

5-13-2022

Phosphorus enriched modified-Douglas fir biochar as a soil amendment

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Phosphorus enriched modified-Douglas fir biochar as a soil amendment

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A Dissertation

Submitted to the College of Arts and Sciences

Mississippi State University

in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy

in Chemistry

in the Department of Chemistry

Mississippi State, Mississippi

May 2022

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2022

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Title of Study: Phosphorus enriched modified-Douglas fir biochar as a soil amendment

Pages in Study: 190

Candidate for Degree of Doctor of Philosophy

ABSTRACT

Biochar application as a soil additive is gaining global acceptance. In this era of climate change, biochar use for improved soil productivity is not just a sustainable eco-friendly substitute to synthetic fertilizer, but a noble contributor to the fight against climate change. Although biochar has been accredited with some environmental and agricultural benefits, most studies concentrated on agricultural and biowaste products as feedstocks. This research was designed to explore P-enriched modified-Douglas fir biochar potential as a soil additive. Using corn as a test crop, greenhouse studies were performed on acidic sandy soil, comparing phosphorus enriched modified-Douglas fir biochar efficacy to a commercial synthetic triple superphosphate fertilizer and a control treatment. Incubation studies were also performed to evaluate the liming and heavy metal immobilization efficacies. Firstly, P-enriched modified-Douglas fir biochar's ability to release plant soluble P was investigated. At various P enrichment concentration, soil plant availability P from P enriched modified-Douglas fir biochar treatments differed insignificantly from superphosphate fertilizer treatment. The direct correlations between both K and Mg recoveries with available soil P, suggested P enriched modified-Douglas fir biochar potential to supply multiple plant nutrients. Secondly, the influence of P uptake on plant growth and P use

efficiency was examined. The greater agronomic P use efficiency obtained in P enriched modified-Douglas fir biochar ($\sim 32 \text{ kg kg}^{-1}$) than the triple super phosphate fertilizer ($\sim 17 \text{ kg kg}^{-1}$) treatment confirmed P enriched modified-Douglas fir biochar potential as a multiple nutrient released soil additive. Thirdly, biochar-supported phosphate (BP) effectively reduced Pb^{2+} mobility in simulated contaminated soil. Pb^{2+} reacted with phosphate from $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ embedded in the biochar supported phosphate at $\text{pH} < 7$ forming a less bioavailable $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$. Finally, the amendment of acidic soils with modified P-enriched modified-biochar improved soil buffering capacity because of its enhanced ash contents, alkalinity, and surface functional groups. Spectroscopic methods were used to analyze biochar, soil, and plant materials extracts. Several other analytical methods including BET and thermogravimetric analyses were used to characterized biochar. These findings suggest that the use of phosphorus enriched modified-Douglas fir biochar in agricultural soil is a feasible relatively low-cost, effective, and environmentally sustainable soil management and P recycling strategy

DEDICATION

This work is dedicated to the Almighty God. To him be the glory, praises, and honor forever, Amen. To my children; John Francis Miti, Faith Ellene Lakareber and Eugene Dwight Mugisha, and husband Nyeko Martine. Thank you for the support, sacrifice, and encouragement.

ACKNOWLEDGEMENTS

I am indebted to my advisor Professor Todd E. Mlsna who has been more than an advisor but a “father” to me away from home. Your, tolerance, commitment, patience professionalism, and caring attitudes influentially guided and encouraged me to be focused.

I extend my sincere gratitude to Dr. Jac J. Varco who gave me an immeasurable amount of technical, materials, and social support to do my research. Your generosity and loving hearts made this journey a success.

To all my committees, Dr. David O. Wipf, Dr. Amanda Patrick, and Dr. Deb Mlsna. I genuinely appreciate your continued support and technical contributions.

I wholeheartedly thank the US department of state and the Fulbright organization for the physical and technical contributions towards this course. “Without your support and funding, this journey would not be possible.” I also appreciate the Government of the Republic of Uganda and Gulu university fraternity for giving me a study leave.

I cannot forget Mississippi State University, administrative staff, and students from the Department of Chemistry for the knowledge, cooperation, and support extended to me during my academic encounter. Kathy Johnsey, Taylor Fultz, Damonique Maclin, Sara Stevenson and Kathryn McTaggart, thank you for your unconditional support. I acknowledge the Department head, Prof Denis Smith, and all other faculty members for making the Department a ‘life’ changing home. I would like to thank Dr. Joseph Emerson, and Dr. David O. Wipf for their compassionate roles as graduate coordinators, Ms. Teresa Brown for her guidance in my TA duties, Navarathna

Chanaka, Sean Stokes and Sanchez Arana Daniela for their technical and instrument support. In a special way, I would like to thank Professor Charles U. Pittman Jr., Andrew Dygert, Donnadiou Bruno and Rooban Venkatesh K.G. Thirumalai for their technical help and devotion during my research. I sincerely convey my gratitude and appreciation to Eric A. Laiche (Greenhouse facility coordinator), Jaime Berry, Julianna Mills, Solomon Sabrina, Tanner Myers, Comer, J. Mike, Lunn Garrett, Prashan M. Rodrigo, Raymond Awoyemi Femi, Naba Krishna Das, Awolesi Oluwafemi, Felix Atsar, Hellen Stephanie, Karl Mukeba, Shelar Ketki, Eugene Caldon, Acheampong Edward, Regmi arma, Mudugamuwa hewage Jayamini, Mary Frances Nakamya, Margaret Khaita, Mawuli Deegbey, Eyram Asempa and Ms Bonnie for making my years at MSU an unforgettable one.

I would like to acknowledge the contributions of my late Uncle Stephen Opira Munu, Grandmother Mrs. Christine Adokorach Munu, and Great grandmother Mrs., Eseja Akello Oola for their love, care, and protection even at a time when life seems to have no meaning anymore. You persistently encouraged us never to give up. May your souls rest in eternal peace.

I wish to acknowledge the support and great love from my family, my husband, Dr. Martine Nyeko; my children, Eugene Dwight Mugisha, Faith Ellene Lakareber and John Francis Miti; my Parents, siblings, and friends. Your prayers, patient, and love kept me going.

Above all, I thank the almighty God for seeing me through with his grace, love, health, favor, guidance, peace, hope, provision, and mercies. To you be the glory and honor forever and ever. Amen

“May God the Almighty bless you all abundantly”

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Background

Phosphorus (P) was discovered by Hennig Brand, in Hamburg, Germany in 1669 but an understanding of its key role in soil fertility and crop growth emerged centuries later.¹ Although P is the 11th most abundant element constituting $\sim 0.12\%$ of earth's crust,² its deficiency is considered a major limiting factor in crop productivity.³ P deficiency is caused primarily by the reactions of P, added to agricultural soil in the form of fertilizers and manure, into less soluble compounds after binding with metal cations.⁴ Many agricultural lands require yearly addition of P fertilizers to improve soil productivity. Excessive application of P fertilizers is a major cause of eutrophication of water bodies.⁵ It is estimated that \$2.2 bn is spent annually in the United States combating eutrophication.⁶ Therefore, minimizing P losses from agricultural runoff can be an important step towards P recycling and the realization of several UN goals on sustainability.⁷

Biochar is a carbonaceous substance formed by pyrolysis of biomass under reduced or oxygen free conditions.⁸⁻⁹ Recently, researchers have demonstrated the advantages of using biochar as a soil additive for sustainable crop production.¹⁰⁻¹² Biochar has an unique combination of characteristics¹³ which enhances cation/anion exchange capacity, water and nutrient retention,¹⁴ carbon (C) sequestration,¹⁵ microbial activities,¹⁶⁻¹⁷ and soil buffering capacity.¹⁸ Moreover, biochar enriched with plant nutrients can be used in agricultural soil as a slow released fertilizer.¹⁹⁻
²⁰ Other environmental merits linked to biochar amendment in agricultural soil include clean

energy production (biochar is a byproduct of some biofuel production), solid waste management and reduction of toxic minerals mobility and availability in soil.²¹ Biochar properties depend on several factors including the type of biomass feedstock, pyrolysis conditions, post-production processes, and soil type.^{17,22} Despite the many proven benefits of biochar as a soil amendment, very little is known about the potential of P-enriched modified-Douglas fir biochar as a soil additive. Information on P availability from P-enriched modified-Douglas fir biochar for plant uptake is inadequate. In addition, biochar's ability to ameliorate acidic soil, and immobilize heavy metals is not well known.

Douglas fir biochar is a product from Black Owl Biochar, (Biochar Supreme Inc. Environment Ultra). It is a commercial by-product from bio-syngas production. The biochar is reported to have a large surface area ($\geq 500 \text{ m}^2/\text{g}$), this is a property that can enhance nutrient retention.²³ However, this biochar's net surface charges are reduced ($\text{pH}_{\text{pzc}} \sim 6.7$) at typical soil pH (5-7). This limits its adsorption ability for anionic species such as phosphate. Impregnating the biochar with salts such as aqueous Al, Fe, Mg, Zn and Mn chlorides is reported to improve both surface functionalities and phosphate adsorption ability.²¹ It has been shown that Douglas fir biochar modified with Fe_3O_4 can absorb phosphate from wastewater.²⁴ However, the use of excess Fe^{2+} , Al^{3+} and Mn^{2+} as treatment agents may cause phytotoxicity in soil or severely limit P availability.²⁴⁻²⁵ Excess Fe^{2+} acts as an electron donor, accelerating redox reactions in plant cells.²⁷ Mn^{2+} produces reactive oxygen species and interferes with the metabolism of essential metals²⁸ and Al^{3+} inhibit root hair growth, root elongation, and lateral root development,²⁹ Furthermore, oxides of iron or aluminum in soil form insoluble complexes and precipitates.³⁰⁻³¹ Akgül et al.,³² reported higher PO_4^{3-} sorption capacity for Mg^{2+} than Fe^{3+} , Al^{3+} , and Mn^{2+} ions modified biochar. Mg^{2+} is essential for the synthesis of nucleic acids and proteins, photosynthesis, and enzyme

activation in plants.³³ In addition, Mg^{2+} hydroxide, oxides, and carbonates increase soil pH which enhances heavy metals immobilization through precipitation.³⁴

The application of P enriched modified-Douglas fir biochar in agricultural soils is expected to minimize nutrient loss from stormwater runoff, which will reduce commercial fertilizer application rates and surface water contamination. Biochar retention of heavy metals also reduces plant heavy metal uptake and the potential risk of transfer to humans via the food chain. Modifying biochar with basic cations increases ash content and acid amelioration ability. This dissertation focused on the potential of P enriched modified-Douglas fir biochar for soil amendment by; 1) examination of the availability and uptake of phosphorus from P- enriched modified-Douglas fir biochar; 2) assessing the impact of P uptake from P enriched modified-Douglas fir biochar on crop growth and P use efficiency; 3) exploring heavy metal immobilization and 4) the acid ameliorating potential of Douglas fir biochar supported-phosphate. The study hypothesized that the use of P enriched modified biochar as a soil amendment shall offer a comparative performance as conventional fertilizers with minimal risk for environmental contamination.

1.2 Literature review

This review of the literature focused on the challenges and opportunities of biochar use as a soil additive. The roles of P in plants, soil P forms, and sources, plants uptake of soil P, plant soil P use efficiency, mechanisms of soil P fixation, methods of biochar production from various feedstocks, post-production treatments, and biochar effects on soil properties are discussed.

1.2.1 Plants soil P functions

Phosphorus (P) is a constituent of many proteins and enzymes. It is required for the transfer of genetic characteristics from one generation to the next. P promotes root, flower and fruit development allowing early maturity.^{31,35–37} Both the DNA and RNA structures are held together by P bonds and P is a component of ATP, the plants "energy unit".³⁸ Grant et al.,³⁸ reported that P deficiency in agricultural soil lowers uptake and use efficiency of other vital plant nutrients. This restricts plant growth, delays maturity, reduces the forage quality, and increases susceptibility to diseases.

1.2.2 Soil P forms and sources

Soil P exists in both organic and inorganic forms. Organic phosphate is a derivative of biological processes resulting from the uptake of inorganic phosphate. The organic P may be converted to inorganic P by mineralization processes facilitated by soil microorganisms (Fig.1.1)³⁹ and P is typically returned to the soil in the form of plant residues or microbial and animal manures.⁴⁰

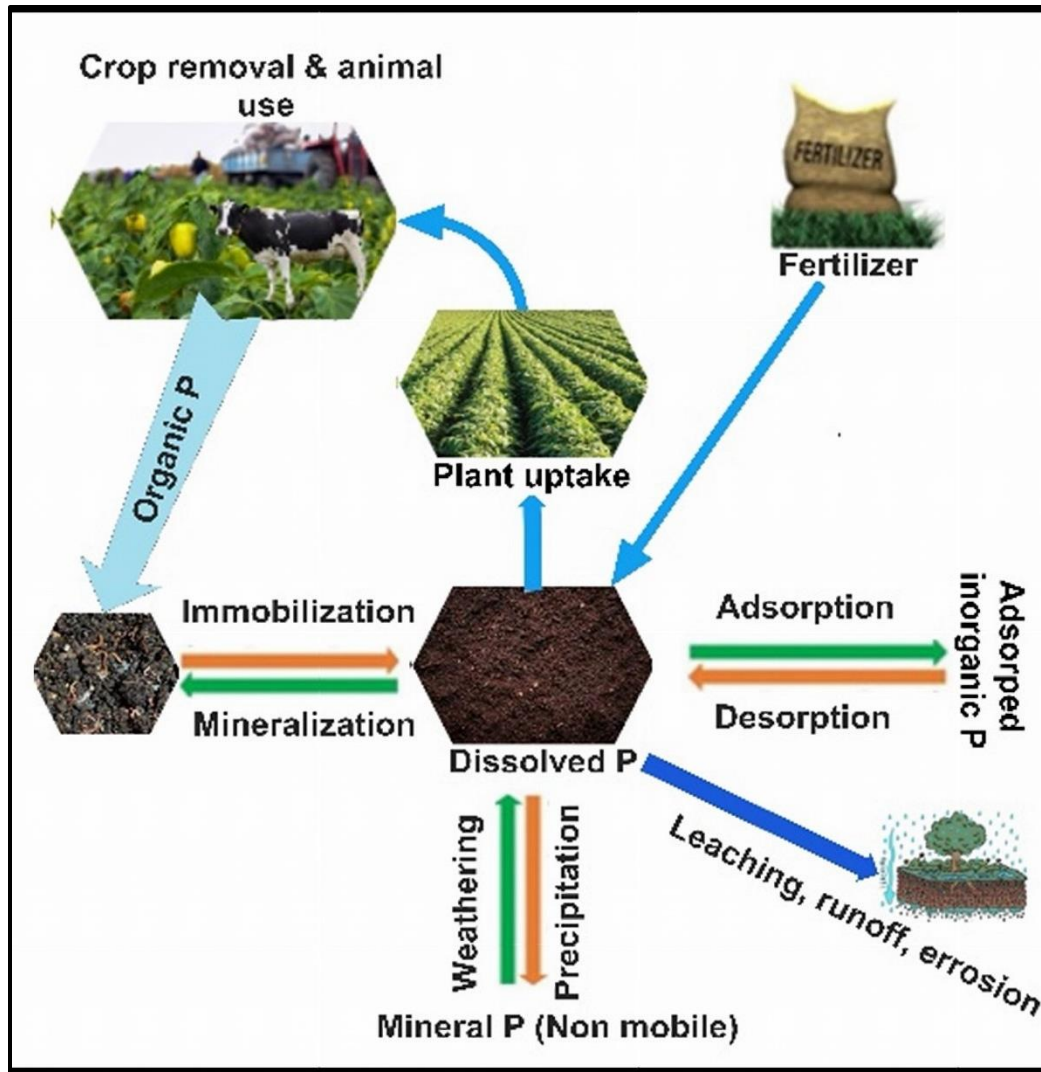


Figure 1.1 P transformation from fertilizer, manure, and plant residue in soil

1.2.2.1 Soil organic P

Huang et al.⁴⁰ grouped soil organic phosphate into three classes depending on the nature of phosphorus bonds (Fig.1.2).

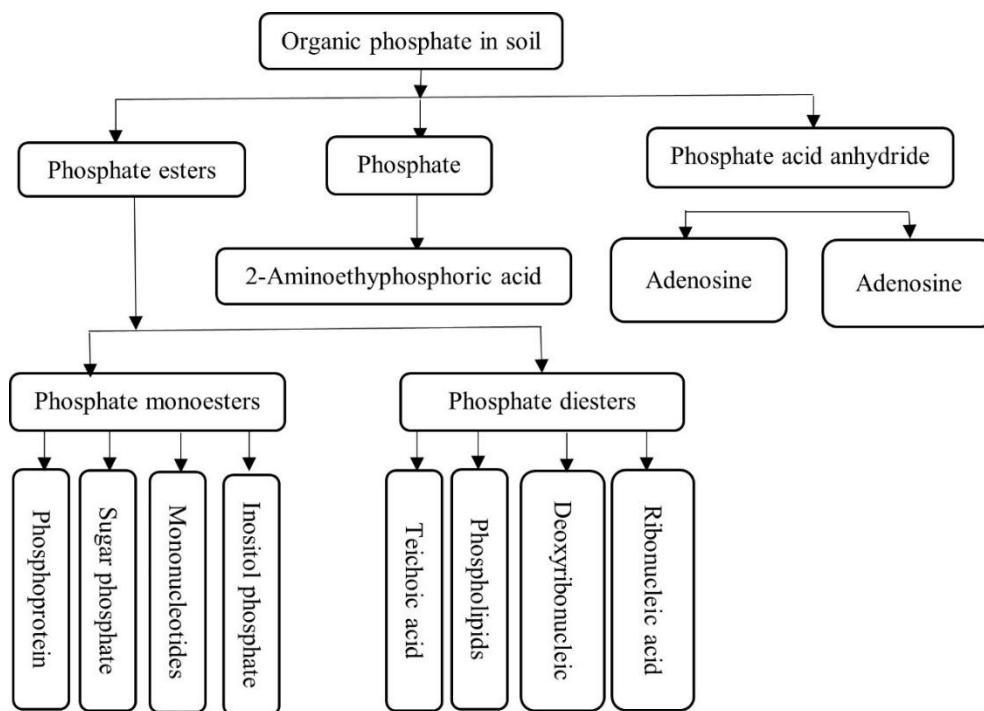


Figure 1.2 Classification of organic phosphate in soil

The first category, phosphate ester, consists of phosphate monoesters and phosphate diesters. The most abundant form of phosphate esters in the soil is phosphate monoester existing primarily as inositol phosphate under aerobic conditions. Phosphate diester comprises mainly the nucleic acids (DNA and RNA), phospholipids, and teichoic acids. Their abundance in soil follows the increasing order of teichoic acids < phospholipids < nucleic acids (DNA and RNA). Because microorganisms rapidly degrade the diesters, they are usually found in lower concentrations than inositol phosphate (monoester) which is persistent and hence bioaccumulates in soil.⁴¹

The next class is phosphoric acid anhydride made up of phosphate monoester and anhydride bonds. The two most widely known phosphoric acids anhydrides are adenosine diphosphate (ADP) and adenosine triphosphate (ATP). They are vital for biochemical energy transfer. However, they

are not often detected in soil because they readily degrade in the environment. The last type is the phosphonates group, which differs from other carbon-oxygen-phosphorus (C–O–P) bonds containing phosphorus in that, it is only made of carbon-phosphorus (C–P) bonds. It was first detected in the environment in the form of 2-aminoethylphosphonic acids.

1.2.2.2 Soil inorganic P

The inorganic phosphates found in soil are mainly in the form of primary minerals such as apatite, strengite, and variscite.³⁹ Depending on soil pH, secondary P minerals, including calcium (Ca), iron (Fe), and aluminum (Al) phosphates, can as well occur. Moreover, inorganic phosphate may be added directly to the soil in highly soluble forms, such as in triple super phosphate [TSP, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] fertilizer. Plants absorb phosphate in this form (H_2PO_4^-) directly through their roots. The rate at which mineral phosphate such as apatite is solubilized in soil is related to plant P uptake rates.⁴²

1.2.3 Plant soil P uptake

Plants absorb phosphorus from the soil through their root hairs, root tips, and the outermost layers of root cells.⁴³ Mycorrhizal fungi that live in association with the roots of numerous crops can also facilitate phosphorous uptake. Phosphorus from the soil is taken up by plants primarily ($\text{pH} < 7$) in the form of orthophosphate ion (H_2PO_4^-),⁴⁴ but in some cases ($\text{pH} > 8$), it may be absorbed in the form of secondary orthophosphate (HPO_4^{2-}). Once absorbed by the plant, phosphorus may be stored in the root or transported to other parts and through various chemical reactions, the phosphorus is incorporated into organic compounds, including nucleic acids (DNA and RNA), phosphoproteins, phospholipids, sugar phosphates, enzymes, and energy-rich phosphate compounds such as adenosine triphosphate (ATP).⁴⁵ Waskom,⁴⁶ reported that

phosphate ion moves throughout the plant, perform various reactions necessary for plant growth, and subsequently returns to the soil surface as plant biomass or animal wastes and residues.

1.2.4 Soil P use efficiency

P use efficiency is the ability of plants to take up and effectively use available soil P for healthy growth.⁴⁷ Approximately 10-25 % of P added in the form of fertilizer or manure is used by plants in most tropical agricultural soils.⁴⁸ Low P use efficiency in agricultural soil results from fixation.⁴⁹⁻⁵¹ The process of fixing soluble phosphorus in soil depends on various factors including soil pH, soluble Fe, Al and Ca content, clay content, organic matter content,⁵² and microbial activity.⁵³⁻⁵⁵ Other reasons for the low P use efficiency in agricultural soil is the loss of available P from fertilizer and manures by runoff, soil erosion losses of organic, mineral and adsorbed forms of P and to a smaller extent, leaching into water bodies.^{46,56-58} This has resulted in eutrophication causing harmful algal blooms, dead zones, and fish kills.

1.2.5 Phosphorous fixation in soil

Despite the large quantity of total phosphorus in the soil, only a small fraction is available to soil biota, mainly due to chemical fixation.⁵⁵ P fixation is the alteration of soluble P from fertilizers and manure into insoluble forms in the presence of clay minerals as well as cations such as Al, Fe, Ca, and Mg.^{59,64-65} Although soil pH does not directly influence phosphorus availability, it regulates how iron, aluminum, and calcium interact with phosphorus in the soil.^{52,61} Figure 1.3 illustrates how soil pH affects phosphorus availability in soil by manipulating the interaction of soil available P with iron, aluminum, and calcium.⁶²

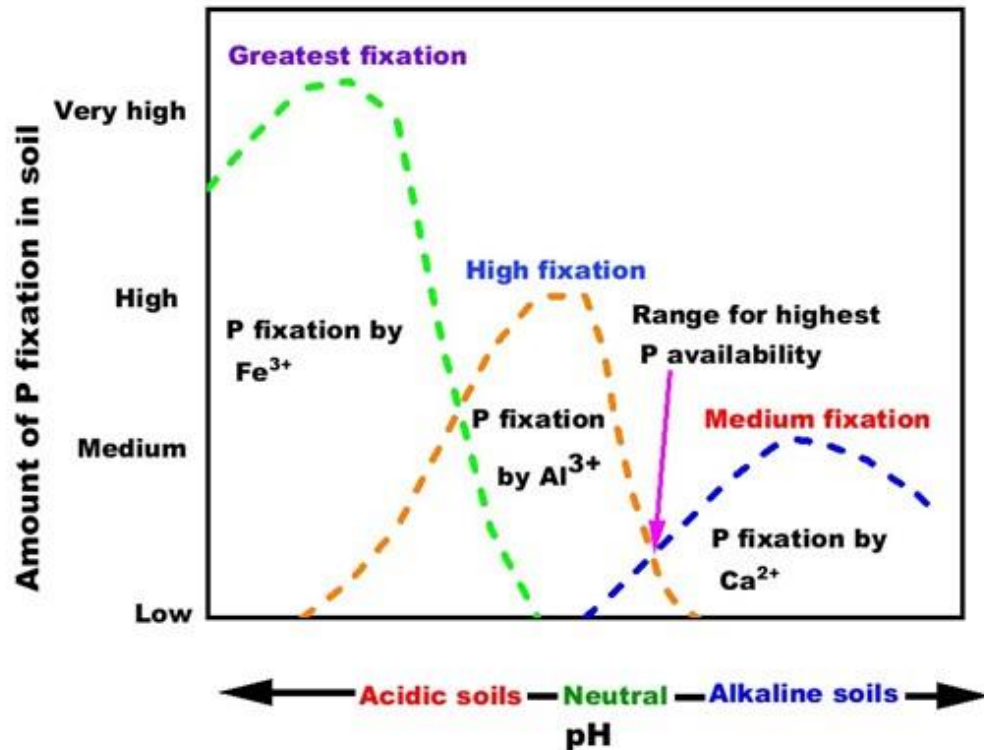


Figure 1.3 Influence of pH on phosphorous fixation in soil (adapted and modified with permission from Penn et al.,⁶²)

The interaction of these cations with phosphorus impacts phosphorus availability in the soil for plant uptake. For alkaline soils ($\text{pH} > 7$), soils' iron and aluminum minerals are almost insoluble, whereas soluble calcium is plentiful.^{49–63} The high concentrations of calcium ions react with available phosphorus (inorganic form), forming insoluble compounds and inhibiting plant uptake. At pH less than 5, calcium ion concentrations are reduced as the minerals dissolve and leach out of the soil, but the concentrations of iron and aluminum ions are high due to the increased solubility of their minerals.^{59,64} Consequently, these ions react with soil's available phosphorus to form their respective insoluble (fixed) phosphates. Other factors influencing phosphorus fixation include the amount of organic matter, clay content and type, temperature, and microorganisms.⁶⁵

1.2.5.1 Mechanism of soil phosphorous fixation

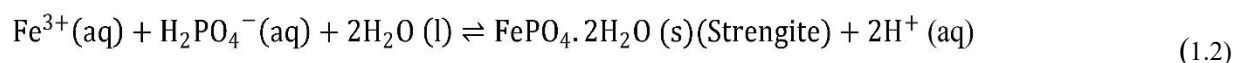
Understanding phosphorus fixation in the soil is vital because it provides insight on the nature of phosphate soil transformation and availability, when added as a fertilizers.^{31,66} Bolland et al.⁵⁰ attributed phosphorus fixation in the soil to the three types of sorption: 1) Chemical sorption in which low soluble secondary inorganic phosphate precipitates from soil solution with divalent/trivalent cations, 2) physicochemical or exchangeable absorption which fixes phosphate ions onto the surfaces of clay minerals and colloidal particles, and 3) biological sorption involving phosphorus immobilization by life activity of microorganisms.

1.2.5.2 Phosphorous fixation by organic matter

Phosphate fixation is reduced following compost application because humus coat Fe oxides and Al oxides during decomposition^{31,51,57}. Organic matter also forms complexes with organic phosphate, which enhance soil P availability. Moreover, the organic matter can release phosphate in soil via mineralization reaction⁶⁷

1.2.5.3 Phosphorous fixation in acidic soil

Phosphorus fixation in acid soil involves both precipitation and adsorption reactions, where precipitation is thought to dominate over a short reaction period.⁵⁹ At low pH<5, Al³⁺ and Fe³⁺ concentrations are high in both the exchangeable and soil solution-phase because of the dissolution of their respective mineral oxides. These ions react with phosphate, precipitating their respective insoluble complex,⁶¹ as shown by equations 1.1 and 1.2.



The products are precipitated from solution or absorbed onto the surfaces of iron /aluminum oxides or clay particles.^{52,68} The adsorption is ascribed to the large specific surface areas and many adsorption sites associated with the clay minerals and oxides of Al/Fe. Further reactions could occur in which the phosphate is blocked in Fe/Al oxide nanopores, thus making it unavailable to plants. Figure 1.4 illustrates the formation of the inner-sphere complex.

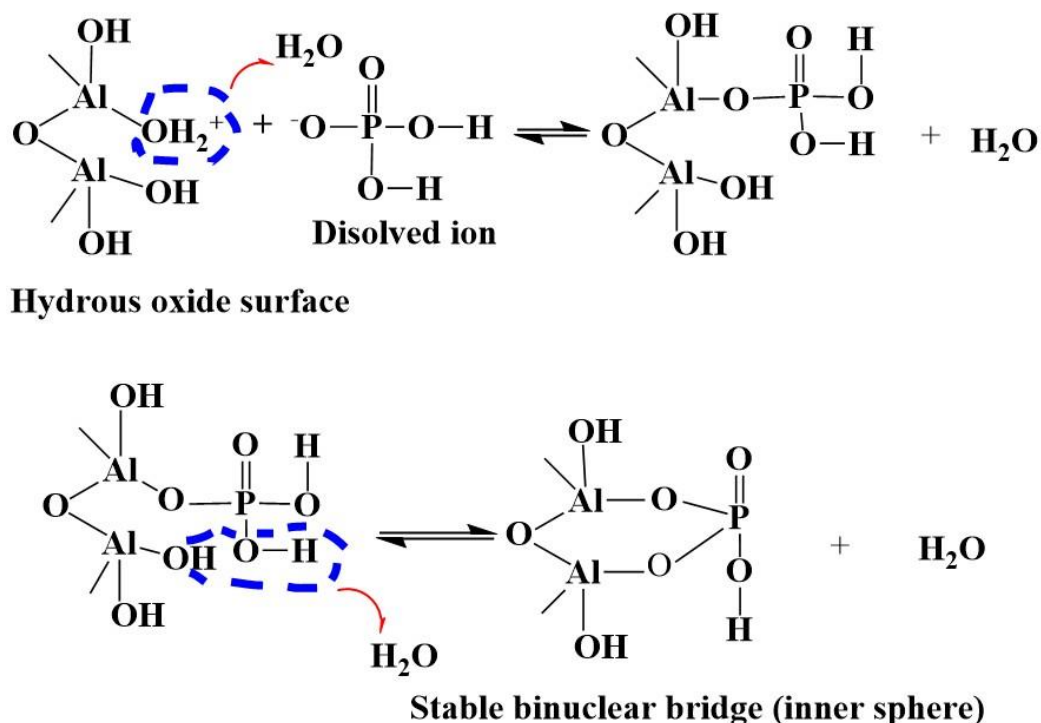


Figure 1.4 Formation of inner sphere complex

1.2.5.4 Phosphorous fixation by silicate clay minerals

Another way to fix P in soil is the reaction of phosphates with silicate clays. Clay sized soil ($<2 \text{ mm}$) are clay mineral consisting of groups of hydrous aluminosilicates.⁶⁹ Whereas a 1:1 clay mineral such as kaolinite ($\text{Al}_2\text{SiO}_5(\text{OH})_4$) consists of a tetrahedral layer and an octahedral layer

bonded through common oxygen atoms, 2:1 clays such as Montmorillonite (smectite) and mica (illite) have an octahedral layer sandwiched between two tetrahedral layers.⁷⁰ Figure 1.5 illustrates the structural differences of kaolinite, montmorillonite and mica. Kaolinite carries no charge, but montmorillonite and mica are charged due to isomorphic substitution. The isomorphic substitution involves the replacement of silicon in a tetrahedral site by aluminum or aluminum in an octahedral site is substituted by a magnesium atom. Montmorillonite and muscovite (mica) differ in that, instead of water molecules between the layers, the mica sheet is occupied by potassium ions.

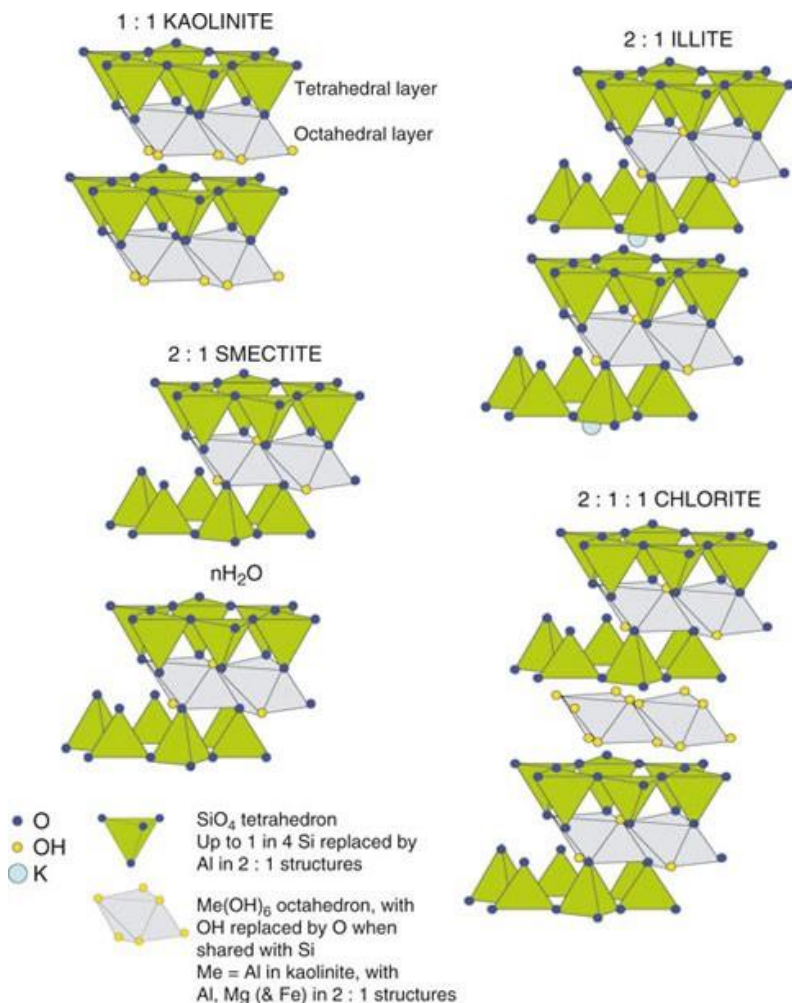


Figure 1.5 Structural differences in kaolinite, montmorillonite (smectite) and mica (illite/muscovite).

Figure adapted with permission from Chesworth et al.,⁷¹

Therefore, both negative and positive charges in clay minerals are created because of isomorphous substitution. For example, one negative charge is created by the substitution of one Al^{3+} for a Si^{4+} in the tetrahedral layer. Positive charge often results from the replacement of a lower valence cation by a higher valence (e.g Fe^{2+} by Fe^{3+}). These charges are responsible for the ion exchange and or the adsorption of ions onto the surfaces of clay minerals. Phosphate fixing

by clay minerals is of two types – anion exchange and through linkages. On the edges of clay minerals such as kaolinite, the oxygen functional groups (silanol and aluminol) are the primary reactive surfaces for adsorption reactions.⁷² Fig. 1.6 illustrates functional groups (aluminol and silanol) and their protonation and deprotonation states on the edge of kaolinite mineral.

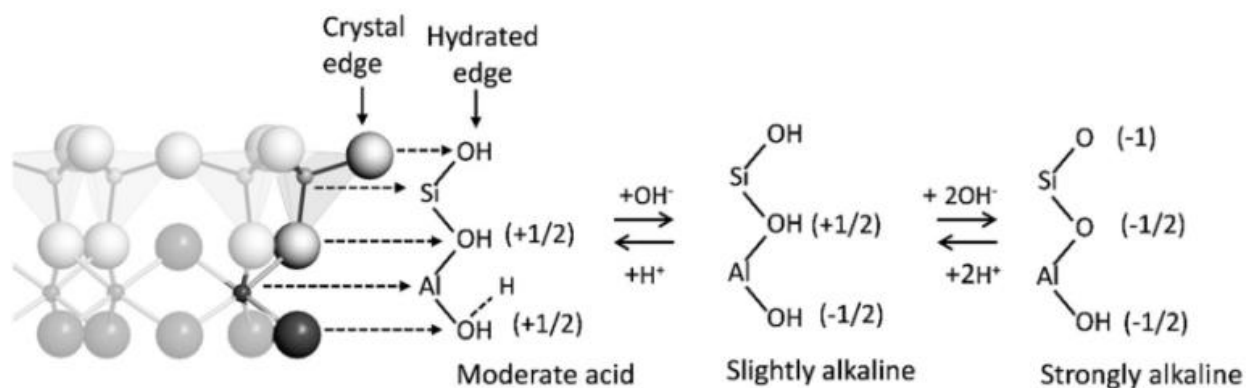


Figure 1.6 Functional groups (aluminol and silanol) and their protonation and deprotonation states on the edge of kaolinite mineral.

Figure 1.6 adopted with permission from D. Strawn.⁷²

1.2.5.4.1 Anion Exchange

In soil, phosphate ions are retained by silicate clay minerals such kaolinite (1:1 clay) by anion exchange. Anion exchange is driven by the attraction of an anion to a positively charged surface resulting in the replacement of another anion.⁶² In this process, anions attached to the hydroxyl group of an aluminum atom exposed at a broken edge or planar surface is replaced by a phosphate ion.^{51,73} Studies have shown that P sorption onto variable charged mineral surfaces decrease with a rise in soil pH due to a reduction in surface positive charge.⁶² As pH rises beyond the soil mineral's point of zero charge (pHpzc), the surface becomes more negative and retains less P due to electrostatic repulsion. However, if pH is less than the pHpzc, P sorption on the

mineral surfaces improves because the surface has more positively charged sites to attract P anions.

Figure 1.7 shows how phosphate ions replace sulfate ions at the edge of clay minerals.

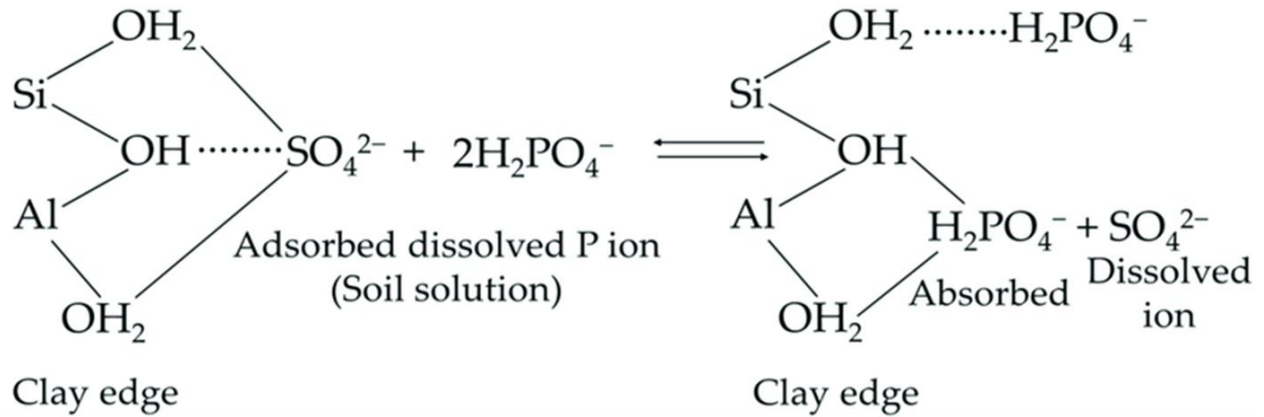


Figure 1.7 Adsorption of phosphate ion on clay minerals by anion exchange

1.2.5.4.2 By linkages

Like anion exchange reactions, phosphate adsorption occurs onto variable charged minerals including Al and Fe oxides/hydroxides and 1:1 mineral by ligand exchange. In this process, a strong covalent bond is formed between the phosphate and an atom with an unsatisfied valence on the mineral surface (equation 1.3).⁶² Many researchers have reported that phosphate fixation is more significant for clays with lower SiO₂ ratios.^{49,61,74} For example, 1:1 clay can fix considerably more phosphate than 2:1 clay.

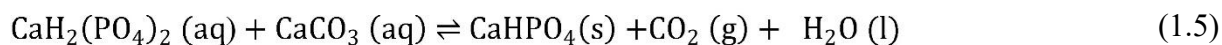


In addition, phosphorus can be fixed by clay minerals forming clay–Ca–H₂PO₄ linkages (equation 1.4).

