.3.4 Ammonium-N concentration

Ammonium-N concentration was significantly reduced by the application of raw CP relative to the control while there were no significant difference between biochars and controls (Figure 5.3 A and B). A rapid increase was observed within the first 14 days of incubation in the Luvisol (Figure 5.3 A), reaching a peak that lasted from day 14 to 42, followed by a subsequent decrease between day 42-84 for all treatments, except for CP. After day 84, ammonium-N was below detection for all treatments up to day 112, followed by a slight increase, with the highest at 2.619 mg kg⁻¹ after 140 days. In the Ferralsol, ammonium-N concentration decreased among all treatments, approaching levels below detection after 21 days and remained low up to 112 days of incubation, after which there was a slight increase in all treatments, with the highest having 2.513 mg kg⁻¹ (Figure 5.3 B). Only the PB and CP had lower ammonium-N than the control after 14 days of incubation, with no differences among treatments for all other sampling periods.

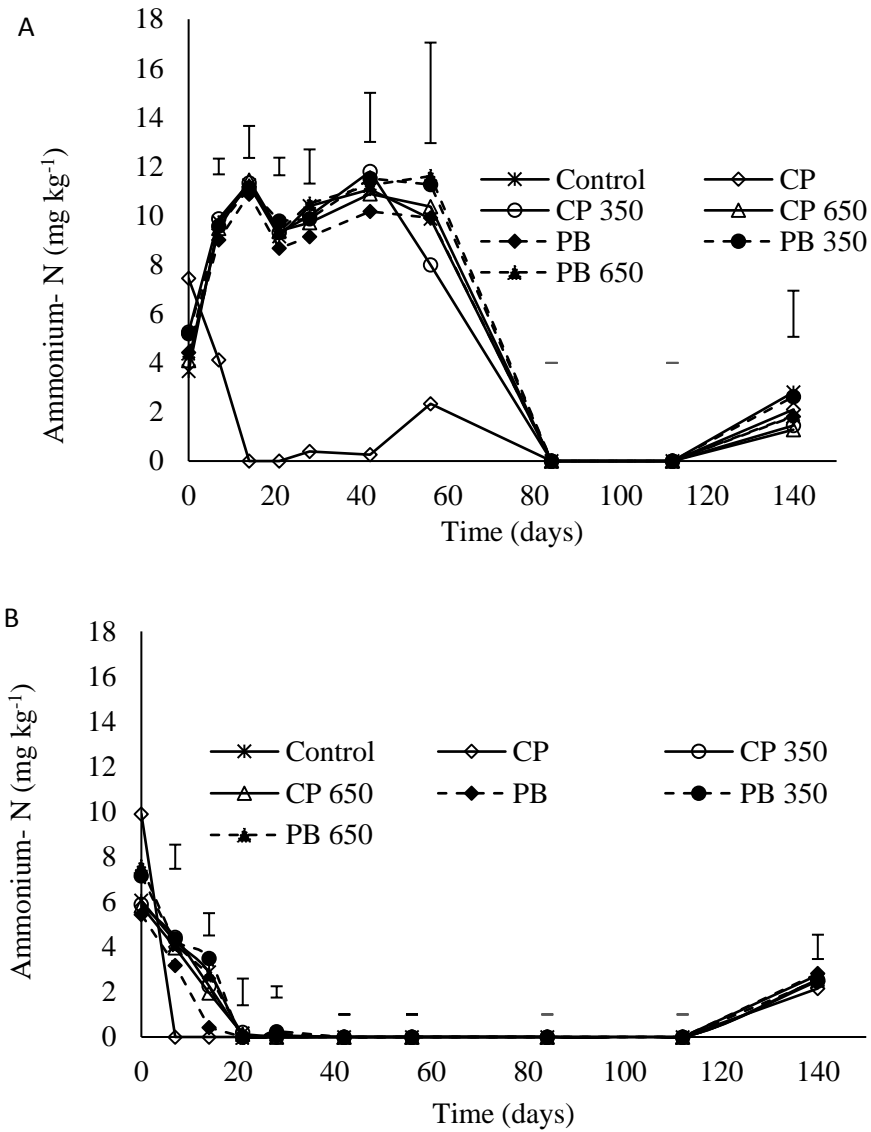


Figure 5.3 Concentrations of ammonium-N during incubation from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB= Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.3.5 Nitrate-N concentration

Application of raw CP significantly reduced nitrate-N concentration compared to the control and all other treatments, (Figure 5.4 A and B). The concentration of nitrate N was generally higher in the Ferralsol than the Luvisol throughout the incubation. The initial concentrations were around 3 mg kg⁻¹ for Luvisol and 42 mg kg⁻¹ for Ferralsol. There were no significant differences among all other treatments on nitrate-N concentration in both soils throughout the incubation, except the PB after 112 days of incubation in the Luvisol (Figure 5.4 A and B). The nitrate-N rapidly increased between 56 and 84 days of incubation in the Luvisol (Figure 5.4 A), while in the Ferralsol the rapid increase in concentration occurred within the first 14 to 21 days (Figure 5.4 B).