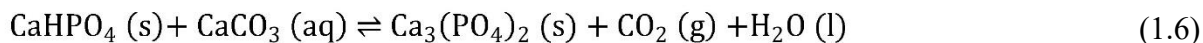


1.2.5.5 Phosphate fixation in alkaline soil

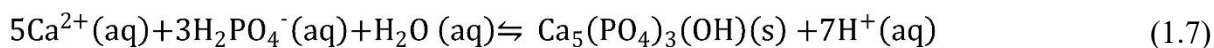
In neutral-to-calcareous soils, such as those found in semi-arid and arid regions, or in humid areas where lime is continuously applied in soil, P fixation is mostly by precipitation reactions.^{39,59} In this process, phosphate precipitates with calcium ions forming dicalcium phosphate $[\text{CaHPO}_4]$ which is slightly soluble (Equation 1.5). Later, $[\text{CaHPO}_4]$ is transformed into a more stable form such as tricalcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ and hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$. These forms of phosphate are less available to plants at alkaline pH due to low solubility³⁵ (Equations 1.6 & 1.7).



Dicalcium phosphate (slightly soluble)



Tricalcium phosphate (less soluble)



Hydroxyapatite (least soluble)

Adsorption on calcium carbonate⁷⁵ and clay minerals⁷⁶ may also occur.

1.2.5.6 Biological fixation of phosphates

Like other processes, biological fixation is an essential process in soil. Microorganisms fix soluble phosphates through immobilization in their cellular materials,⁷⁷ interactions (chelation) by organic substances secreted by the roots, and the decomposition of products of soil organic matter such as humic materials.⁵³ It is reported that phosphates fixed biologically are more soluble than

those fixed inorganically because organic matter is susceptible to decomposition and mineralization processes.⁵⁴

1.2.6 Biochar production and composition

Biochar is a black carbonaceous substance produced at temperatures greater than 300 °C from the pyrolysis of organic materials under reduced oxygen conditions.⁷⁸ The thermal decomposition of organic material (pyrolysis) has been grouped into slow, fast, and flash pyrolysis based on the reaction rate.²¹ In slow pyrolysis, the residence time is longer, but heating rates and pyrolysis temperatures are lower than in fast pyrolysis. During pyrolysis, biomass can be converted into syngas (CO, CO₂, H₂), bio-oil, and biochar.⁷⁹ In practice, slow and fast pyrolysis processes are the common methods used for the production of biochar due to its simplicity and applicability at varying scale.²²

The thermal transformation of biomass to biochar produces substances with high C concentrations and changes in both the nature and concentrations of mineral nutrients.⁸⁰ Many studies have suggested that increased nutrient and carbon concentrations in biochar are responsible for long-term soil fertility and C stability when added to soil^{81–82}. Therefore, biochar is more chemically recalcitrant and resistant to biological breakdown than the corresponding organic feedstock.¹¹ Thus biochar is known to enhance stable soil organic C pools for long-term carbon sequestration.⁸³

Biochar produced at high pyrolysis temperatures have increased aromaticity with high C and inorganic minerals (K, Ca, Mg, Fe, P).^{18, 81} The authors reported that high pyrolysis temperatures biochar typically have low O/C and H/C ratios, cation exchange capacity and yield because these materials have fewer surface oxygen-containing functional groups such as hydroxyl, ether, lactone, carbonyl, carboxyl and phenolic than biochars produced at lower temperatures.^{84–85}

Biochar is a heterogeneous material with both stable and labile components.⁸⁶ Volatile matter, carbon, moisture and mineral matter (ash) are the major biochar constituents.⁸⁷ Biochar contains other elements including O, S, Ca^{2+} , Mg^{2+} , K^+ , H, and heavy metals to variable amounts.⁸⁸ The variations in nutrient contents is ascribed to the nature of biochar feedstocks and pyrolysis conditions.⁸¹

1.2.7 Biochar modification

While the chemical and physical properties of biochar are largely linked to the nature of feedstock and pyrolysis conditions, research has shown that both biochar's physical and chemical characteristics can be altered by modification.²² The process of modification of biochar requires implanting various ingredients into the biochar's structure either before or after pyrolysis.²¹ Pre-pyrolysis activation includes the treatment of biochar feedstock while post-pyrolysis modifications involve the treatment of the biochar itself.

The most common techniques for modification of biochar reported in the literature are the physical activation or chemical treatments (Fig 1.8), which include; surface oxidation and reduction, impregnation, clay mineral modification, thermal plasma processing, high-temperature ammonification, and the use of microorganisms.^{21,89} Modification of biochar can enhance performance by increasing surface area, introducing certain functional groups, improving pore structure and inducing activated surface oxygen species. Yakout et al.⁷⁹ modified rice straw biochar with KOH, H_2O_2 , KMnO_4 , HNO_3 , and H_2SO_4 . They found that treatment of biochar with KOH, H_2O_2 and KMnO_4 increased surface area. In contrast, the surface area was reduced after treatment with H_2SO_4 and HNO_3 . Sizmur et al.⁸⁹ reported an increase in surface area and phosphate adsorption capacity after modifying biochar with clay minerals, MgCl_2 , and MgO . Moreover, the authors suggested that the adsorbed phosphate could slowly be released in soil as fertilizer.

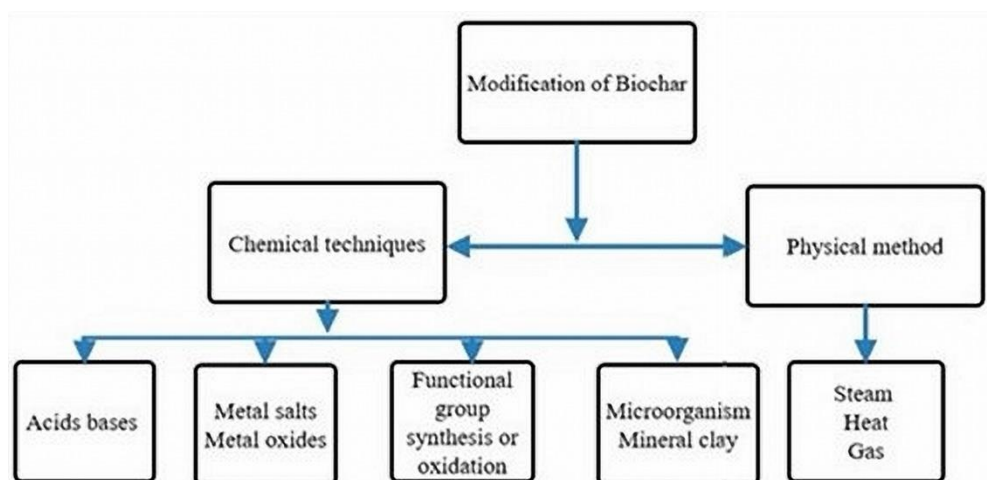


Figure 1.8 Biochar modification methods

1.2.8 Biochar as a fertilizer

Biochar has been proven to improve plant growth by enhancing soil physical, chemical, and biological properties including; water holding capacity, nutrient retention and availability, anion/cation exchange capacity (A/CEC), soil pH, and by providing an appropriate habitat for microbial communities.⁸⁸ The superficially high resistance of biochar to biological and chemical processes in soil with the residence time of hundreds to thousands of years enables its long-term ecological and agronomic advantages.⁹⁰ Consequently, the addition of biochar to agricultural soils has been proven as an alternative, cost-effective and sustainable strategy for enhancing soil fertility and nutrient use efficiency.^{9,91} However, the success of each biochar for soil amendment is significantly influenced by its chemical and physical nature and other environmental aspects such as soil type.⁸⁸

Biochar amendments result in alteration of soil chemical properties including an increase in soil cation/anion exchange capacity, nutrient contents, and pH.⁸⁸ Soil cation/anion exchange capacity, defined as the measure of soil capacity to hold exchangeable cations/anions has been

shown to improve after biochar application in soil.⁹² Many researchers have shown that biochar addition in agricultural soils increases CEC because of the presence of negatively charged surface functional groups.^{11,93} Enhanced cation/anion exchange capacity of soil due to biochar's large surface area, negative surface charge, and porous structure is suggested to be responsible for the reduction in nutrient losses /leaching after biochar addition in soil.⁹⁴ Moreover, some studies have demonstrated that the applied biochar can directly supply nutrients for plant uptake and growth.^{9,93} Therefore, fertilizer application needs can be reduced because of improved nutrient use efficiency following biochar amendments.⁸³ Research has shown that biochar cation exchange capacity increases over time after soil application because of exposure to O₂ and water, and the occurrence of biotic and abiotic oxidation which increases biochar surface functional groups.⁹⁵

Kose et al.,⁷⁸ reported that biochar's pore space provides suitable habitat for microorganisms by protecting them from potential predators and dehydration. Biochar also supplies microorganisms with C and mineral nutrients.⁹⁶ Moreover, some fungi establish a symbiotic relationship with plant root fibers which enables better nutrient uptake by plants.⁸³

Biochar amendment can increase soil pH which results in a reduction in the quantity of exchangeable Al³⁺.⁹⁷ Studies have indicated that biochar amendment in acidic soils lowers the mobility of toxic elements while enhancing K, Mg, Ca and P availability, and thus increasing crop productivity while reducing lime application needs.^{18,97} The pH of biochar in water ranges from 4 to 12 with a steady rise in pH as pyrolysis temperatures increases.⁹⁸ The increase in biochar pH at higher pyrolysis temperatures is attributed to enhanced concentrations of basic cations especially oxides, carbonates and hydroxides of K, Ca, Mg and Na.⁹⁹ Likewise, biochar ash content has been reported to increase with a rise in pyrolysis temperatures.

1.2.9 Biochar effects on soil pH buffering capacity

Soil pH is important because it affects plant growth by controlling both nutrient availability and microbial activities.¹⁰⁰ Many soil minerals help to buffer against pH variations whenever an acid or base is added. While oxides, hydroxides and carbonates of calcium, potassium, and magnesium buffers soil at higher pH values,¹⁰¹ aluminum oxides and iron hydroxides are the main buffering agents in acid conditions.¹⁰² At intermediate pH, the soil is largely buffered by exchange reactions, soil organic matter, and mineral weathering¹⁰¹. In general, clay soils rich in organic matter tends to have a higher buffering capacity than sandy soils.¹⁰³

Several studies have suggested biochar amendments as a way of ameliorating acidic soils.^{92,99–100}. Most biochar is basic with calcium carbonate equivalent (CCE) ranging from ~6 to ~30%.⁹⁸ According to Hue,⁹⁸ biochar alkalinity is largely derived from carbonates, other inorganic alkalis such as oxides and hydroxides, surface functional groups and soluble organic compounds. Baninajarian & Shirvani¹⁰⁶ reported reduced phosphate fixation in acid soil amended with sugarcane bagasse biochar due to enhance pH and cation exchange capacity. Biochar impacts soil buffering capacity by controlling the rate of adsorption and desorption of ionic species in soil.

Biochar surface functional groups such as carbonyl, carboxyl, and hydroxyl adsorb nutrients through ionic exchange, electrostatic interaction, complexation and chemical precipitation.¹⁰⁷ Fig. 1.9 illustrates a conceptual structure of biochar surface consisting of various functional groups.⁹⁸ These surface functional groups are generated further as biochar ages in soil due to environmental oxidation. As surface functional groups increase, biochar ability to absorb heavy metals such as Cd^{2+} and Pb^{2+} soil also increases. This reduces heavy metal mobility, bioavailability, potential risk of water contamination as well as transfer to humans through the food chain.

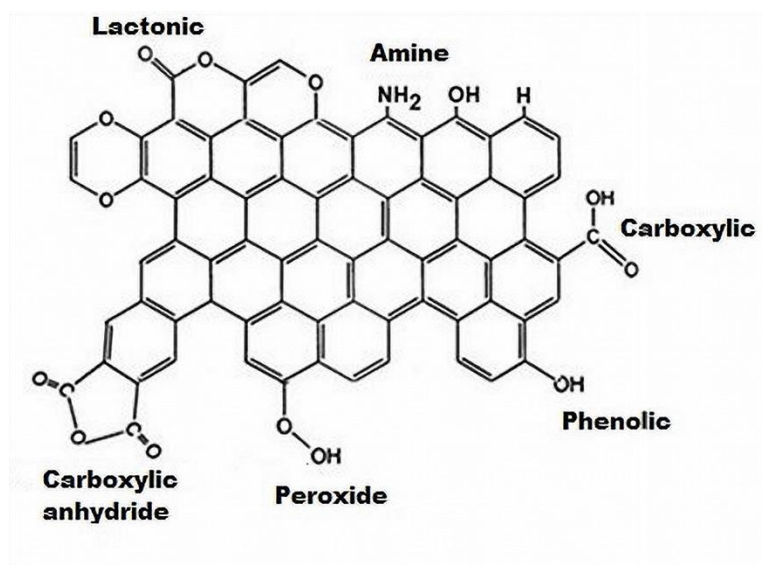


Figure 1.9 A conceptual structure of biochar surface

1.3 References

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CHAPTER II

PHOSPHOROUS AVAILABILITY FROM MAGNESIUM MODIFIED P-ENRICHED
DOUGLAS FIR BIOCHAR AS A CONTROLLED RELEASE FERTILIZER

Published in “Soil Use and Management”. 2021, 00, 1-12. <https://doi.org/10.1111/sum.12751>

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2.1 Abstract

Phosphorus (P) is one of the essential elements required for plant growth and development. However, worldwide, many agricultural soils can be deficient in P. The use of fertilizers and manures as a source of P can be costly, limited in supply in some regions of the world and ecologically unfavorable. Nutrient enriched biochar has been suggested as a relatively cost-effective and eco-friendly P source. This study investigated P availability from Douglas fir biochar modified with magnesium chloride and potassium hydroxide solutions only (B), and P enriched modified Douglas fir biochar B50, B100, and B150 corresponding to B treated with 50, 100, and 150 mg P L⁻¹ solutions of potassium phosphate monobasic. Triple super phosphate fertilizer (FC), and a control treatment without phosphate added (C) used as a reference treatment. Treatments were added to soil in varied amounts to obtain the same P rate of 30 kg P ha⁻¹. Above ground biomass dry weight yield ($R^2 = 0.7$), and plant height ($R^2 = 0.86$) improved with P contents. After harvest, residual soil P for the FC treatment was significantly greater than all other treatments (P -value = 1.78×10^{-6} , $R^2 = 0.8$). Plant height and aboveground dry weight biomass was greater with B150 compared to B50 at the same total P loading, suggesting that the greater P concentration of

the biochar (B150) resulted in less tightly bound P and was therefore more available for plant uptake. This study showed promise of utilizing P enriched Douglas fir biochar as a slow-release P fertilizer.

Keywords: P-enriched Douglas fir biochar, Nutrient management, P availability, Sustainability, soil amendment.

2.2 Introduction

Phosphorus (P) is one of the 18 essential elements for plant growth and development. However, in many agricultural soils worldwide, plant available P may be insufficient due to many factors including low soil P mineral content, and soil properties which influence adsorption mechanisms such as CaCO_3 , Al and Fe oxides contents.¹ P fixation involves the conversion of soluble phosphate into insoluble forms, which inhibit its accessibility by plants.² In acidic soils ($\text{pH} < 5.5$), P fixation occurs when soluble P reacts with Fe^{3+} and Al^{3+} oxides and hydroxides to form minerals strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) and variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), respectively. In calcareous soils ($\text{pH} \geq 7.5$), soluble P can react with the Ca^{2+} ion, forming dicalcium phosphate (CaHPO_4) and sequentially to a less soluble form such as octacalcium phosphate $\{\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}\}$. The resulting compounds are relatively insoluble substances that limit plant labile soil P.³ Therefore, soluble P released from manures or fertilizers applied to soil can be adsorbed, fixed or precipitate with time and so, continued availability of added P for plant use may be restricted.⁴

Many studies have related low crop productivity and yield to insufficient supply of soil P,^{5–6} not only due to its role in plant nutrition but it also lowers the efficiency to uptake and utilization of other essential plant nutrients.⁷ Synthetic fertilizer or manure are commonly used to provide labile P needed by plants for optimum growth. However, long term use of manures and fertilizers to meet crop P demands has been linked to eutrophication.^{8–9} Research has shown that

approximately £75–114 million and \$2.2 billion are spent annually in the UK and USA, respectively, on related eutrophication problems.⁸ Therefore, to realize the UN Sustainable Development Goals (SDGs) 2, 3, 6, 12, 13, and 15,¹⁰ stake holders and policy makers need to find more holistic approaches to soil management challenges.¹¹

Recent studies have documented the potential for biochar to contribute to sustainable soil management¹¹ due to its unique properties including large specific surface area, internal porosity, and rich polar and nonpolar surface sites.¹² Biochar, a by-product of biomass pyrolysis under limited oxygen conditions, has a porous carbonaceous structure with various functional groups.¹³ Biochar can hold nutrients, improve soil water holding capacity, sequester greenhouse gases, enhance soil cation exchange capacity (CEC), reduce nutrient leaching,¹⁴ and improve microbial activity.¹³ Furthermore, studies have noted that biochar enriched with P slowly releases labile P into the soil^{15–16} thereby minimizing required application rates of P and cost of fertilizers.¹⁷ However, pyrolysis temperature, treatment methods, and cations used to modify biochar may affect its surface functional groups, pore structure, and the capacity to adsorb and release labile P.¹⁷ For example, tea biochar activated with Mg^{2+} had greater sorption capacity for PO_4^{3-} than when treated with Fe^{3+} , Al^{3+} , and Mn^{2+} ions.¹⁸ Similarly, a study by Yang et al,¹⁹ using biochar layered double hydroxide (BC-LDH) composites derived from fabricating corn straw with Mg/Al, Ni/Fe, and Zn/Al respectively, achieved greater P sorption capacity with B-Mg/Al-LDH-1 (152.1 mg g⁻¹) than B-Ni+Fe-LDH-1 (78.3 mg g⁻¹) and B-Zn/Al-LDH-1 (64.9 mg g⁻¹). The authors ascribed the variations in P sorption capacities of the BC-LDH to the variation in electronegativity ($Mg < Al < Zn < Ni \approx Fe$) which caused increased electric repulsion between the BC-LDH ($Ni/Fe > Zn/Al > Mg/Al$) and phosphate (HPO_4^{2-} , $H_2PO_4^-$) ions. Peng et al²⁰ used Mg/Al layered double hydroxides biochar produced from corn straw waste at 350, 550, 750, and

950°C and obtained maximum P sorption capacity of 286.2 mg/PO₄^{3-/g} and 215.8 mg/PO₄^{3-/g} at pH 6.0 with the AMOST (950-Mg/Al-A) and conventional (950-Mg/Al) methods, respectively. They ascribed greater P sorption attained with AMOST (950-Mg/Al-A) over the conventional method (950-Mg/Al) to its larger BET surface area and exposed sorption sites. However, P sorption at a high loading (15wt%) of LDHs impregnated on biochar was reduced, due to pore blockages.

Douglas fir biochar, a commercially available by-product of syngas production, has demonstrated a relatively high P adsorption capacity of 91.3 mg g⁻¹ ²¹ and so, could serve as an alternative source of inexpensive and eco-friendly raw material for the production of slow release P fertilizer source to help achieve greater sustainability in agricultural production. However, it is unclear whether the P adsorbed by Mg²⁺ modified Douglas fir biochar would be plant available when applied to soil. Therefore, this study aimed to assess the bioavailability of P in soil amended with Mg²⁺ modified Douglas enriched with P, by looking at relationships between plant tissue P concentrations, residual extractable soil P, and overall plant growth.

2.3 Materials and methods

2.3.1 Soil collection and preparation

A Stough fine sandy loam (coarse-loamy, siliceous, semiactive, thermic Fragiagiuic Paleudults) (pH = 5.5) was used for this study. The soil was collected from a depth of 0- to 15-cm and was air-dried, thoroughly mixed, and sieved to remove any gravel and plant debris prior to placing in experimental pots. The initial bulk soil following crushing and sieving through a 1 cm mesh was analyzed for selected chemical properties at the Mississippi State University extension service plant and soil testing laboratory (Table A.1).

2.3.2 Preparation of magnesium modified Douglas fir biochar.

Commercial Douglas fir biochar was obtained from Biochar Supreme Inc., Bellingham Washington. It was derived from Douglas fir following the procedure described by Karunanayake et al.,²² The production process for modified Douglas fir biochar (B) involved weighing 200 g of previously ground and sieved Douglas fir biochar (particle size $\leq 350 \mu\text{m}$) into 1000 mL beaker and adding 400 mL of a 5% solution of MgCl_2 (wt/v) with constant stirring to form a uniform slurry. To the slurry, 200 mL 2M solution of KOH was added and the mixture stirred at a speed of (500 rpm) with a magnetic stirrer for 2 h, followed by aging at 25°C for 24 h. The treated biochar (B) was oven-dried at 100°C for 48 h and stored in sealed plastic containers.

2.3.3 Preparation of P-enriched Douglas fir biochar

Phosphate enriched biochar was produced by mixing 100 g of ($\text{MgCl}_2 + \text{KOH}$) treated biochar (B) with 400 mL of potassium phosphate monobasic solution. Treatments included a 50 mg P L^{-1} (B50) solution of potassium phosphate monobasic mixed with the treated biochar to form a slurry. Similarly, 100 and 150 mg P L^{-1} solutions derived from potassium phosphate monobasic were mixed with treated biochar to form B100 and B150 treatments, respectively. The products were then left to equilibrate overnight before oven drying at 100°C to constant weight. The resultant products were stored in sealed plastic containers at room temperature until used.

2.3.4 Determining available (extractable) potassium, magnesium, and phosphorus concentrations of Unmodified Douglas fir Biochar (UDB), modified Douglas fir Biochar (B), and modified P enriched Douglas fir biochar (B50, B100, and B150).

The available (extractable) K and Mg concentrations of UDB, B, B50, B100, and B150 were determined by the method described by Marta et al.²³ Briefly, 1 g (W) of air-dried samples of UDB, B, B50, B100, and B150 were measured using an analytical balance and placed in

individual 35 mL polypropylene tubes. To each tube and its contents, 20 mL (V) of 1 M HCl was added, and the mixture was shaken for 2 h at 25°C on a reciprocating shaker. The tubes and their contents were left to stand overnight before filtering the supernatant through Whatman number 42 filter paper. The potassium and magnesium concentrations of the filtrate were determined using atomic absorption spectrophotometry (model SHIMADZU AA-7000) at 202.6 nm and 285.2 nm, respectively. The available (extractable) potassium and magnesium (g kg^{-1}) were calculated from

$$\text{K or Mg} = \frac{\text{Concentration (K or Mg)} \times V}{W \times 10^3}.$$

The available (extractable) P was determined by weighing 0.35 g (W) of air-dried samples of previously ground and sieved (<2 mm) UDB, B, B50, B100, and B150 into a 50 mL polypropylene centrifuge tube. To each tube, 35 mL (V) of 2% formic acid (formate) solution was added, and the tubes and their content ultrasonicated for 10 minutes to allow for thorough wetting of the biochar.²³ The samples were then shaken in a reciprocating shaker for 30 minutes at 25 °C. The tubes were centrifuged at $\sim 2500 \times g$ for 10 minutes before filtering through a Whatman number 41 filter paper. The P concentration (C_p) in the filtrate was determined by the ascorbic acid method using a UV spectrophotometer (model SHIMADZU UV-2550) at a wavelength of 880 nm

The available P (g kg^{-1}) was calculated from $P = \frac{C_p \times V}{W \times 10^3}$.

2.3.5 Analyzes of surface morphology and elemental composition of Unmodified Douglas fir Biochar (UDB), modified Douglas fir Biochar (B), and modified P enriched Douglas fir biochar (MPB).

The morphology and elemental composition of UDB, B, and modified P enriched Douglas fir biochar (MPB) were analyzed with scanning electron microscopy (SEM) and SEM-EDX at 5 kV using a JEOL JSM-6500F FE instrument. X-ray diffraction (XRD) analysis was done to determine their structural and chemical compositions. The analysis was performed using a

SmartLab X-ray diffractometer by scanning 2θ from 0° to 90° at $1^\circ/\text{min}$. The SmartLab X-ray diffraction system was used to acquire a XRD spectrum under the same conditions. For modified P enriched biochar, only B100 was analyzed as a representative.

2.3.6 Greenhouse Experiment

The experiment was conducted in a greenhouse located on the campus of Mississippi State University ($33^\circ 27' 22'' \text{ N} / 88^\circ 47' 44'' \text{ W}$) between February and April 2019 using corn (*Zea mays* L.) variety DeKalb 67-44 as the experimental crop. Treatments were arranged in a randomized complete block design with four replications using plastic pots measuring 15 cm X 15 cm. Treatments included a control with no amendment applied concentrated superphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) as a fertilized control (FC), and biochar treatments of B, B50, B100, and B150 mg P L^{-1} . A 30 kg P ha^{-1} application rate was used for FC, B, B50, B100, and B150 treatments so that each treatment received an equivalent rate of applied P (30 kg P ha^{-1}). Each pot was perforated at the bottom to allow for drainage and aeration, and treatments were thoroughly mixed with 2.5 kg of air-dried soil/pot and either C (no amendment), FC (0.074 g), B (9.7 g), B50 (2.0 g), B100 (1.0 g), or B150 (0.73 g) treatments. Four seeds of DeKalb corn variety 67-44 were planted per pot and at the V2 growth stage, plants were thinned to two per pot. Nitrogen fertilizer was applied in the form of ammonium nitrate (34-0-0) at a rate equivalent to 120 kg N ha^{-1} based on the weight of soil in each pot. Watering was done daily to maintain soil moisture at around 80% field capacity by weighing using balance. After harvest, 5 soil cores from each pot was homogenized, air-dried, crushed to pass a 10-mesh sieve, and tested for pH (2:1 di H_2O : soil) using a Fisher Scientific Model 25 Accumet pH meter (Denver, CO) following the method described by Thompson et al.,²⁴ and extractable nutrients (P, K^+ , Mg^{2+} , and Ca^{2+}) were determined following

the Mississippi State Extension Service Soil Test Method²⁵⁻²⁶ using an Avio 200 ICP-OES (Perkin Elmer, Waltham, MA) to determine nutrient concentrations in the extracted solution.

2.3.6.1 Plant and Soil analyses

Whole plants were harvested 31 d after planting by cutting with a scalpel just above the soil line. Just before harvest, plant height was measured (V6 growth stage). Harvested plant material was oven-dried at 65°C until a constant weight was obtained. Dry matter yield was recorded, and then oven-dried plants were ground to pass through a 40-mesh sieve. Plant tissue was analyzed using a modified dry ashing procedure²⁷ with nutrient elements quantified using an Avio 200 ICP-OES (Perkin Elmer, Waltham, MA). Plant nutrient content was calculated using plant tissue nutrient concentration and dry matter weight.

2.3.6.2 Statistical analysis

Regression analysis was performed for plant height, dry matter yield, plant P content, and extractable soil nutrient levels using Microsoft excel 365 software. Analysis of variance (ANOVA) and Fisher's Least Significant Difference (LSD) at a 95% confidence limit was performed to detect differences among treatment means using Origin pro-8 software. Also, Pearson correlation coefficients of both plant and residual soil nutrient contents were determined.

2.4 Results and Discussions

2.4.1 Available potassium, magnesium and phosphorus concentrations of biochar

Concentrations of available K and Mg in the biochar significantly increased after modification. In contrast, P concentrations slightly decreased following modification. However, available P concentrations increased following treatment of modified Douglas fir biochar with

potassium phosphate solutions. The increase in P concentrations of P enriched Douglas fir biochar was in the order of $150 \text{ mg P L}^{-1} > 100 \text{ mg P L}^{-1} > 50 \text{ mg P L}^{-1}$ (Fig.2.1).

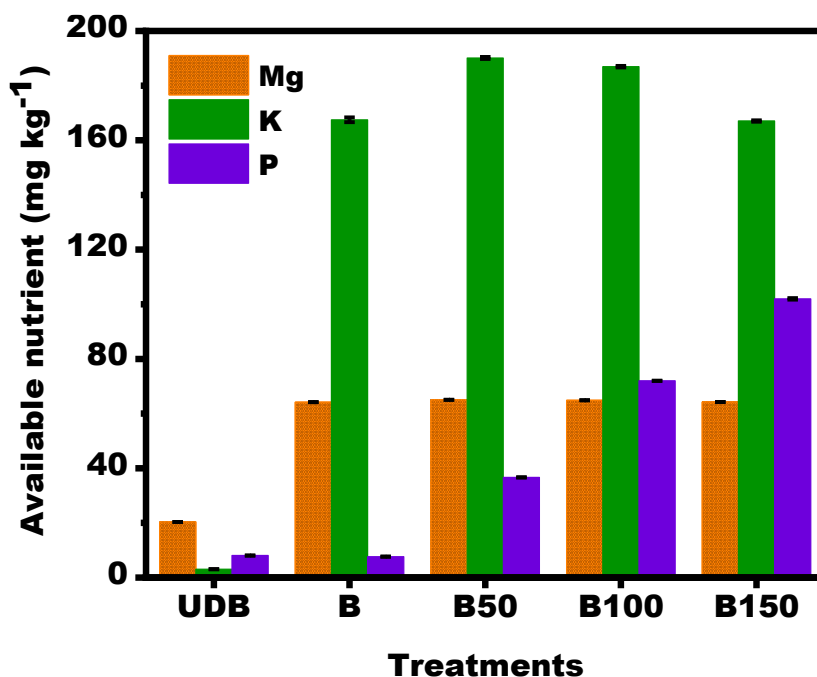


Figure 2.1 Available K, P, and Mg in unmodified Douglas fir biochar (UDB), modified Douglas fir biochar (B), and P enriched modified Douglas fir biochar (B50, B100, and B150). Error bars represented as the standard error of the mean of 3 replicates.

While available K and Mg concentrations increased following modification of biochar, there was a small decline in available P concentration (Fig.2.1). However, the concentration of available P significantly increased after treatment with different potassium dihydrogen phosphate solution concentrations. The decrease in P concentration following the modification of biochar may be due to the reaction of Mg ions from the modification solution with biochar phosphate forming less soluble compounds such as $\text{Mg}_3(\text{PO}_4)_2$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and MgHPO_4 (Equations. 2.1, 2.2 & 2.3).



According to Akgül et al.²⁸ phosphate sorption by metal impregnated biochar is enabled by the coating of magnesium hydroxide on biochar surfaces. Therefore, the formation of less soluble compounds decreases the fast release of available P in solution which can result in long term release of available P.

Similarly, percent yield of available P improved in the order B150 > B100 > B50 (Table 2.1). However, the percent available yield for both K and Mg were comparable across B, B50, B100, and B150 treatment. The percent yield was calculated using the expression:

$$\% \text{ yield} = \frac{\text{Available (P, K, or Mg)} \times 100}{(\text{concentration of nutrient in untreated biochar} + \text{concentration of nutrient in treatment solution})}$$

This expression assumes that each nutrient in solution was completely adsorbed by the biochar.

Table 2.1 Percentage (%) yield of available P, K and Mg from B, B50, B100 and B150

Treatment	% Yield		
	P	Mg	K
B	NA	0.128	0.150
B50	13.17	0.130	0.170
B100	33.91	0.129	0.167
B150	45.55	0.128	0.149

B = MgCl₂ + KOH treated Douglas fir biochar, B50, B100 and B150 were B treated with 50, 100 and 150 mgPL⁻¹ solution of KH₂PO₄ respectively

As expected, the percent yield of available P increased with increasing P concentration in Biochar (Table 2.1) and the percent yield for K and Mg were relatively comparable for B, B50,

B100, and B150 treatments. Identical concentrations of K and Mg were used for treatment of UDB, therefore this result was predictable. Interestingly, even with the low P concentrations in biochar compared to Mg and K, a relatively larger proportion of available P was released suggesting that P in the biochar was more weakly adsorbed or occurs as more soluble compounds.

2.4.2 Surface morphology and structural chemical composition

Scanning electron microscopy (SEM) micrographs and energy dispersive spectroscopy (SEM/EDS) spectra for untreated Douglas fir biochar (UDB), $\text{MgCl}_2 + \text{KOH}$ modified Douglas fir biochar (B), and Modified P enriched Douglas fir (MPB) are shown in figures (2.2 and 2.3 respectively). Modification of UDB altered its surface morphology. Prior to activation, the UDB possessed a distinct honeycomb surface structure, following activation, B and MPB appeared more heterogeneous, with trapped crystal particles.

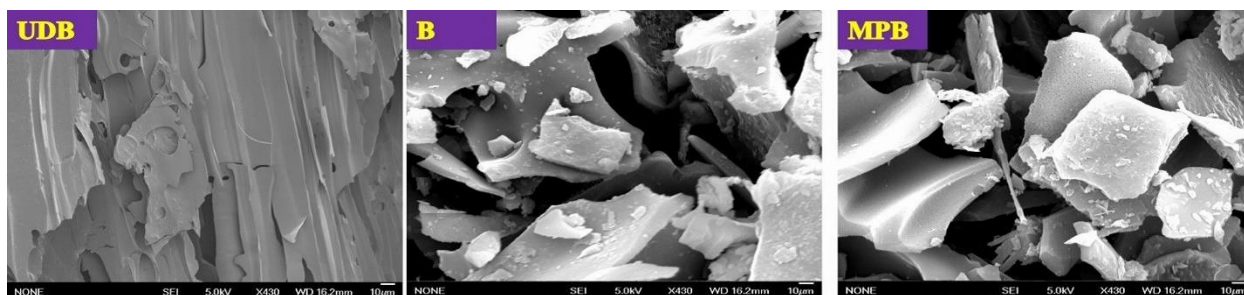


Figure 2.2 Scanning electron microscope (SEM) images for unmodified Douglas fir (UDB), modified Douglas fir biochar (B) and modified p enriched Douglas fir biochar (MPB).

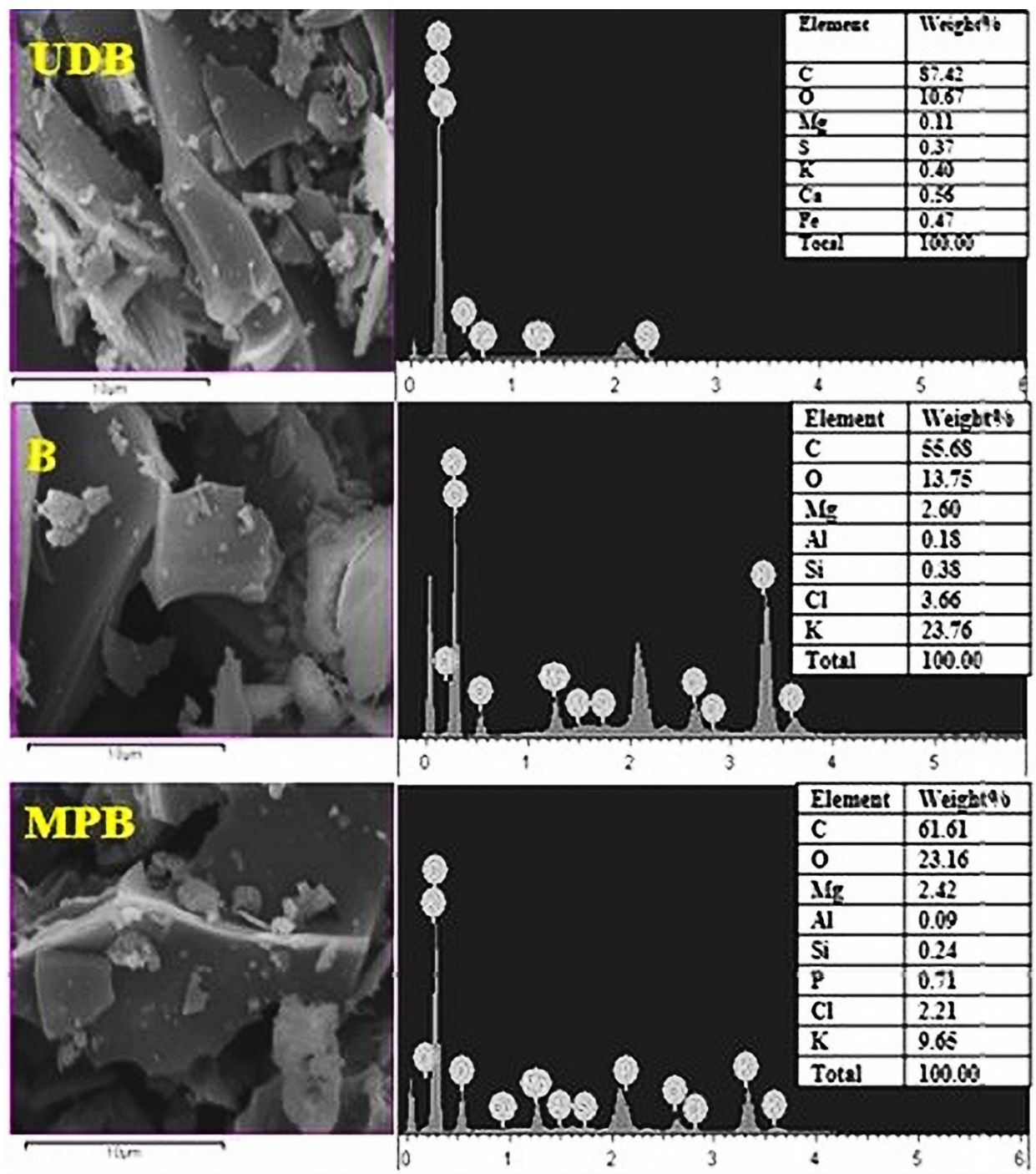


Figure 2.3 Energy-dispersive X-ray (EDX) spectra for unmodified Douglas fir (UDB), modified-Douglas fir biochar (B) and modified p-enriched Douglas fir biochar (MPB).

The peaks from X-ray diffraction techniques (Fig. 2.4), were identified by matching in qualX 2.0 Software. XRD patterns for UDB displayed the presence of two broad peaks, similar to graphene, between $2\theta = 20^\circ$ to 30° and 40° to 50° . These peaks are perhaps due to graphite diffraction.²⁹ Additional sharp peaks were identified as mixed inorganic components including calcite,³⁰ brucite, dolomite, quartz, and periclase (not shown).³¹ New peaks emerged in B providing evidence for the presence of MgO ($2\theta = 28.46^\circ, 44.05^\circ, 60.79^\circ, 43.88^\circ$)³² and Mg(OH)₂ at ($2\theta = 37.93^\circ, 50.17^\circ, 58.67^\circ, \text{ and } 73.8^\circ$).^{33–35} Furthermore, additional peaks emerged in MPB due to hydrated Mg₃(PO₄)₂ at $2\theta = 4.65^\circ, 6.16^\circ, 31.9^\circ, 53.23^\circ$ and, MgHPO₄ at $2\theta = 4.65^\circ, 5.73^\circ, 6.80^\circ, 13.18^\circ, 16.51^\circ$.^{36–38}

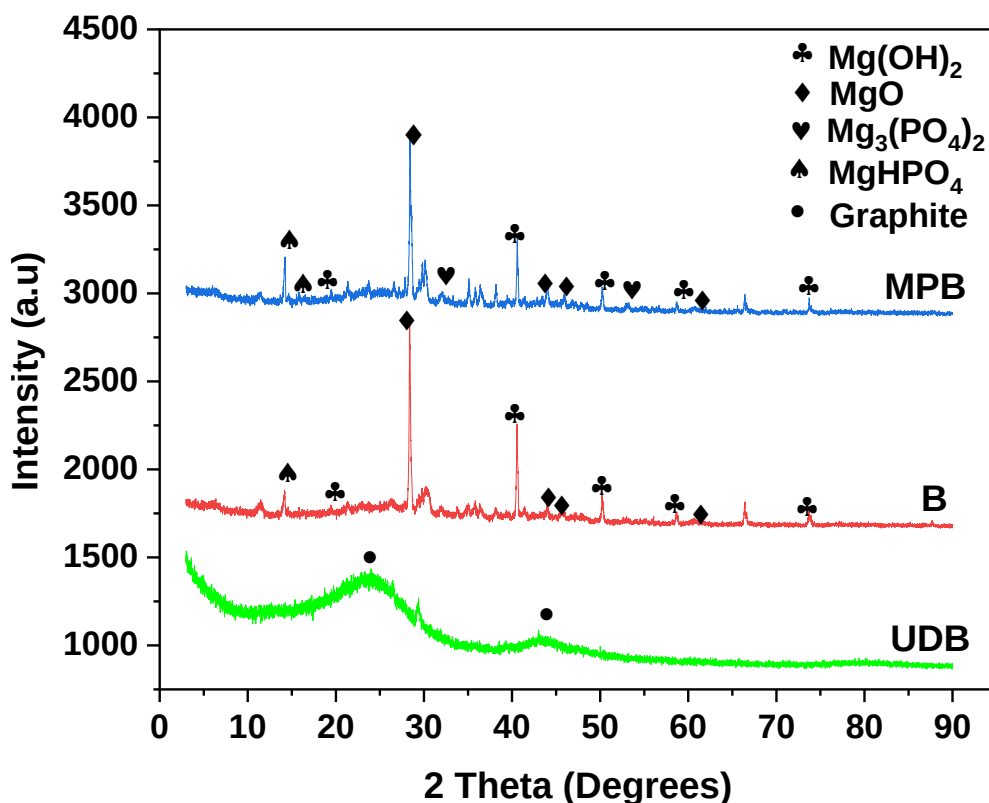
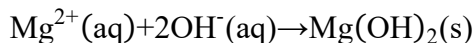


Figure 2.4 XRD spectra for Unmodified Douglas fir (UDB), modified Douglas fir biochar (B) and Modified p enriched Douglas fir biochar (MPB).