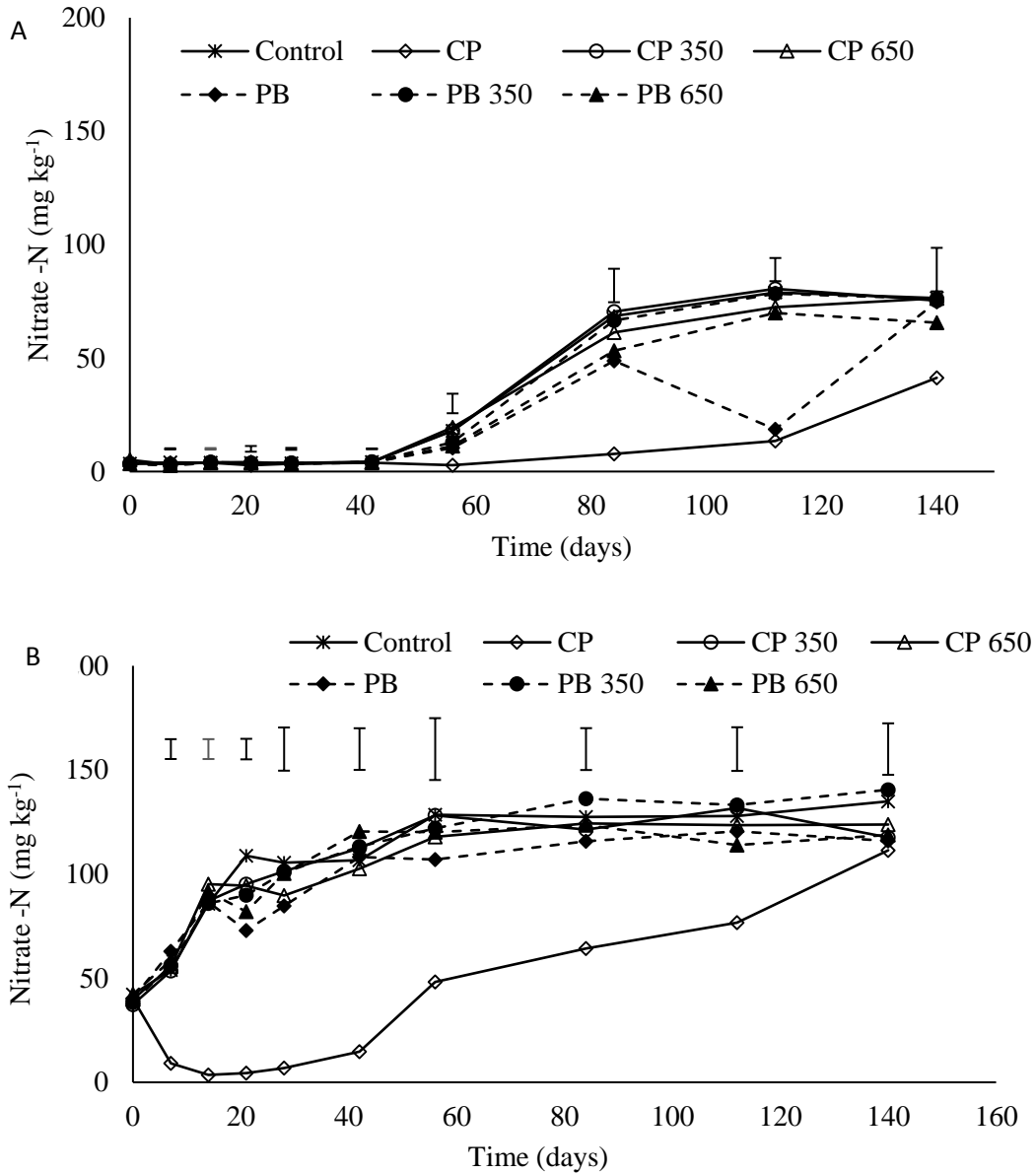


Figure 5.4 Concentrations of nitrate-N during incubation from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB= Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD ($P<0.05$).

5.3.6 Extractable P

The Luvisol generally had lower extractable P than the Ferralsol. In the Luvisol soil, there were no significant treatment effects on extractable P except after 14 and 112 days of incubation (Figure 5.5 A). After 14 days of incubation, the extractable P was higher in the CP based biochars and the PB treatment than PB based biochar and CP treatments and the control. The PB based biochars had higher extractable P than the other treatments after 112 days of incubation.

There were three peaks of extractable P in the Ferralsol (Figure 5.5 B). After seven days of incubation, extractable P was higher in the CP based biochars followed by the PB treatment and the control, with the PB based biochar and the CP treatments having lower. After 14 days, the extractable P was in the order PB650>PB>PB350=CP650=CP350=control >CP (Figure 5.5 B). All biochar treatments were not significantly different in extractable P after 42 and 56 days of incubation with the CP and control treatments having lower. After 112 days, the CP350 had higher extractable P than PB and PB650 treatments, with all other treatments being similar.

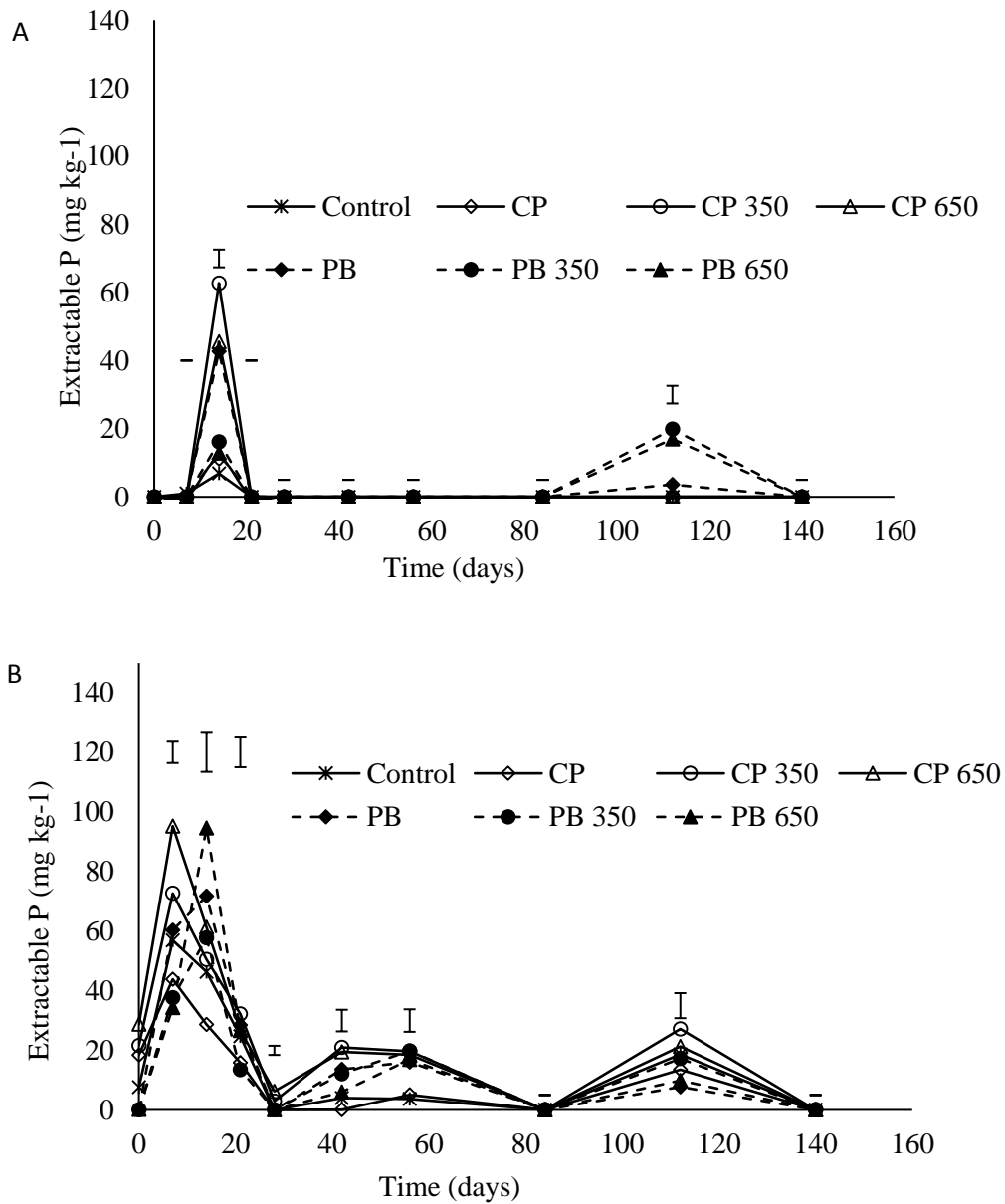


Figure 5.5 Concentrations of Extractable P during incubation from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB= Pine bark; CP 350 = Cull potato biochar at 350 °C; CP 650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.3.7 Extractable K

Addition of raw CP and CP biochars to soil significantly increased extractable-K concentration when compared to PB, PB biochar and the control treatments for both soils and at all sampling periods (Fig 5.6 A and B). The increase in extractable-K was greater for higher temperatures (CP 650°C > CP 350°C > CP) for both soils. Pyrolysis temperature did not affect extractable K in treatments with PB biochars. Although the results appeared to fluctuate between sampling periods, there was no major change throughout the incubation. Generally, the Ferralsol had higher exchangeable K than the Luvisol throughout the experiment.

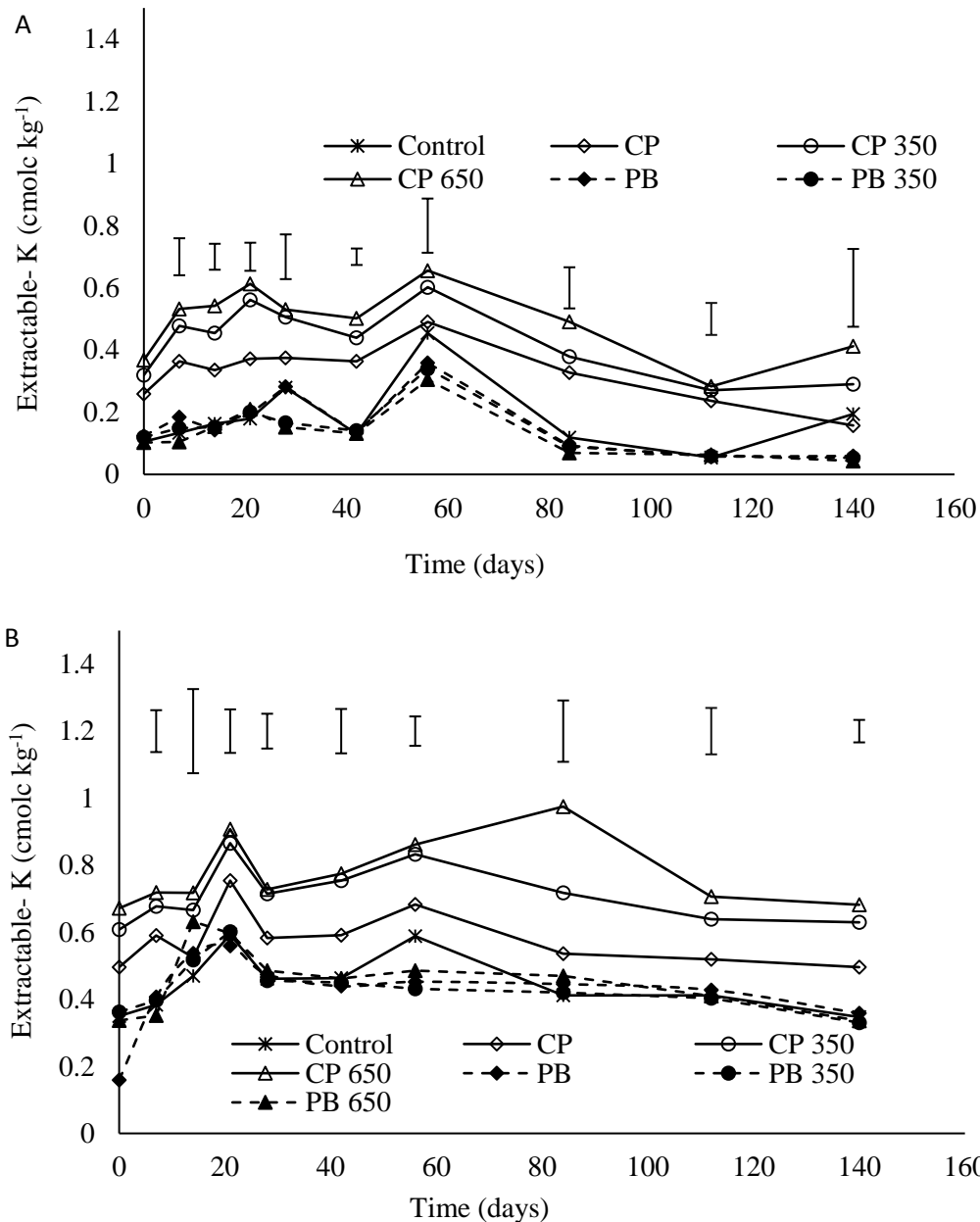


Figure 5.6 Concentrations of exchangeable K during incubation from (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB= Pine bark; CP 350 = Cull potato biochar at 350 °C; CP650= Cull potato biochar at 650 °C; PB 350= Pine bark biochar at 350 °C; PB 650= Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.3.8. *Changes in soil pH*