Results from SEM (Fig.2.2) revealed that modification of UDB altered its surface morphology. Prior to activation, the UDB possessed a distinct honeycomb structure suggesting the tube-like structure from plant cells. However, with activation and enrichment, the surfaces of B and MPB appeared more heterogeneous, with trapped crystal particles. The SEM-EDX results (Fig.2.3) indicated that the major constituents of UDB, B and MPB were C, O, Ca, K, Si, and Mg. However, weight percentages corresponding to K and Mg in B and MPB were greater than that of UDB due to activation with MgCl_2 and KOH. In addition, MPB had P (0.71%) revealing that modification and enrichment of biochar increased its nutrient contents.

XRD results indicated that P exists in the form of hydrated $\text{Mg}_3(\text{PO}_4)_2$ and MgHPO_4 (Fig. 2.4). Since $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ is more soluble ($\text{pK}_{\text{SP}} = 5.83$) than $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ ($\text{pK}_{\text{SP}} = 23.7$) and $\text{Mg}_3(\text{PO}_4)_2$ ($\text{pK}_{\text{SP}} = 23.28$),³⁹ it is therefore likely that enrichment of B with potassium phosphate solution enhanced the content of more soluble MgHPO_4 in B50, B100, and B150. The increased solubility of MgHPO_4 in B50, B100, and B150 is probably responsible for their better P availability compared to B.

In contrast, the low release of Mg could possibly be due to the precipitation of Mg^{2+} in the form of less soluble forms such as $\text{Mg}(\text{OH})_2$ ($\text{pK}_{\text{SP}} = 10.86$)⁴⁰ at increased Mg^{2+} and OH^- concentration.



Sohi and Angst⁴¹ in their study to establish K, Mg, and P released by biochar noted that, both P and Mg were gradually released from biochar suggesting its suitability for use as a slow release fertilizer

2.4.3 Crop response to biochar P loadings

Treatments B150 and the Control (C) had the tallest and shortest plant heights, respectively (Supporting information Fig. A.1). Also, the fertilizer control treatment (FC) had the second-tallest plant height recorded, while B100 and B50 treatments resulted in comparable plant heights. Plant dry weight yield followed a similar trend as for plant height (Supporting information Fig. A .2).

An analysis of variance ($\alpha = 0.05$) indicated significant differences in plant heights between treatments ($R^2 = 0.5$, P -value = 0.01). Both B150 and FC treatments showed significant differences in their mean plant heights compared with C. Regression analysis of the biochar treatments showed that plant heights increased with increasing P_2O_5 % biochar treatments ($R^2 = 0.88$, P -value = 0.01). This indicated that plants performed better with increasing rates of P loaded onto biochar even though P application rates were equal (Table 2.2).

Table 2.2 Treatments effects on corn growth

Treatment	Plant height (cm)	DW yield (g pot ⁻¹)
Control	22.1 ± 0.67 ^c	1.17 ± 0.08 ^b
FC	29.4 ± 2.64 ^{ab}	1.45 ± 0.38 ^{ab}
B	22.6 ± 0.68 ^c	1.25 ± 0.14 ^b
B50	25.7 ± 1.67 ^{bc}	1.38 ± 0.19 ^b
B100	25.7 ± 2.49 ^{bc}	1.37 ± 0.21 ^b
B150	31.5 ± 2.04 ^a	1.61 ± 0.21 ^a

DW yield = Above ground biomass dry weight yield. Values represented for plant height and DW yield are averages of four replicates ± standard error of the mean. Different letters (superscripts) indicate significant differences ($P < 0.05$) among treatments according to Fisher's LSD test.

A similar trend was observed for plant P content. Results indicated that both P content and plant height corresponding to FC treatment varied significantly from those of C and B treatments but was similar to the B150 treatment. Regression analysis showed positive correlations ($R^2 = 0.86$, P-value = 0.007) between average plant heights and mean P content (Supporting information Fig. A. 3 A₁). Similarly, there was a significant positive relationship ($R^2 = 0.7$, P-value = 0.03) between average plant P content and mean dry weight yield (Supporting information Fig.A.3 A₂).

Plant growth may be affected by many factors, including sunlight, temperature, genetics, water, and nutrient availability. However, for this study, the primary limiting factor was soil available P. The effect of sunlight was minimized by using a completely randomized experimental design. Soil moisture levels were maintained near field capacity to ensure adequate water availability.

Although fertilizer (FC) had the highest percentage of P₂O₅ (46%) compared to other treatments (Supporting information Fig. A.1), insignificant differences were observed in plant heights corresponding to FC and B50, B100, and B150 treatments. Differences were noted however, between FC and C and B treatments. Significant variations between C and B treatments and the FC treatment was likely due to their inability to release relatively sufficient available P for plant recovery compared to the FC, B50, B100, and B150 treatments. Also, the insignificant difference in P content and plant height observed between the FC treatment and P enriched Biochar (B50, B100, and B150) treatments is likely due to the slow release of available P by P enriched Douglas fir biochar which subsequently resulted in enhanced plant growth. The biochar P release rate was likely due in part to its liming property, which causes an increase in soil pH leading to the repulsion of phosphate anions by making soil particle surfaces more negatively charged and

reducing Fe and Al solubilities. The increased repulsion of phosphate resulted in decreased P sorption by the soil, making it more readily available for plant uptake.

Plant growth is directly correlated to the presence of available P in soil. Therefore, the positive relationship between plant P contents and growth parameters (dry weight yield and plant height) can be due to the slow release of available P into the soil from the P enriched Douglas fir biochar, which may have resulted in improved plant P uptake and hence plant growth on this P testing soil. Besides, the insignificant difference between P uptake between the FC and P enriched Douglas fir biochar treatments, the results suggests a similarity in their ability to supply available P for plant uptake. Enhanced plant growth following the application of different P sources in soil has been reported in the literature by many researchers.^{42–45} For example, increased dry weight yield following poultry manure-derived biochar has been shown.⁴⁴ The enhanced growth observed was ascribed to an increase in available macronutrients supplied by the applied sources. Furthermore, both plant height and dry weight yields improved following the applications of different types and amounts of manures to the soil.⁴⁵

There was a general decline in soil pH following harvest regardless of treatment. Relatively greater soil pH was observed in B, B50, B100, and B150 treatments compared to the C and FC treatments. Except for B150, which did not indicate a significant difference in soil pH from the FC treatment, all other treatments showed a decline ($R^2 = 0.6$, P-value = 0.002) in soil pH compared to both C and FC treatments (Fig. 2.5).

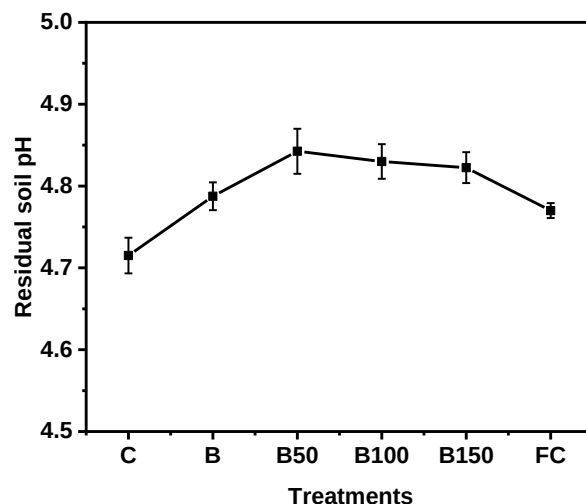


Figure 2.5 The effect of C, B, B50, B100, B150, and FC treatments on residual soil pH. Errors bars shown as the standard error of the mean ($n = 4$).

The pH presented is that of the soil sampled after harvest. The initial soil pH was 5.5 (1:2, soil: water) and declined for all treatments, but reductions were less for biochar treatments possibly due to high concentrations of basic cations (calcium, potassium and magnesium oxides and hydroxides) in biochar resulting in a liming effect. The nitrogen fertilizer used in this study was ammonium nitrate which can contribute to acidity with the nitrification of NH_4^+ to NO_3^- the decline in pH.⁴⁶ Organic matter including biochar are also known to absorb Al^{3+} thus reducing potential acidity. Other studies⁴⁷⁻⁴⁸ have also reported improved plant growth (corn) following biochar application. Numerous reasons including liming effects, increased soil water-holding capacity and physical property improvement, and increased surface area for nutrient adsorption have been hypothesized in the literature for improved crop yield following biochar application in soil.⁴⁹ Researchers⁴⁷⁻⁴⁸ have claimed that biochar's liming ability was the principal reason for enhanced plant growth on acid soils due to a reduction in Al^{3+} and Fe^{3+} activities and hence improved P availability for plant use.

2.4.4 Variations of K and Mg contents with treatments

In general, K and Mg plant contents showed similar trends as P contents. However, unlike P content, the FC treatment recorded a lower K/Mg content ratios than biochar treatments (Fig. 2.6). There were weak positive correlations between P plant content and Mg ($r^2 = 0.3$) /K ($r^2 = 0.2$) contents.

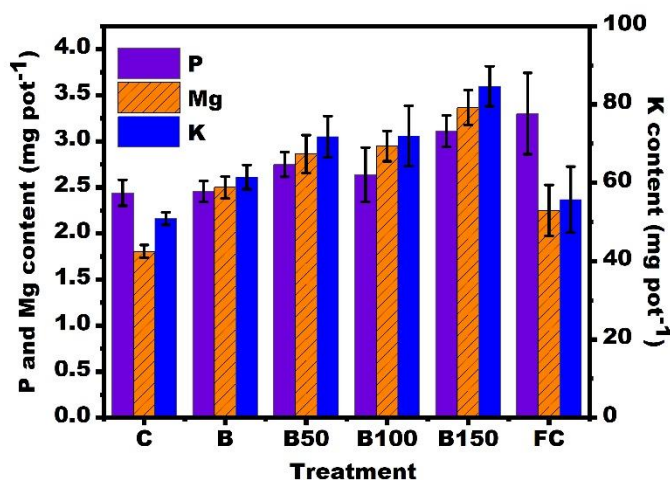


Figure 2.6 The effect of biochar enrichment rate on nutrient contents of corn plants as compared to an untreated biochar and a commercial fertilizer. Errors bars shown as the standard error of the mean of 4 replicates.

Analysis of variance showed significant differences in both K ($R^2 = 0.56$, P-value = 0.006) and Mg ($R^2 = 0.7$, P-value = 0.0001) contents between various treatments. Also, regression analysis showed positive plant growth responses with both soil K/Mg ($R^2 = 0.54$, P-value = 0.09) contents (Supporting information Fig. A.4 A₁ & A₂ respectively). Although FC and C treatments did not record significant differences in their K/Mg contents, the K/Mg contents for the FC treatment differed significantly from those of biochar treatments. In addition, regression analysis (Supporting

information Fig. A.4 A₃) showed K content increased with Mg content ($R^2 = 0.97$, P-value = 0.0005).

Results showed weak positive correlations between P content and Mg ($r^2 = 0.3$) /K ($r^2 = 0.2$) contents. The increased plant K and Mg contents compared with P contents may indicate the necessity for soil available P to improve K/Mg uptakes. For example, in this work, greater plant K/Mg contents were observed for the FC treatment than for the C treatment. Similar results were reported by Saleque et al.⁵⁰ in which both K and Mg contents of different rice varieties correlated positively with P concentrations signifying negative impacts of soil P deficiency on K and Mg recovery.

Furthermore, increased plant K and Mg contents associated with biochar and P enriched biochar treatments in comparison to the FC and C treatments can be due to the ability of biochar and P enriched biochar to release soluble K and Mg for plant use. The successive modification of biochar with magnesium chloride and potassium hydroxide solution, prior to enrichment with potassium phosphate solution, can partly explain the enhanced soluble K and Mg associated with biochar and enriched biochar treatments. These results suggests that, in addition to available P, modified P enriched biochar may have the potential to supply soluble K and Mg required for plant growth. Improved crop yield following Mg application was reported by Guo et al.⁵¹ They noted that growth responses to magnesium was directly influenced by both soil pH (acidic>neutral>alkaline) and Mg concentration {deficient ($< 6 \text{ mg kg}^{-1}$) > moderately deficient ($< 60\text{-}120 \text{ mg kg}^{-1}$) > relatively enough ($>120 \text{ mg kg}^{-1}$)}. In this study, the soil was acidic (pH = 5.5) and both Mg (15 mg kg^{-1}) and K (44.5 mg kg^{-1}) tested low. Therefore, soil conditions may partly explain the growth responses linked to improved Mg and K availability and recovery.

Regression analysis (Supporting information Fig. A.4 A₃) showed plant K content increased with Mg content ($R^2 = 0.97$, P-value = 0.0005). This observation contrasts with the antagonistic effect between K and Mg uptake reported in the literature.^{52–53} High soil test K generally results in Mg deficiency in crops grown on soils that are low in Mg, whereas crops grown on soils high in Mg can suffer K deficiency if grown on soil low in K. For this study, our soil was acidic and deficient in both K (low soil test) and Mg. Therefore, the addition of biochar modified with both Mg and K simultaneously supplied both nutrients for plant uptake. Consequently, this observation may suggest that the concurrent addition of K and Mg may enhance their uptake by plants. However, more studies are necessary to validate this view.

2.4.5 Residual soil test P (STP), K (STK) and Mg (STMg) levels

Following harvest, residual soil P, K, and Mg levels were determined. Results showed the greatest and lowest STP corresponded to the FC and C treatments, respectively (Fig.2.7).

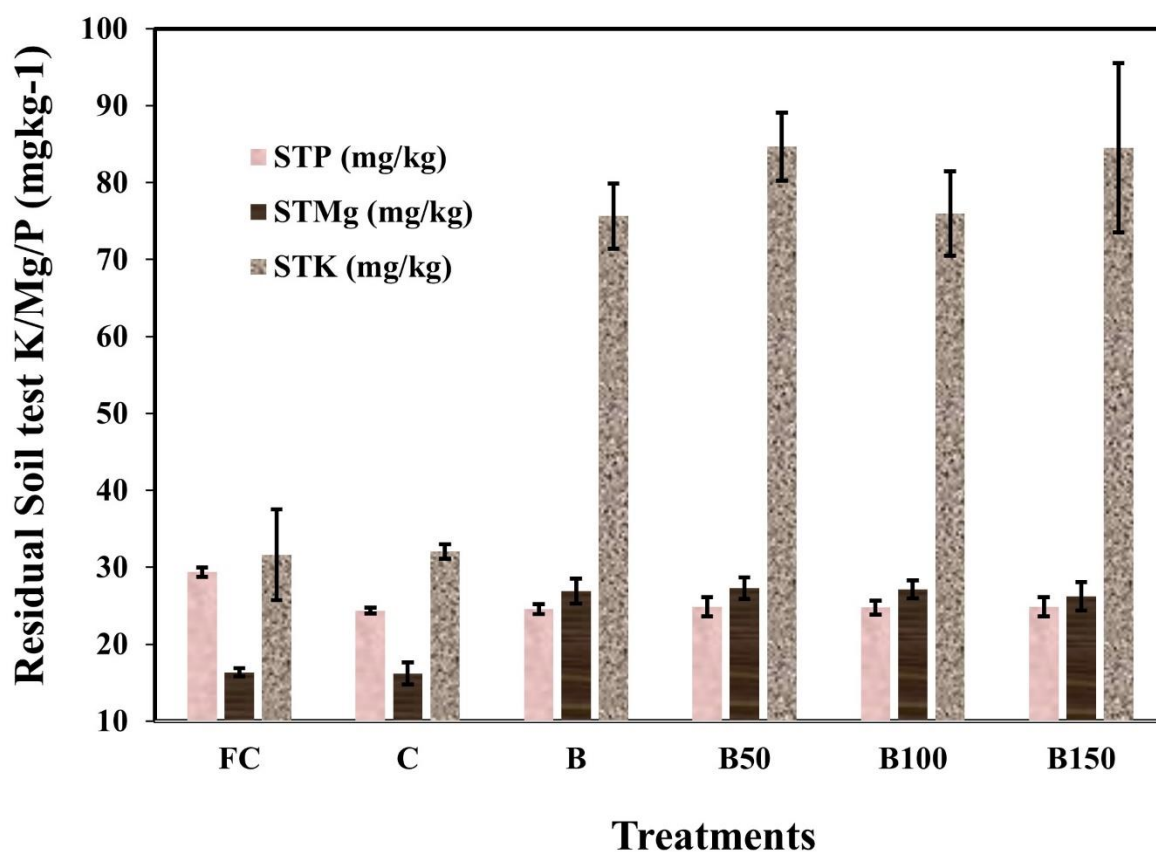


Figure 2.7 The influence of C, B, B50, B100, B150, and FC treatments on soil residual P (STP), K (STK) & Mg (STMg) test levels. (Errors bars shown as standard errors of the mean, n=4).

However, biochar treatments had comparable STP with the C treatment. A Fisher LSD test indicated that STP for the FC treatment differed significantly ($P\text{-value} = 1.78 \times 10^{-6}$, $R^2 = 0.8$) from both the control and all biochar treatments. Furthermore, the application of both modified Douglas fir biochar and P enriched modified Douglas fir biochar significantly increased both residual STK ($P\text{-value} = 4.54 \times 10^{-11}$, $R^2 = 0.9$) and STMg ($P\text{-value} = 1.29 \times 10^{-10}$, $R^2 = 0.9$) levels compared to the control and FC treatment (Fig.2.7). All biochar treatments had greater STK/Mg levels than the C and FC treatments.

While residual STK and STMg levels were greater for the B, B50, B100, and B150 treatments than for the FC and C treatments, residual STP levels for B, B50, B100, B150 and C treatment were lower than for the FC treatment. (Fig.2.7). The similarity in residual STP for the control and P enriched Douglas fir biochar treatments could signify increased crop removal of available P associated with P enriched Douglas fir biochar treatments as the applied rate at 30 kg P ha⁻¹ is considered low. However, additional P may remain, as adsorbed P for B50, B100, and B150 treatments may not be completely extracted as it may be too tightly bound to the biochar. This bound P may behave as a slow-release fertilizer in subsequent seasons, or the lower STP exhibited by P enriched Douglas fir biochar compared to FC may suggest the need for using a greater concentration of phosphate for biochar enrichment. Further studies are needed for clarification. In addition, the high residual STK and STMg associated with modified Douglas fir biochar and P enriched Douglas fir treatments further suggest that the modification of Douglas fir biochar with magnesium chloride and potassium hydroxide solutions may be responsible for the increased STK and STMg levels compared to the C and FC treatments.

2.5 Conclusions and recommendations

The current study investigated plant and soil availability P from nutrient enriched Douglas fir biochar at various P enrichment concentrations and compared to commercial fertilizer. While the control treatment resulted in the least growth, B150 and FC had the greatest growth response. P contents was greatest for the FC treatment due to its high-water soluble P content. However, insignificant differences were observed between P contents for the FC treatment and B50, B100, and B150 treatments indicating a similar ability of P enriched Douglas fir biochar to release available P for plant use. Recovery of K and Mg were directly correlated with available soil P, suggesting that P enriched modified Douglas fir biochar had the potential to supply soluble K and

Mg needed for plant growth. Generally, P enriched Douglas fir biochar showed potential as a slow-release fertilizer; however, more studies are necessary to investigate the effects of simultaneous application of K and Mg in other soil types with different fertilizer sources. We also recommend more research to establish optimal P loading rates for biochar enrichment.

2.6 Acknowledgments

Mississippi State University, Department of Chemistry. Fulbright Organization and US Department of State for Scholarship awarded to Beatrice Arwenyo

2.7 Conflict of interest

Authors declare no conflict of interest

2.8 References

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CHAPTER III

UPTAKE OF PHOSPHOROUS FROM MODIFIED P-ENRICHED DOUGLAS FIR BIOCHAR AND ITS EFFECTS ON CROP GROWTH AND P USE EFFICIENCY

(To be submitted to Journal of Geoscience and Environmental Protection)

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3.1 Abstract

The potential use of biochar as a sustainable soil amendment has recently gained global recognition. The use of biochar as a soil additive is attributed to its ability to improve soil chemical, physical and biological properties. Studies have shown that biochar amendments can enhance soil nutrient retention and availability, pH, water holding capacity, microbial activity and sequester carbon. In this study using corn (*Zea mays* L) as an experimental crop, the influence of P availability from modified P enriched Douglas fir biochar (PEB), triple super phosphate fertilizer (SPF), and modified Douglas fir biochar (MB) on plant growth and P Use Efficiency (PUE) were compared. The rate of P applied (0, 30, 60, 90 and 120 kg ha⁻¹) was calculated based on % P content of each soil additive. Except for MB treatments, P recovery, crop growth and P Use efficiency increased with application rates. The maximum above ground dry matter yields corresponding to PEB, SPF and MB treatments were estimated at 3488 kg ha⁻¹, 2449 kg ha⁻¹ and 639 kg ha⁻¹, while their respective agronomic P use efficiency (AGE) rates were 32 kg kg⁻¹, 17 kg kg⁻¹, 0.5 kg kg⁻¹. Also, recovery of K, Mg, Ca, Zn, Fe, Cu, B and Mn improved in both PEB (p value < 0.0003, r² > 0.9) and SPF (p value < 0.0058, r² > 0.9)

treatments. More studies at field scale are needed to demonstrate the practicability of using Modified P enriched Douglas fir biochar for soil amendments.

Keywords: Nutrient uptake, Crop biomass yield, P enriched biochar, P use efficiency, soil amendment, Fertilizer

Highlights

- Modification of biochar with magnesium sulphate and potassium hydroxide significantly improved biochar's liming ability
- Availability of soil P influenced uptakes of other essential nutrients
- P enriched modified Douglas fir biochar recorded greater P use efficiency than the reference super phosphate fertilizer treatment

3.2 Introduction

The world's population is constantly growing and so the demands for food, fiber, and biofuel¹⁻² or the growing needs of these essential requirements to be met for future generations, sustainable agricultural productivity is an inevitable requirement. Even with the use of improved crop varieties, machineries, pesticides and better nutrient management strategies to improve crop yields,³ lesser yields than expected have often been realized in many agricultural soils due to insufficient Phosphorus (P), a key nutrient for ideal crop yield.⁴ Consequently, P fertilizers and manures have increasingly been used to improve crop production. However, P losses from applied fertilizers and manures due to runoff, erosion of top soil and leaching makes it less (10%) efficient,⁵ expensive and subsequently, presents significant risks of environmental pollution such as eutrophication which affects both social and economic development.⁶⁻⁷ Therefore, the search for more environmentally sustainable crop production practices remains an indispensable goal.

Recently, research has demonstrated that, P use efficiency can be improved through the adoption of the 4Rs (Right of fertilization sources, Right rate, Right timing, and Right placement) management strategies.⁸ The 4Rs management system integrates practices which emphasize optimization of crop yield and agronomic efficiency while limiting undesirable environmental impacts and conserving P resources. However, making nutrient management decisions based on the 4Rs strategies relies on site-specific conditions such a soil type, climate, and cropping history. For example, Grant and Flaten⁸ reported that planting crops during cold weather such as early spring, limits plant access and uptake for available P and thus amplifies the risk of P deficiencies. Biochar, a byproduct of pyrolysis of biomass under reduced oxygen conditions, is known for its advantageous properties in soil including increased water and nutrient holding capacity, improved microbial activities and buffering ability.^{2,9} Lately, studies have proposed the use of biochar enriched with plant nutrients for sustainable soil fertility and improve nutrient use efficiency.¹⁰⁻¹¹ Research has also shown that activation of biochar with chemical reducing/oxidizing agents and metal salts can enhanced biochar sorption capacity for inorganic compounds including PO_4^{3-} .¹² Akgül et al.,¹³ reported that biochar modified with Mg^{2+} had greater sorption capacity for PO_4^{3-} than those activated with Fe^{3+} , Al^{3+} , and Mn^{2+} ions. Furthermore, unlike Fe^{3+} , Al^{3+} , and Mn^{2+} which are toxic to plants in large quantities,¹⁴⁻¹⁵ Mg^{2+} is an essential nutrient necessary for the maintenance of enzyme activities including polymerases, kinases and H^+ -ATPase.¹⁶ However, biochar's efficacy in agricultural soil is reported to be regulated by many attributes including pyrolysis temperature, feed stock material, soil type, climatic condition and biotic interactions.¹⁷

Modified P enriched Douglas fir biochar obtained by sequential treatment of Douglas fir biochar, a byproduct from syngas production, with magnesium sulphate, potassium hydroxide and potassium phosphate monobasic can be an ecofriendly, inexpensive soil additive compared to

conventional soil additives such as chemical fertilizer and manures. Besides other beneficial uses of biochar modified P enriched-Douglas fir biochar may offer additional benefits including greater nutrient contents than biochar derived from crop residues and less risks for soil contaminations when compared to biochar derived from manures, poultry litter, and biosolids. Whereas nutrient availability from biochar enriched with phosphate have been reported,^{2,10} there is still a need to explore P uptake from modified P enriched Douglas fir biochar and its ultimate influence on crop growth and P use efficiency. The purpose of this study therefore was to investigate P uptake, compare plant growth responses, and predict P use efficiency from soil amended with modified P enriched Douglas fir biochar, triple super phosphate fertilizer $\{(Ca(H_2PO_4)_2 [0\ 46\ 0])\}$ (SPF) and modified Douglas fir biochar (MB).

3.3 Materials and Methods

3.3.1 Preparation of Douglas fir biochar

Biochar was obtained from Douglas fir, a commercial byproduct from syngas production (Black Owl Biochar, supreme company). Raw Douglas fir chips (~ 3-inch lengths) were auger-fed into an updraft gasifier for a ~1-3 s residence time at a temperature of about 900–1000 °C. The dried biochar was ground, sieved through 50 mm mesh and stored in closed vessels. This biochar was designated as Douglas fir biochar (DFB).

3.3.1.1 Preparation of Modified Douglas fir biochar (MB)

Modified biochar was made by sequential modification of DFB with 0.52 M magnesium sulfate ($MgSO_4$) and 5 M potassium hydroxide (KOH) solutions. All chemicals were of analytical standard (Sigma Aldrich).

3.3.1.2 Treatment of DFB with Magnesium sulphate solution

Magnesium sulphate solution was prepared by dissolving 50.15 g of anhydrous magnesium sulphate powder in deionized water to make 800 mL of the solution in a clean glass beaker. To 200 g of previously ground and sieved (300-250 μm particle size) DFB, the 800 mL magnesium sulphate solution was slowly added and stirred to a uniform slurry. The slurry was placed on a magnetic stirrer (rpm = 500) for 6 h, at $\sim 24^\circ\text{C}$ to ensure uniform mixing and left to stand for 24 h to allow reaction to fully go to completion. After 24 h, the excess solution was filtered, and the residue dried in an oven at 80°C to a constant weight. The magnesium sulphate treated biochar was then stored in a tight container after cooling to room temperature ($\sim 24^\circ\text{C}$).

3.3.1.3 Treatment of magnesium sulphate modified biochar with potassium hydroxide solution

Potassium hydroxide solution was prepared by carefully weighing and dissolving 280.5 g of potassium hydroxide pellets in 1000 mL of deionized water in a volumetric flask. To the previously prepared magnesium sulphate modified biochar in a clean glass beaker, 800 mL of 5 M potassium hydroxide solution was slowly added while stirring until a uniform slurry was formed. The slurry was left on a magnetic stirrer (rpm = 500) for 6 h at $\sim 24^\circ\text{C}$ and then allowed to stand for 24 h at $\sim 24^\circ\text{C}$. The residue was dried in an oven at 80°C to constant weight after filtering the excess solution. The product formed (MB), which was kept in a tight container after cooling to $\sim 24^\circ\text{C}$ before use.

3.3.1.4 Preparation of P enriched modified Douglas fir biochar (PEB)

Potassium phosphate solution was prepared by dissolving 219.7 g of potassium phosphate monobasic (KH_2PO_4) in deionized water up to 1000 mL in a volumetric flask. P enriched modified biochar was prepared by mixing 100 g of MB with 400 mL solution of potassium phosphate

monobasic in a beaker while stirring to form a homogeneous slurry. The slurry was stirred on a magnetic stirrer (rpm =500) at ~24 °C for 6 h and left to stand for 24 h at ~24 °C before filtering excess solution and then oven drying to constant weight at 80 °C). The final product was cooled to ~24 °C and kept in tight containers until use.

3.3.2 Characterization of DFB, MB and PEB

3.3.2.1 Surface area, pore size and pore volume analysis

The surface area, pore volume and pore size of PEB, MB and DFB were determined based on N₂ adsorption technique using the Bruner, Emmett, and Teller (BET) method. Samples were degassed for 6 h at 180 °C prior to measurements. About 0.1 gram of each biochar sample was analyzed at 77.3 K with a MicroActive for TriStar II Plus Version 2.03.

3.3.2.2 Determination of surface morphology and elemental compositions

Surface morphology and elemental compositions of the PEB, MB and DFB were examined by SEM and SEM-EDS techniques. The measurements were done at 5 kV using a JEOL JSM-6500F FE instrument. Structural chemical compositions were investigated by X-ray diffraction (XRD) using a SmartLab X-ray diffractometer by scanning 2θ from 0° to 90° at 1° min⁻¹ using the SmartLab X-ray diffraction system with monochromatized Cu K α radiation ($\lambda = 0.6465944$ Å).

3.3.2.3 Determining pH, liming potential, ash content and total metal concentrations of DFB, PEB and MB

Biochar pH and liming capacity were determined following procedures described by Singh et al.¹⁸ To 5 g of air-dried samples of DFB, PEB and MB measured into a 100 mL centrifuge tubes, 50 mL of deionized water was added, and the mixture shaken on a mechanical shaker for 1h at room temperature. The pH of the suspensions was recorded using an HI3221 pH meter after 30 minutes of standing.

The liming potential was obtained by weighing 0.5 g dry samples of PEB, MB, DFB and CaCO₃ in a polypropylene tube. To the samples, 10.0 mL of 1M HCL was added and shaken for 2h at room temperature. After shaking and standing overnight, the supernatants were filtered with

Whatman number 1 filter papers. The filtrates were titrated with a 0.5 M NaOH solution using phenolphthalein as an indicator. Standard CaCO₃ (previously dried at 105°C) was used as a reference sample, and 1 M HCl was used as blank. The liming capacity was obtained from:

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

Where M=Standardized molarity of NaOH (mol L⁻¹),

b = Volume of NaOH consumed by blank (mL)

a = Volume of NaOH consumed sample (mL),

W = mass of sample (g),

10⁻³ converts volume from mL to L

100.09 (g mol⁻¹) = molar mass of CaCO₃ and

2 = Number of H⁺ consumed per mole of CaCO₃.

To determine a sample's ash content, 1.0 g of biochar sample, dried overnight in an oven at 105°C, was ashed in a muffle-furnace at 650 °C for 8 h. After cooling, the remaining ash was weighed, and ash content calculated from: $\% \text{ ash} = \frac{\text{Remaining mass after cooling (g)} \times 100}{\text{Original weight (g)}}$

The ash was then digested by heating with 5.0 mL nitric acid (70% Sigma Aldrich) and 2.0 mL of hydrochloric acid (37% Sigma Aldrich) on a hot plate at 150° C. The digested samples were then diluted with deionized water, filtered with Whatman number 41 filter paper, and brought to 100mL. The samples were then analyzed for Mg, Ca, K and P using an Elan DRC II ICP-MS spectrometer.

3.3.3 Greenhouse experiment

3.3.3.1 Soil sample collection and preparation

A Stough fine sandy loam (coarse-loamy, siliceous, semiactive, thermic Fragiatic Paleudults) was used for this study. The soil was collected from a depth of 0 to 15 cm and was air-dried, thoroughly mixed, and sieved to remove stones and plants debris before putting into experimental pots. Prior to potting, the soil was analyzed for selected chemical properties (Table B.1) at the Mississippi State University plant and soil testing laboratory.¹⁹ The sandy loam soil had very low organic matter. Low organic matter levels have been previously reported in sand soils,²⁰ mainly due to soil texture, drainage, climate and soil management.

3.3.3.2 Experimental pots set up and management

The experiment was conducted in a greenhouse located at the Mississippi State University campus (33° 27' 22" N / 88° 47' 44" W) in Starkville. The experiment was conducted between September and November 2019 using corn (*Zea mays* L.) variety DeKalb 67-44 as the experimental crop. Three treatments; concentrated super phosphate fertilizer (SPF) as a standard, magnesium sulphate plus potassium hydroxide modified biochar (MB) and P enriched modified biochar (PEB) were arranged in a randomized complete block design with four replications each at five different application rates of 0, 30, 60, 90 and 120 kg P ha⁻¹. For each soil additive, the quantity corresponding to each application rate was calculated based on its % P concentration (19.8, 9.6 and 4.2% for SPF, PEB and MB respectively). Plastic pots measuring approximately 12 cm by 18 cm were used. Each pot was perforated at the bottom to allow for drainage and aeration and treatments were thoroughly mixed with 4.5 kg of air-dried soil/pot. Prior to mixing, soil in each pot was limed with 2.3 g of calcium carbonate. Five seed of DeKalb corn Hybrid 67-44 were planted per pot and 6 days after planting, plants were thinned to two per pot. Nitrogen fertilizer

was applied in the form of ammonium nitrate (34-0-0) at a rate of 200 kg N ha⁻¹ in three separate applications (50 kg N ha⁻¹, 50 kg N ha⁻¹ and 100 kg N ha⁻¹ after 8, 14 and 21 days from planting. Watering and weeding were done as required. At harvest, whole plants were cut at the soil surface. After harvest, soil from each pot was air-dried, crushed to pass a 10-mesh sieve, and tested for pH (2:1di H₂O:soil) using a Fisher Scientific Model 25 Accumet pH meter (Denver, CO), and extractable nutrients (P, K⁺, Mg²⁺ and Ca²⁺) were determined using the Mississippi State Extension Service Soil Test method ¹⁹⁻²¹ and Avio 200 ICP-OES (Perkin Elmer, Waltham, MA).

3.3.3.3 Leave chlorophyll concentrations, plant height and biomass dry weight yield

A chlorophyll meter (SPAD-502 Plus.) was used to take readings on two separate dates. The first and second readings were taken 20 and 28 d after planting. At each sampling date, two uppermost fully expanded leaves were selected in each pot. Three SPAD readings were taken around the midpoint of each leaf blade approximately 30 mm apart, on one side of the midrib. Six SPAD readings were averaged to represent the mean SPAD value of each pot. Plants were harvested 35 d after planting by cutting with a scalpel just above the soil line. Prior to harvest, plant heights were measured. Harvested plant material was oven-dried at 65 °C until constant weight was obtained, and dry matter yield was recorded using an analytical balance.

3.3.3.4 Plant nutrients uptake

The oven-dried plants were ground to pass through a 40-mesh sieve. Plant tissue was examined following a modified dry ashing procedure²² with nutrient elements (P, K, Mg, Ca, Fe, Zn, B, Mn and Cu) measured with an Avio 200 ICP-OES (Perkin Elmer, Waltham, MA). Plant nutrient uptake was calculated from plant tissue nutrient concentrations and dry matter weight.

$$\text{Plant nutrient uptake} = \frac{\% \text{ nutrient (P/Mg/K/Ca)} \times \text{Dry weight (g pot}^{-1}\text{)}}{100}$$

3.3.3.5 P use efficiency

To ascertain the effect of fertilizer application on crop yield, the Agronomic P use efficiency (AGE) in (kg kg^{-1}) was obtained from the equation: $\text{AGE} = \frac{(Y-Y_0)}{F}$ where Y = yield of harvested portion of crop with nutrient applied; Y_0 = yield of harvested portion of crop with no nutrient applied; F = amount of nutrient applied.

3.3.4 Statistical analyses

Regression analyses, correlations coefficients and ANOVA were used to assess the associations between variables at 95% confidence level. The data obtained were processed using Microsoft excel 365 and origin pro 2019b software. Each value used represented the average of the four replicates.

3.4 Results and discussions

3.4.1 Surface area, pore size and pore volume

Surface area analysis indicated that modification of biochar resulted in reduction of both surface area and pore volume. The surface area decreased after the modification of Douglas fir biochar (DFB) to MB from $514.567 \text{ m}^2 \text{ g}^{-1}$ to $14.640 \text{ m}^2 \text{ g}^{-1}$ (~97 %) while pore volume reduced from $0.192 \text{ cm}^3 \text{ g}^{-1}$ to $0.005 \text{ cm}^3 \text{ g}^{-1}$ (> 97 %). P enrichment of the modified Douglas fir biochar reduced the surface area even further (Table B.2). The blockage of pores by modification agents and their aggregate can explain the reduction in surface area following modification of DFB. The incomplete blockage obstructs the passage of N_2 to micropores. According to Kose et al.,²³ the micropores are the primary determinant of the surface area, and the amount of volume of nitrogen adsorbed by biochar corresponds to its pore volume and surface area. Similar observations were reported previously.²⁴

3.4.2 Surface morphology and elemental compositions

The surface morphology of DFB, MB and PEB were determined by SEM (Fig. B.1). DFB had a smoother surface with honeycomb structures ascribed to fibrous structure from plant cells. DFB had the greatest BET surface area recorded. For MB and PEB, the surfaces showed wide irregular shaped structures with crystal particles bound to their surfaces due to modification and enrichment. These trapped crystal particles can block pores and partly explain the reduction of pore volume and surface area noted in MB and PEB.

The surface elemental compositions of DFB, MB and PEB, were analyzed using SEM/EDX. The corresponding peaks and the atomic percentage of each element are shown in Fig. B.2. Generally, biomass derived biochar samples are composed of C, O, Mg, K and Si. Modification of DFB increased the weight percentages of O, Mg, and K in MB from (9.50-33.95%), (0.18-2.24%) and (0.43-9-23.52%) respectively. Although P enrichment of MB did not show substantial effect on K% weight (23.52-23.38), it did significantly reduce the weight percent of Mg (2.24-0.9) in PEB.

The structural composition of samples was studied using X- ray diffraction (Fig.3.1). The XRD patterns for DBF showed two broad peaks similar to that of graphene between $2\theta = 20^\circ$ to 30° and 40° to 50° .²⁵⁻²⁶ These peaks are ascribed to graphite diffraction. Other sharp peaks showed mixed inorganic components mostly calcite at $2\theta = 12.24^\circ$ (1 0 4)²⁷, brucite at $2\theta = 7.96^\circ$ (0 0 1)²⁸ and dolomite at 12.8° (1 0 4) (cod no. 00-900-1245). In addition, new peaks showed up in MB signifying the existence of MgO at $2\theta = 38^\circ$ (1 1 1), 42° (200), 67° (3 1 1)²⁹ and Mg(OH)₂ at $2\theta = 7.80^\circ$ (0 0 1), 15.78° (1 0 -1), 20.85° (1 0 -2), 45.01° (3 0 2).³⁰ Furthermore, additional peaks in PEB matched MgHPO₄ at $2\theta = 4.16^\circ$ (2 0 0)³¹ and Mg₃(PO₄)₂ at $2\theta = 9.68^\circ$ (1 2 0).³²

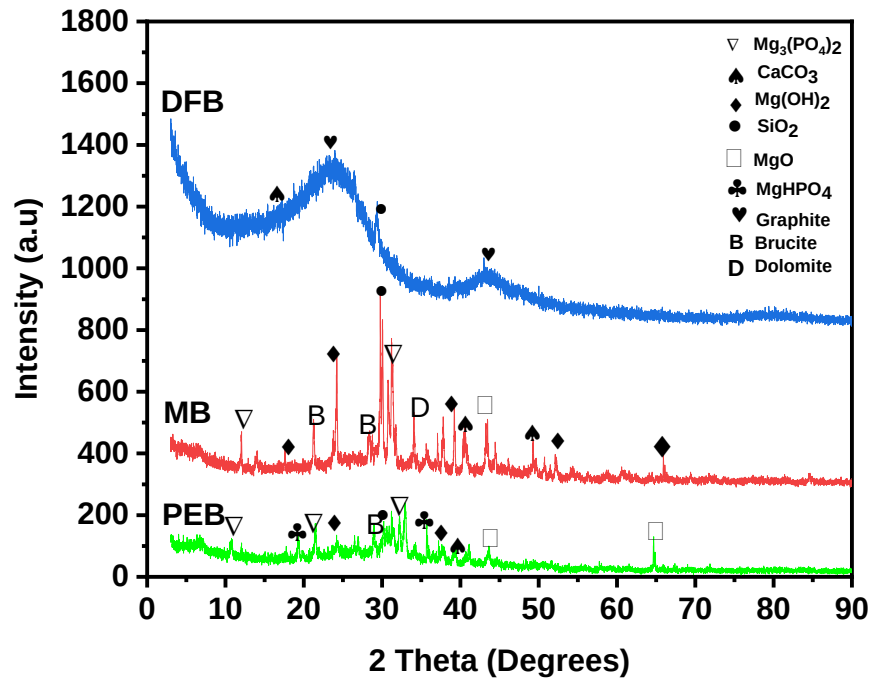


Figure 3.1 XRD pattern for Douglas fir biochar (DFB), modified Douglas fir biochar (MB) and modified P-enriched biochar (PEB)

3.4.3 The pH, liming capacity, ash content and total metal concentrations

Modified Douglas fir biochar (MB) had the highest pH (11.8) and liming capacity (53.3 % CCE). DFB and PEB had pH values of 11.3 and 10.9, respectively. The corresponding liming capacities were 39.7 and 36.9 % CCE, respectively (Fig.3.2). Liming potential and pH were positively correlated ($r = 0.9$) indicating their interdependency.

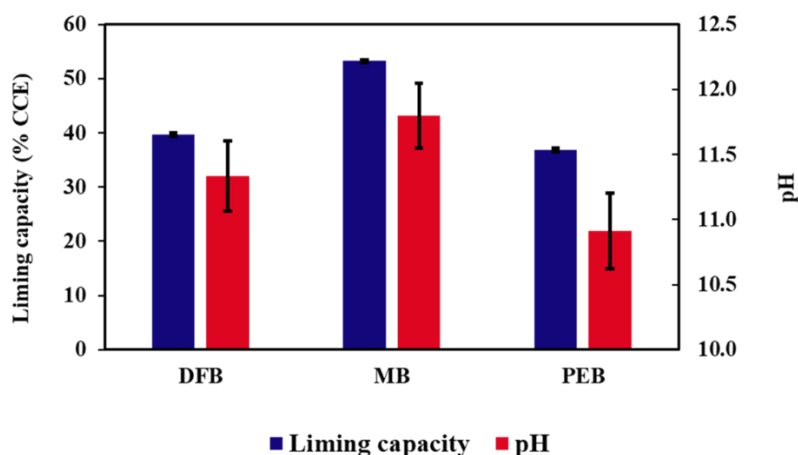


Figure 3.2 pH and liming capacity of Douglas fir biochar (DFB), Modified Douglas fir biochar (MB) and Modified P enriched biochar (PEB), CCE= Calcium carbonate equivalence. (Values shown are mean of three replicates, errors bars shown as standard deviation)

Activation of DFB with MgSO_4 and KOH significantly increased both ash content and total metal concentrations (Table B.3). The increased total metal concentrations following modification correlates well with the high ash content associated with MB and PEB. The more alkaline pH and liming ability associated with MB can be explained by the greater concentrations of magnesium and potassium associated with MB as revealed by EDX and total metal concentrations. Increased pH with liming ability and ash content was previously reported by Rehrah et al.³³

3.4.4 Nutrient content

Macronutrient content was affected by application rates across all treatments (Fig.3.3). Significant variations in nutrient recovery were observed in both PEB ($r^2 \geq 0.8$, $p\text{-value} \leq 0.03$) and SPF ($r^2 \geq 0.9$, $p\text{-value} \leq 0.01$) treatments. However, no significant differences were recorded in MB treatment ($r^2 \leq 0.6$, $p\text{-value} \geq 0.1$). Although the PEB treatment had greater P, K and Ca recoveries than the SPF treatment, Mg recovery was comparable for both treatments. High positive

correlations ($r > 0.9$) were observed for all nutrient contents for the PEB and SPF treatments. For the MB treatment however, no substantial variations were observed for all nutrients content with increasing application rate, but both Mg and Ca contents were positively correlated with P content ($r = 0.6$ and 0.9 , respectively). However, K content correlated negatively with P ($r = -0.3$), Mg ($r = -0.8$) and Ca ($r = -0.3$) contents.

In this study, phosphorus was the limiting nutrient as observed by the very low initial P soil test (Table B.1). Soil, P is known for its roles in plant growth and development including storage and production of energy, reproduction, and enhancing shoot and root growth.^{34–36} Reduced root growth and development, limits nutrient uptake and water use efficiency and subsequently, plant growth. In this study, the lower nutrient content observed with the MB treatment is likely due to its inability to release available phosphate which subsequently affected the uptake of Ca, Mg and K despite their availability in soil. P, K, Ca, and Mg plant contents increased with increasing PEB and SPF treatments. However, a greater increase was observed for the PEB treatment due to its ability to replenish P, K, Mg, Ca for plant growth. The increased nutrient content observed for the PEB, and SPF treatments could indicate that P has a role in facilitating the uptake of other nutrients (Mg, K and Ca). Increased Mg, K and Ca contents following P fertilization has been previously reported.^{37–38}

For the MB treatment, uptake of P, Mg, K and Ca plant contents did not differ much with application rates. Both Mg and Ca contents were positively correlated with P content ($r = 0.6$ and 0.9 respectively). However, K content correlated negatively with both Mg and Ca contents ($r = -0.8$, -0.3 , respectively). Furthermore, the residual soil P levels compared to Control (0 kg p ha^{-1}) did not vary significantly with those of the MB treatment regardless of the application rates. In addition, residual soil test results showed increasing levels of extractable K, Mg and Ca associated

with the MB treatment. Therefore, the low level of available P from the MB treatment could have affected root development and hence reduced contents of K, Mg and Ca. Besides, the observed reduction in K content with increasing Mg and Ca contents could be due to antagonistic effects in which the presence of Mg and Ca in high concentration reduced K content. Several studies have reported antagonistic plant removal effects between magnesium, calcium and potassium^{38–39}

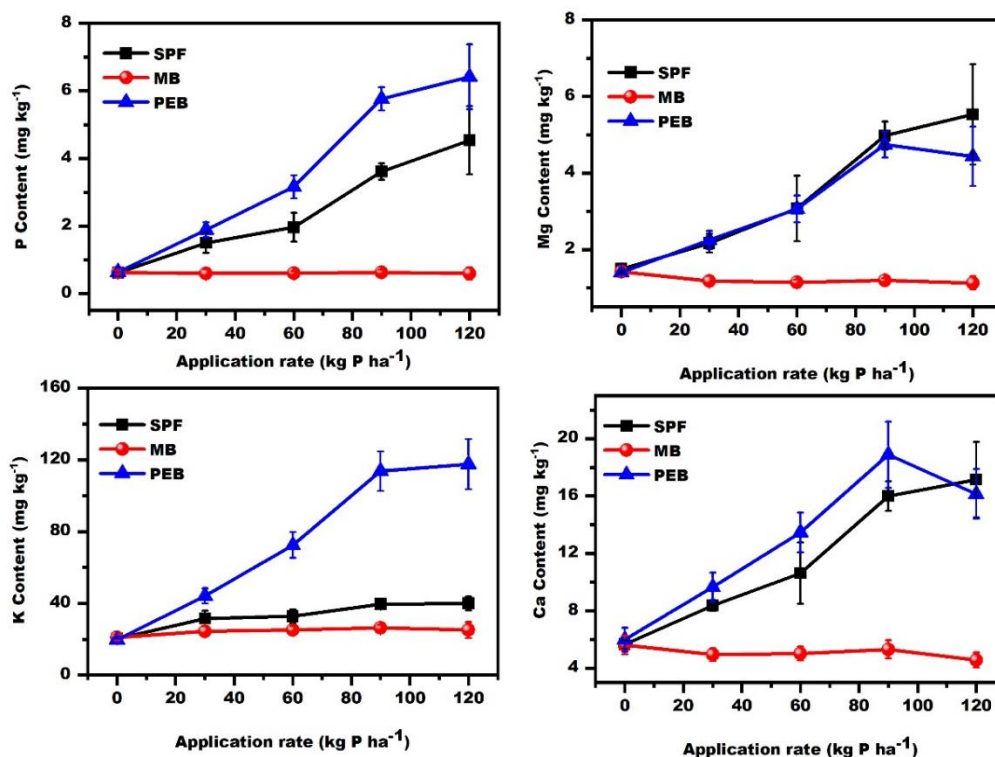


Figure 3.3 Variations of P, Mg, K and Ca contents with application rates of triple super phosphate fertilizer (SPF), modified P enriched biochar (PEB) and modified biochar (MB), (plotted values are mean of four replicates with standard deviation as error bars)

Results from micronutrients analysis indicated plant nutrient contents increased with application rates for both SPF and PEB (Fig 3.4). Regression analysis showed significant variations in micronutrients contents for both SPF (p-value < 0.0026, $r^2 > 0.94$) and PEB (p-value

< 0.003, $r^2 > 0.96$) treatments with application rates except for Cu content which varied insignificantly with application rate for the PEB treatment (p-value < 0.057, $r^2 > 0.75$). Variations in micronutrient contents for the MB treatments (Fig.3.4) however were insignificant (p-value > 0.08). Although B (p value = 0.027, $r^2 = 0.79$), Zn (p-value = 0.93, $r^2 = 0.003$) and Cu (p-value = 0.78, $r^2 = 0.03$) contents did not show a clear trend, Fe (p-value = 0.08, $r^2 = 0.69$) and Mn (p-value = 0.18, $r^2 = 0.5$) contents decreased with increasing application rates. Similarly, positive correlations ($r > 0.86$) were observed between micronutrient contents and application rates for both SPF and PEB treatments. In addition, correlations between P content and micronutrient recoveries were positive for both SPF and PEB treatments ($r > 0.9$). For the MB treatment, except for K ($r = 0.8$), Zn ($r = 0.05$) and Cu ($r = 0.17$) which had positive correlations with application rates, P ($r = 0.49$), Mg ($r = 0.72$), B ($r = 0.12$) and Mn ($r = 0.7$) were negatively correlated.

In addition to macronutrients, plant requires micronutrient for optimum growth and yield.⁴⁰ The soil serves as the major source for micronutrients⁴¹. Availability of micronutrients in soil are greatly influenced by soil pH. According to Hart et al.⁴² except for Mo, availability of micronutrients decreases with increasing soil pH and that deficiencies rarely occur in soil with pH values less than 6.5. In this study, the effect of pH was unlikely since post-harvest soil test results indicated pH values ranged from (5.9-6.2) for the SPF treatment and (6.0 to 6.6) for both MB and PEB treatments. The main determinant of micronutrient contents in this case, therefore, was increased growth resulting from fertilizer formulation (PEB, MB and SPF). The rise in micronutrient contents for both SPF and PEB treatments may indicate the influence of soil available P on micronutrient recovery. Furthermore, the positive correlations between P content and micronutrient contents for the SPF and PEB treatments can partly be explained due to enhanced P availability and plant growth. The unclear trend or decreased plant nutrient contents

for the MB treatment was likely due to deficiency of available P and less dry matter yield. Increased plant micronutrient contents (Zn, Mn, Cu and Fe) with P fertilization has been previously reported by Fageria et al.³⁷

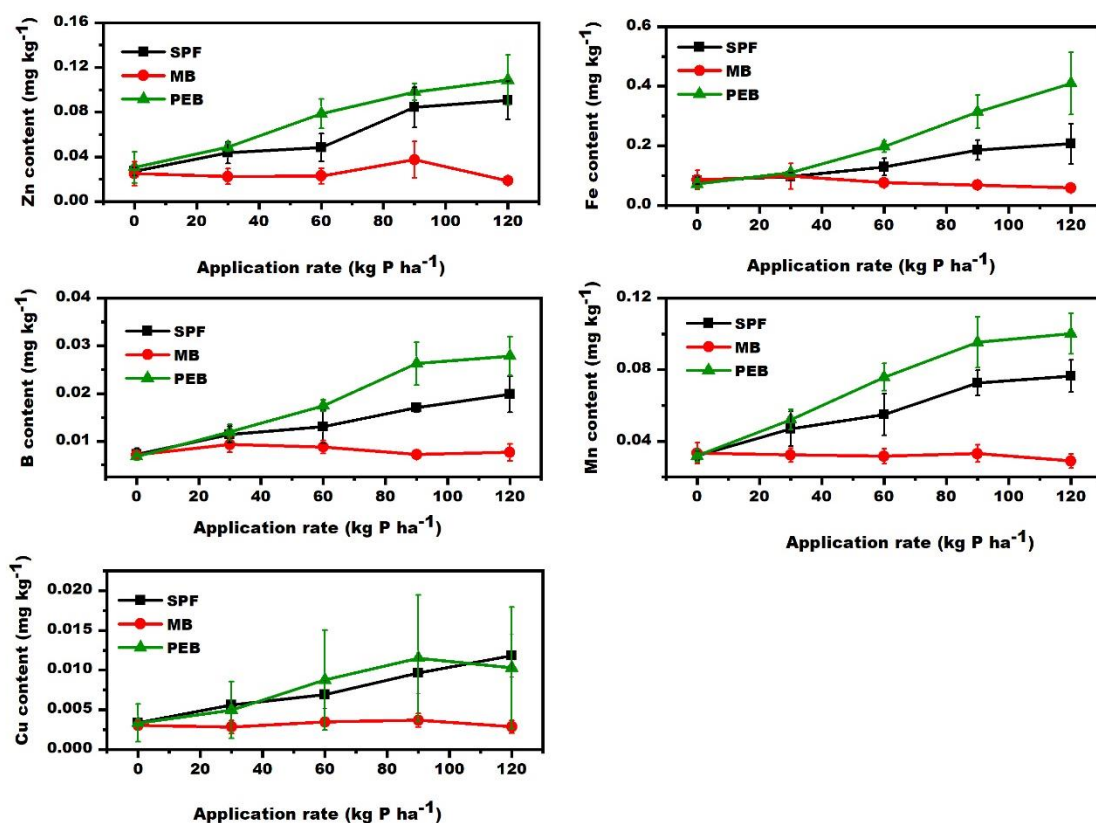


Figure 3.4 Variations of application rates with micronutrient contents (Fe, Cu, B, Mn and Zn) in super phosphate fertilizer, (SPF); modified P enriched biochar, (PEB); and modified biochar, (MB) treatments. Values shown are average of four replications, error bars shown as standard deviation)

3.4.5 Leaf chlorophyll concentration and dry weight yield

Treatments with P fertilizer exhibited significantly greater levels of leaf chlorophyll as indicated by SPAD readings. SPAD readings was greatest for the SPF treatment irrespective of application rates (Fig.3.5). The increase in chlorophyll levels with application rates was significant

for both SPF ($r^2 = 0.86$, P value < 0.0000) and PEB ($r^2 = 0.64$, p-value = 0.0025) treatments. In contrast, MB treatment showed decreasing chlorophyll levels with rising application rates ($r^2 = 0.17$, p-value = 0.57). Regardless of treatment, chlorophyll levels correlated positively with tissue P concentrations ($r > 0.8$). Within treatments, SPAD readings for the PEB and SPF had positive correlations ($r > 0.9$). MB recorded weak negative correlations with both PEB ($r = 0.2$) and SPF ($r = 0.3$) treatments.

Since P fertilization influenced plant removal of other nutrients, the effects of plant P removal on chlorophyll seems to be indirect and complex. In this study, we observed increasing contents of other nutrients with P fertilization. Jawale et al.⁴³ suggested that uptake of other essential nutrients such as Mg, N and Fe by maize plants influences chlorophyll formation because they regulate photosynthesis, respiration, cell division and protein formation. Therefore, increased chlorophyll levels linked to SPF and PEB treatments can be ascribed to their ability to supply available P which in turn aided the recovery of other essential nutrients responsible for chlorophyll formation in maize plants (Figs. 3.3 and 3.4, respectively). This result is consistent with those of Rietra et al.⁴⁴ who observed increased chlorophyll concentration in rice with increasing P application rates.

Application of both PEB and SPF resulted in a greater total aboveground biomass yield of maize compared to the MB treatments (Fig. B.3 and B.4, respectively). Simple regression analysis indicated response in dry weight yield to application rates was significant for both PEB (p-value $= 1.7 \times 10^{-9}$, $r^2 = 0.90$) and SPF (p-value $= 1.2 \times 10^{-6}$, $r^2 = 0.88$). However, no response to increasing MB (p-value = 0.41, $r^2 = 0.22$) was found. Dry weight yield responses to nutrient applications were quadratic for both SPF and PEB treatments (Fig.3.5). Maximum dry weight yield corresponded to

an application rate of 90 kg P ha⁻¹ for PEB (3488 kg ha⁻¹) and MB (639 kg ha⁻¹) and 120 P kg ha⁻¹ for SPF (2449 kg ha⁻¹) treatments. Similar observations were recorded for plants heights (Fig.3.5).

Plant growth response to amendment rates depends on a source's nutrient content and availability for plant uptake. Other factors that can influence plant growth include microbial activity, water availability and nutrient release from the biochar or mineralization.⁴⁵ Multiple variables have been cited for the effects of biochar on increasing crop yield. Some of them include liming effects, increased water-holding capacity, structural soil improvement, increased surface area for nutrient adsorption, and improved microbial activities⁴⁶⁻⁴⁸. For this study, biomass dry weight yield at 0 kg P ha⁻¹ was comparable for all treatments (602.6 kg ha⁻¹, 592.8 kg ha⁻¹ and 605 kg ha⁻¹ for SPF, MB and PEB, respectively). Yield response was mainly influenced by the source's nutrient content and availability. Furthermore, since adequate nitrogen was added to all treatments, any variation in growth should have been minimal unless adsorption or immobilization of the added N from fertilizer was affected.

Therefore, differences in available P, Mg, and K could be responsible for the variations in biomass yield corresponding to PEB, SPF and MB treatments. In this experiment, except for the SPF treatment, both PEB and MB treatments had additional magnesium and potassium due to the biochar's modification with magnesium sulphate and potassium hydroxide. Although all treatments had phosphate, the % P in MB (4.16) treatment was much less compared to PEB (9.57) and SPF (19.78). Therefore, the lower biomass yield observed for the SPF treatment than the PEB treatment despite its greater % P concentration may have been partially due to an inadequacy of Mg and K. For the PEB treatment, biochar's increased K, Mg and P concentrations as a result of chemical modification and enrichment could be responsible for the enhanced plant growth. In addition, biochar's soil conditioning properties including liming ability and improved microbial

activities may have allowed the PEB treatment an additional advantage. For MB however, the low % P concentration and recovery may have affected uptake of both K and Mg regardless of their availability and hence the reduced growth response. Improved plant growth with nutrient uptake was also reported by Sial et al.⁴⁵

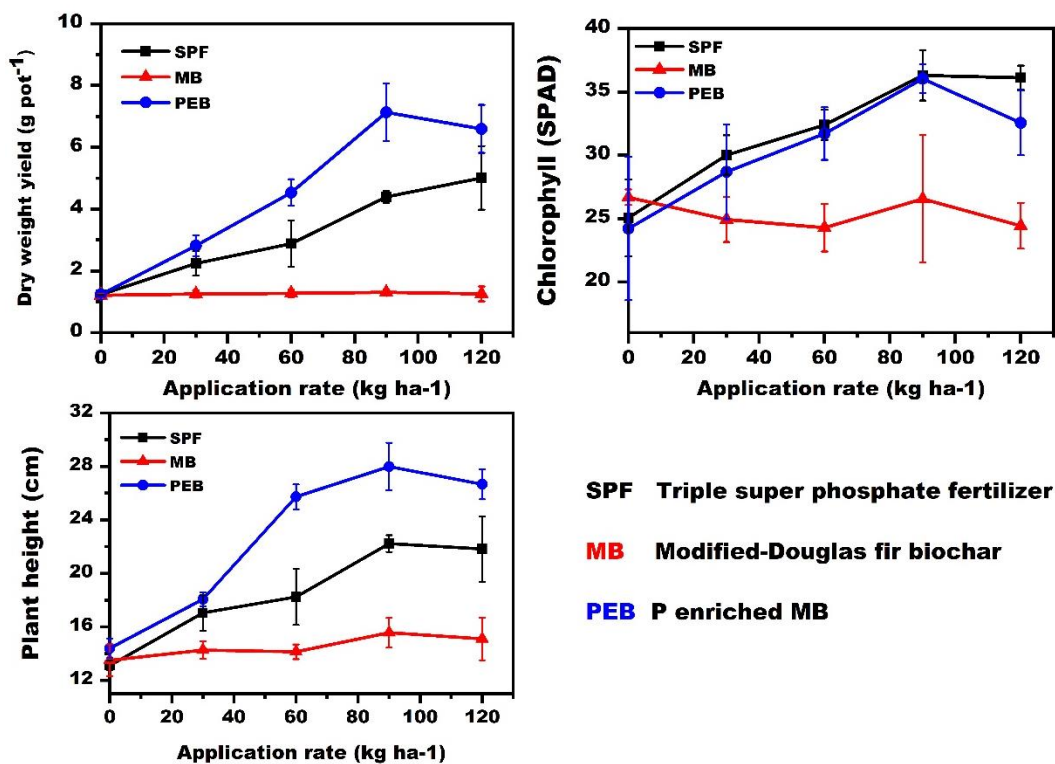


Figure 3.5 Variations of dry weight yield, plant heights and plant leaf's SPAD readings with application rate. (Values shown are average of four replicates, error bars indicated as standard error of the Mean)

3.4.6 P use efficiency

Phosphorus use efficiency (PUE) can be defined as a yield increase per kg P fertilizer added.⁴⁹ It is related to P sources, environmental factors, soil chemical properties, and crop management.⁵⁰ Though there are many ways of calculating P use efficiency, in this study, the

agronomic P use efficiency was used as the objective of the study was to compare P use efficiency associated with SPF, MB and PEB treatments at different application rates. The agronomic P use efficiency (AGE) is used as a short-term indicator of the impact of applied nutrients on productivity. It also provides information on how much productivity improvement was gained by use of nutrient inputs as well as an aid to identify the optimal level of nutrients required for improved yield.⁵¹ In this way, negative economic and environmental impacts associated with excessive fertilizer applications can be avoided.

Regardless of treatment, PUE showed a quadratic response to both PEB and SPF application rates (Fig. 3.6). The largest P use efficiencies corresponded to an application rate of 90 kg P ha⁻¹ (32 kg kg⁻¹, 17 kg kg⁻¹ and 0.5 kg kg⁻¹ for PEB, SPF and MB respectively). Since the greatest AGE for MB treatment was very low, its maximum AGE was not estimated. The approximate maximum agronomic P use efficiencies for PEB and SPF treatments were 32 kg kg⁻¹ and 18 kg kg⁻¹ respectively, corresponding to application rates of 76 Kg P ha⁻¹ and 81 kg P ha⁻¹. Although there are many factors influencing P use efficiency: including soil test P levels, soil pH, water status, soil mineralogy, crop variety, timing and rate of application, fertilizer placement and fertilizer formulation,⁵⁰ for this study, PUE was primarily affected by fertilizer formulation. The effect of pH was minimized by liming prior to planting. Other factors were controlled and hence unlikely to have influenced PUE. Overall, these results indicated the ability of these P sources to supply this nutrient under very low soil test P conditions

The larger P use efficiency linked to the PEB treatment can be explained by the ability of PEB biochar to provide other essential nutrients (Mg and K) in addition to P. Also observed in this study was increased uptake of micronutrients associated with PEB (p -value < 0.003, r^2 > 0.94 except for Cu (p -value = 0.057, r^2 = 0.75) and SPF (p -value < 0.0058, r^2 > 0.94) treatments. Rietra

et al.⁴⁴ stated that fertilizer nutrient use efficiency can be improved if fertilizer were formulated such that antagonistic effects among nutrients were minimized. In this study therefore, residual soil test results indicated synergetic interactions between P and the rest of the nutrients for both PEB and SPF treatment. These observations confirm that the application of PEB or SPF facilitated uptake of K, Mg, Ca, Fe, Zn, B, Mn and Cu by plants. This was further indicated by the positive correlations between P content and K, Mg, Ca, Fe, Zn, B, Mn, and Cu contents for both SPF and PEB treatments ($r > 0.9$).

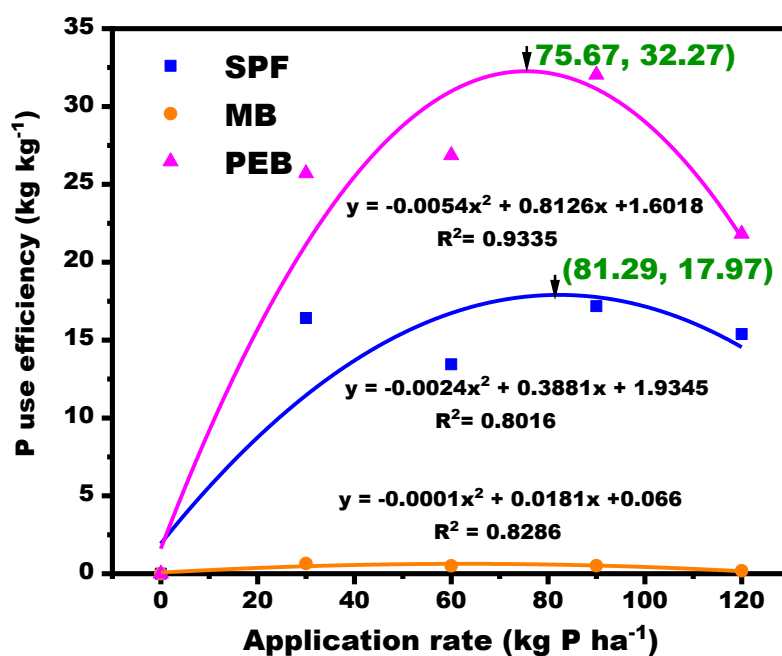


Figure 3.6 The influence of application rates of P-enriched biochar (PEB), superphosphate fertilizer (SPF) and modified biochar (MB) on agronomic P use efficiency (AGE)

3.4.7 Soil residual P, K, Mg and Ca

Following harvest, soil residual nutrients were tested. Across all treatments (Fig.3.7), regression results showed an increase in soil residual P (p value ≤ 0.04). In addition, residual soil test K and Mg concentrations were significantly increased by MB and PEB (p value < 0.003). In contrast, there was a reduction in soil residual potassium and magnesium concentrations by SPF (p value = 0.04 and 0.6 respectively). Irrespective of treatment, there was an insignificant rise in soil residual Ca concentrations (p value > 0.07).

For the MB treatment, P uptake did not respond to rate of MB, only a slight increase in soil residual P resulted for MB indicating MB could be containing some fixed P which was unavailable for plant uptake. Whereas for the PEB and SPF Treatments, increasing residual P in response to application rates may indicate their ability to release available P for plant uptake. Results indicated the AGE increased in the order PEB > SPF > MB with corresponding optimal values of 32 kg kg⁻¹, 18 kg kg⁻¹ and 0.5 kg kg⁻¹.

In this study there was no substantial variation in soil test Ca response across all treatments. Ca deficiency is not commonly encountered in soil environments which are limed as is the case for this study.³⁵ Most soils contain adequate Ca needed for plant growth. Moreover, the amount of Ca required for optimal growth is not as great as for N, P and K.

For the SPF treatment, the decline in soil test K and Mg levels indicated that, as more P was added to the soil, plant demand for K and Mg increased as well. Since there was no external replenishment for either K or Mg in this study for the SPF treatment, the soil was the only source for Mg and K. For MB and PEB treatments however, EDX results previously showed increased K and Mg concentrations following chemical modification of biochar. Therefore, as application rates

increased, more K and Mg were added to soil resulting in their accumulation. Therefore, these results indicate that application of P facilitated removal of other nutrients as previously noted.

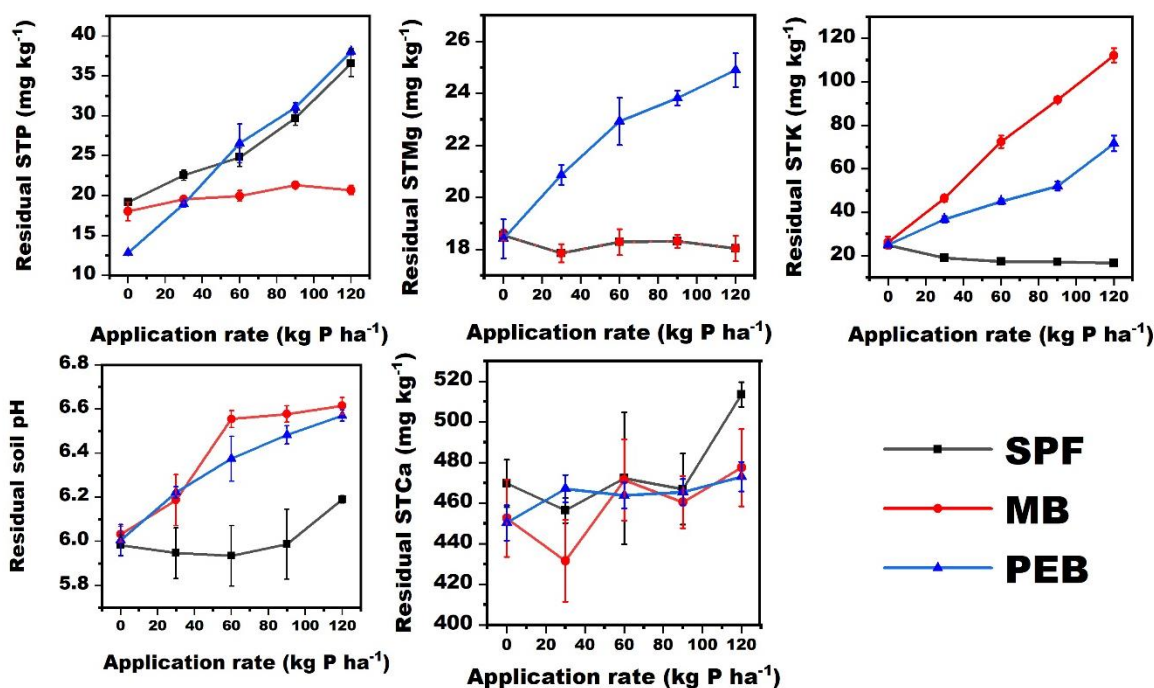


Figure 3.7 Variations of application rates with residual soil test pH, and macronutrients in modified P-enriched Douglas fir biochar, (PEB); modified Douglas fir biochar, (MB) and super phosphate fertilizer (SPF) treatments (Values shown are mean of four replicates, error bars shown as SEM)

3.5 Conclusions and recommendations

In this study, P recovery from PEB and MB, its impact on plant growth and P use efficiency was investigated in comparison with standard triple superphosphate fertilizer (SPF). Results indicated P removal significantly increased with application rates of both SPF and PEB, demonstrating their ability to provide plant available P. Maximum crop yields for the different

treatments corresponded to applications rates of 90 kg P ha⁻¹ for PEB and MB, and 120 kg P ha⁻¹ for SPF. Their optimal agronomic P use efficiencies increased in the order PEB> SPF >MB. These results showed that, greater P recovery and hence yields associated with SPF and PEB treatments in comparison to MB were due to their ability to supply available P, which in turn facilitated the uptake of other essential nutrients (K, Mg, Ca, and micronutrients). Therefore, these results provide evidence for the potential application of PEB as a multiple nutrient fertilizer. However, these results were under controlled growth conditions and 35 d of growth. Further research under field conditions is needed to validate P availability from PEB and plant growth responses, and P use efficiency to establish its practicability.

3.6 Acknowledgements

Mississippi State University, Department of Chemistry. Fulbright Organization and US Department of State for the scholarship awarded to Beatrice Arwenyo

3.7 Conflict of interest

Authors declare no conflict of interest.

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CHAPTER IV

LEAD IMMOBILIZATION IN SIMULATED POLLUTED SOIL BY DOUGLAS FIR
BIOCHAR-SUPPORTED PHOSPHATE

(Published in *Chemosphere*. **292**, (2022) **133355**.)

<https://doi.org/10.1016/j.chemosphere.2021.133355>

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4.1 Abstract

This study compared the lead (Pb^{2+}) immobilization efficacy of biochar-supported phosphate to conventional in-situ heavy metal immobilization methods (with lime, neat biochar and phosphate). The biochar-supported phosphate was obtained by treating Douglas fir biochar (BC) with anhydrous calcium chloride and potassium dihydrogen phosphate. The amount of Pb^{2+} immobilized was determined by comparing the concentration of ammonium nitrate extractable Pb^{2+} lead from lead-spiked soil (without amendment) to that of a 30 d incubation with (a) lead-spiked soil plus 5% (wt./wt.) biochar supported-phosphate, (b) lead-spiked soil plus 5% (wt./wt.) untreated Douglas fir biochar, (c) lead-spiked soil plus 5% (w/w) lime and (d) lead-spiked soil plus 5% (wt./wt.) potassium dihydrogen phosphate. The control (lead-spiked soil without amendment) produced the largest quantity ($96.08 \pm 9.22 \text{ mg L}^{-1}$) of NH_4NO_3 -extractable Pb^{2+} , while lead-spiked soil treated with 5% (wt./wt.) biochar-supported phosphate gave the lowest amount of NH_4NO_3

extractable Pb^{2+} ($0.3 \pm 0.2 \text{ mg L}^{-1}$). XRD and XPS analyses showed mechanism for immobilization of Pb^{2+} by BP occurs at $\text{pH} < 7$ due to dissolution of Hydroxyapatite embedded in BP during modification, followed by precipitation of insoluble $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$. The residual lead fraction in the lead-spiked soil increased by 20.9% after amendment with BP, while the oxidizable fractions increased by 21.3% after amendment with BC suggesting complexation of Pb^{2+} by ligand functional groups on BC surfaces. These results indicate that biochar-supported phosphate is a candidate to reduce lead mobility (bioavailability) in polluted soil. This treatment may lower Pb^{2+} uptake by plants and minimize water contamination by Pb^{2+} .

Keywords: Heavy metals, Biochar supported-phosphate, Insitu-immobilization, bioavailability, simulated polluted soil.

4.2 Introduction

Over 10 million heavy metal-polluted sites have been reported globally with net economic consequences of nearly US \$10 billion annually¹. Lead, cadmium, and arsenic contaminations constitute more than 50% of the polluted sites. The continued bioaccumulation of heavy metals in soil poses a significant health threat to plants, animals, and humans.²⁻⁴ Lead (Pb^{2+}) in particular can remain in the environment for more than 150 years.⁵ Lead uptake by crops has been previously linked to plant phytotoxicity with a consequent adverse impact on humans due to metal transfer through the food chain.⁶⁻⁷ Ingestion of lead from contaminated food can lead to learning difficulties in children, neuron toxicity, kidney diseases and cancer.^{2,8} Therefore, the development of an effective and eco-friendly technique for minimizing lead bioavailability from contaminated soil is crucial.

Many methods have been developed for heavy metal remediation from contaminated

soil.⁹ Conventional methods include phytoremediation, soil washing, electrokinetic treatment, soil isolation, vitrification, sorption, liming, and precipitation using phosphates.^{10–12} Phytoremediation is eco-friendly, but only suitable for moderately contaminated soil. It can also cause secondary pollution.¹³ Electro-kinetic treatment, soil isolation, and vitrification methods are laborious and costly.¹⁴ The use of chelating agents for washing poses a significant groundwater contamination risk.¹⁵

In-situ immobilization techniques, using lime, phosphate, and biochar, are considered relatively inexpensive and easy to manage.¹⁶ Therefore, they have been used widely. The technique is believed to reduce heavy metal bioavailability,¹⁷ and lower plant uptake through adsorption and formation of stable precipitates and complexes.¹ Lime application causes an increase in soil pH and co-precipitation hydroxides and carbonates.¹⁸ Phosphate use forms insoluble precipitates such as pyromorphite-type minerals $[\text{Pb}_5(\text{PO}_4)_3\text{X}]$; $\text{X} = \text{F}, \text{Cl}, \text{B}, \text{or OH}$] which lowers lead mobility.¹⁰ Biochar immobilizes heavy metals by adsorption, through ion exchange, co-precipitation, complex formation, electrostatic interactions, and physical sorption.^{19–}
²¹ It is unclear whether the combination of lime, phosphate, or biochar for lead immobilization is superior to the individual traditional immobilization methods. The phosphate sorption ability of calcium derived adsorbent has been previously shown.²² While phosphate application in isolation could result in eutrophication of water bodies ²³, binding phosphate to calcium treated biochar slows phosphate release into soil.²⁴ In August 2021, the United Nations intergovernmental Panel on Climate Change (IPCC) forecast that adding huge amount (10^9 tons/yr) of biochar in soil combats the growth of atmospheric CO_2 while improving soils. Thus, for reducing heavy metal mobility, biochar supported phosphate is an important choice to demonstrate. Moreover, biochar addition to soil does not only sequesters carbon originally obtained from organic biomass that

would otherwise release CO₂ by combustion or decay, but also serve as a suitable waste management alternative.²⁵ The oxidative aging of biochar during exposure to water and oxygen generates hydroxyl, carboxyl, and carbonyl functions on BC which readily sorb heavy metals.^{26–}
²⁷ Compared with neat biochar, chemical modified-biochar has demonstrated better sorption capacity for contaminants due to improved surface area and surface functional groups. Ye et al.²⁸ separated Pb from natural-aged microplastic using magnetic biochar with porosity and graphitization (PGMB) and obtained removal efficiency of 37.95 and 33.78% in the presence of HPO₄²⁻ and HCO₃⁻ respectively. They attributed this to the buffering action of HPO₄²⁻ and HCO₃⁻ causing pH rise and thus promoting precipitation, complexation and reduced mobility of Pb²⁺. Kong et al.²² used BC-HAP recovered from phosphate sorption from wastewater to extract uranium from wastewater. While sorption capacity of neat Hydroxy apatite was 934.57 mg g⁻¹, the sorption capacity of BC-HAP improved with increasing P content. They observed sorption capacity of 485.43, 675.67 and 917.43 with BC-HAP containing 5%, 10% and 25% phosphorus respectively. Chen et al.,²⁹ got improved heavy metal sorption by biochar in soil after the addition of Hydroxyapatite/Calcium Silicate Hydrate (HAP/CSH). They ascribed the enhanced heavy metal sorption by the Biochar Facilitated Hydroxyapatite/Calcium Silicate Hydrate (BC-HAP/CSH) to increased quantity of oxygen-containing functional groups including carboxylate, carboxyl, and hydroxyl, which offers additional adsorption sites for heavy metals.

The main objective of this study was to assess the lead immobilization efficacy in soil by biochar-supported phosphate from a simulated lead-polluted soil and compare this treatment to the individual use of lime, phosphate, or biochar alone. It is hypothesized that, the hydrolysis of biochar supported-phosphate in soil would reduce Pb²⁺ mobility, bioavailability and so, potential transfer to human via food chain.

4.3 Materials and Methods

4.3.1 Preparation of Douglas fir biochar (BC) and biochar-supported phosphate (BP).

Douglas Fir biochar (BC) is a commercial product (Black Owl Biochar, Biochar Supreme Inc. Environment Ultra) obtained as a by-product from bio-syngas production. The biochar was prepared according to the method reported by Bombuwala et al.³⁰ In this method, green Douglas fir wood chips were introduced into an air-fed updraft wood gasifier at ~900-1000 °C for a residence time of ~1–30 s.

Biochar-supported phosphate was obtained by treating BC with anhydrous calcium chloride and potassium dihydrogen phosphate (Fig. C.1). BC (50 g) was treated with anhydrous calcium chloride (25 g) to enhance its phosphate sorption ability. All chemicals used were of analytical grade (Aldrich Sigma). Deionized water (400 mL) was added to 50 g of previously ground and sieved BC ($\leq 350 \mu\text{m}$ particle size) in a 1000 mL beaker with continued stirring to form a uniform slurry. The slurry was then heated to about 37 °C. Then, 25 g of anhydrous calcium chloride was added and stirring was continued for 30 min. Then, 25 g of potassium dihydrogen phosphate was added and stirring continued for another 30 min. The pH of the slurry was then adjusted to about 10 using aqueous potassium hydroxide (10 M KOH) and aged for 24 h. The aged slurry was vacuum filtered through Whatman number 1 filter paper. The residue was washed three times, each with 200 mL of deionized water, and oven-dried at ~1 atm pressure for ~48 h to constant weight at 80 °C. The biochar-supported phosphate (BP) was kept in seal containers for later use.