For the Luvisol, there were significant differences throughout the incubation except for day 7 and 84 (Figure 5.7 A). The soil pH was higher for CP based biochars than the PB treatment, PB based biochar, CP treatment and the control. In Ferralsol, there were 3 peaks (Figure 5.7 B). Throughout the incubation period soil pH was higher in the CP based biochars with CP 650°C having higher soil pH relative to the PB treatments and the control. All treatments were not significantly different in soil pH after 28 and 56 days of incubation with the CP 350 °C being higher after day 28 and PB being higher after day 56.

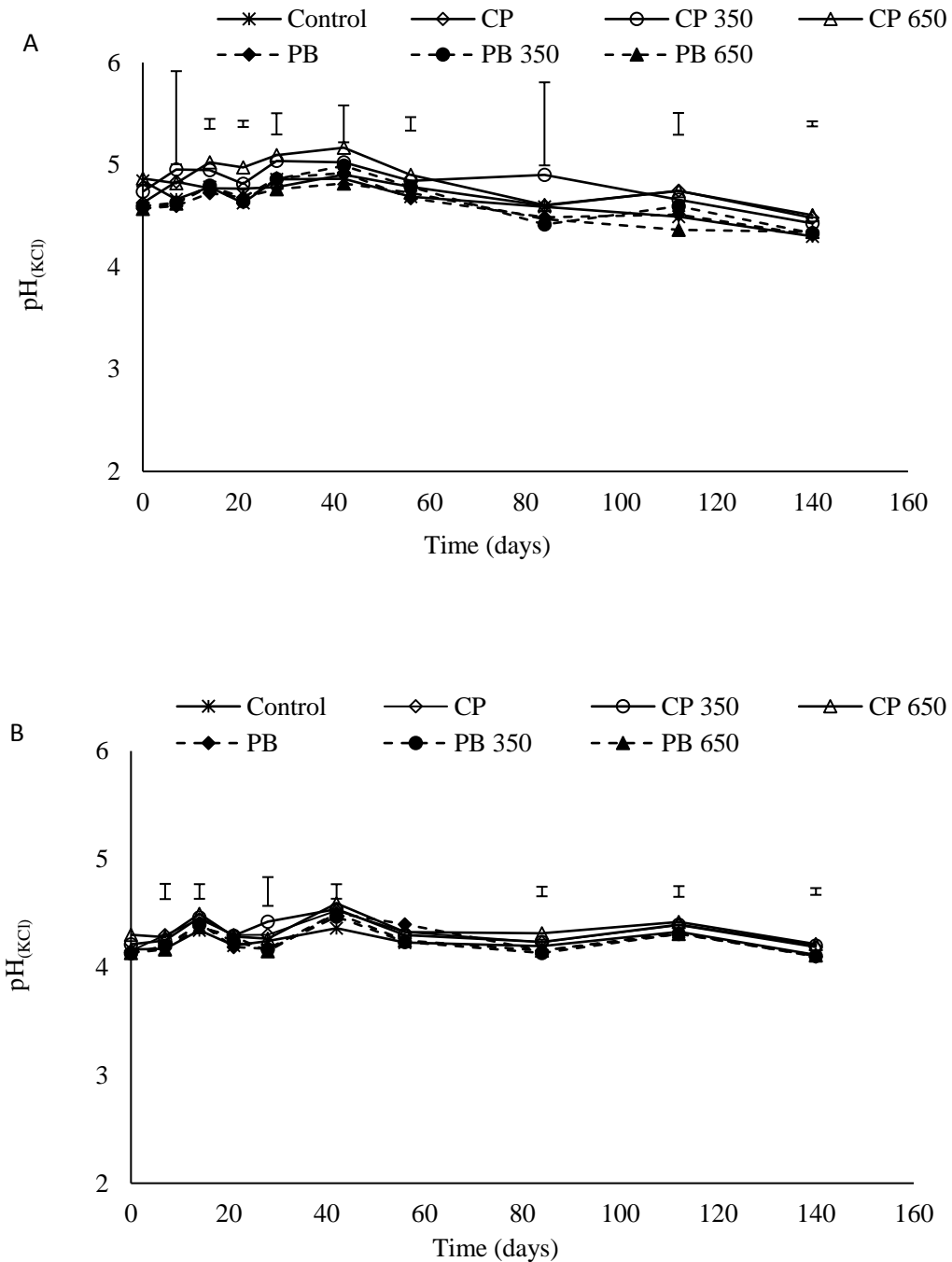


Figure 5.7 The pH (KCl) during incubation of (A) Luvisol and (B) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperature. CP = cull potato; PB = Pine bark; CP 350 = Cull potato biochar at 350 °C; CP650 = Cull potato biochar at 650 °C; PB 350 = Pine bark biochar at 350 °C; PB 650 = Pine bark biochar at 650 °C. The vertical error indicates LSD (P<0.05).