4.3.2 Characterization of Douglas fir biochar (BC) and biochar-supported phosphate (BP)

The surface area, pore volume and average pore size diameter were analyzed by the BET (Brunauer, Emmet, and Teller) N₂ adsorption method at 77.3K with a Micromeritics Tristar II Plus Version 2.03 surface area analyzer. The morphology of both BC and BP was examined with scanning electron microscopy (JEOL JSM-6500F FE-SEM operated at 5 kV), and the elemental contents were determined using scanning electron microscopy-electron diffraction energy (SEM-EDX) spectroscopy. Powder x-ray diffraction scrutinized the crystalline content of BC and BP before and after a 30-d incubation with lead-spiked soil using a Rigaku's Smartlab X-ray diffraction system employing Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation generated at 40 kV and 44ma. The XRD patterns were obtained by scanning 2θ from 3° to 90° with 0.05° step at a the rate of 4° min^{-1} .

The pH and ash contents of BC and BP were determined following the method described by ³¹ with some modification. The pH was measured using a Hanna pH meter (model HI 3221) after shaking the biochar samples for 1h in deionized water at a 1:10 (wt./v) ratio. The ash content was determined by heating 1.0 g of oven-dried biochar samples (at 105°C for 24 h) in an open-top porcelain crucible at 650°C in a muffle furnace for 15 h. A (Elementar unicube, Germany) elemental analyzer was used to determine the elemental composition (C, H, N, S) of BC and BP by combustion. The amount of organic oxygen (%O) was calculated by difference ($\text{O}\% = [100 - (\text{C} + \text{H} + \text{N} + \text{S} + \text{Ash})]$).

4.3.3 Determining pH point of zero charge (pH_{pzc})

The solution pH at which the net surface charge on the absorbent (BC and BP) is zero (the PZC) was determined from ~0.1 g BC and BP samples, which were placed in 50 mL polypropylene tube and mixed with 20 mL of 50 mgL⁻¹ Pb²⁺ solution. The mixtures were then shaken for 24 h in a mechanical shaker (200 rpm) at room temperature. These slurries were then filtered through Whatman number I filter paper. The final pH of the filtrates were measured using the Hanna pH meter for pH values ranging from 1 to 14. The desired solution pH was adjusted using 1M NaOH or 1M HCl solutions. The PZC was obtained by plotting ΔpH (initial-final pH) values against the initial solution pH.

4.3.4 Soil sampling and incubation

These experiments were carried out on Pb-spiked soil. Soil was collected at a depth of 0-15 cm from an agricultural field located at Mississippi State University. The soil was sieved to remove roots and stones, air-dried, homogenized, and passed through a 2 mm sieve before use. The initial soil pH (5.64) was measured following the method described by.³² An air-dried soil sample (10 g) was added into a 50mL plastic beaker. Then, 20 mL of deionized water was added using an auto dispenser and the mixture stirred with a glass rod until all soil was suspended. The slurry was then stirred for 1 h and then allowed to stand for a 30 min interval before measuring the pH using a Fisher Scientific Model 25 Accumet pH meter (Denver, CO). In addition, the soil was analyzed for P, Mg, Ca, K and Na contents (Table C.1) following the Mississippi State University soil testing (Lancaster method) procedure as described by.³³ Air-dried and sieved soil samples (5 g) were placed into 125 mL plastic Erlenmeyer flasks. Then, 5 mL of solution A (0.05M HCl) was added using an autopipette, and it was left to stand for 10 min. Next, 20 mL of solution B (prepared by mixing 900 mL glacial acetic acid, 65.2 g malonic acid, 120 g malic acid, 12 g ammonium

fluoride, 30 g aluminum chloride hexahydrate, 300 mL concentrated ammonium hydroxide and then diluting to 10 L with deionized water after adjusting the solution pH to 4.0) was added to each flask using an autopipette, and the mixture shaken for 10 min on a mechanical shaker (250 cycles min^{-1}). The suspension was filtered through Whatman number 2 filter paper, and the filtrate analyzed for P, Mg, Ca, K and Na using an Avio 200 ICP-OES (Perkin Elmer, Waltham, MA).

A 3 kg soil sample was spiked with Pb to a 300 mg kg^{-1} level using a $\text{Pb}(\text{NO}_3)_2$ solution. The USEPA maximum acceptable soil lead level for gardening soil is 100 mg kg^{-1} of soil.³⁴ However, the acceptable soil lead levels set by environmental protection agencies varies by country.³⁵⁻³⁶ The lead-spiked soil was incubated for 14 d at 25°C with a moisture content at 100% field capacity initially, which was then maintained at 80% of water by adding deionized water throughout the duration. After the 14-d incubation, the soil was air dried at 25°C for ~ 7 d and stored at room temperature.

4.3.5 Determining the lead immobilization efficacy

The lead immobilization efficacy of BP was evaluated in comparison to BC, lime and potassium dihydrogen phosphate, each used individually. The treatments used included: 1) Pb-spiked soil (Control), 2) lead-spiked soil plus 5% BP (wt./wt.), 3) lead-spiked soil plus 5% BC (wt./wt.), 4) lead-spiked soil plus 5% lime (wt./wt.) and 5) lead-spiked soil plus 5% potassium dihydrogen phosphate (wt./wt.). Each treatment was performed in triplicate and arranged in a randomized design. The different treatments were incubated for 30 d at 25°C with their water holding levels maintained at 80% capacity. The sample containers were covered with parafilm with holes pierced into them for aeration. After incubating for 30 d, the soil samples were air-dried and their ammonium nitrate extractable lead concentrations were determined following the procedure described by.³⁷ This procedure entails weighing 2 g of the air-dried soil samples in a 50

mL polypropylene tube and adding 5 mL of 1 M ammonium nitrate solution to each (soil solution ratio of 1:2.5), followed by shaking in a reciprocating shaker at 200 rpm for 2 h at room temperature. After shaking, the tubes were removed, and their contents filtered using Whatman number one filter paper. The ammonium nitrate extractable lead concentrations of the filtrate were determined using ICP-MS. The lead immobilization percentage (IP) was obtained from:

$$IP = \frac{\text{NH}_4\text{NO}_3 \text{ extractable lead concentration of the (control-amended soil)} \times 100\%}{\text{NH}_4\text{NO}_3 \text{ extractable lead concentration of the control}}$$

The pH and electrical conductivity of the incubated soil samples were determined at a soil-water ratio of 1:2.5 using the Hanna pH meter and a Hanna edge electrical conductivity meter, respectively. The elemental contents of the incubated soil samples were also analyzed using an elemental analyzer (Elementar unicube, Germany).

The effect of BP dose on Pb^{2+} bioavailability was evaluated. The lead-spiked soil (control), lead-spiked soil plus 1% of BP (wt./wt.), lead-spiked soil plus 2.5% of BP (wt./wt.) and lead-spiked soil plus 5% PB (wt./wt.) were each incubated for 10 days with their moisture levels maintained at 80% at 25 °C. After incubation, the soil was air-dried, homogenized, and extracted with 1 M NH_4NO_3 . Its NH_4NO_3 -extractable lead concentration was determined by ICP MS as described before.

To evaluate the mobility and bioavailability of lead in lead-spiked soil before and after amendment with BC and BP, total lead concentration was determined following EPA method 3050B.³⁸ Modified version of Tessier sequential extraction³⁹⁻⁴⁰ was employed to determine the different fraction of lead species in soil. Detailed procedure is shown in Table A4.1 The concentration of Pb^{2+} in the extract was determined by atomic absorption spectrophotometer (model SHIMADZU AA-7000) at wavelength 283.3 nm.

4.3.6 Immobilization mechanism of Pb²⁺ onto BP

To establish the mechanism of adsorption of Pb²⁺ onto BC and BP, Batch experiments was employed. The adsorption kinetic was determined by adding 25 mL of 50 mg L⁻¹ Pb²⁺ solution to ~ 0.1 g of adsorbent placed in a 50 mL polypropylene tube. The supernatant pH was adjusted to 6.5 to mimic soil pH required for optimum nutrient availability. The samples were shaken at 25 °C at 200 rpm for 0.08, 0.25, 0.5, 1, 2, 4, 6, 9, 12, 24 and 48 h. After filtering the supernatant through Whatman number 41 filter paper, Pb²⁺ concentrations in the filtrates were quantified by atomic absorption spectrophotometer. The adsorption isotherm was obtained by adding 25 mL of 5, 10, 15, 20, 30, 40, 50 and 70 mg L⁻¹ Pb²⁺ solution to ~ 0.1 g of adsorbent placed in a 50 mL polypropylene tube. After adjusting the supernatant pH to 6.5, The tubes were shaken at 200 rpm for 24 h at 25 °C. The supernatant was filtered and Pb²⁺ concentrations determined using atomic absorption spectrophotometer. XPS analyses of BC and BP before and after a 30-d incubation with lead-spiked soil was performed

4.4 Results and discussions

4.4.1 Soil physiochemical properties.

The preliminary soil test results showing physiochemical properties are shown in (Table C.2). The soil was sandy, acidic with low P, K and Mg concentrations.

4.4.2 Characterization of Douglas fir biochar (BC) and biochar-supported phosphate (BP)

The pH, ash content, BET surface area, pore volume, pore size diameter, and elemental composition of both BC and BP are shown in (Table C.3).

Modifying BC to BP with anhydrous calcium chloride and potassium dihydrogen phosphate lowered the BC surface area from 578.9 to 360.5 m²g⁻¹ in BP. However, both pore

volume and average pore size diameter increased from 0.07 in BC to 0.12 cm³g⁻¹ in BP and 4.55 in BC to 13.40 Å in BP, respectively.

The nitrogen adsorption curve (Fig.4.1), for Douglas fir biochar was a type I isotherm indicating formation of micropores, whereas that for BP was a type II adsorption signifying the presence of mesopores and macropores. The nitrogen adsorption capacities of BC and BP increased rapidly when the relative pressure was less than 0.3. This rise at low relative pressure can be due to monolayer adsorption. Between relative pressures of 0.2 to 0.7, however, the slopes were small due to multilayer adsorption. At a relative pressure greater than 0.8, a large increment in adsorption capacity was observed in BP which could be from the capillary condensation within mesopores and macropores. According to Yakout et al.,³², the decrease in surface area following modification with H₂SO₄ is caused by micropore destruction by modifying agents resulting in greater meso- and macropores fractions. However, the uptake of phosphate to generate BP was done at a very low temperature. So, destruction of micropores originally present in BC would be unlikely. Thus, the decrease in surface area after modifying BC to BP could have risen from micropore blockage by the deposition of phosphate compounds on biochar surface. Furthermore, Table C.3 confirms that the ash content rose from ~3.4 to ~38.1wt.% after modifying BC to BP. This finding agrees with Leng et al.,⁴¹ who observed a reduced surface area in biochar containing significant ash contents due to extensive pore blockage.

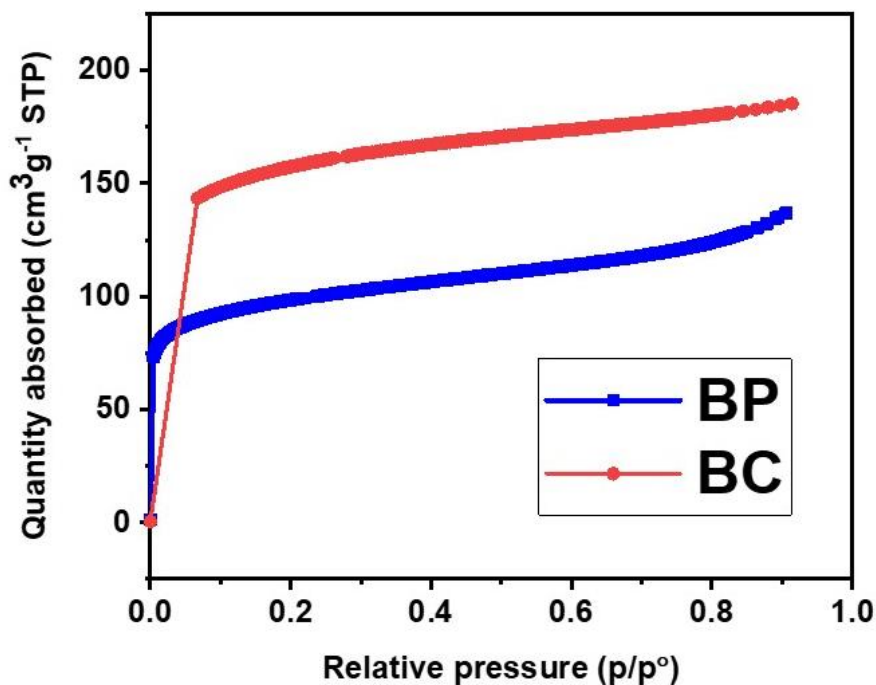


Figure 4.1 N_2 adsorption at 77.300 K of Biochar-supported phosphate (BP) and Douglas Fir biochar (BC)

The elemental contents of C, H, O, N and S changed after modifying BC to BP. While there was a reduction in the amount of N% (0.12 to 0.08), C% (79.4 to 50.86), H% (1.79 to 1.37) and O% (15.12 to 9.5). The quantity of S% and P%, respectively, increased from ~ 0.01 and ~ 0.5 in BC to ~ 0.07 and ~ 5.8 in BP after the modification. Also, BP had a larger molar H/C ratio (0.32) than BC (0.27). The large increase in P% confirms substantial phosphate surface deposition occurred on BP.

Biochar with O/C ratios of < 0.2 meet the criteria for highest stability with half-life of more than 1000 years in soil irrespective of the production temperatures (300-1000°C).⁴² Therefore, both BC and BP, with approximate molar O/C ratios of about 0.14, will sequester carbon for a long time in soil. Also, molar O/C ratios are directly correlated to the amount of oxygen groups on biochar

surfaces. The molar O/C ratio for BC was slightly less than that of BP. Similarly, BP had a larger molar H/C ratio than BC. The slightly larger molar O/C and H/C ratios in BP are attributed to the addition of phosphate species (HPO_4^{2-} , H_2PO_4^-) to BC during modification. The addition of H_2PO_4^- or HPO_4^{2-} to BP resulted in an improved Pb^{2+} immobilization, because Pb^{2+} reacts with H_2PO_4^- to form insoluble and immobile lead-phosphate compounds such as $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ at $\text{pH} < 7.5$. The formation of insoluble lead compounds due to reaction of Pb^{2+} with phosphates species in soil at $\text{pH} < 7$ was reported by Jensen et al.,⁴³

BC and BP have low nitrogen concentrations like many wood-derived biochar. Elemental analysis indicated both BC (751.8) and BP (741.6) had high molar carbon to nitrogen (C/N) ratios. The carbon-to-nitrogen ratio is among the vital chemical parameters considered in soil amendments because it helps to predict mineralization and nitrogen release into soils. A molar C/N ratio in soil greater than 25:1 results in N immobilization, where inorganic nitrogen (NH_4^+ and NO_3^-) is transformed into organic forms,⁴⁴ hence making it unavailable for plant use. Similarly, amending soil by switch grass biochar increased N immobilization but reduced the total inorganic nitrogen due to the high switch grass molar C/N ratio.⁴⁴ Therefore, the use of significant amounts of BC or BP for soil amendment should be accompanied by the application of nitrogen fertilizer for proper plant growth.

The SEM micrographs of both BC and BP are shown in (Fig. C.2). The images of both BC and BP showed the presence of micropores, mesopores and macropores which consisted of tube-like structures much of which reflects the original wood morphology. The morphology of BP exhibited more mesopores and macropores than BC. The larger number of mesopores and macropores found in BP is consistent with the surface area decrease going from BC to BP (BET results) in which both pore diameter and pore volume increased. The decreased surface area in BP

could have risen from the blockage of micropores by the deposition of phosphate compounds on the biochar surface. Leng et al.,⁴¹ reported that micropores strongly correlate with biochar's surface area.

The SEM-EDX elemental composition analyses of BC and BP are shown in (Fig. C.3). SEM-EDX employs a spot diameter of 4-6 μm , penetrating to a depth of $\sim 5.3 \mu\text{m}$. BC and BP surfaces are heterogeneous, so SEM-EDX analyses of many locations are needed to obtain a representative analysis of these surfaces. Analyses of four BC locations gave C (84 to 87%), O (9.9 to 12%), P (0.5 to 1.1%), Ca (0.5 to 1.6%) and K (0.86 to 1.75%). After phosphate uptake, the corresponding analyses of four BP locations exhibited: C (50.8 to 64.9%), O (20.4 to 33.0%), P (4.7 to 5.8), Ca (7.1 to 8.2%) and K (0.66 to 1.35%). The molar Ca/P ratio ranged from ~ 1.1 to 1.2. The theoretical molar Ca/P for $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{PO}_4)_6(\text{HO})_2$ are 1.33 and 1.67, respectively.⁴⁵ These analyses reflect the deposition of phosphate as $(\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O})$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{HO})_2$, CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and related calcium salts on the BP surface. This lowers the contribution by carbon, which was covered partially by deposition and raises the oxygen surface region amount. The bulk analyses in Table 4.1 are for the entire sample, not just the surface and near surface region which EDX-probed to a depth of $\sim 5.3 \mu\text{m}$. The EDX values confirm successful surface region deposition of phosphorus on BP during the modification of BC with calcium chloride and potassium phosphate.

The XRD patterns for BC and BP before [A] and after a 30-d incubation with lead-spiked soil [B] are shown in (Fig.4. 2). The BC XRD spectra revealed two broad peaks comparable to that observed for layered graphene between $2\theta = 20^\circ$ to 30° and 40° to 50° . These peaks are due to graphitic-like diffraction formed as lignocellulostic structures are partially aromatized during pyrolysis and typical aromatic stacking occurs with d-spacing of ~ 3.4 to $3.5 \text{ \AA}$.⁴⁶ The major new

peaks exhibited by BP appeared at 2θ approximately 9.4° , 26° and 53° . These result from octacalcium phosphate (OCP, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), [ICDD number 261056].⁴⁷ Further peaks at $2\theta = 28.23^\circ$, 32.05° , 40.28° , 46.66° , 49.41° and 64.18° matched the diffraction pattern of hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [JCPDS ICDD card Number 09-0432].⁴⁷⁻⁴⁸ These crystalline species form during hydrophosphate deposition in the BP formation. Other amorphous poorly crystallized P-containing species may also be present on BP that are not observed by XRD.

After a 30-d incubation with lead spiked soil, all peaks matched to lead hydroxyapatite ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, (JCPDS card number 01-087-2477).⁴⁹ This indicate that, both BC and BP immobilize Pb^{2+} in soil through the transformation of (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) into a more stable [hydroxypyromorphite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$].

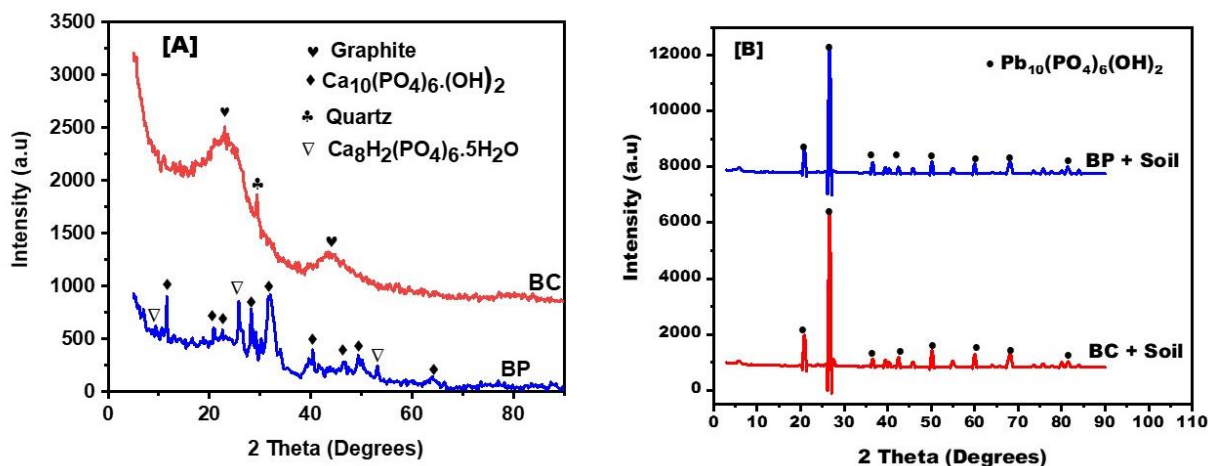


Figure 4.2 XRD patterns of BC and BP Before (A) and after a 30-d incubation with lead-spiked soil (B)

4.4.3 pH point of zero charge

The pH point of zero charge (pHpzc) value corresponds to the point where the net surface charge of the adsorbent is zero.⁵⁰ BC and BP exhibit pHpzc values of 6.7 and 9.5 respectively (Fig.4.3). Therefore, anionic species will be attracted, at solution pH values lower than 6.7 to BC surfaces and 9.5 to BP surfaces. Above their pHpzc values, the removal of cationic species will be favored.⁵¹ Since lead (II) is cationic, its removal by BC and BP is favored at pH > 6.7 and 9.5, respectively. However, free ionic Pb^{2+} exists at pH < 7.⁵² At pH > 7, hydrolysis to lead hydroxide and hydrous oxides occurs, so Pb^{2+} sorption is typically studied only below pH 6.5 to avoid precipitation. The absorption of Pb^{2+} is suppressed by electrostatic repulsion between the positively charged BP surface (pzc 9.5). Thus, Pb^{2+} immobilization by both BP and BC at pH < 7 occurs by precipitation (PbO and lead hydroxide) and complexation of insoluble octacalcium phosphate, hydroxyapatite and other such species.

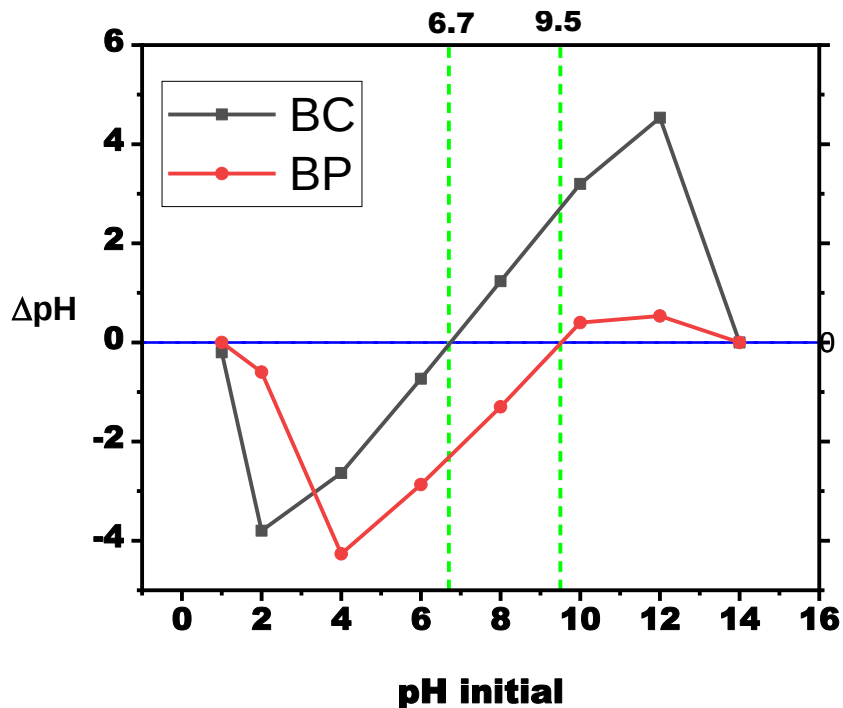
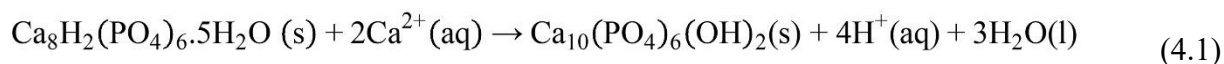


Figure 4.3 Point of zero charge (pHpzc) determinations of BP and BC

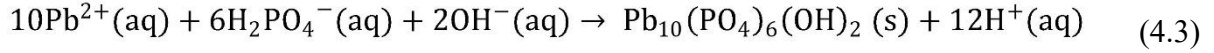
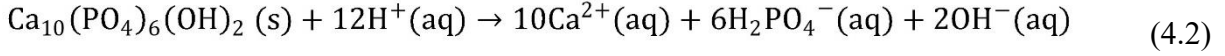
The XRD results indicated the phosphorus-containing crystalline species on BP are mostly octacalcium phosphate (OCP, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) and hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). In the presence of water, OCP in soil can be converted to more thermodynamically stable hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) on the release of H^+ as illustrated in equation 4.1.⁴⁸



(OCP) (Hydroxyapatite)

The use of hydroxyapatite for heavy metal immobilization from contaminated soil has been reported^{53,16}. According to Zeng et al.,¹⁶ the main Pb^{2+} immobilization mechanisms by hydroxyapatite include surface complexation, precipitation, cation exchange, and adsorption. In acidic soil, hydroxyapatite dissolves (equation 4.2), then, Pb^{2+} is adsorbed by the formation of

complex lead phosphate precipitates (equation 4.3), in which Pb^{2+} reacts with dihydrophosphate. Pb^{2+} also exchanges with Ca^{2+} forming insoluble Pb-containing hydroxyapatites, $\text{Pb}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$.



4.4.4 The lead immobilization efficacy

The lead immobilization efficacies of BP, BC, lime and potassium phosphate monobasic are compared to the unamended soil spiked with $\text{Pb}(\text{NO}_3)_2$ (control) in (Fig.4.4a). The control comparison examined NH_4NO_3 extractable lead concentrations from lead-spiked soil shown in (Fig. 4.4b). This control is compared with lead-spiked soil plus 5% BP (wt./wt.), lead-spiked soil plus 5% BC (wt./wt.), lead-spiked soil plus 5% lime (wt./wt.) and lead-spiked soil plus 5% potassium dihydrogen phosphate (wt./wt.) in (Fig.4.4b). All are shown after a 30-d incubation period in (Fig.4.4a and b), respectively.

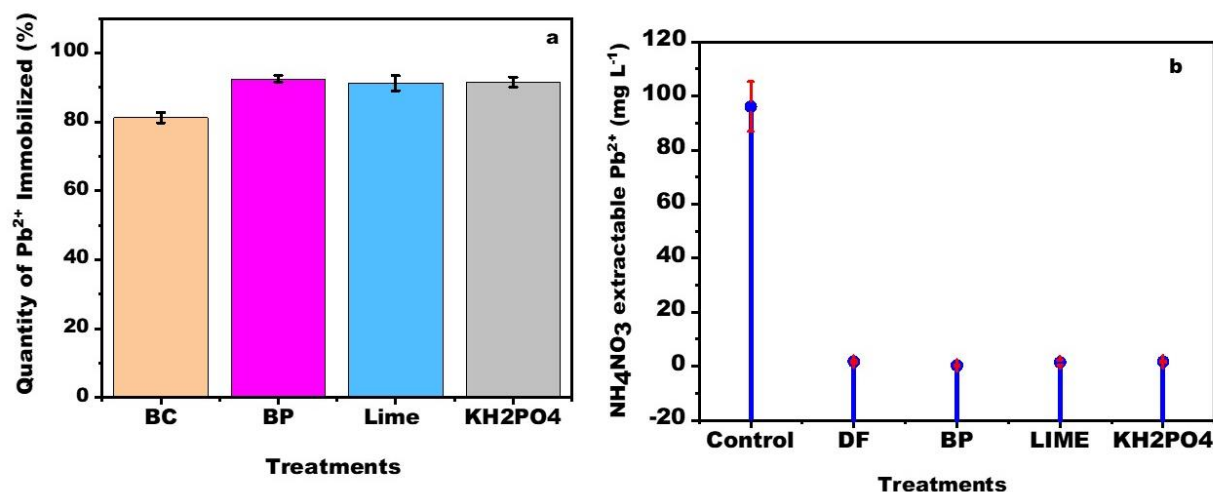


Figure 4.4 The Pb²⁺ immobilization efficacy of BP, BC, lime, and potassium dihydrogen phosphate compared to the control (a) and the NH₄NO₃ extractable Pb²⁺ concentration of control (unamended lead -spiked soil), lead-spiked soil plus 5% BC, lead-spiked soil plus 5% BP, lead-spiked soil plus 5% lime and lead-spiked soil plus 5% KH₂PO₄ (b) after a 30d incubation period at room temperature. (Values are average of n =3, error bars shown as SD)

The lowest amount of NH₄NO₃ extractable Pb²⁺ ($0.3 \pm 0.2 \text{ mg L}^{-1}$) was found in the lead-spiked soil amended with 5% BP. The largest amount of extractable Pb²⁺ came from the control ($96.08 \pm 9.22 \text{ mg L}^{-1}$) experiments. Clearly, the BP soil amendment immobilized successfully the Pb²⁺. The amounts of NH₄NO₃ extractable Pb²⁺ obtained from the lead-spiked soil amended with 5% BC, lime and KH₂PO₄ were 1.7 ± 0.38 , 1.43 ± 0.90 and $1.70 \pm 0.27 \text{ mg L}^{-1}$, respectively. BC, lime and KH₂PO₄ worked well to immobilize Pb²⁺ but not as well as BP. The Pearson correlation coefficient between residual soil pH (pH after incubation) and the NH₄NO₃ extractable Pb²⁺ was negative ($r = -0.5$), indicating that pH played a role in the immobilization of Pb²⁺ in the soil. When soil pH is increased, the negative charge density on soil surfaces and the [OH⁻] in the H₂O increases. This in turn, can facilitate immobilization of positively charged Pb²⁺ by precipitation as Pb(OH)₂. This enhances adsorption on soil charged sites and or formation of PbOH⁺ species which

is favorably adsorbed compared to Pb^{+2} . Several other studies have reported reduced solubility and mobility of Pb^{2+} with rise in pH.⁵⁴⁻⁵⁵

The incubation of the lead-spiked soil with 5% BC, BP, and lime increased soil pH from 5.67 to 6.87, 6.2, and 7.1, respectively (Table 4.1). The pH was slightly reduced (by ~ 0.07) in soil treated with KH_2PO_4 . The electrical conductivity rose from 75.9 to 82.7, 176.6, 652.7 and 2607.7 in lead-spiked soil treated with lime, BC, BP and KH_2PO_4 , respectively. The C/N ratio rose from 0.08 to 0.16, 3.1, 6.45, and 149.8 in lead-spiked soil treated with KH_2PO_4 , lime, BC, and BP, respectively. However, H/C ratio was reduced from 12.1 to 11.5, 2.2, 1.0 and 0.6 following amendment with KH_2PO_4 , lime, BP, and BC, respectively.

Table 4.1 Selected properties of lead-spiked soil after incubating for 30-d with different amendments verses the control

Property	Control (Unamended soil)	Soil + BC	Soil+BP	Soil + lime	Soil + KH_2PO_4
pH	5.67 ± 0.15	6.87 ± 0.06	6.20 ± 0.10	7.10 ± 0.10	5.60 ± 0.10
EC ($\mu S cm^{-1}$)	75.93 ± 5.19	176.60 ± 9.52	652.67 ± 14.57	82.73 ± 4.46	2607.67 ± 131.11
C%	0.15 ± 0.02	4.50 ± 0.68	3.10 ± 0.33	0.78 ± 0.09	0.22 ± 0.04
N%	2.17 ± 0.28	0.84 ± 0.27	0.03 ± 0.01	0.36 ± 0.15	1.60 ± 0.23
H%	0.16 ± 0.00	0.24 ± 0.03	0.26 ± 0.03	0.14 ± 0.02	0.21 ± 0.01
S%	0.00 ± 0.00	0.01 ± 0.02	0.07 ± 0.04	0.00 ± 0.00	0.00 ± 0.00
H/C Ratio	12.10 ± 0.86	0.63 ± 0.01	0.99 ± 0.02	2.19 ± 0.05	11.49 ± 2.19
C/N Ratio	0.08 ± 0.02	6.48 ± 1.15	149.80 ± 21.58	3.09 ± 1.88	0.16 ± 0.03

EC = Electrical conductivity, data shown are mean ± SD, n =3

Information on soil pH, electrical conductivity, molar C/N and H/C ratios are vital parameters for predicting soil productivity because they control nutrient availability. While a

reduction in the molar H/C ratio occurred in all treatments, a general increment in the soil pH, electrical conductivity, and the molar C/N ratio was observed. Improvements in both soil electrical conductivity and pH following the application of biochar and lime have been previously reported.⁵⁶ The rise in the electrical conductivity is attributed to increased salt contents (ash content) following the amendments. The increased soil pH can be ascribed to the presence of oxides, carbonates, and hydroxides of Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} in the additives used (lime, BC and BP). The increment in soil pH after incubation with BP was much smaller than that induced by unmodified BC. The slight increase in the soil pH treated with BP is likely due to octacalcium phosphate $[(\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O})]$ hydrolysis, which releases H^{+} .

Soil microbes' accessibility to C and available N correlates with molar H/C and C/N ratios, respectively. Soil additives with molar C/N ratios values lower than 25:1 indicate their ability to provide sufficient nitrogen needed for microbes to use applied carbon.⁵⁷ The lower molar H/C ratios associated with BC and BP amendments are related to their recalcitrant nature, stability, and ability to mitigate climate change via carbon sequestration. Also, larger molar C/N ratios observed in BP treatment reveal low nitrogen availability, implying nitrogen immobilization (conversion of inorganic nitrogen to organic nitrogen) is more favorable. Increased molar C/N ratios in soil after biochar amendment was previously reported with pine wood biochar because of its low N contents.⁵⁸ In the same study however, a reduction in soil molar C/N ratios was observed after poultry litter biochar amendment based on its greater N contents. So, the effect of biochar application on soil molar C/N ratio depends on the feedstock used. Thus, the use of biochar produced from low N feedstocks, such as BC for soil amendment, should be complemented by nitrogen fertilizer application.

4.4.5 The effect of BP dose on lead (II) immobilization efficiency

The lead immobilization efficiencies for the control compared to lead-spiked soils amended with different BP doses is shown in (Fig. C.4 [A]). The control gave the highest NH_4NO_3 -extractable Pb^{2+} concentrations (98.9 mg L^{-1}). The lead-spiked soils amended with 1%, 2.5%, and 5% of BP had NH_4NO_3 -extractable Pb^{2+} concentrations values of 12.7 mg L^{-1} , 8.4 mg L^{-1} , and 8.1 mg L^{-1} , respectively. The lead (II) immobilization efficacy improved with increasing BP dose. However, the NH_4NO_3 extractable lead (II) concentrations in lead-spiked soil amended with 2.5% (8.4 mg L^{-1}) and 5% (8.1 mg L^{-1}) of BP did not differ significantly. At a BP application rate of only 1% (wt./wt.) to the lead spiked soil, BP reduced Pb^{2+} bioavailable by $\sim 87\%$ versus the control within 10 d of treatment. Both 2.5% and 5% (wt./wt.) treatment rates lowered Pb^{2+} by $\sim 92\%$ versus the control, suggesting BP's potential to lessen Pb^{2+} accumulation in humans through food chain. The mobility and bioavailability of lead in lead-spiked soil before and after amendment with BC and BP was examined. Before amendment, Pb was largely in the form of residual (50.2%) and Fe-Mn oxides bound (28.3%). After amendment, the distribution of different lead species changed (Fig. C.4[B]). The Organic fraction increased from 6.8% (control) to 28.1% in BC and 9.0% in BP, respectively. Similarly, Fe-Mn oxides forms increased from 28.3% (control) to 43% in BC. The residual fraction rose by 20.9% in BP. In contrast, the Exchangeable fraction decreased from 5.4% (control) to 2.7% in BC and 2.5% in BP, respectively. Similarly, the carbon-occluded form decreased from 4.5% (control) to 2.0% in BC and 2.5% in BP. This result concurs with earlier study in which, an increase in residual fraction and a decline in exchangeable fractions of Pb^{2+} in soil was reported after amendment with rice hull biochar.⁵⁹ Since the residual fraction is associated with the crystalline structure of the mineral and usually not easily extracted, the rise in residual fraction in BP further signify its potential to immobilize and lower Pb^{2+} bioavailability and

environmental risk. Also, the increase in organic fraction after amendment suggest sorption of Pb^{2+} on BC or BP surface functional groups via complex formation.

4.4.6 Immobilization mechanism of Pb^{2+} onto BP

Pseudo first order and pseudo second order adsorption kinetic models were used to predict the mechanism of Pb^{2+} adsorption onto BC and BP. Kinetic results obtained are shown on Fig. 4.5. The rate constants, coefficient of determination and adsorption capacities for the adsorbents are shown on Table C.4. The adsorption of Pb^{2+} onto both BC and BP were best described by pseudo second order kinetic implying that Pb^{2+} adsorption on both BC and BP occurred via chemisorption.