5.4 Discussion

The increase in CO₂-C emission in the first 3 days, with no significant differences among all treatments, (Figure 5.1 A and B), could be due to rapid increase in activities of microorganisms due addition of moisture (Iovieno and Bååth, 2008) or dissociation of carbonates (Bruun *et al.*, 2014) as supported by the high peak for the acidic Ferralsol . The results corroborates with Miller *et al.* (2005), who observed an increase in microbial activity following rewetting a dry soil and also Bruun *et al.* (2014) who reported a sharp CO₂-C emission in an acidic soil due to carbonates dissociation. The increase in CO₂-C, particularly in the biochar treatments, compared to the control in the Luvisol, coincides with increase in pH, extractable P and ammonium-N, suggesting that liming of the soil by the biochars increased pH and availability of P and enhanced activity of microorganism, resulting in SOM decomposition and mineralization of C (CO₂-C) and N. The delayed peak in treatments with PB biochar, in both soils, could be because of slower increase in pH as a result of lower acid neutralizing power (CCE). The explanation for low CO₂-C after 28 days of incubation for all treatments in both soils is the result of moisture, as watering was skipped during this day. However, the decrease in CO₂-C emission beyond 42 days of incubation (Figure 5.1 A and B) could be due to depletion of substrate (labile soil C pool) for microorganisms with increase in incubation period. The higher cumulative CO₂-C in amended soil compared to the control in the Luvisol was possibly due to higher C added through the amendments. Although the amendments were added at the same C rate, PB and PB biochars had higher cumulative CO₂-C than the CP and CP biochars (Figure 5.1 A). The explanation of the higher CO₂-C in the PB and PB biochar treatments than CP and CP biochars is not clear. However, the lower CO₂-C for CP could be due to the low water soluble carbohydrates in the raw feedstock. It would be expected that the higher CCE and lower C:N of CP biochars could have increased microbial activity and CO₂-C than PB biochars. For PB, the PB350 had higher cumulative CO₂-C than PB650 and PB treatments supporting the view that low temperature biochar releases more CO₂-C compared to high temperature biochars (Ippolito *et al.*, 2012). However, for CP biochars CO₂-C increased with increased pyrolysis temperature, possibly because of liming of the soil, increasing microbial activity. The CO₂-C may be also derived from the CaCO₃ of the biochar which is said to be an abiotic process, and occurs mostly for high pyrolysis temperature biochars attributed to high CaCO₃ content.

The generally lower CO₂-C (and cumulative CO₂-C) in Ferralsol than the Luvisol was a result of differences in soil characteristics, including lower pH, and exchangeable Ca and Mg in the Ferralsol (Table 4.4). The pH (KCl) in the Luvisol ranged 4.6 to 5.1 (5.6 to 6.1 in water) while it ranged from 4.1 to 4.6 (5.1 to 5.6 in water) in Ferralsol, with only the CP650 being higher than pH 4.5 (pH 5.5 in water). The lower soil pH in the Ferralsol would have limited microbial activity, irrespective of treatment. The effects of biochar addition on CO₂-C emission therefore appears to depend on the characteristics of the soils, especially the level of acidity. Similar findings were reported by (Keith *et al.*, 2011) and (Fang *et al.*, 2014) that more C was being mineralised in high pH soils relative to low pH soils due to high microbial biomass. (Fang *et al.*, 2014), reported that biochar-C mineralisation varied in soils of contrasting properties, and that biochar-clay interactions contribute significantly to the stabilisation in the variable charge soils than in soils dominated by permanent charge. In addition, Brodowski *et al.* (2005) showed that there is a chemical interaction between the oxidized biochar surfaces and the functional groups of clay minerals and native SOC. The Luvisol (moderately weathered with high clay content) could be dominated by permanent charge clay minerals limiting ligand exchange reaction, hence making the biochar susceptible to microbial breakdown. The acidic pH of Ferralsol (highly weathered) may contribute to enhanced organo-mineral association through ligand exchange reactions (Gu *et al.*, 1994). This could occur between Al oxides and carboxyl and phenolic groups through electrostatic process (Cheng *et al.*, 2006) and possibly due to stabilisation through micro-aggregates. Ferralsol are dominated by micro-aggregates (Totsche *et al.*, 2018) protecting C from microbial process (Lal, 2004).

The addition of the biochars to the Ferralsol resulted in suppressed CO₂-C emission (and cumulative CO₂-C) compared to the control, possibly due to adsorption of recalcitrant biochar-C by Al and Fe oxides, particularly in a highly acidic soil with limited microbial activity. This view was supported by the CO₂-C results of the CP treatment, which was higher than the control, while the lower levels for the PB was a result of the extremely higher C:N ratio of the pine bark (204:1) than CP (35:1). Yu *et al.* (2020) reported that acidic soils have the ability to retard SOM decomposition by limiting activities of microorganisms and enzyme activities. The increase in pH after biochar application might be to levels not conducive for microbial activity, which for bacteria community they are conducive in alkaline pH whereas neutral to slightly acid pH favours fungal communities (Rousk *et al.*, 2009). The higher CO₂-C in the feedstock treatments (CP and PB)

could be due to easily accessible C or substrate to the microorganisms which would result in increased decomposition. The pyrolysis of the feedstocks and subsequent application sequesters C relative to direct application of feedstocks in the Ferralsol.

The increase in ammonium-N for Luvisol for the first 14 days could be the result of SOM decomposition and N mineralisation releasing ammonium-N. This coincides with the high CO₂-C emission and the increasing pH. A similar observation was reported by Cao *et al.* (2017) using rice hull biochars. The peak which lasted from day 14-42 (Figure 5.3 A) was attributed to slower rate of nitrification, as supported by lower nitrate-N results in the Luvisol. The rapid decline in ammonium-N between days 42-84 (Figure 5.3 A), in the Luvisol coincided with decline in CO₂-C and the increase in nitrate-N from day 42 (Figure 5.4 A) and is attributed to nitrification. While in the Ferralsol, ammonium-N declined from the beginning of incubation, the decrease was associated with increase in nitrate-N, suggesting that N mineralization occurred rapidly and that the conditions in this soil were more conducive for nitrification. The lack of accumulation of ammonium-N could be explained by higher aeration in the Ferralsol, with its lower clay content (23 %), than Luvisol (39% clay), favouring nitrification by heterotrophs and autotrophs which facilitate nitrification in acidic soils (Boer and Kowalchuk, 2001), due to the abundance of oxygen in the moist soil. These findings are coherent with Zhao *et al.* (2013) who reported a decline in soil pH after applying crop residue biochar due to nitrification. The CP reduced ammonium-N availability than the control possibly due to immobilization of the N by microorganisms. Cull potatoes showed N immobilisation, possible due to high labile C /volatile matter (Table 4.2) without sufficient nitrogen (C: N = 35:1). As a result the microbes scavenge nitrogen from the soil environment, resulting in N immobilisation (Robertson and Groffman 2006). Nitrogen immobilization including the readily available N, associated with raw CP suggests that more N fertilizer will be required compared to the control while pyrolysis of the material does not affect the fertilizer requirements when compared to the control. However, the Luvisol is dominated by the ammonium-N and lower nitrate-N than the Ferralsol soil for the first 56 days. However, the higher nitrate-N in the Ferralsol (Figure 5.4B) could partly be explained by higher contents in the original soil than Luvisol (Figure 5.4 A). The same trend was observed for extractable P in the original soils, possibly due to remnants of fertilisers added to the cultivated soil, compared to the uncultivated soil from Luvisol.

The increase in extractable P concentration for biochars and its relative feedstocks from day 7-14 for Luvisol (Figure 5.5 A) and day 0-14 for Ferralsol (Figure 5.5 B) could be attributed to increase in soil pH (Li *et al.*, 2019). The increase in soil pH increases the negative surface charges which will cause less adsorption of P increasing its availability. Similar observations have been reported where P availability increased following biochar application (Cui *et al.*, 2011; Nelson *et al.*, 2011). Naeem *et al.* (2016) reported a decrease in P adsorption to Fe with biochar application and the desorbability of adsorbed P to increase. Additionally, the increase in soil pH promotes activities of microorganism and abundance, favouring organic matter decomposition and mineralisation of organic P. The high extractable P in CP biochars could be explained by the higher P concentration (Table 4.4), as well as their liming effects. This suggests that CP needs to be pyrolysed to ensure that P is available while NO_3^- and NH_4^+ are not affected. The sharp decrease after day 14 for Luvisol is possibly due to microbial immobilization, considering the high $\text{CO}_2\text{-C}$ in a soil low in available P (Table 5.2). At day 84, the increase in P could be explained by release of previously immobilized P by microorganisms, thus causing an increase at day 112.

The soil pH was increased due to the application of CP biochar for most sampling days, however, PB did not influence soil pH. The enhancement in soil pH for CP biochars (350 and 650°C) was due to their liming effect (CCE of 11.5 and 17.5 %) associated with their high pH values (11.1 and 12.1) as on Table 4.4. Several authors have reported an increase in soil pH after biochar application across different soils (Ameloot *et al.*, 2013), due to the higher pH of the biochars, which is positively correlated to the pyrolysis temperature and depends on the feedstock. The negatively charged carboxyl groups could be another possible explanation for the increased soil pH in CP biochar treated soils. Chintala *et al.* (2014) elucidated that the negatively charged functional groups on the biochar surfaces bind with the H^+ ion from soil solution hence reducing H^+ ions in the soil solution consequently increasing soil pH. The increase in pH due to addition of CP biochars could reduce P fixation, increase microbial activity and decomposition of organic matter, resulting in mineralization of C ($\text{CO}_2\text{-C}$), N and P.

Application of CP biochars significantly increased available K and maintained it up to 140 days in both the soils (Figure 5.6 A and B). The high exchangeable soil K throughout the incubation, where CP biochars were added, was because K is not organically bound in the plant tissue and when plant decomposes K is released immediately (Van Lith *et al.*, 2008), as such availability is minimally

affected by incubation time. The higher exchangeable K in soils treated with CP biochars of increasing pyrolysis temperature, could be explained by the high K (22.7 mg/kg) in the feedstock. Although the K in the biochars decreased with pyrolysis, this might mean that the K was absorbed in the net negative charge surfaces and becomes bioavailable once applied to the soil or a stable compound was formed (K_2CO_3) (Van Lith *et al.*, 2008). Similarly other authors reported an increase in soil K after amendment with crop residue biochar (Shafie *et al.* 2012; Singh *et al.*,2019). The lack of significant effect when PB biochars were added to the soil, could be linked to the low levels of K in PB such that even the biochars cause no significant change. The generally higher soil K in the Ferralsol than Luvisol for all treatments, can be explained by the composition of the original soils (Table 4.4). In the context of applying CP as source of K, it is ideal to use pyrolysed CP to ensure that NO_3^- and NH_4^+ are not limited.

5.5 Conclusion

The study has shown that CO_2 -C emission as a result of amendment with different biochars varies in soils of contrasting properties. Application of biochar to the Luvisol increased CO_2 -C emission, while in the more acidic Ferralsol it suppressed CO_2 -C emission, when compared with unamended control and the feedstocks. Pine bark biochars emitted more CO_2 -C in Luvisol than in Ferralsol. It can be concluded that the effectiveness of application of biochars for carbon sequestration is affected by biochar characteristics and soil type. Application of biochars did not affect ammonium and nitrate-N when compared to the control for the contrasting soils, while the cull potato feedstock caused N immobilisation. However, the form of mineral N dominating for extended periods depended on soil type, with more ammonium-N in the Luvisol and nitrate-N in the Ferralsol for the first 56 days. Application of cull potato biochars to two contrasting soils increased available P, K and soil pH compared to pine bark biochars. Cull potato waste should thus be applied as biochar to increase pH, available P, and exchangeable K with no negative effects of N immobilisation. Research on the application of cull potato biochars on nutrient availability and its liming ability in South Africa is fairly recent. Further research, on the applications of the CP biochar and its cost-benefit analysis, especially on crops grown on contrasting soils, is of paramount importance to provide a strong scientific knowledge on optimal utilizing the products of these organic wastes in agriculture.