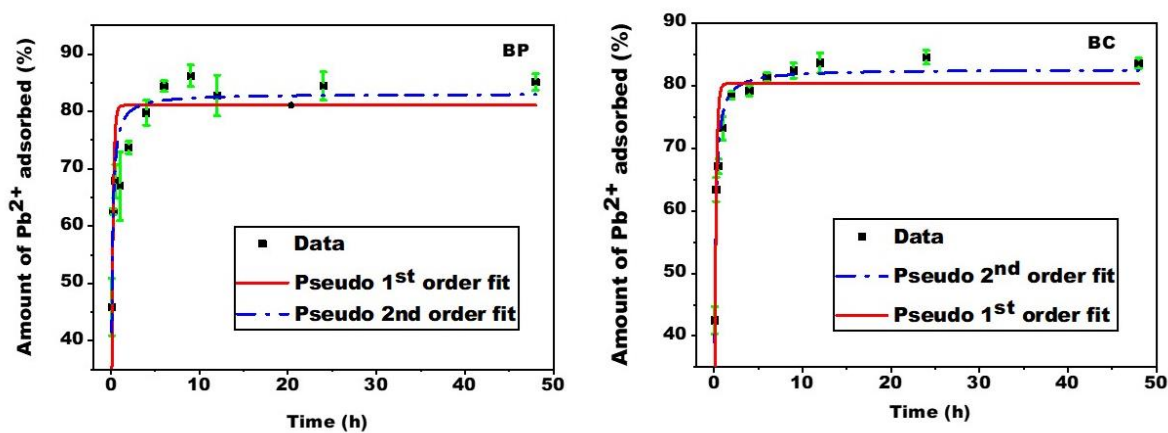


Figure 4.5 Adsorption kinetic for Pb^{2+} onto BC and BP at 25°C. Values used are mean of $n=3$, error bars shown as standard deviation

The adsorption isotherms were fitted by Freundlich and Langmuir models (Fig.4.6). The adsorption experiment indicated both BC and BP were effective in removing Pb^{2+} . The adsorption capacities of 122.03 mg g^{-1} and 102.75 mg g^{-1} were obtained with BC and BP respectively. The corresponding K_L coefficients were 0.065 and 0.12 M mg^{-1} . The sorption of Pb^{2+} ion on BC was

best fitted by Langmuir model signifying that sorption on BC surface was monolayer. However, the adsorption onto BP was best fitted by the Freundlich model (Table C.5) indicating the adsorption process was heterogeneous. Table C.6 compares Pb^{2+} adsorption capacities of both BC and BP with other absorbent reported in the literature. XRD analysis of Lead spiked soil amended with BC or BP confirms that the mechanism of immobilization of Pb^{2+} by BP was due to the dissolution of HAP, followed by the precipitation of lead hydroxyapatite. The XRD diffraction patterns changed from those of OCP and HAP in BP to a phase of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ in soil amended with BP. Therefore, the immobilization of lead ion by BP is majorly due to the dissolution of HAP followed by precipitation of lead hydroxyapatite (Pb-HAP). Fig A4.5 illustrates the mechanism of Pb^{2+} immobilization by BP. Some studies have proposed that lead removal by HAP can occur through ion exchange process which takes place at the HAP surface.⁶⁰ For lead immobilization by BP, this mechanism is unlikely because it occurs at $\text{pH} < 7$. Also, the distribution of different lead species in soil before and after amendment indicated increased Organic fraction from 6.8% (control) to 28.1% in BC and 9.0% in BP, respectively. This suggest Pb^{2+} could be strongly sorbed onto BC or BP surface via complex formation with the ligand surface functional groups such as hydroxyl, carboxylic, and phenolic. Sorption of heavy metal on biochar surfaces was also reported by.⁶¹

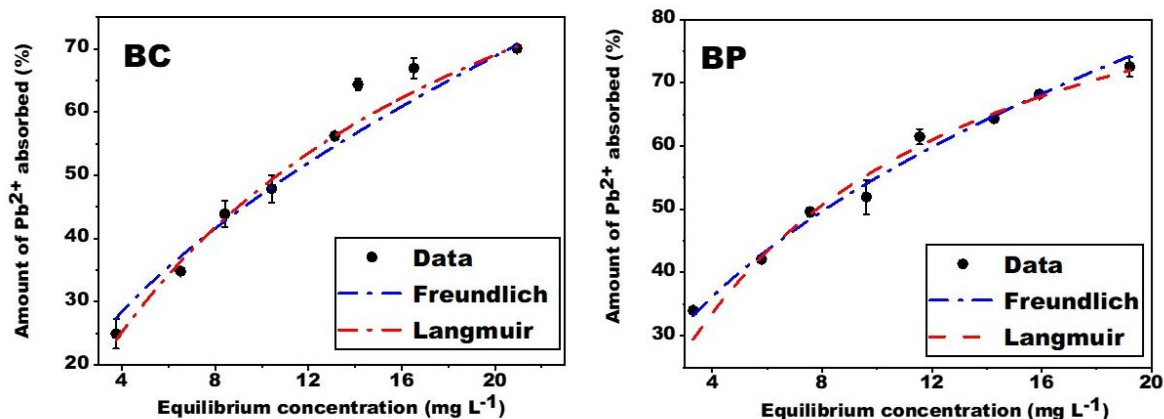


Figure 4.6 Adsorption isotherm for Pb^{2+} onto BC and BP at 25°C. Data presented are average of $n=3$, error bars are shown as standard deviation

XPS spectra for BC, BP, lead-spiked spoil, lead-spiked soil amended with %BC and lead-spiked soil treated with 5% BP are shown in (Fig. C.6). Before treatment, the binding energies of O1s, P2p and Ca2p corresponding to BP were 531.6, 134.0 and 348.3 eV respectively, all matching binding energy for HAP.⁶² The Pb4f peak observed in the lead-spiked soil at binding energy 140.15 eV is consistent with the values for $Pb(NO_3)_2$. After treatment with BC and BP, the appearance of Pb 4f peaks at binding energies 139.74 eV and 139.19 eV respectively confirms the formation of Pb-OH and $Pb-PO_4^{3-}$ bonds.⁶³

4.5 Conclusions and recommendations

The efficacy of using biochar supported phosphate (BP) over the traditional in-situ heavy metal immobilization methods (lime, potassium dihydrogen phosphate and biochar) was investigated. At an application rate of just 1% wt./wt., BP lowered Pb^{2+} bioavailability by 87% compared to the control within 10 d. The distribution of different lead species indicated a decline in the exchangeable lead forms from 5.4 to 2.5%, whereas the residual form increased by 20.9%

following amendment. The acid promoted formation of insoluble lead-containing hydroxyapatite was the main mechanism driving Pb^{2+} immobilization by BP. This result confirms that biochar-supported phosphate can effectively reduce Pb^{2+} mobility in contaminated soil, thus minimizing the possibility of Pb^{2+} uptake by plant and the likely transfer to humans through food chain. Besides carbon sequestration due to biochar's recalcitrant nature in soil, binding phosphate to biochar slows phosphate release, which minimizes water contamination and the related economic consequences. Additional research is recommended to establish the long-term effect of BP amendments on soil physical, chemical and biological characteristics. Also, future application of BP for immobilization of Cd, Hg and As should be examined.

4.6 Acknowledgements

Mississippi State University, Department of Chemistry. Fulbright Organization and US Department of State for the scholarship awarded to Beatrice Arwenyo.

4.7 Conflict of interest

Authors declare no conflict of interest.

4.8 References

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CHAPTER V

CONTRIBUTION OF MODIFIED P-ENRICHED BIOCHAR TO THE PH BUFFERING CAPACITY OF ACID SOIL

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(To be submitted to Journal of Environmental Management)

5.1 Abstract

Biochar can directly hold cations in soil because of the negative charge that exists on its surfaces. Besides, improving soil cation exchange capacity, the negative charges on biochar surfaces can buffer acid soil by protonation and deprotonation mechanisms. Moreover, biochar can ameliorate soil acidity due to the presence of oxides, carbonates, and hydroxides of its basic cations (Ca, Na, K, and Mg). Both biochar surface functional group and basic cation concentrations can be altered by modification with chemical agents (Chemerys, 2017; Godwin et al., 2019). These modifications could affect its soil pH buffering capacity. However, information concerning the impact of modified biochar application on soil pH buffering capacity is still scanty. This study investigated the pH buffering capacity of acidic soil amended with three P-enriched modified Douglas fir biochars and compared this buffering capacity to amendment with untreated Douglas fir biochar. These three P-enriched biochars, designated CCPP, CAPP and MSPP, were prepared by treating Douglas fir biochar, respectively, with: 1) anhydrous calcium chloride (CaCl_2) and potassium phosphate monobasic (KH_2PO_4), 2) calcium carbonate (CaCO_3) and diammonium phosphate $\{(\text{NH}_4)_2\text{HPO}_4\}$ and 3) an aqueous solution of magnesium sulfate (MgSO_4), potassium

hydroxide (KOH) and potassium phosphate monobasic (KH₂PO₄). The acid soil was then treated with biochar samples in biochar: soil ratios of 0%, 10%, 30%, and 50% (w/w), followed by incubation for 30 d at room temperature with soil moisture levels maintained at 80% of field capacity. The soil-biochar mixtures were titrated with 0.1 M aqueous HCl solutions and the resultant pH values determined. The amount of H⁺ added to soil-biochar mixture was plotted against pH. The pH buffering capacities of the soil and the soil-biochar mixtures were obtained from the graph's slope. The soil pH buffering abilities were largely dependent on the added biochar's alkalinity and ash contents.

Keywords: Biochar, pH buffering capacity, soil acidity, alkalinity, cation exchange capacity.

5.2 Introduction

Soil acidification is a natural process that has been escalating due to anthropogenic activities.¹ Soil acidity is caused by the dissociation of organic and inorganic acids, acid deposition, continued application of ammonium-based nitrogen fertilizers and excess uptake of basic cations by plants versus replenishment rates.²⁻⁴ Excessive soil acidification affects plant growth by inducing nutrient deficiencies, especially those of phosphorus, calcium, magnesium, and molybdenum.⁴ Phosphorus and molybdenum deficiencies result from adsorption of nutrients present in soil solutions by clay minerals, iron oxides and aluminum oxides at low pH (<5), forming insoluble phosphates and molybdates.^{5,6} In addition, acid soil pH levels induce increased solubility and plant uptake of heavy metals such as cadmium.^{7,8} Furthermore, excessively acidic soil pH values can induce elemental toxicities in plants due to increased aluminum, iron, manganese, and zinc solubilities and uptake.^{9,10} Moreover, available plant nutrients (N, P, K) decline in acidic conditions because microbial activity deteriorates.⁴ This can lower biological

nitrogen fixation and nutrient mineralization (mobilization).¹¹ These two processes are vital for creating plant-available forms of nutrients. Therefore, managing soil pH is vital for maintaining agricultural productivity.

Conventionally, lime/limestone (calcium carbonate)¹⁰ and similar compounds including dolomitic limestone,¹² quicklime, hydrated lime, marl, chalk, oyster shells, fluid lime,^{13,14} and wood ashes¹⁵ have been used to neutralize soil acidity. However, conventional liming agents are ineffective in improving subsurface soil acidity due to low solubility and slow movement into deeper soil depths. Extensive use of liming materials could cause supply shortages and inflated costs,¹⁶ limiting access to these agents to farmers in developing countries. Consequently, using biochar as a low-cost liming alternative for ameliorating soil acidity has been suggested.^{17,18}

Biochar is a carbonaceous material formed from pyrolysis of carbon-rich biomass under oxygen deficient or oxygen-free conditions.¹² Recently, research on biochar as a soil additive has increased due to its long term ability to improve soil physical, chemical and water retention properties,¹⁹ microbial activity,²⁰ ion exchange capacity and P retention and use efficiency.^{6,21} Negatively charged biochar surfaces can adsorb exchangeable soil cations.^{22,23} Moreover, negative biochar surface charges can buffer soil acidity.¹⁸ Biochar addition raises soil pH because metal cations compete with H^+ ions for cation exchange surface sites.¹² Mg, Ca, Na and K embedded in biochar as oxides, carbonates and hydroxides hydrolyze to form hydroxide ions that increase soil pH. Moreover, binding phosphate to biochar has been shown to slow down phosphate release, making it a suitable alternative for sustainable agriculture.²⁴ Excessive release of phosphate in the environment causes eutrophication of water bodies. In addition, phosphate treated biochar has been shown to exhibit greater heavy metal immobilization capacity from polluted soil than neat biochar.²⁵⁻²⁷ Soil has been previously amended with hydroxyapatite/calcium silicate

hydrate (HAP/CSH) treated biochar.²⁶ Heavy metal reduction increased with phosphate content of the amendment material. Compared to the control, this work achieved Cd reduction of $\geq 27.7\%$. The improved heavy metal sorption by the Biochar Facilitated Hydroxyapatite/Calcium Silicate Hydrate (BC-HAP/CSH) was attributed to greater amounts of oxygen-containing functional groups such as carboxyl, hydroxyl, and carboxylate which gave additional adsorption sites for heavy metals.²⁶ Furthermore, the use of P-enriched biochar could provide an eco-friendly approach to solid waste management. In addition to enhance soil fertility, P-enriched biochar application to soil sequesters carbon that would otherwise release toxic gases such as CO and CO₂ via combustion or decay.²⁸

Sequential modification and enrichment of a high surface area, porous Douglas fir biochar with magnesium chloride, potassium hydroxide and potassium dihydrogen phosphate, followed by addition to soil has been shown to improved soil pH and basic cation concentrations.²⁹ Thus, application of P-enriched biochar could be even more effective at buffering soil acidity than untreated biochar. This hypothesis is untested. Therefore, we investigated the ability of P-enriched biochar to buffer soil acidity, while assuming this influence could depend on cations used in the modification.

5.3 Methods and materials

All chemicals used were analytical grade (Sigma Aldrich). The purpose of using different modifying agents was to assess if different modifications would enhance Douglas fir biochar as a soil pH buffer. Basic soil cations included potassium, sodium, calcium, and magnesium. However, high sodium concentrations contribute to sodicity and salinity which can affect plant growth negatively.³⁰ Thus, three P-enriched biochars were prepared using K⁺, Ca²⁺ and Mg²⁺. The first designated as CCPP was made using anhydrous calcium chloride and potassium dihydrogen

phosphate as modifying agents. Calcium carbonate and diammonium phosphate were used to prepare CCAP. Finally, magnesium sulfate, potassium hydroxide and potassium dihydrogen phosphate were combined to make MSPP.

5.3.1 Origin of Douglas fir biochar (DFB)

Douglas fir biochar is a commercial product (Black Owl Biochar, Biochar Supreme Inc.) obtained as a by-product from bio-syngas production. The production method, previously discussed by,³¹ included the introduction of green Douglas fir wood chips into an air-fed updraft wood gasifier at ~ 900 - 1000 °C for a residence time of ~ 1 – 30 s. The biochar had a relatively high surface area of ~ 616 m²/g, low ash contents (~ 1.6 %) and an alkaline pH (~ 8).

5.3.2 Preparation of P-enriched biochar

Prior to chemical modification treatments, Douglas fir biochar (DFB), was ground and sieved to a particle size ≤ 350 μ m. P-enriched biochar was obtained by treating the sieved Douglas fir biochar with 1) CaCl₂ and KH₂PO₄ (CCPP), 2) CaCO₃ and (NH₃)₂HPO₄ (CAPP) and 3) MgSO₄, KOH and KH₂PO₄ (MSPP).

5.3.3 Preparation of CCPP

DFB, ~ 50 g, (≤ 350 μ m particle size) and deionized water, 400 mL, were mixed in a beaker to a uniform slurry and heated to ~ 37 °C with constant stirring. To this slurry, 25 g of anhydrous CaCl₂ was dissolved and stirred for 30 min. Then, 25 g of KH₂PO₄ was dissolved in this slurry, stirred and the pH was adjusted to 10 with 10 M KOH (aq.) with continued stirring for 2 h. The slurry was aged for 24 h at room temperature and then vacuum filtered through Whatman number 1 filter paper. The CCPP was washed four times each with ~ 200 mL of deionized water, oven-

dried at ~1 atm pressure to constant weight (~70.39 g) at ~80°C for 48 h and kept in an air-tight container until use.

5.3.4 Preparation of CCAP

To DFB, ~50 g, and 400 mL of deionized water was stirred to a uniform slurry in a 1000mL beaker. After warming to ~60°C, ~20 g of CaCO_3 was added and stirred for 30 min more. Then ~13 g of diammonium phosphate was added. The resulting slurry was stirred continuously for 72 h at room temperature; the product (CCAP,) was filtered, washed four times each with ~200 mL of deionized water, oven-dried at ~1 atm pressure to constant weight (~ 63.29) at ~80°C for 48 h and stored as described previously for CCPP.

5.3.5 Preparation of MSPP

To ~200 g of previously ground and sieved DFB (300-250 μm particle size), 800 mL of 0.52 M aqueous magnesium sulfate solution was slowly added and stirred to a uniform slurry. This slurry was uniformly mixed with a magnetic stirrer (rpm = 500) for 6 h, at ~24 °C and left to stand for 24 h. Then, excess solution was filtered through Whatman number 1 filter paper, and the residue was washed four times each with ~500 mL of deionized water, oven-dried at ~1 atm pressure to constant weight to constant weight (~ 216.47 g) at 80 °C for 48 h. Thus, ~16 g of MgSO_4 remained in the modified biochar at this stage. Then, to the magnesium sulfate-modified biochar, 800 mL of 5 M potassium hydroxide solution was slowly added while stirring (rpm =500) to provide a uniform slurry for 6 h at ~24 °C. This was aged for an additional 24 h at ~24 °C, vacuum filtered through a Whatman number 1 filter paper, and then oven-dried for 48 h at ~1 atm pressure and 80 °C to constant weight (~244.18 g). A 100 g amount of this modified Douglas fir biochar was mixed with 400 mL of 1.61 M L^{-1} aqueous potassium dihydrogen phosphate while

stirring to a homogeneous slurry. stirring was continued for an additional 6 h at rpm =500 at ~24 °C and then the slurry was aged for 24 h at ~24 °C. The excess solution was filtered through Whatman number 1 filter paper and the residue oven-dried at ~1 atm pressure to constant weight (149.6 g) at 80 °C for 48 h. The product, MSSP, was cooled to ~24 °C and kept in a tight container until use.

5.3.6 pH stabilization reaction time

The time needed for pH stabilization was determined following acid addition to all soil and biochar samples. Air-dried soil or biochar samples (DFB, CCPP, CAPP and MSPP) ~2.5 g were added to a 50 mL polypropylene tube (in triplicate). To each sample, 0, 1 or 2 mL of 0.1 M HCL acid was added, and the total volumes were increased to 25 mL with deionized water. The samples were placed in a reciprocating shaker (200 rpm) at room temperature for 24 h. Then the slurry pH was measured after 24, 48, 72, 96, 120, 144, 168, 192 and 216 h using a Hanna pH meter (model HI 3221).

5.3.7 Determining pH and electrical conductivity

Biochar pH and electrical conductivity (EC) were determined by accurately weighing ~5.0g each of air-dried DFB, CCPP, CAPP or MSPP into 100 mL polypropylenes tubes.³² Deionized water (50 mL) was added to each tube, and they were shaken at 200 rpm for 1h at ~25°C. After standing for 30 min, the pH and EC were determined using a Hanna pH meter and a Hanna edge electrical conductivity meter, respectively.

5.3.8 Biochar alkalinity, acid functional groups, ash contents and metal concentrations (Mg, K, Ca and P)

The alkalinity of DFB, CCPP, CAPP and MSPP were measured by the acid-base titration method described by Xu et al.,¹ The alkalinity was expressed as mmol of H⁺ reacted per gram of air-dry biochar, calculated from the quantity of hydrochloric acid consumed by biochar samples. To each biochar sample (0.5 g) in a 50 mL polypropylene tube, 20 mL of deionized water was added. This mixture was shaken for 2 h at 25° C. The samples were titrated at 0.5 mL per min with 0.1 M HCl to the end point of pH 2.0. The alkalinity was obtained from the quantity of HCl consumed by each sample during the titration.

Acid groups on the biochars were analyzed by the Boehm method.³³ This assumes that NaHCO₃ neutralizes only carboxylic acid groups (pK_a ≤ 6.4), Na₂CO₃ neutralizes carboxylic acids and lactones (pK_a ≤ 10.3), and NaOH neutralizes all acids including phenolic groups (pK_a <13). Approximately 1.0 g of each biochar sample was placed in a 100 mL plastic bottle. Then, 50 mL of 0.05 M NaHCO₃, Na₂CO₃ or NaOH was added, and the mixtures were shaken 24 h at 25°C. The supernatant was filtered, and 20 mL of each solution was titrated with a 0.2 M HCl acid solution. Blank samples (no biochar added) were used for each base titrant. All treatments were analyzed in triplicate. The total surface acidity and the carboxylic acid fractions were calculated as moles neutralized by NaOH and NaHCO₃, respectively.

Previously oven-dried (~105 °C) biochar ~1.0 g samples were added to a pre-weighed crucible to measure the ash content by heating in a muffle furnace at 650 °C for at least 6 h. After cooling, the mass of crucibles and their contents were measured, and the ash content calculated from

$$\% \text{ ash content} = \frac{\text{Weight of ash (g)} \times 100}{\text{Original weight of samples (g)}}$$

The metal concentrations were determined by weighing ~ 0.2 g of biochar samples in a crucible, then ashing in a muffle furnace for 8 h at 650 °C. After cooling to ambient temperature, 5.0 mL of HNO₃ acid and 2.0 mL of HCl acid were added to each vessel. The mixtures were heated at 150°C on a hot plate to dryness. After cooling to ambient temperature, 10 mL of deionized water was added to dissolve the ash before filtering through Whatman number 1 filter paper. The filtrates were then analyzed for Mg, Ca, P, and K with an ICP-MS model (ELAN DRC II) after appropriate dilution with deionized water.

The surface morphologies were analyzed by scanning electron microscopy (SEM, (JEOL JSM-6500F FE-SEM operated at 5 kV). The elemental distributions on DFB, CAPP, MSPP and CCPP were measured using scanning electron microscopy-electron diffraction spectroscopy (SEM-EDS). The specific surface area, pore size diameter and average pore volume were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77.3K using a Micromeritics Tristar II Plus Version 2.03 surface area analyzer. The crystallinities were examined by powder X-ray diffraction with a Rigaku's Smartlab X-ray diffraction system using Cu-K α (λ = 1.54 Å) radiation generated at 40 kV and 44 ma. The XRD patterns were taken by scanning 2θ from 5 ° to 90 ° with 0.05 ° steps at a rate of 4 ° min⁻¹. The peaks were identified by matching in qualX 2.0 Software.

5.3.9 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was done with a DTG-Q50 device using ~5 mg samples of DFB, CCPP, CAPP and MSPP. These were heated from room 25 °C to 1000 °C at a rate of 10 °C min⁻¹ in a nitrogen flow rate of 50 mL min⁻¹. The first derivative of the TGA curves were then calculated to establish the loss in mass over the temperature range used. The recalcitrance index

(R_{50}) of the biochar samples was calculated from the expression, $R_{50, \text{ sample}} = \frac{T_{50, \text{ sample}} \times 100 \%}{T_{50, \text{ graphite}}}$ where, $T_{50, \text{ graphite}}$ and $T_{50, \text{ sample}}$ are the temperatures at which the graphite and biochar sample weight decreased by 50%, respectively.³⁴

5.3.10 ATR-FTIR analysis

DFB, CCPP, CAPP and MSPP (~1.0 g) were oven-dried at ~1 atm pressure and 60 °C for 24 h, ground and sieved to (250-300 μm particle size). Surface functions were analyzed using a Nicolet 6700FT-IR instrument with an attenuated total reflectance (ATR) accessory. FTIR spectra from 400 scans were recorded and averaged in the wavenumber range 4000–500 cm^{-1} with 2 cm^{-1} resolution

5.3.11 Determining soil buffering capacity and electrical conductivity.

A sandy surface soil (0-20 cm) was collected from the Mississippi State University research farm, air-dried, homogenized, ground, and sieved through 2 mm mesh before analysis. Prior to use, the soil was analyzed for physical and chemical properties at Mississippi State University soil testing laboratory (Table D.1), following the Lancaster Soil Test method described by Cox.³⁵ The soil had an initial pH of 5.64.

Soil buffering capacities were determined on 2.5 g samples in 50 mL polypropylene tubes, to which 0, 0.25, 0.5, 1, 2, 4, and 6 mL of 0.1 M HCl was added. In each tube, 0.05 M aqueous CaCl_2 was added to minimize variation of ionic strength. Deionized water was added to bring each total volume to 25 mL. All suspensions were equilibrated 24 h at 25°C and then removed from the shaker to equilibrate for another 7 d, during which the samples were shaken at 200 rpm for 2 min daily to re-suspend the sample. After 8 d of equilibration, pH was measured using the pH meter.

Then soil buffering capacity was obtained from the slope of a plot of the amount of acid added against solution pH. Soil electrical conductivity was determined following method by Mylavarapu et al.³⁶ Briefly, 10 mL of deionized water was added to 5 g of air-dried soil (at room temperature) in a polypropylene tube (in triplicate). These slurries were equilibrated on a reciprocating shaker (200 rpm) for 4h before filtering through Whatman number 42 filter paper. The EC was measured as described for the biochar in section 5.3.7 above.

5.3.12 Effect of Incorporating biochar on soil buffering capacity and electrical conductivity

To assess the influence of incorporating biochar on soil buffering capacity/electrical conductivity, air-dried soil was mixed with biochar samples at a (biochar:soil) ratio of 0 %, 10 %, 30 % and 50% (wt/wt). DI water was added to the mixtures to maintain water holding capacity near 80% of field capacity. After incubating at ~25°C for 30 days, soil/biochar was air-dried at room temperature, and pH buffering capacity/electrical conductivity were determined as for soil in section 5.3.11 above. Extractable nutrients and base cation exchange capacities of the incubated soil was also determined from Mississippi state soil testing laboratory as for the initial soil analysis.

5.4 Results and discussions

5.4.1 Time required for pH stabilization

Following acid additions at amounts of 0 mmol H⁺ kg⁻¹, 20 mmol H⁺ kg⁻¹ and 40 mmol H⁺ kg⁻¹, the pH stabilized within 72 h for MSPP, 96 h for neat soil, CCPP, and CCAP. The pH stabilized after 192 h for DFB. Also, the pH of MSSP after addition of 20 mmol H⁺ kg⁻¹ did not differ from that of 0 mmol H⁺ kg⁻¹ (Fig 5.1. a - e). In both cases, the pH values after 24-48h was 10.9 but changed to 11 after 72-216 h.

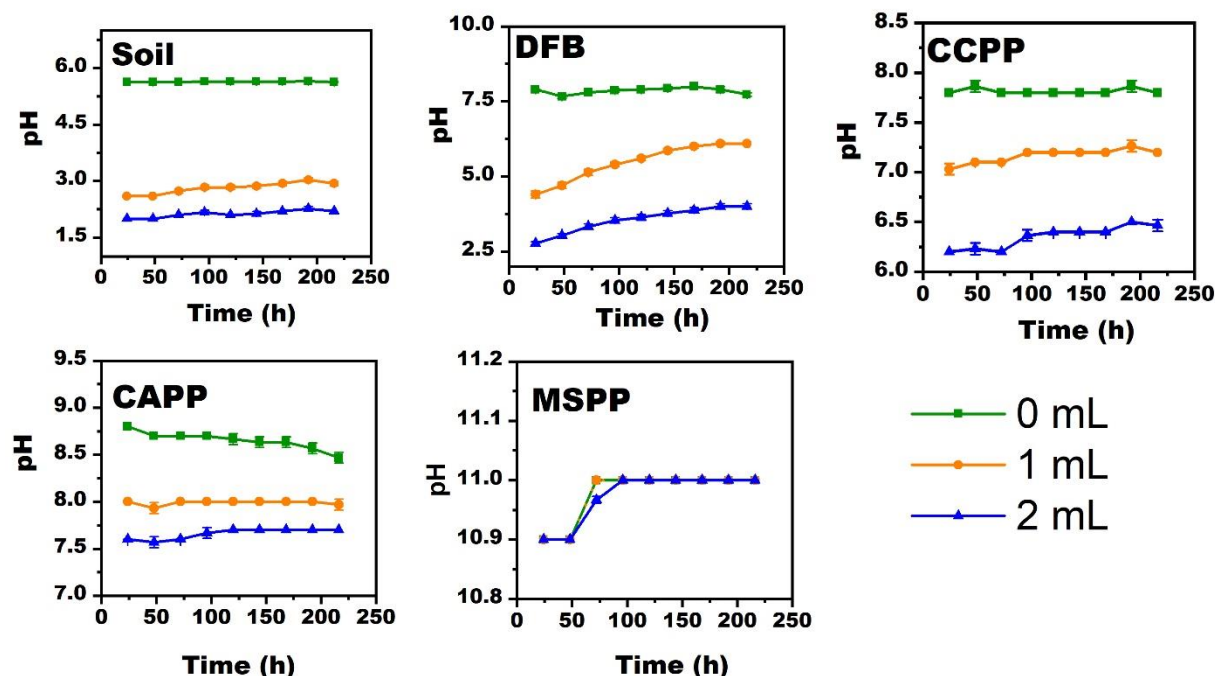


Figure 5.1 Time required to reach a stable pH after dilute acid addition of 0 mmol H^+kg^{-1} , 20 mmol H^+kg^{-1} and 40 mmol H^+kg^{-1} for a) neat soil (Soil), b) unmodified Douglas fir biochar (DFB), c) Douglas fir biochar treated with CaCl_2 and KH_2PO_4 (CCPP), d) Douglas fir biochar treated with CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ (CAPP) and e) Douglas fir biochar treated with MgSO_4 , KOH and KH_2PO_4 (MSPP). Values shown are mean, $n = 3$ and error bars shown as standard error of the mean

The pH versus time plots for neat soil, MSPP, CCPP and CCAP are shown in Fig. 5.1. In each case the difference between stabilized pH and initial pH (after 24 h) ranged between 0 to 0.3 units. For Douglas fir biochar however, the difference was 1.70 and 1.23 for 20 mmol H^+kg^{-1} and 40 mmol H^+kg^{-1} addition, respectively (Fig. 5.1).

The pH stabilization of neat soil, CAPP, CCPP, MSPP, and Douglas fir biochar occurred within 72 to 192 h after acid addition. The stabilization time varied for each material. Variable stabilization times have been reported for compost and oak biochar in other titration experiments.^{21,37} During compost titrations, pH stabilizes within 72 h after acid addition.³⁷

Mukherjee and colleagues²¹ reported that oak biochar pH stabilized within 2 h. Since stabilization time depends on the material, the longest time (192 h) was chosen for determining pH buffering capacities of neat soil and soil-biochar mixtures.

5.4.2 Biochar pH and electrical conductivity

The modified biochars exhibited significantly increased pH (Fig. 5.2) and EC (Table 5.1) values. The largest electrical conductivity increase upon modifying DFB was achieved with MSPP (1734 $\mu\text{S cm}^{-1}$). The other EC increases over DFB were 68 $\mu\text{S cm}^{-1}$ for CCAP and 1074 $\mu\text{S cm}^{-1}$ for CCPP. Similarly, MSPP, CCAP, and CCPP resulted in pH increases of 3.4, 1.3, and 0.3 units, respectively, over DFB. Numerous studies have reported biochar pH and EC increases are related to its ash content.^{38,39} In this study, the electrical conductivities were positively correlated with biochar's ash content ($r = 0.75$). Moreover, the ash contents were positively correlated to Mg, Ca, K, and P concentrations ($r \geq 0.4$). Therefore, the rise in EC following modification is ascribed to the increased salt content in the modified biochar. Similarly, the pH increase is attributed to rise in concentration of Ca^{2+} , Mg^{2+} , and K^{+} after modification.

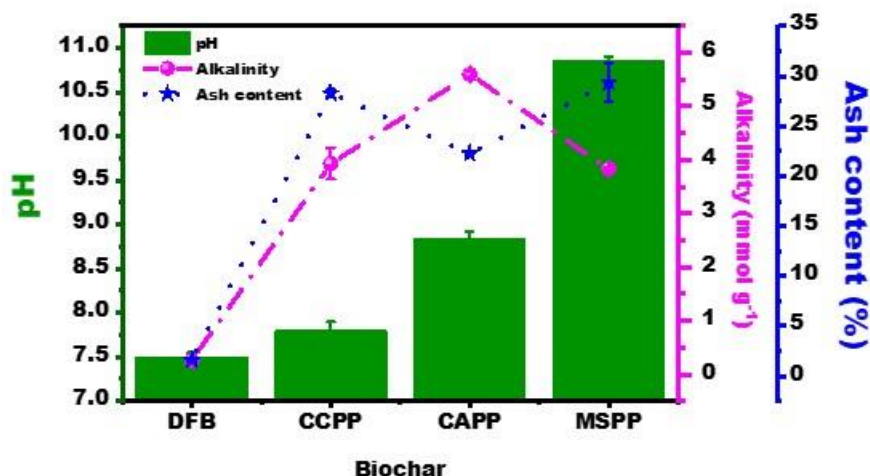


Figure 5.2 Alkalinity, ash content and pH for DFB: untreated Douglas fir biochar; CCPP: $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar; CCAP: $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ treated Douglas fir biochar and MSPP: $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar (Values shown are mean of $n=3$, error bars shown as standard error of the mean)

Table 5.1 Biochar's electrical conductivity (EC), acid functional groups amount and mineral concentrations

Biochar ^a	EC ($\mu\text{S cm}^{-1}$)	Acid functional groups (mmol g^{-1})				Metal concentrations (g kg^{-1})			
		phenolic	lactonic	carboxylic	Total	Mg	Ca	K	P
DFB	134.2 ± 3.21	0.023	0.013	0.004	0.04	0.95	3.40	0.45	0.01
CCPP	1208.7 ± 5.21	0.037	0.011	0.003	0.05	0.81	110.13	4.43	50.23
CCAP	201.8 ± 3.63	0.031	0.008	0.004	0.04	0.55	130.53	0.63	10.95
MSPP	1868.0 ± 40.5	0.024	0.005	0.003	0.03	23.64	0.14	68.50	0.18

^aDFB: Untreated Douglas fir biochar; CCPP: $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar; CCAP: $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ treated Douglas fir biochar; MSPP: $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar. Values shown are calculated using mean of $n = 3$

5.4.3 DFB, CAPP, CCPP and MSPP characterization

Total alkalinity varied extensively among the treated biochars treatments (0.27-5.60 mmol g^{-1}), with CCAP and DFB having the highest and lowest values, respectively (Fig. 5.2). Biochar pH measured in water rose with increasing total alkalinity ($r = 0.43$), but regression analysis indicated this variation was insignificant ($r^2 = 0.18$, P- value = 0.5).

Boehm titration of the acidic surface functions (lactonic, carboxylic, and phenolic) of all modified biochars measured a reduction versus DFB in both carboxylic (except for CCAP which did not differ), and lactones groups but an increase in phenolic groups (Table 5.1). The decrease in lactones followed the order CCAP> MSPP> CCPP, while the increase in phenolic functional groups followed the order CCPP> CCAP >MSPP. Biochar's pH decreased as the amount of all surface acid functional groups rose with correlation coefficients of ($r = 0.5, 0.8$ and 0.5) for carboxylic, lactonic and phenolic groups, respectively.

The modifications of Douglas fir biochar significantly enhanced both its metal concentrations (Table 5.1) and ash content (Fig. 5.2) irrespective of modification methods. MSPP had the largest increase in ash content (27.7%). Ash contents increased for CCPP (26.7%) and CCAP (20.7%), respectively. Ash contents for all biochars were positively correlated to Mg, Ca, K, and P concentrations ($r \geq 0.4$). Regression analysis indicated a positive, but insignificant correlation between ash contents and pH ($p\text{-value} = 0.4, r^2 = 0.35$).

An insignificant difference in pH of DFB and CCPP existed, despite the variation of their alkalinities. The highest (0.05 mmol g^{-1}) and lowest (0.03 mmol g^{-1}) total acidic functionals belong to CCPP and MSPP, respectively, while the total quantity of acid functions on DFB were comparable to that on CCAP (0.04 mmol g^{-1}). The total acid functionality was mostly due to the high pK_a (>7) phenolic groups especially for MSPP and CAPP. Thus, their contribution to pH can be insignificant. The lower pH of DFB versus CCAP and MSPP results from the greater contribution of its low pK_a lactones ($pK_a \sim 4$ to 7) and carboxylic acid ($pK_a \sim 2$ to 4) groups. The higher alkalinity of the modified biochars versus DFB could be due to a rise in base saturation after modification. Since biochar pH is influenced by both acid functional groups and nutrient

elemental concentrations,¹² the correlation between pH and total alkalinity suggests that pH may not solely be a result of biochar alkalinity.

Boehm titration indicated a reduction in carboxylic acid and lactone groups and an increase in phenolic groups on modification of DFB. Hence, enhancing phenolic concentration by modification could raise biochar pH. Furthermore, impregnation of biochar with basic metal salts increased its metal concentrations (Mg, Ca and K) and ash contents as shown by positive correlations between ash contents and Mg, K, Ca, and P concentrations ($r \geq 0.4$). Previous studies linked biochar's pH, ash content, and EC to their mineral metal concentrations.^{12,40} The increase in ash content after modification comes from the additional amounts of inorganics added. The enhanced concentrations of K, Mg, P and ash in MSPP versus DFB, CCAP, and CCPP explains its greater pH and EC. Gezahegn et al.,¹² analyzed biochars from 19 wood feedstocks, confirming that increases in pH, EC and ash content were highly correlated to biochar's mineral concentrations, particularly Ca and K. Therefore, results from this study suggest that biochar's alkalinity/liming value are largely controlled by its ash content (particularly Ca, Mg, and K), and by pH to a smaller degree. Accordingly, the low alkalinity shown by DFB despite its high pH indicate a smaller pH effect on biochar's alkalinity. These results agree with those of Shi et al.¹⁶

DFB, CCPP, CAPP and MSPP displayed heterogeneous surface morphologies (Fig. D.1). So, SEM images were taken from three different locations. DFB exhibited large internal pores originating from the wood structure. The xylem and phloem vascular structure have been maintained by the carbon matrix in DFB's images. Upon modification to CAPP, CCPP and MSPP, the morphology appeared more complex due to mineral aggregates on the surfaces. These mineral phases partially filled or blocked pores, lowering CAPP, CCPP and MSPP surface areas. BET surface areas (Table D.2) confirmed the reduction of DFB's surface area by ~254, ~264 and ~612

m² g⁻¹ after modification to CAPP, CCPP and MSPP, respectively.

SEM-EDX elemental surface region compositions of DFB, CAPP, CCPP and MSPP were taken from three locations in each to obtain a representative analysis (Fig. D.2). SEM-EDX interrogates to a depth of ~5.3 µm with a spot diameter of 4-6 µm. DFB exhibited, average C, O, P, Ca, K and Mg values for the three locations of ~87.04, ~9.47, ~0.84, ~0.71, ~1.54, ~0.10 %, respectively. After modifying to CAPP, CCPP and MSPP, the averaged analyses of three locations gave ~76.31, ~64.67 and ~31.12 C %, respectively. The corresponding values for % O, P, Ca, K and Mg are shown in Table 5.2.

Table 5.2 Average percent elemental composition analysis from three locations

Biochar ^a	Elemental composition (%)				
	O	P	Ca	K	Mg
CAPP	9.66	5.85	7.02	7.25	0.00
CCPP	20.29	6.41	1.17	0.79	24.40
MSPP	33.07	5.12	0.11	0.1	5.55

^aCCPP: CaCl₂ + KH₂PO₄ treated Douglas fir biochar; CCAP: CaCO₃ + (NH₄)₂HPO₄ treated Douglas fir biochar; MSPP: MgSO₄ + KOH + KH₂PO₄ treated Douglas fir biochar.

The average molar Ca/P ratios for CAPP and CCPP were ~0.93 and ~0.88, respectively. The theoretical molar Ca/P for CaHPO₄, CaHPO₄·2H₂O, Ca₈H₂(PO₄)₆·5H₂O and Ca₁₀(PO₄)₆·(HO)₂ are 1.00, 1.00, 1.33 and 1.67, respectively,⁴¹ suggesting phosphate deposited mostly as CaHPO₄ and CaHPO₄·H₂O on CAPP and CCPP surfaces. XRD analyses of MSPP revealed phosphate occurred as MgHPO₄·3H₂O and Mg₃(PO₄)₂·5H₂O. These depositions raise the amount of surface oxygen. In contrast, the carbon contribution drops as the surface is partly covered by mineral depositions. Pore blockages at the surface agrees with the decline in MSSP, CCPP and CAPP BET surface area compared to DFB (Table D.2). Pore blockages by surface deposition was previously reported by.⁴²

The XRD analyses of DFB, CCPP, MSPP and CAPP (Fig. D.3) identified the mineral species deposited. DFB XRD spectra showed two broad peaks like those of layered graphene between $2\theta = 20^\circ$ to 30° and 40° to 50° , attributed to graphitic-like diffraction created as lignocellulostic structures are partly aromatized during pyrolysis.⁴³

New peaks inorganic appeared in MSPP, CCPP and CAPP. In MSPP, major diffractions were observed due to MgO at $2\theta = \sim 43^\circ$ [JCPDS file No. 45-0946],⁴⁴ Mg(OH)₂ at $2\theta \sim 19^\circ$ and $\sim 38^\circ$ [JCPDS card no. 00-007-0239],^{45,46} hydrated MgHPO₄·3H₂O [JCPDS No. 72-0023] and Mg₃(PO₄)₂·5H₂O [JCPDS No. 35-0329].⁴⁷ Both CAPP and CCPP exhibited major diffractions at $2\theta = \sim 11.6^\circ$, $\sim 21^\circ$, $\sim 28.4^\circ$, $\sim 32^\circ$, $\sim 40.6^\circ$, $\sim 46.8^\circ$, $\sim 49.9^\circ$ and $\sim 64.2^\circ$ matching those of hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂ [JCPDS card Number 09-0432].^{48,49} CCPP additional peaks at $2\theta = 9.4^\circ$, 26° and 53° matched octacalcium phosphate (OCP, Ca₈H₂(PO₄)₆·5H₂O), [ICDD number 261056].⁴⁹

CAPP also contained calcium carbonate (CaCO₃) diffractions at $2\theta = \sim 29.4^\circ$, $\sim 39.6^\circ$ and $\sim 48.4^\circ$ [ICDD PDF No. 5-0586]⁵⁰ and dibasic calcium phosphate dihydrate (CaHPO₄·2H₂O, Brushite) diffractions appeared at $2\theta = \sim 23^\circ$, $\sim 29^\circ$ and $\sim 31.4^\circ$ [ICDD PDF No. 09-077].⁵⁰ Other amorphous P-containing species might be present on CAPP, CCPP and MSPP but would not be observed by XRD due to their poor crystalline order.

5.4.4 Thermogravimetric analysis (TGA)

TGA thermograms of DFB, CAPP, CCPP and MSPP conducted under nitrogen at 10 °C min⁻¹ are shown in Fig 5.3. All samples lost mass going upto 1000°C due to progressive carbonization. CCPP did not differ much from DFB but CCAP underwent a sharp mass loss at $\sim 700^\circ\text{C}$ perhaps because of excess CaCO₃ in this sample undergoing its well-known decomposition reaction to CaO.^{51,52} Its limited CaCO₃ content prevented a greater mass loss.