6. CHAPTER 6: GENERAL DISCUSSION, CONCLUSION AND RECOMMENDATIONS

6.1 General discussion

Significant amount of potato wastes are generated worldwide and end up in landfills. The disposal of these materials pose significant environmental challenges due to their high nutrients and carbon which can pollute ground water by leaching, while CO₂, N₂O and odour contribute negatively to air quality (Matsakas *et al.*, 2017). Conversion of potato wastes to biochars can be an effective approach to counteract these negative effects. While numerous studies on different biochars (including pine bark, commonly available in SA) have been widely published, limited work has been done on potato waste biochar. The type of feedstock and pyrolysis conditions used in biochar production are the keys factors in determining biochar's properties (Sohi *et al.* 2010; Spokas *et al.* 2012; Singh *et al.* 2015). Application to agricultural soils could minimize C emissions to the atmosphere through storage in stable form and could also be important in recycling nutrient, depending on the characteristics of the biochar. The overall objective of this research was to investigate the effects of pyrolysis temperature and type of feedstock on the characteristics of the biochar from cull potatoes and potato peels relative to pine bark, and their effects on CO₂-C evolution and availability of macro-nutrients in two contrasting soils.

The study showed that potato waste biochars had lower yield than pine bark biochar due to the higher volatile matter and lower lignin content (Sun *et al.*, 2017). The lower yield was attributed to thermal degradation of lignocellulosic components, release of water vapour and carbon monoxide during pyrolysis (Kloss *et al.*, 2012). Increasing pyrolysis temperature decreased biochar yield for all feedstocks, due to further degradation of the volatile material (Kloss *et al.*, 2012). This view was supported by the decline in volatile matter, total H and O and surface functional groups and increase in ash content as pyrolysis temperature increased for all feedstocks.

The higher ash content, extractable phosphorous, extractable potassium, pH and acidic neutralizing ability (calcium carbonates equivalent) in potato waste biochars, compared to pine bark biochar, could be explained by the higher concentrations of those parameters in the raw feedstocks. The

higher ash content and pH supported the liming potential or acid neutralizing power (calcium carbonate equivalent) of potato waste biochars, more so for those produced at 650°C.

When applied to an acidic soil, the biochar from cull potato increased soil pH while pine bark and its biochars did not result in any change. This effect was associated with inherently high pH of the potato waste biochar, which translated to high CCE. Although the materials were applied at similar calcium carbonates equivalent (CCE) rates, the potato waste biochar resulted in greater increase in soil pH than that from pine bark. The differences are due to the dissimilarities in the kinetic dissolution of alkaline salts in the ash of biochars and the presence of negatively charged surface functional groups (higher in potato waste biochar), which binds H^+ and remove them from the soil solution (Mohan *et al.*, 2018). The effectiveness of the biochars in neutralizing soil acidity could enhance microbial activity, CO_2 -C evolution and availability of plant essential nutrients in amended soils, especially where high concentrations of volatile matter occurs. Volatile matter acts as a source of labile carbon for micro-organisms and therefore enhances CO_2 -C evolution when added to soil (Tomczyk *et al.*, 2020). The higher carbon content in pine bark biochars, suggested a higher carbon sequestration potential than potato-waste derived biochars. However, the addition of cull potato and pine bark waste and biochars derived from these materials showed different trends in CO_2 -C evolution from two contrasting soils, suggesting that soil type is particularly important in carbon sequestration due to the addition of the biochars.

Cumulative CO_2 -C was lower for the amended Ferralsol than the control and the cull potato feedstock suggesting sequestration of biochars and soil organic matter C possibly due to the expected limited mineralization of the recalcitrant biochar-C (Lal, 2004; Liu *et al.*, 2012). The higher cumulative CO_2 -C from the amendments than the control, in the Luvisol was not as expected, but it was most likely explained by added C, compared to the control. Addition of biochars with more recalcitrant C, would be expected to decrease CO_2 -C emission when compared to the control, yet the opposite was observed. Also against expectations, pine bark and its biochars, which had C/N >200, had higher cumulative CO_2 -C than cull potato and its biochars, with C/N of 30-49, in the Luvisol, yet the materials were applied at the same rate of carbon. There was no clear explanation to this observation. The CO_2 -C from cull potato biochar in the Luvisol increased with increase in pyrolysis temperature. This could be explained by increasing acid neutralising power of the biochars which could have increased microbial activity resulting in increased CO_2 -C

emission. The CO₂-C may be also derived from the CaCO₃ of the biochar which is said to be an abiotic process, and occurs mostly for high pyrolysis temperature biochars attributed to high CaCO₃ content. The generally higher CO₂-C in the Luvisol than the Ferralsol, irrespective of amendment could be explained by the characteristics of the soils, especially the level of acidity. Previous reports indicate that more C is mineralised in high pH soils than where pH is lower due to higher microbial biomass and activity (Keith *et al.*, 2011; Fang *et al.*, 2014). The Ferralsol had lower pH which ranged from 4.1 to 4.6 (5.1 to 5.6 in water), while the Luvisol had high pH which ranged from 4.6 to 5.1 (5.6 to 6.1 in water). Interactions of the biochar and soil colloids could also have contributed in the CO₂-C evolution results.

Biochar-clay interactions have been reported to contribute to C stabilisation in the variable charge soils than in soils of permanent charge resulting to variation in biochar-C mineralisation in soils of contrasting properties (Fang *et al.*, 2014). The Luvisol (moderately weathered) used in this study has high clay (39%) and pH 4.67 (pH 5.67 in water) than the Ferralsol (23% clay), which had pH 3.97 (pH 4.97 in water). As such the Luvisol could have more permanent charge clay minerals limiting ligand exchange reaction, and this coupled with higher pH and microbial activity could make the biochar-C susceptible to microbial breakdown. The acidic pH of Ferralsol (highly weathered) may contribute to enhanced organo-mineral association through ligand exchange reactions (Gu *et al.*, 1994) between Al oxides and carboxyl and phenolic groups through electrostatic process (Cheng *et al.* 2006) and possibly due to stabilisation through micro-aggregates (Lal, 2004). The application of organic wastes and their biochars contributes nutrients like nitrogen (N), phosphorus (P) and bases, and the decomposition could result in mineralization. When applied at the same rate of C, cull potato and its biochars supplied 196-350 kg N/ha while pine bark and its biochars supplied 41-50 kg N/ha.