MSPP exhibits major weight losses from 350-1000 °C after minor weight losses from 30 – 350 °C. MSSP showed the largest first weight loss (~6.2%) between 30-242 °C likely due to water of hydration losses from inorganics. MSSP also contains KOH which above 600°C causes activation reactions resulting in carbon losses, pore diameter and surface area increases. The low temperature weight losses for CCPP and DFB were comparable (1.3%) occurring between 30-170°C and 97.2-180°C, respectively. CCAP showed greatest thermal stability at the start with an initial weight loss of ~1.9% between 326.6 - 383°C. In all cases, the initial weight loss involves elimination of chemically unbound moisture. MSPP undergoes major weight loss at ~350°C which accelerates above 700°C. Major weight loss for DFB, CCAP, and CCPP occurred at much greater temperatures (> 600°C). A drop in biochar thermal stability after MgO impregnation is known.⁵³ The calculated recalcitrance index (R50) for MSPP was ~0.99. However, the recalcitrance index (R50) for DFB, CCAP and CCPP were not calculated because the weight loss of 50% was not realized upto 1000°C. A biochar with a recalcitrance index (R50) > 0.7 is considered a class A biochar with carbon sequestration potential similar to graphite.⁵⁴ The recalcitrance indices (R50) corresponding to DFB, CCPP and CAPP are likely to be >1. MSPP's reduced recalcitrance index (R50) due to its higher alkali content and known for KOH activation. R50 value of wheat straw biochar increased from ~0.46 to ~0.55 after washing to remove alkali contents.⁵⁵ Mineral content analysis followed the orders MSPP > CCPP > CAPP > DFB (for K), MSPP > DFB > CCPP > CAPP (for Mg²⁺), CAPP > CCPP > DFB > MSPP (for Ca²⁺) and CCPP > CAPP > MSPP > DFB (for P).

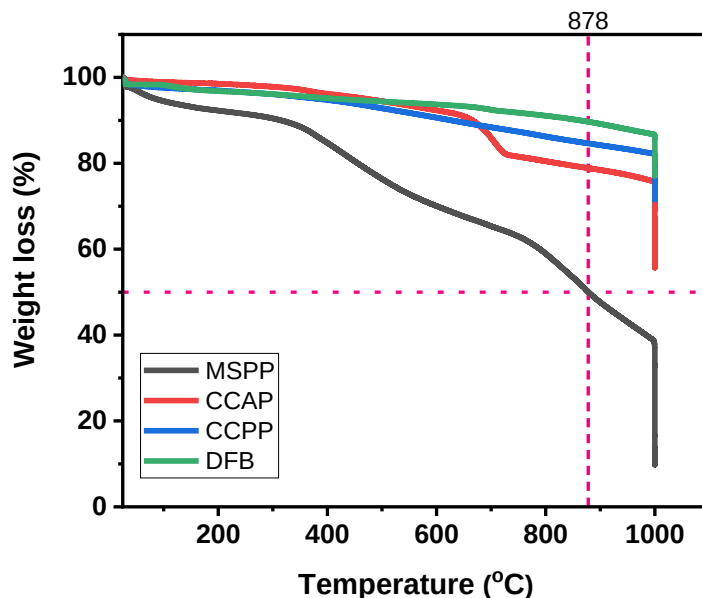


Figure 5.3 TGA thermograms for unmodified Douglas fir biochar (DFB), Douglas fir biochar treated with CaCl_2 and KH_2PO_4 (CCPP), Douglas fir biochar treated with CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ (CCAP) and Douglas fir biochar treated with MgSO_4 , KOH and KH_2PO_4 (MSPP) at heating rate of $10\text{ }^\circ\text{C min}^{-1}$ for heating temperatures range of 25 to $1000\text{ }^\circ\text{C}$.

5.4.5 FTIR-ATR analysis

FTIR-ATR analyses (Fig. 5.4) were run to identify surface functional group changes on treated biochars. The FTIR-ATR spectra for DFB, CCPP (CaCl_2 plus KH_2PO_4 modified Douglas fir biochar), CCAP (CaCO_3 plus $(\text{NH}_4)_2\text{HPO}_4$ modified Douglas fir biochar) and MSPP (MgSO_4 plus KOH plus KH_2PO_4 modified Douglas fir biochar) are shown in (Fig. 5.4).

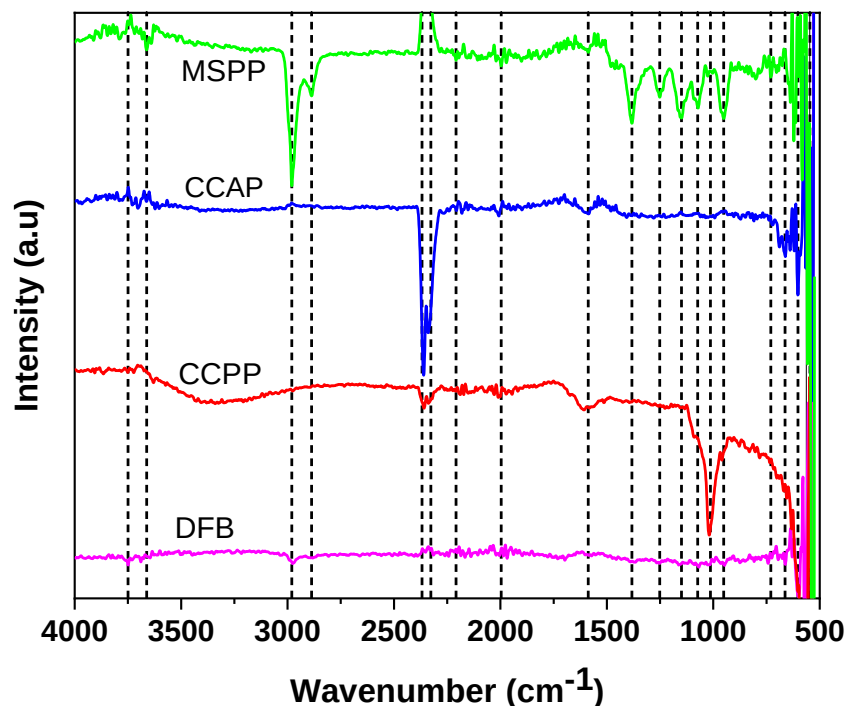


Figure 5.4 FTIR-ATR spectra for unmodified Douglas fir biochar (DFB), $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ modified Douglas fir biochar (CCPP), $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ modified Douglas fir biochar (CCAP) and $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ modified Douglas fir biochar (MSPP)

Weak absorptions between $3670\text{--}3550\text{ cm}^{-1}$ are due to hydrogen-bonded hydroxy groups in the chars phenol, $\text{Mg}(\text{OH})_2$ and hydroxyapatite.⁵⁶ Bands at 2971 and 2887 cm^{-1} were assigned to asymmetric and symmetric sp^3 hybridized C–H stretches.⁵⁷ C–O stretching at 1252 , 1150 , 1149 cm^{-1} were assigned carboxylic acids, variscite and phenols respectively. Bands due to CO_3^{2-} ions occurred at 1382 cm^{-1} , 880 , 860 and 711 cm^{-1} . Absorption at 638 , 622 and 613 cm^{-1} were attributed to stretching of Mg–O–Mg bonding in $\text{Mg}(\text{OH})_2$. Phosphates were observed at 1072 and 950 cm^{-1} due to P–O symmetric and asymmetric stretching, respectively. P–OH vibrations ascribed to HPO_4^{2-} occurred at 1588 cm^{-1} .^{58,59}

5.4.6 Soil buffering capacity and electrical conductivity

Soil buffering capacity is the amount of acid required to reduce the pH of a unit mass of soil by 1 unit.⁶⁰ Buffering capacity was obtained from the slope of the linear regression fit of the amount of H^+ ion added to soil versus pH responses.

The soil pH decreased in proportion to the quantity of acid added ($r^2 > 0.9$). The unamended soil buffering capacity was $8.00 \text{ mmol kg}^{-1} \text{ pH}^{-1}$. This capacity can be influenced by CEC, organic matter and clay content which affect protonation and deprotonation in soil. The sandy loam soil used here was low in clay and organic matter. Soil pH buffering capacity is primarily affected by variations in CEC. Soil pH buffering capacities determined from HCl addition for 20 different soil samples ranged from 3.2 to $57.7 \text{ mmol kg}^{-1} \text{ pH}^{-1} \text{ unit}$.⁶¹ Buffering capacities varied from 9.1 to $32.1 \text{ mmol kg}^{-1} \text{ pH}^{-1}$ in 24 acidic soils signifying that soil properties impact pH buffering capacity¹.

5.4.7 The effects on soil buffering capacity and electrical conductivity of incorporating biochar

The pH response of our soil/biochar mixtures to acid addition were fitted with a linear regression function. The regression results were significant for CCPP, CCAP, and MSPP samples ($p \text{ value} \leq 0.01$ with $r^2 \geq 0.9$) but insignificant for the unamended soil and soil amended with DFB. The buffering capacities ranged from $(8.23 \pm 0.17 - 82.63 \pm 1.42 \text{ mmol kg}^{-1} \text{ pH}^{-1})$ over all samples assessed. The highest and lowest improvements were recorded with CCAP and DFB, respectively (Fig. 5.5a).

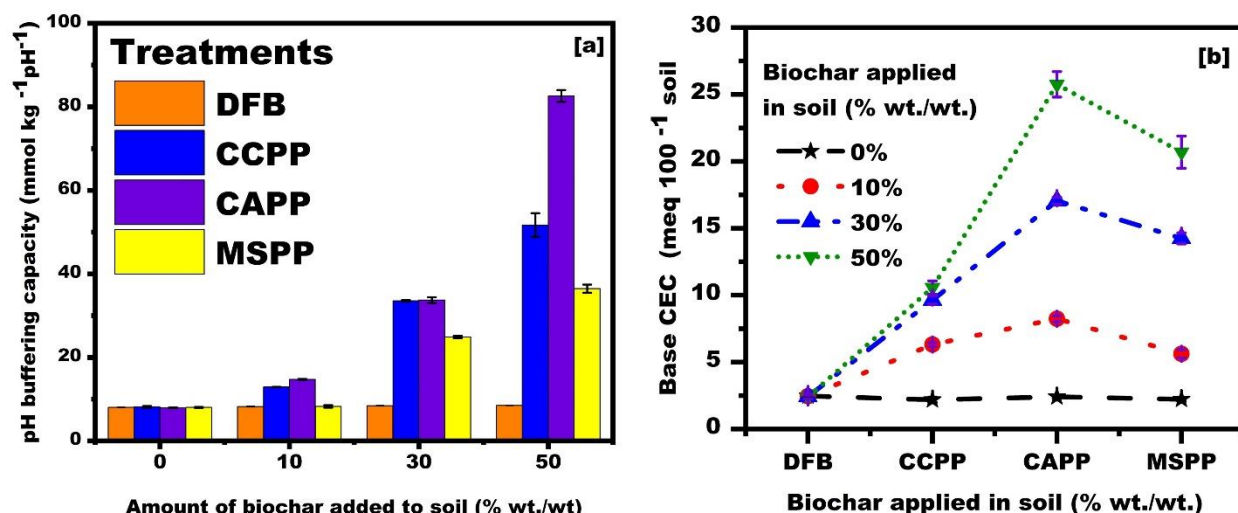


Figure 5.5 Influence of biochar amendment on; (a) the soil pH buffering capacity (BC) and (b) Cation exchange capacity (CEC) after a 30-day incubation with DFB = Unmodified Douglas fir biochar, CCPP = Douglas fir biochar modified with $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$, CCAP = Douglas fir biochar treated with $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$, and MSPP = Douglas fir biochar modified with $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$. (Values used = average of 3 replicate, errors bars shown as Standard error of the mean).

Both pH buffering capacity and the cation exchange capacity (Fig. 5.5 a and b, respectively) increased with a rise in the quantity of biochar added to soil (50% > 30% > 10% > 0%). However, the increase in the buffering capacity for soil amended with DFB was much less than the increase induced with CCPP, CAPP, and MSPP.

Besides the oxygen-containing groups on the biochars surface, which buffer acid soil by protonation and deprotonation at low and high pH, respectively, the modified biochars contain added oxides, hydroxides and carbonates of bases such as Mg, K, and Ca which can enhance their ash content, alkalinity, and pH.¹ In this study, DFB had the lowest alkalinity, ash content, and pH (Fig 5.2). Since biochar's buffering capacity is associated with its alkalinity^{62,63}, the low buffering capacity of DFB is due to its low concentrations of basic cations and alkalinity. Improvement in both alkalinity and pH buffering capacity followed the order CCAP > CCPP > MSPP > DFB (Fig.

5.2 and 5.5a, respectively). Residual soil CEC followed the order CAPP>MSPP>CCPP>DFB (Fig. 5.5b). Also, the residual soil CEC was highly correlated ($r \geq 0.9$), with the soil buffering capacity (Fig. D.4). MSPP had higher concentrations of K and Mg, but greater concentrations of Ca were present in CCAP and CCPP than MSPP. Therefore, Ca concentrations in biochar seem to exert a greater influence on alkalinity and buffering capacity than Mg and K. The affinity for exchange sites varies for different cations based on their charge (valence) and size (hydrated radius).⁶⁴ The greater the charge, the stronger the ion is attracted to the negatively charge surface by electrostatic forces. For example, $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$. Hence, Ca^{2+} is preferred to Mg^{2+} and K^+ because of its smaller effective hydration radius⁶⁵ and larger charge density. In addition, the greater solubility of calcium hydroxide in water makes it a stronger base than magnesium hydroxide. Magnesium hydroxide has a larger lattice energy than calcium hydroxide requiring more energy to form Mg^{2+} and OH^- ions in solution, lowering its solubility. Since pH buffering capacity depends on cation exchange sites, soil additives containing Ca^{2+} are likely to create greater impacts than those containing Mg^{2+} and K^+ . Ca^{2+} benefits from greater exchange site affinities and lower lattice energy.

Incorporating biochar in soil significantly increased soil electrical conductivity (Fig 5.6). The EC increase was greater in modified biochar-amended soil than by adding DFB because increased salt concentrations released to the soil influences EC. Modified P- enriched biochar (CCPP, CCAP and MSPP) release the metal cation counter ions to HPO_4^{2-} and H_2PO_4^- . Overall, greater metal concentrations and ash contents are released by the p-enriched biochars than DFB. Previously, increased soil EC was reported following biochar amendments,⁶⁶ but this influence depended on the feedstock used. In this study, EC values were within the non-saline range of 0-2000 μscm^{-1} ,⁶⁷ indicating that P-enriched biochars can be used for soil amendment

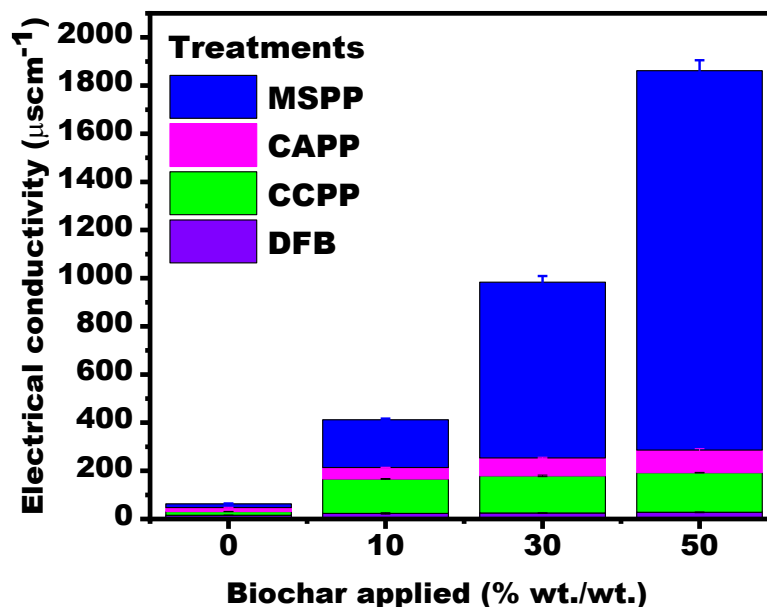


Figure 5.6 The impact of biochar amendment on soil electrical conductivity (EC). DFB = unmodified Douglas fir biochar, CCPP = Douglas fir biochar modified with $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$, CCAP = Douglas fir biochar treated with $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$, and MSPP = Douglas fir biochar modified with $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$. (Values are average of $n=3$. Error bars shown as SEM)

5.4.8 Nutrient release to soil

The extractable nutrient concentrations increased with the amount of biochar amendments added (Fig 5.7). MSPP and CCPP released increasing amounts of extractable P, Ca, Mg and K that were highly correlated to the quantity of biochar applied ($r > 0.9$). CAPP treatments released P, Ca and K amounts that were highly correlated to the amount of biochar applied ($r > 0.9$) but Mg gave a negative correlation ($r = \sim -0.6$) as the mass of biochar increased. DFB soil treatments gave positive, K and Mg correlations to the biochar quantity ($r = \sim 0.9$ and ~ 0.7 , respectively), but increasing the amount of DFB did not significantly affect P concentrations ($r = -0.009$). In addition, the extractable calcium decreased with increasing amount of DFB ($r = -0.9$).

The extractable soil nutrient concentration is an indication of the nutrient availability to plants because of amendment treatments. This increase in extractable P, Ca, Mg, and K as the amount of biochar amendment ratios increased is one measure of the potential for these three P-enriched biochars to function as fertilizers. In addition, MSPP treatments had significantly increased extractable K concentrations, but Ca concentrations were less than those from CCPP and CAPP treatments (Fig. 5.7). The enhanced Ca concentrations from CCPP and CAPP treatments explain the higher alkalinity observed with CCPP and CAPP additions and the role of Ca in regulating pH buffering capacity discussed earlier in section 5.4.7. Furthermore, the negative correlations linked to DFB reaffirm its low ash contents, EC, alkalinity and pH buffering ability.

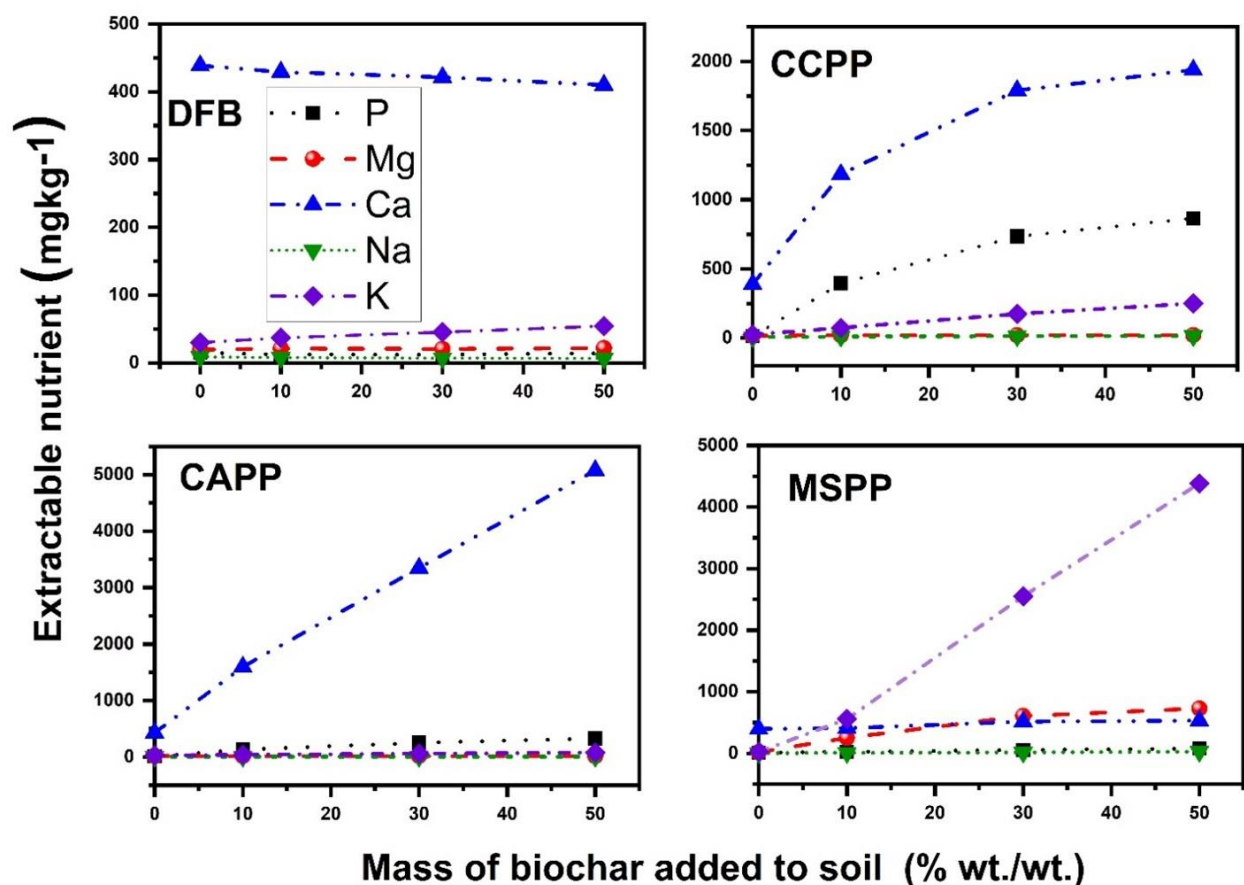


Figure 5.7 Extractable nutrients after incubating soil with different masses of DFB, CCPP, CAPP and MSPP biochar (%wt./wt.)

5.5 Conclusions

Incorporation of modified P-enriched Douglas fir biochar to an acidic soil increased pH buffering capacity. The improved buffering capacity was greater for soil amended with biochar modified with calcium-containing salts. The lower lattice energy associated with calcium hydroxides versus magnesium hydroxide is the probable reason for the greater buffering capacity rise with high Ca²⁺ contents. Also, Ca²⁺ has greater affinity for cation exchange sites compared to Mg²⁺, and K⁺, which is an advantage for biochar treated with calcium salts. The three modified Douglas fir biochars (CCPP, CAPP and MSPP) provided increased pH, ash content (P, K, Mg and

Ca), and alkalinity. Amendment of acidic soils with modified P-enriched biochar provides both liming and fertilization benefits. Overall, modification of Douglas fir biochar had little effect on P-enriched biochars thermal stability. However, high potassium contents promote biochar weight loss at high temperatures, resulting in a reduced recalcitrance index. The biological stability of P-enriched Douglas fir biochar to prove its usefulness in carbon sequestration should be further assessed.

5.6 Acknowledgement

Mississippi State University, Department of Chemistry, Fulbright Organization and US Department of State are thanked for the Scholarship awarded to Beatrice Arwenyo

5.7 Conflict of interest

Authors declare no conflict of interest

5.8 References

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CHAPTER VI

GENERAL CONCLUSIONS AND RECOMMENDATIONS

There is growing acceptance of the use of biochar as a soil additive. In the current era of climate change, the use of biochar for improved soil productivity is not only seen as a viable eco-friendly substitute to synthetic fertilizer, but a noble contributor in fighting climate change. While several agricultural and environmental benefits have been accredited to biochar, most studies focused on agricultural and biowaste products as suitable feedstocks (raw materials for biochar). Other potential sources such as commercial biochar have not been widely investigated. Besides, information on phosphorus enriched modified biochar is scarce.

This research was therefore designed to investigate P-enriched modified-Douglas fir biochar potential as a soil additive. Douglas fir biochar is a commercial by-product from syn gas production. It is available in large scale and can be cheaply obtained (considered to be a waste byproduct). The study specifically looked at P-enriched modified-Douglas fir biochar ability to release soluble P required for plant uptake, improve plant growth and P use efficiency, buffer acidic soil and minimize soil heavy metal mobility.

Greenhouse studies were conducted to compare phosphorus enriched modified-Douglas fir biochar suitability with commercial synthetic triple superphosphate fertilizer and a control (soil without amendment) using corn as experimental crop on acidic sandy soil. Incubation studies were also performed to assess phosphorus enriched modified-Douglas fir biochar liming and heavy metal immobilization efficacies.

Results from this study indicated insignificant differences between soil available P from the P enriched modified-Douglas fir biochar treatments and the commercial triple superphosphate fertilizer treatment. This indicates P enriched modified-Douglas fir biochar ability to release required plant available P. In addition, direct correlations between both K and Mg recoveries with available soil P, suggested P enriched modified-Douglas fir biochar potential to supply plant soluble K and Mg. the greater agronomic P use efficiency obtained from the P enriched modified-Douglas fir biochar ($\sim 32 \text{ kg kg}^{-1}$) than the triple super phosphate fertilizer ($\sim 17 \text{ kg kg}^{-1}$) treatment confirms P-enriched modified-Douglas fir biochar potential use as a multiple nutrient released fertilizer.

Furthermore, biochar-supported phosphate (BP) effectively reduced Pb^{2+} mobility in simulated contaminated soil. The formation of insoluble lead-containing hydroxyapatite at $\text{pH} < 7$ minimizes the possibility of Pb^{2+} uptake by plant and the likely transfer to humans through food chain. The amendment of acidic soils with modified P-enriched modified-biochar provided liming benefits which is consistent with previous research. Modification of Douglas fir biochar with basic salts had little effect on the thermal stability of the resulting products. However, high potassium content seems to promote biochar oxidation, resulting in a reduced recalcitrance index (~ 0.99 in MSPP).

This study offers indicative evidence for P enriched modified-Douglas fir biochar application as a plausible soil additive. In addition to the carbon sequestration and waste management benefits, the results suggested that the use of phosphorus enriched modified-Douglas fir biochar as a soil amendment improves soil buffering capacity, plant available P, heavy metal retention and plant P use efficiency. This reduces the need for continuous fertilization, lime application and the risk of water contamination and plant uptake, and transfer of heavy metal to

human via food chain. This suggest that the use of phosphorus enriched modified-Douglas fir biochar in agricultural soil is a feasible relatively low-cost, effective, and environmentally sustainable soil management and P recycling strategy.

I should emphasize that this study was largely concern with Douglas fir biochar, a commercially available by product from syn gas production. Similar studies need to be done with biochar from different feedstock and pyrolysis conditions. Other possible areas for further research could be to:

1. Investigate the effects of simultaneous application of K and Mg in other soil types with different fertilizer sources.
2. Establish optimal P loading rates for biochar enrichment.
3. Validate the mechanism of P uptake from P enriched modified-Douglas fir biochar in a field experiment scale.
4. Examine future application of BP for immobilization of Cd, Hg and As.
5. Assess the biological stability of P-enriched Douglas fir biochar to prove its usefulness in carbon sequestration

APPENDIX A
SUPPORTING INFORMATION FOR CHAPTER II

A.1 Phosphorous availability from Magnesium P-enriched Douglas fir biochar as controlled released fertilizer

Table A.1 Basic soil properties

Texture	pH	Cation exchange Cations (Milliequivalents Per 100 gm)	Extractable Nutrient Levels (Pounds per Acre)						
			P	K	Ca	Mg	Zn	Na	S
Sandy	5.5	2.01	37	89	388	30	0.60	31	0

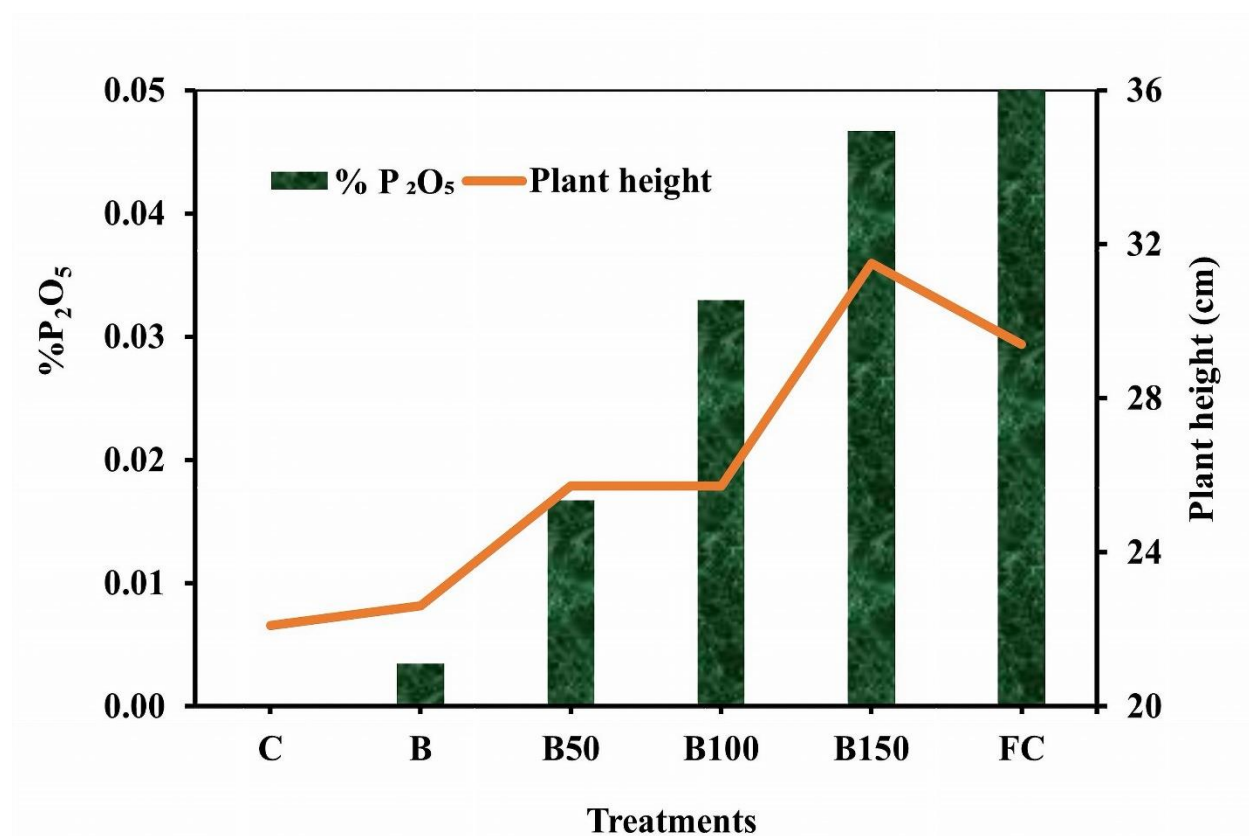


Figure A.1 Influence of % P₂O₅ in Control (C), Modified Douglas fir biochar (B), P enriched Biochar (B50, B100, and B150), and superphosphate fertilizer (FC) treatments on plant heights. To compare to biochar P with the reference superphosphate fertilizer (FC), P loading was converting into units of P₂O₅ (superphosphate fertilizer P₂O₅ % (46 %))

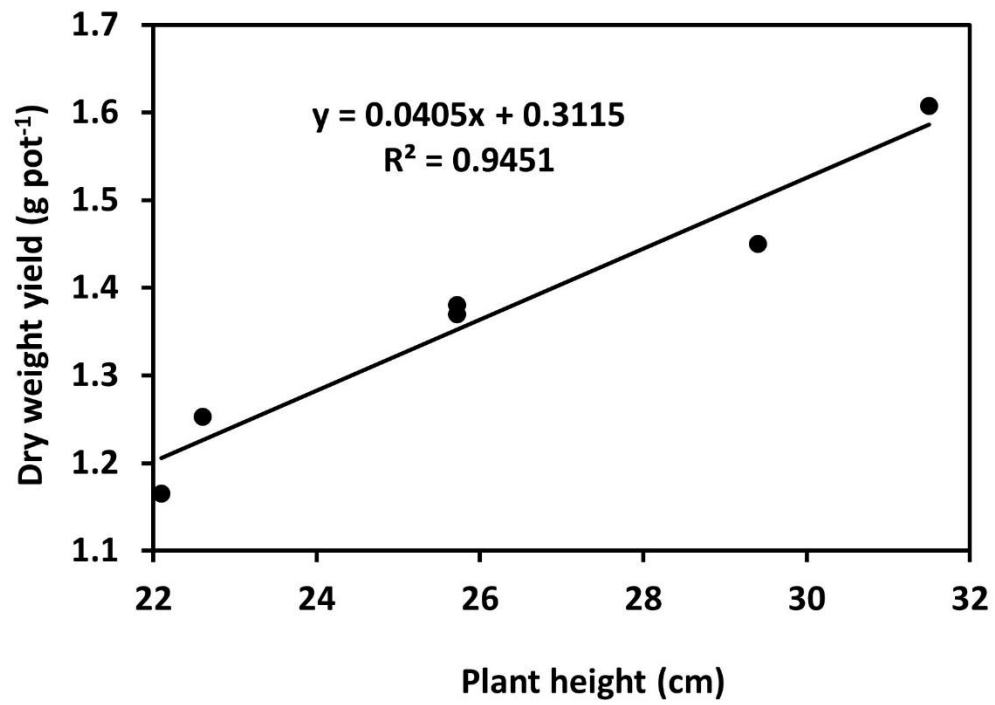


Figure A.2 Regression analysis of average plant height and average above ground biomass dry weight yield (DW yield), p value = 0.001 at 95% confidence level,

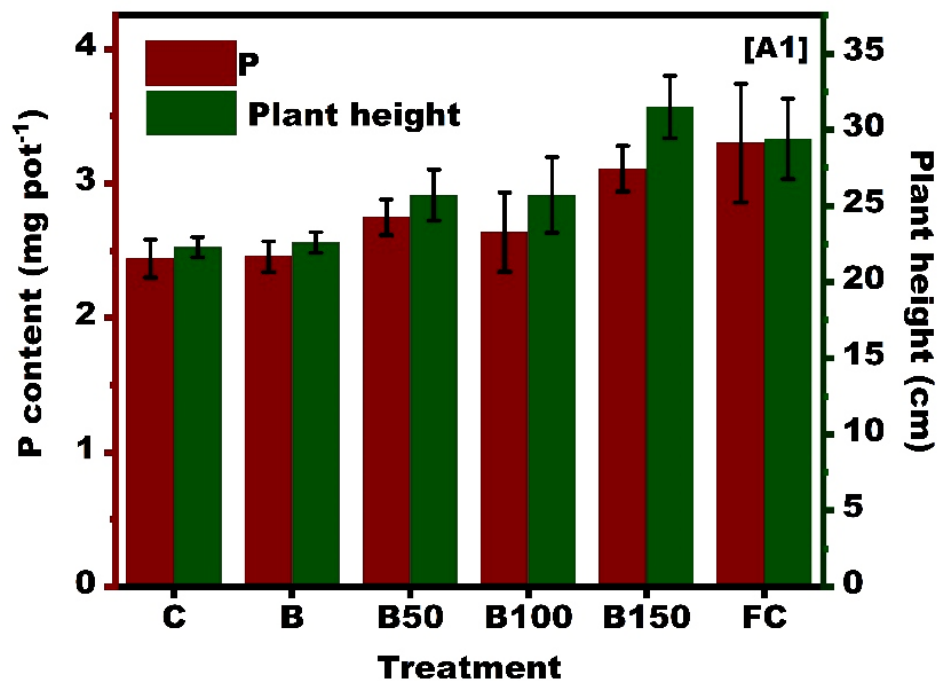


Figure A.3 The influence of P uptake on Plant Height (A₁), and Dry weight yield (A₂) in Control (C), Modified Douglas fir biochar (B), P enriched Biochar (B50, B100, and B150), and superphosphate fertilizer (FC) treatments. (Error bars shown as standard error of mean, n= 4)

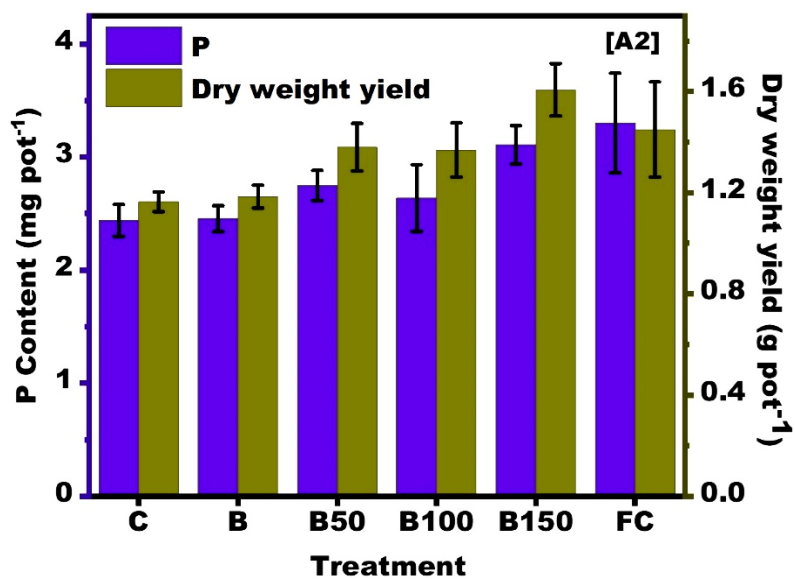


Figure A.3 (Continued)

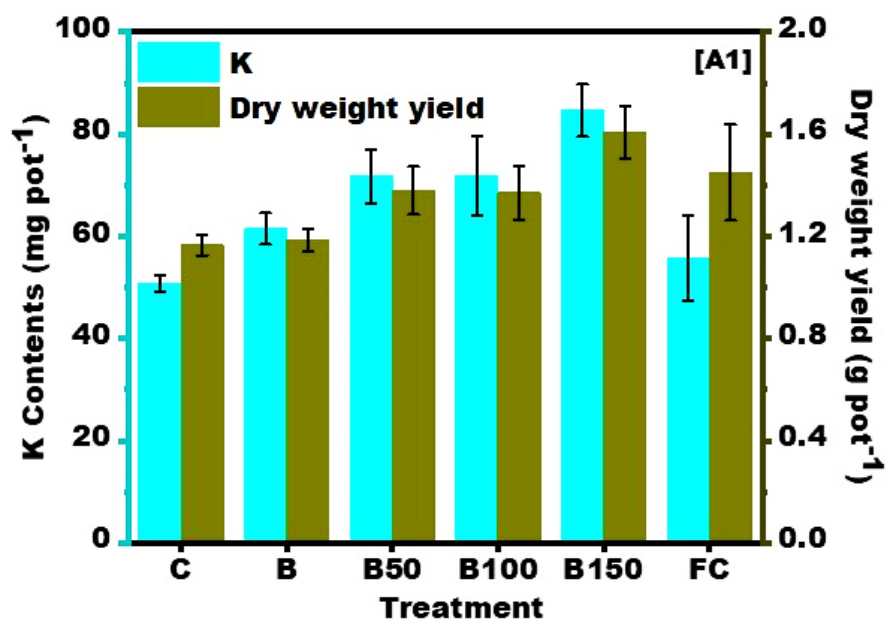


Figure A.4 Variations of Dry weight yield with K uptake (A₁), Dry weight yield with Mg uptake (A₂) and K uptake with Mg uptake (A₃)

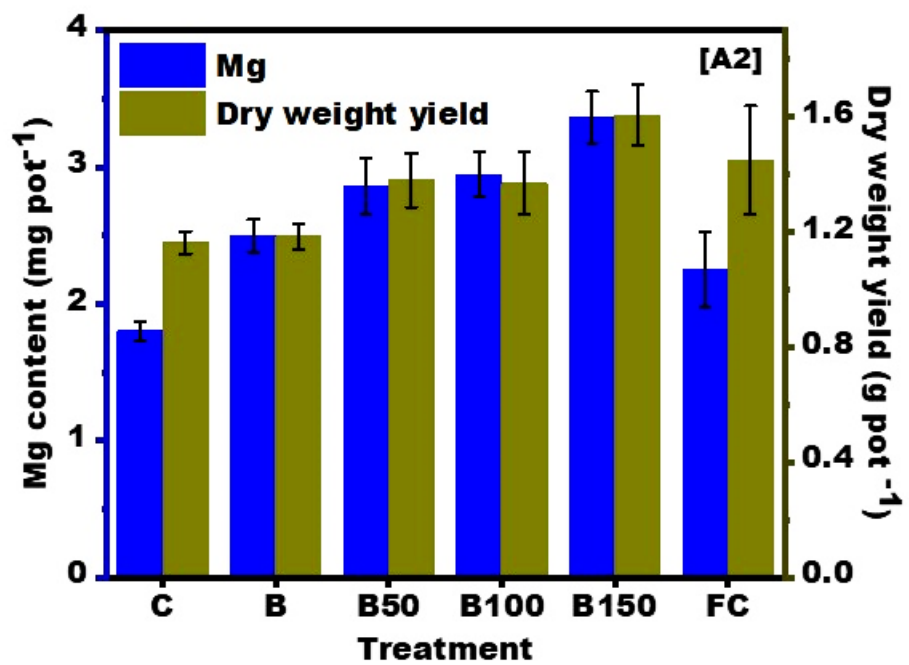


Figure A.4 (Continued)

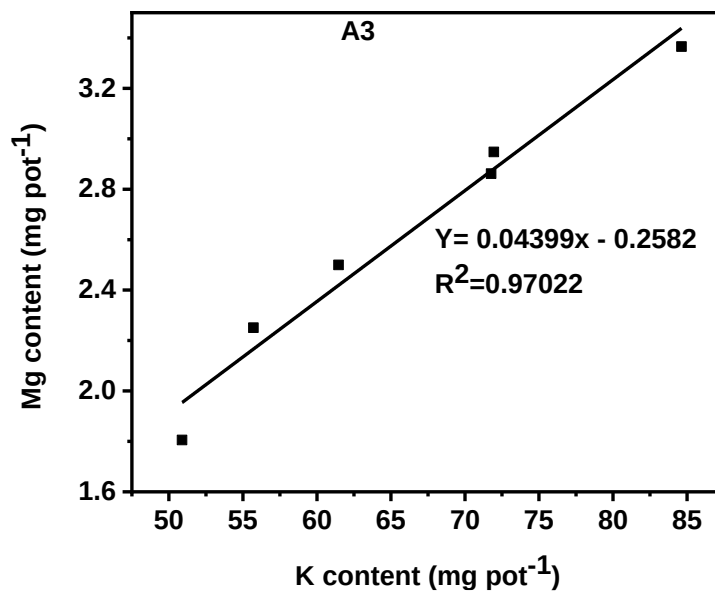


Figure A.4 (Continued)

APPENDIX B
SUPPORTING INFORMATION FOR CHAPTER III

B.1 Uptake of phosphorus from modified P-enriched Douglas fir biochar and its effects on crop growth and P use efficiency

Table B.1 Selected initial soil chemical properties

CEC (cmol kg ⁻¹) ^a	pH	Extractable nutrient levels (kg ha ⁻¹)						% Base saturation		
		P	K	Mg	Ca	Na	Zn	Ca	K	Mg
1.65	5.60	6.28	101.76	15.08	604.28	41.46	0.12	81.52	0.07	3.40

^aCEC= Cation exchange capacity (centimole per kg of soil)

Table B.2 BET Surface analysis of DFB, MB and PEB

Sample ^a	BET surface area (m ² g ⁻¹)	Adsorption average pore diameter (Å)	Total pore volume (cm ³ g ⁻¹)
DFB	514.567	12.465	0.192
MB	14.640	11.934	0.005
PEB	3.134	10.862	0.001

^aDFB = untreated Douglas fir biochar, MB= Douglas fir biochar modified with magnesium sulphate and potassium hydroxide solutions, PEB=P-enriched modified Douglas fir biochar

Table B.3 Ash content, Ca, Mg, K and P concentrations of DFB, MB and PEB

Biochar ^a	Ash content (%)	Total elemental concentration (g kg ⁻¹)			
		Ca	Mg	K	P
DFB	3.07 ± 0.20	45.75 ± 0.62	49.16 ± 0.43	52.86 ± 0.73	41.04 ± 1.29
MB	24.80 ± 0.12	45.01 ± 0.81	112.00 ± 3.27	94.67 ± 3.65	41.55 ± 1.93
PEB	25.10 ± 0.12	45.73 ± 0.56	104.79 ± 2.69	78.70 ± 1.94	95.72 ± 1.64

^a DFB = untreated Douglas fir biochar, MB= Douglas fir biochar modified with magnesium sulphate and potassium hydroxide solutions, PEB=P-enriched modified Douglas fir biochar (values presented = average ± Standard error of the mean, n=3).