Application of biochar from cull potato and pine bark in Luvisol increased ammonium to the same level as the control indicating that the biochar did not affect mineralization of N from SOM in the soil. The higher the CO₂-C evolution in biochar amended soils, and no effect on ammonium-N, when compared with the control, shows that the amendment increases mineralization of C and not N, in this soil. However, the biochar treatment resulted in generally lower nitrate-N compared to high ammonium-N in the Ferralsol, due to slow nitrification due to high clay content (39%). All the ammonium-N because of biochar addition could be the result of SOM decomposition and

mineralisation. Biochar application in the Ferralsol, resulted in lower ammonium availability, and higher nitrate availability, when compared with the Luvisol. The rapid nitrification in the Ferralsol could be due to higher aeration, with the lower clay content (23%), favouring conducive environment for micro-organisms, hence, hindering accumulation of ammonium-N. Additionally, the nitrate-N in the original soils was higher in the Ferralsol than in the Luvisol, possibly due to remnants of fertilisers added to the cultivated soil, compared to the uncultivated Luvisol. The application of raw cull potato feedstock led to N immobilisation possibly as a result of high labile carbon with insufficient N. This implies that pyrolysis of feedstock is a better alternative than application of the raw feedstock as the latter will require additional N fertilisers. In addition to supplying nitrogen, the biochars may also supply other macro-nutrients like phosphorous and potassium.

Biochar from cull potato had higher extractable P than pine bark biochar during incubation, which can be explained by higher concentration added. When applied at the same rate of C, cull potato and its biochars supplied equivalents of 11-21 kg P ha⁻¹ while pine bark and its biochars supplied 0-0.28 kg P ha⁻¹. The differences in added P is explained by the higher P in the cull potato and its biochars. In addition to the added P, the higher P availability in soils amended with cull potato biochar could be attributed to decomposition and mineralisation of native SOM upon biochar addition, which had a higher acid neutralization power (CCE) as shown on Table 3.3. The lower extractable P in the Luvisol than the Ferralsol could be due to microbial immobilisation considering low extractable P (2.73 mg/kg) compared to 18.6 in the Ferralsol (Table 4.1). In addition to C, N and P, cull potato and its biochars also supplied K, which increased its availability when added to the contrasting soils.

Extractable potassium exhibited a similar trend in both soils, with higher extractable K for CP biochars, than PB biochars, and it increased with increasing pyrolysis temperature. The higher extractable K in the cull potato and its biochar could be explained by the higher K added. When applied at the same rate of C, cull potato and its biochars supplied an equivalent of 75-227 kg K ha⁻¹ while pine bark and its biochars supplied 0.003-0.057 kg K ha⁻¹. The higher added K is associated with the high K concentration of (22.7 mg kg⁻¹) the cull potatoes. In Chapter 3,

extractable K in cull potato biochar decreased with increasing pyrolysis temperature, while the reverse was observed in the incubation study (Chapter 4). The decline in extractable K with increase in pyrolysis temperature could be probably due to the bounded K in K_2CO_3 , which is regarded as being a stable compound (van Lith *et al.* 2008). The K may also be bounded to the carboxyl and phenol groups (Nwajiaku *et al.*, 2018), which decreased with pyrolysis temperature, as shown by decline in O/C and H/C (Table 3.2). However, upon addition into the soil the K_2CO_3 may have been solubilised and released the K. Overall, this implies that pyrolysis of cull potato increases extractable K when applied into the soil. The higher extractable K in the Ferralsol than Luvisol, could be explained by the content of high extractable K (0.338 cmol_c/kg) in the original soil.

Addition of cull potato biochars at 10 t C/ha rate slightly increased soil pH relative to pine bark biochars during the incubation experiment. The rate (t C/ha) applied did not reach the recommended rate to neutralise the acidity of the soil, which explains only a slight neutralization of acidity. As a result, some of the micro-organisms are deprived owing to slightly acidic soil pH. The surface functional groups also play a pivotal role in binding the H^+ from soil solution in the negative charged groups (Chintala *et al.*, 2014).

6.2 Conclusion

Potato waste biochar had higher pH, ash, phosphorous, potassium volatile matter and calcium carbonates equivalent, and lower yield and carbon than pine bark. Cull potato biochar pyrolysed at 650°C increased soil pH, especially when applied as lime at 5 t ha⁻¹ in Luvisol and at 30 t ha⁻¹ in the ferralsol. The CO₂-C emission increased in the Luvisol and was suppressed in the acidic Ferralsol, by addition of cull potato biochars, when compared with the control and the feedstock. More CO₂-C was emitted in the Luvisol than in the Ferralsol following pine bark addition. It can be concluded that the effectiveness of application of biochars for carbon sequestration was affected by biochar characteristics and soil type. Ammonium-N and nitrate-N were not affected by addition of biochars when compared to the control in both contrasting soils tested, while cull potato raw feedstock led to N immobilisation. However, the form of mineral N dominating for extended periods varied with soil type, with more ammonium-N in the Luvisol and nitrate-N in the Ferralsol

for the first 56 days. Available P, K and soil pH increased in both the Luvisol and Ferralsol soils following cull potato biochar addition. Conversion of potato waste to biochar could be an alternative waste management approach to counteract the negative impacts of wastes on the environment. In this study, the benefits of pyrolysed potato waste included liming ability, increases of K and P, especially in Ferralsol. Additional benefits were the increase of available P, and exchangeable K with no negative effects of N immobilisation while sequestering C. The application of cull potato biochar as soil amendment could benefit smallholder farmers since it could be relatively inexpensive for them to access it.

6.3 Recommendations

While this work has showed potential for using cull potato biochar as a liming agent and for adding P and K to the soil, the economic impact of cull potato biochar will be influenced by the costs associated with biochar production and quantities of cull potato available. Research on the application of cull potato biochars on nutrient availability and its liming ability in South Africa is fairly recent. The effects of adding potato waste biochar on soil's C, N, P, K and on crop productivity need to be further studied under South African conditions/soils following field conditions. Thus, further research is needed to provide a strong scientific knowledge on the optimal utilization of this product derived from organic wastes in agriculture.

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