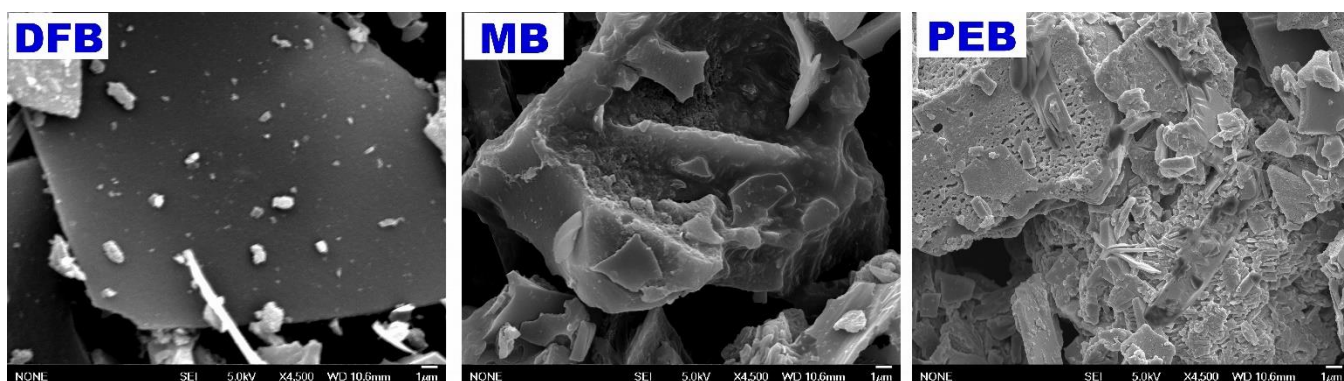


Figure B.1 Scanning Electronic Microscopy (SEM) of biochar before modification (DFB), after modification (MB) and after enrichment with phosphate (PEB)

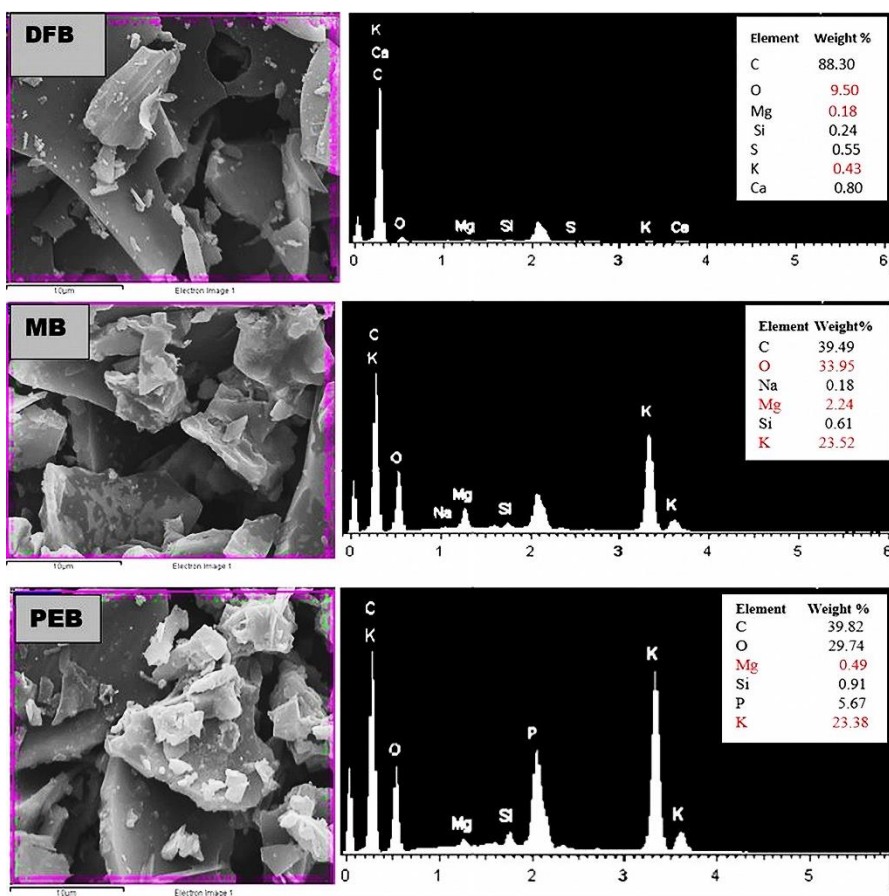


Figure B.2 Energy-Dispersion X-ray Spectroscopy (EDS) images of biochar before modification (DFB), after modification (MB) and after enrichment with phosphate (PEB)



Figure B.3 Plant growth at different application rates of Triple super phosphate fertilizer (SPF), MB plus potassium dihydrogen phosphate (PEB), and Douglas fir biochar plus MgSO_4 Plus KOH (MB).



Figure B.4 Plant growth at 120 kg P ha^{-1} (left) and 90 kg P ha^{-1} (right) application rates after amendment with Triple super phosphate fertilizer (SPF), MB plus potassium dihydrogen phosphate (PEB), and Douglas fir biochar plus MgSO_4 Plus KOH (MB).

APPENDIX C
SUPPORTING INFORMATION FOR CHAPTER IV

C.1 Lead immobilization in simulated polluted soil by Douglas fir biochar-supported phosphate

Table C.1 Sequential extraction procedure for lead in soil

Step	Fraction	Extraction procedure
1	Water soluble	20 mL Deionized water 16 h, 25 °C
2	Exchangeable	20 mL 1 M MgCl ₂ , pH 7 1h, 25 °C
3	Carbonate-bound	20 mL 1 M CH ₃ COONa, pH 5 with CH ₃ COOH, 5 h, 25 °C
4	Fe-Mn oxide-bound	20 mL 0.04 M NH ₂ OH-HCl pH 2 with CH ₃ COOH, 5 h, 96 °C
5	Organic form	5 mL 0.02 M HNO ₃ , 5 mL 30% H ₂ O ₂ 2 h, 85 °C Followed by 5 mL 30% H ₂ O ₂ 2 h, 85 °C Then 5 mL 3.2 M CH ₃ COONH ₄ in 20% HNO ₃ for 0.5 h at 25 °C
6	Residual form	Acid digestion following US EPA method 3050B

Source ¹⁻³

Table C.2 Soil physiochemical properties

Texture	pH	Mineral concentrations (mg kg ⁻¹)				
		P	Mg	Ca	K	Na
Sandy	5.64	8.94 ± 0.01	18.25 ± 0.16	475.42 ± 0.92	26.68 ± 0.36	5.99 ± 0.07

Value shown are mean ± standard deviation, n = 3

Table C.3 Properties of Douglas fir biochar (BC) and biochar-supported phosphate (BP)

Property	BC	BP
pH	9.30	6.63
Ash Content (%)	3.59 ± 0.06	38.12 ± 0.18
N (%)	0.12 ± 0.01	0.08 ± 0.00
C (%)	79.37 ± 0.24	50.86 ± 0.53
H (%)	1.79 ± 0.01	1.37 ± 0.03
S (%)	0.01 ± 0.01	0.07 ± 0.06
O (%)	15.12 ± 0.22	9.50 ± 0.50
C/N ratio	751.80 ± 35.87	741.62 ± 7.65
H/C ratio	0.27 ± 0.00	0.32 ± 0.01
O/C ratio	0.14 ± 0.00	0.14 ± 0.01
BET surface area (m ² g ⁻¹)	578.90 ± 3.21	360.53 ± 0.34
Pore volume (cm ³ g ⁻¹)	0.07	0.12
Average pore diameter (Å)	4.55	13.40

Data are shown as the Mean ± SD, n = 3.

Table C.4 Kinetic parameters of pseudo-first-order and pseudo-second-order expressions

Model	Capacity and constants	Adsorbent	
		BC	BP
Pseudo first order	$q_{\max}$ (mg g ⁻¹)	80.33 ± 1.26	81.06 ± 1.84
	k_1 (min ⁻¹)	5.63 ± 1.11	5.91 ± 0.49
	r^2	0.724	0.858
Pseudo second order	$q_{\max}$ (mg g ⁻¹)	82.63 ± 0.58	83.08 ± 1.45
	k_2 (g mg ⁻¹ min ⁻¹)	0.13 ± 0.01	0.14 ± 0.02
	r^2	0.958	0.928

Table C.5 Freundlich and Langmuir isotherm constants for adsorption of Pb²⁺ ions onto BC and BP

Model	Constants	Adsorbent	
		BC	BP
Freundlich	K_F	13.28 ± 1.87	19.17 ± 0.57
	n	1.82 ± 0.16	2.18 ± 0.06
	R^2	0.972	0.997
Langmuir	$q_{\max}$ (mg g ⁻¹)	122.03 ± 8.16	102.75 ± 0.32
	K_L (Lmg ⁻¹)	0.065 ± 0.01	0.12 ± 0.00
	R^2	0.985	0.988

K_L and K_F are Langmuir bonding term related to interaction energies (Lm g⁻¹) and the Freundlich affinity coefficient (mg(1⁻ⁿ) Ln g⁻¹), respectively. C_e and $q_{\max}$ denotes the equilibrium solution concentration (mg L⁻¹) and the Langmuir maximum adsorption capacity (mg g⁻¹) of the sorbate, respectively. q_e is the quantity of solute adsorbed per gram of the adsorbent at equilibrium (mg g⁻¹), n signify the Freundlich linearity constant and R^2 is the coefficient of determination.

Table C.6 Comparison of pb^{2+} sorption capacities of different adsorbent

Adsorbent	Langmuir			Freundlich			Reference
	Q mg g^{-1}	K_L	R^2	n	K_F	R^2	
Chicken manure biochar (CM)	11.30	3.39	0.471	3.86	12.40	0.036	⁴
Green waste biochar (GW)	6.53	3.91	0.966	7.03	4.34	0.842	⁴
Douglas fir biochar (BC)	122.03	0.07	0.985	1.82	13.28	0.972	This study
Hydroxyapatite (HAP)	121.74	0.15	0.984	1.59	44.26	0.970	⁵
Pine Needle Biochar (PNBC)	31.81	0.02	0.945	1.73	1.67	0.882	⁶
Nano Tricalcium phosphate	761.90	0.02	0.982	4.69	1214.39	0.943	⁷
Douglas fir biochar-supported phosphate (BP)	102.75	0.12	0.988	2.18	19.17	0.997	This study

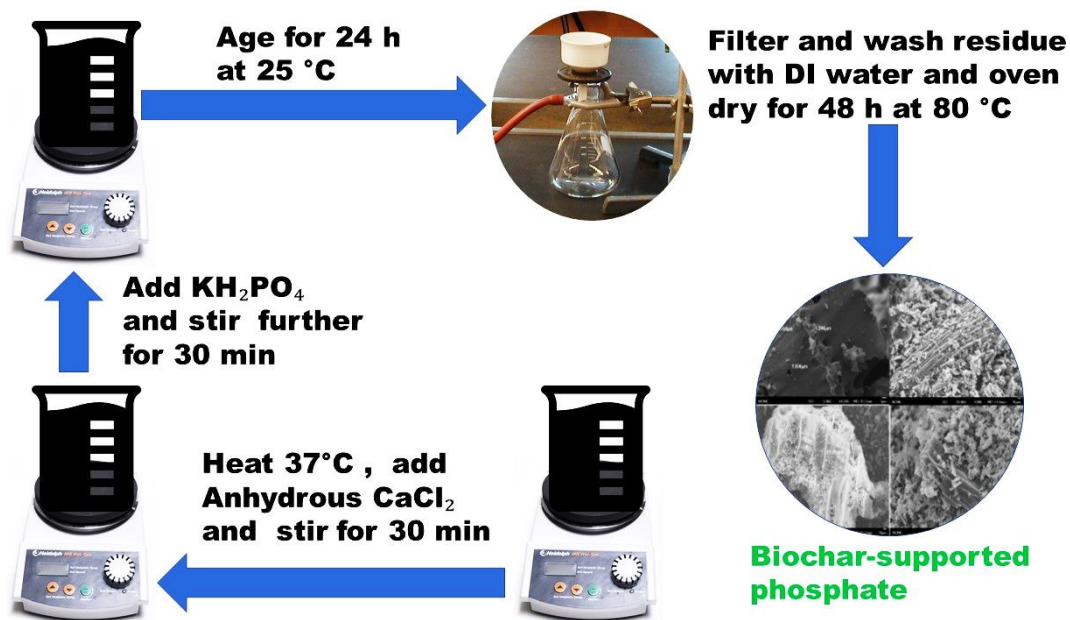


Figure C.1 Preparation scheme for biochar supported phosphate (BP) from Douglas fir biochar (BC), anhydrous calcium chloride and potassium dihydrogen phosphate

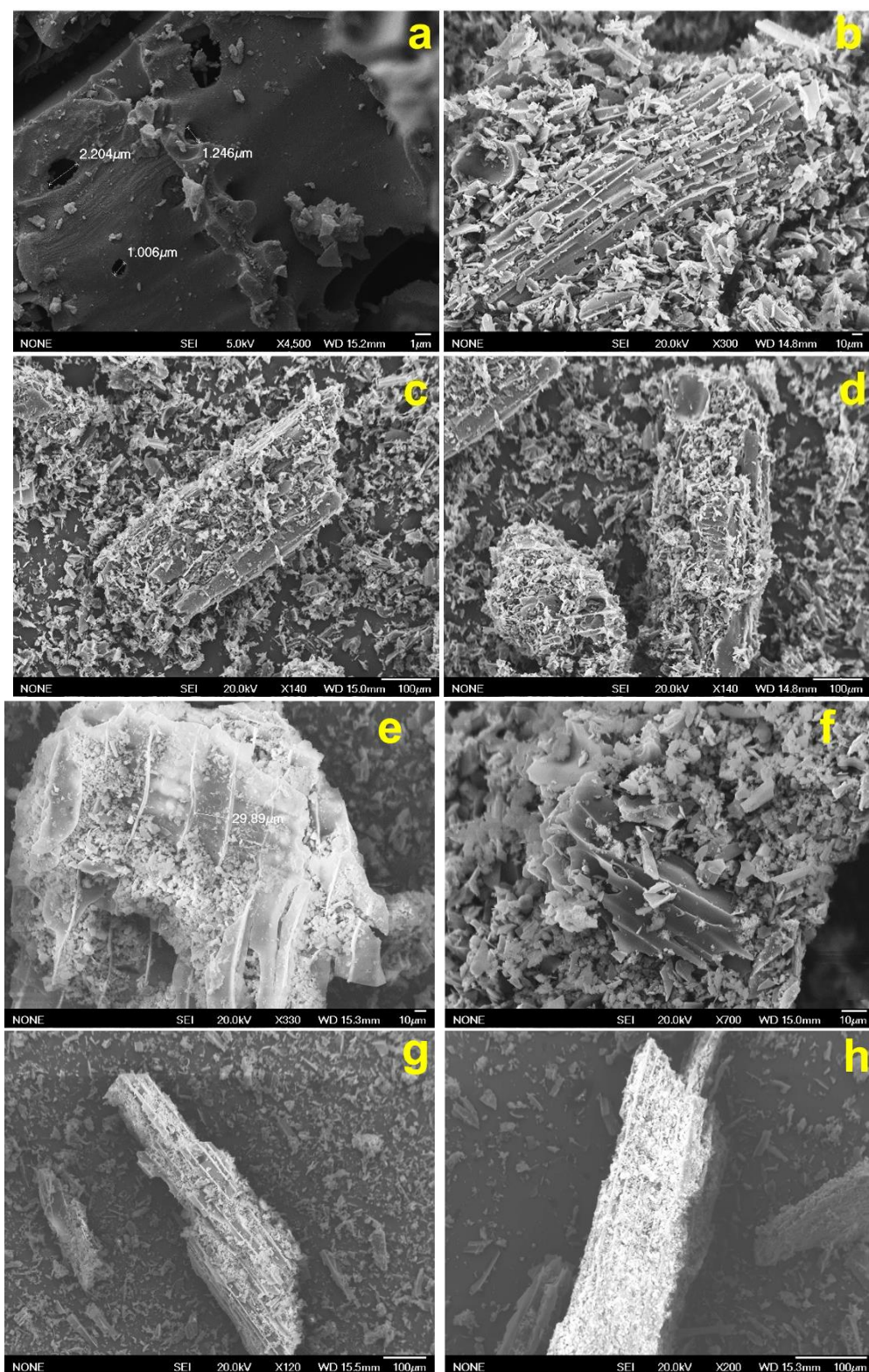


Figure C.2 SEM micrographs for BC (a-d) and BP (e-h)

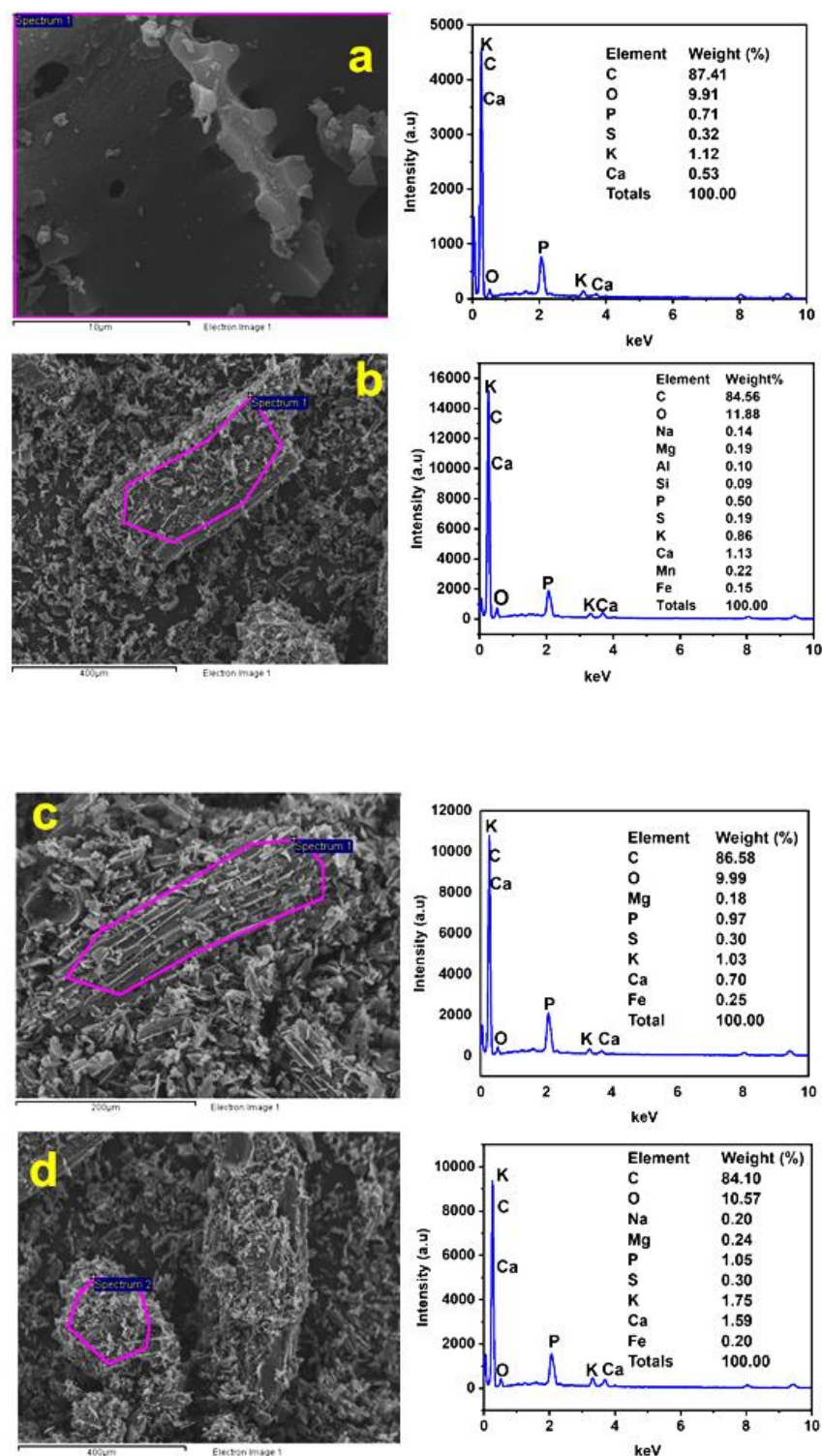


Figure C.3 SEM-EDX images showing the morphology and elemental composition of four locations on the BC surface before (a-d) and after modifying BC to BP with anhydrous calcium chloride and potassium dihydrogen phosphate (e-h).

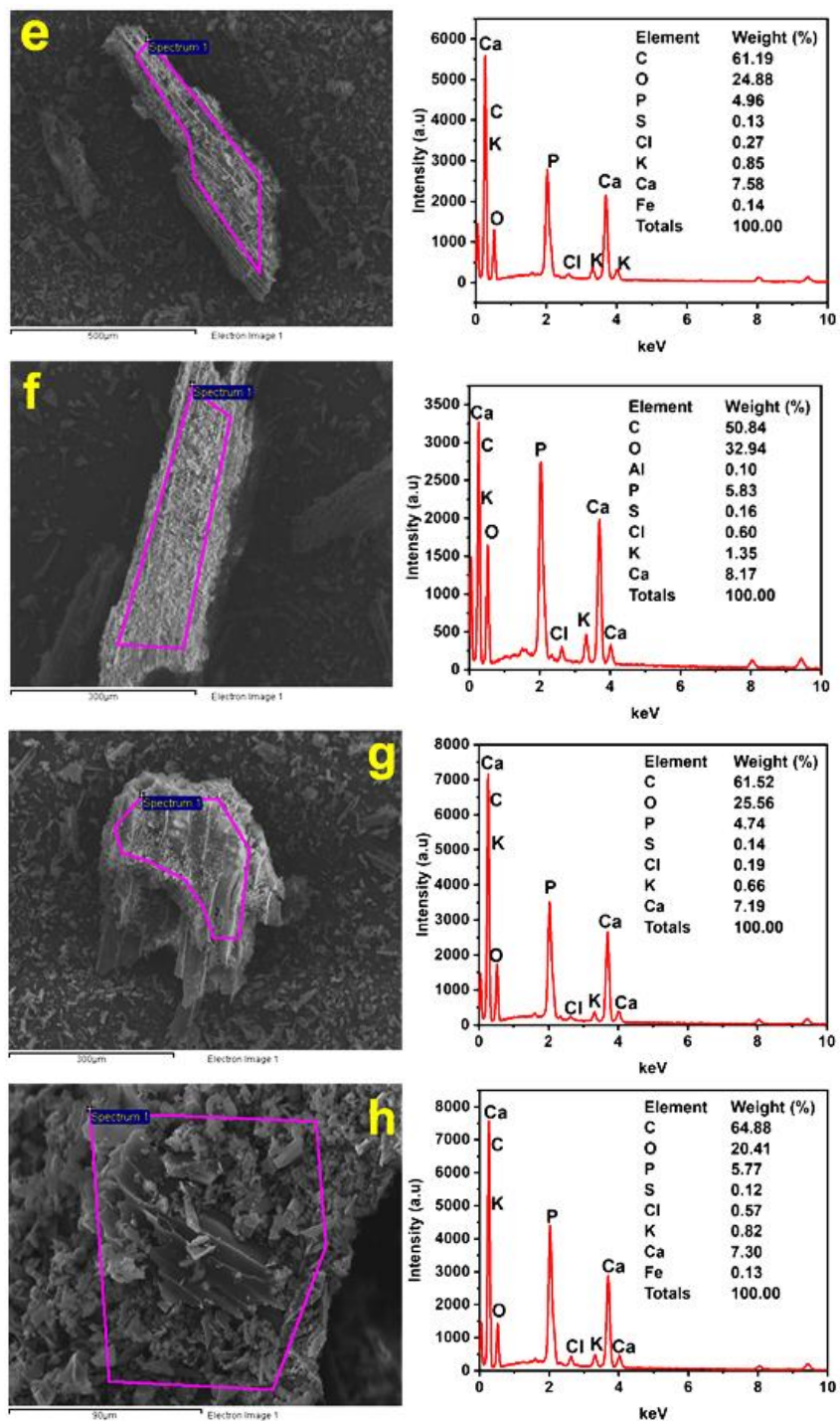


Figure C.3 (Continued)

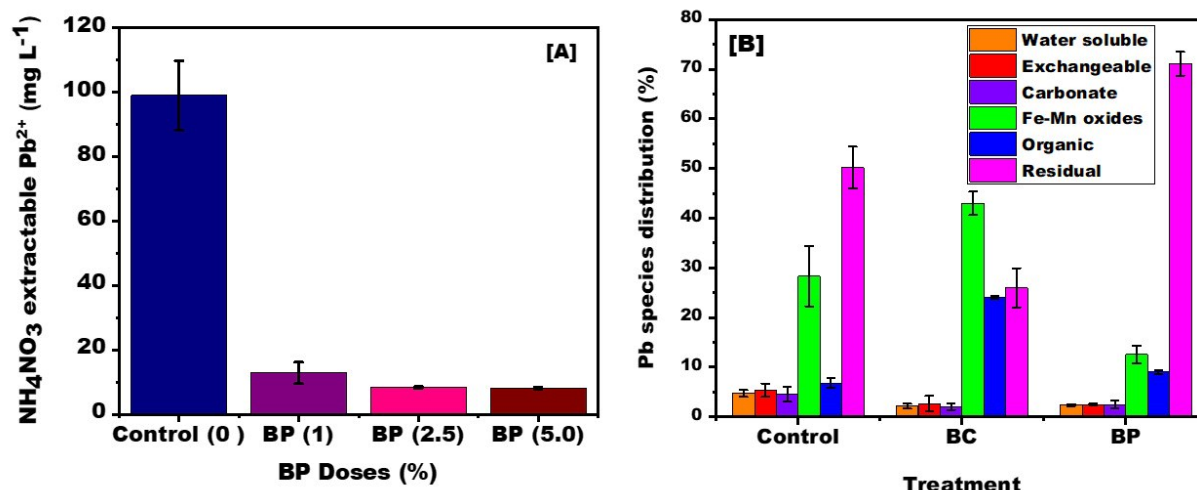


Figure C.4 NH₄NO₃-extractable Pb²⁺ concentration of Pb-spiked soils amended with different doses of BP. Control: (Pb-spiked soil without amendment), BP -1%: (Pb-spiked soil plus 1% BP), BP -2.5%: (Pb-spiked soil plus 2.5% BP), and BP-5%: (Pb-spiked soil plus 5% BP) [A] and distribution of different lead fractions in lead-spiked soil before (control) and after a 30-d incubation with 5% BC or 5% BP [B]. Values used are average of n=3, error bars shown as SD.

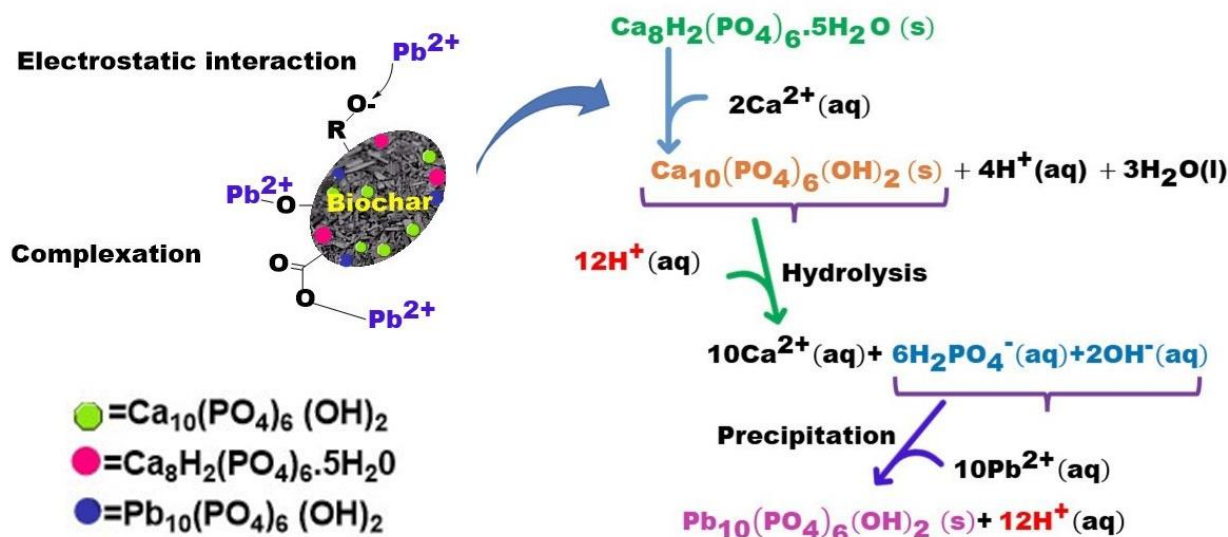


Figure C.5 Immobilization mechanism of Pb²⁺ onto BP

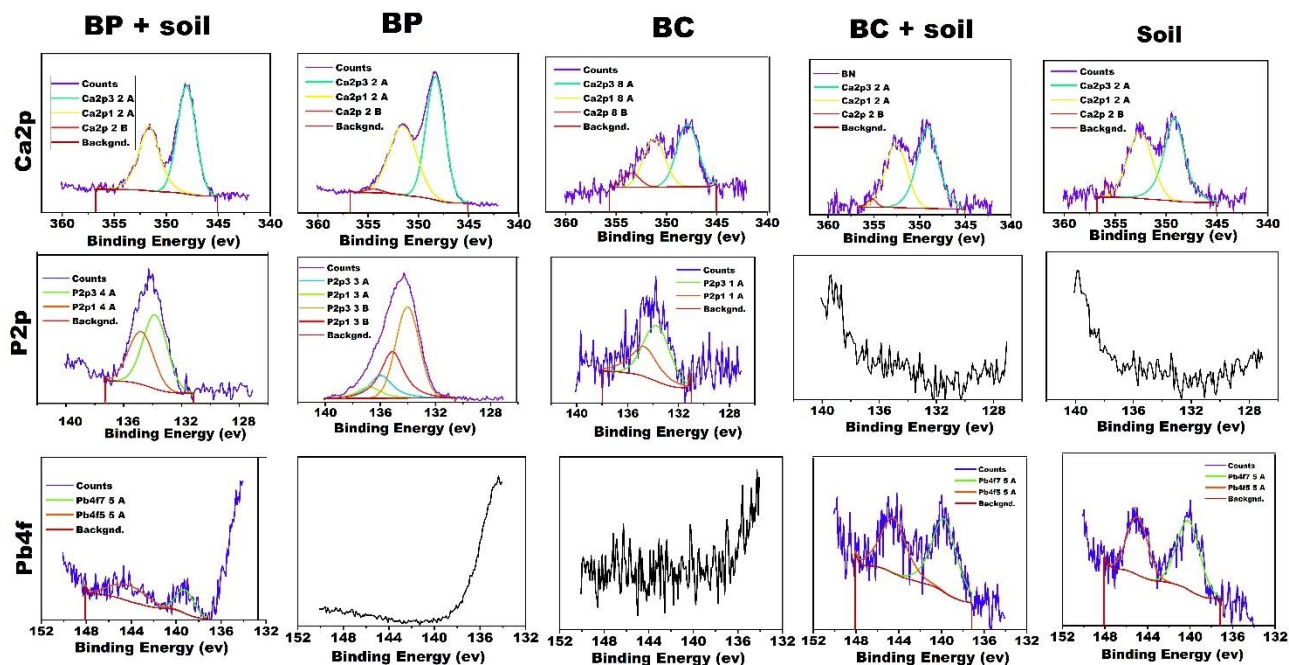


Figure C.6 XPS O1s, Ca2p, P2p and Pb4f spectra for BC, BP, lead-spiked spoil, lead-spiked soil amended with %BC and lead-spiked soil treated with 5% BP after a 30-d incubation.

C.2 References

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APPENDIX D
SUPPORTING INFORMATION FOR CHAPTER V

D.1 Investigating the contribution of modified P-enriched biochar on acid soil's pH buffering capacity

Table D.1 Soil physiochemical characteristics

Texture	pH	CEC	Extractable nutrient concentrations (mg kg ⁻¹)				
			P	Mg	Ca	K	Na
Sandy	5.64	2.62	8.94 ± 0.01	18.25 ± 0.16	475.42 ± 0.92	26.68 ± 0.36	5.99 ± 0.07

CEC = cation exchange capacity in cmol kg⁻¹ soil). (Value shown are mean ± standard deviation, n =3)

Table D.2 Surface area, pore size diameter and average pore volume of DFB before and after modifying to CAPP, CCPP and MSPP.

Parameter	DFB	CCPP	CAPP	MSSP
BET surface area (m ² g ⁻¹)	615.65 ± 0.22	362.13 ± 0.34	351.19 ± 0.74	3.20 ± 0.01
Pore volume (cm ³ g ⁻¹)	0.19	0.11	0.12	0.00
Pore size (Å)	12.47	13.00	13.46	10.86

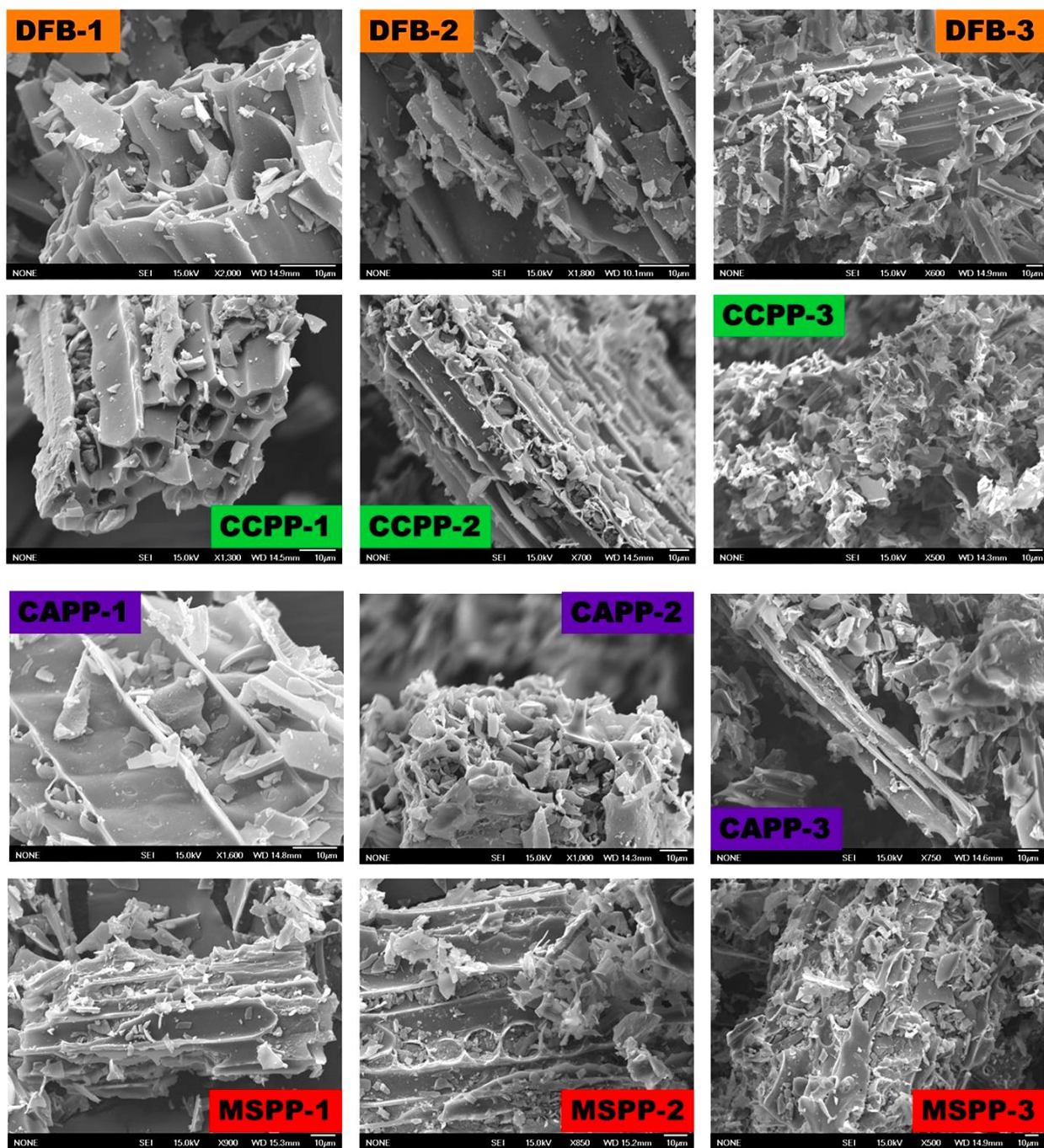


Figure D.1 SEM micrographs for DFB, CCPP, CAPP and MSPP.

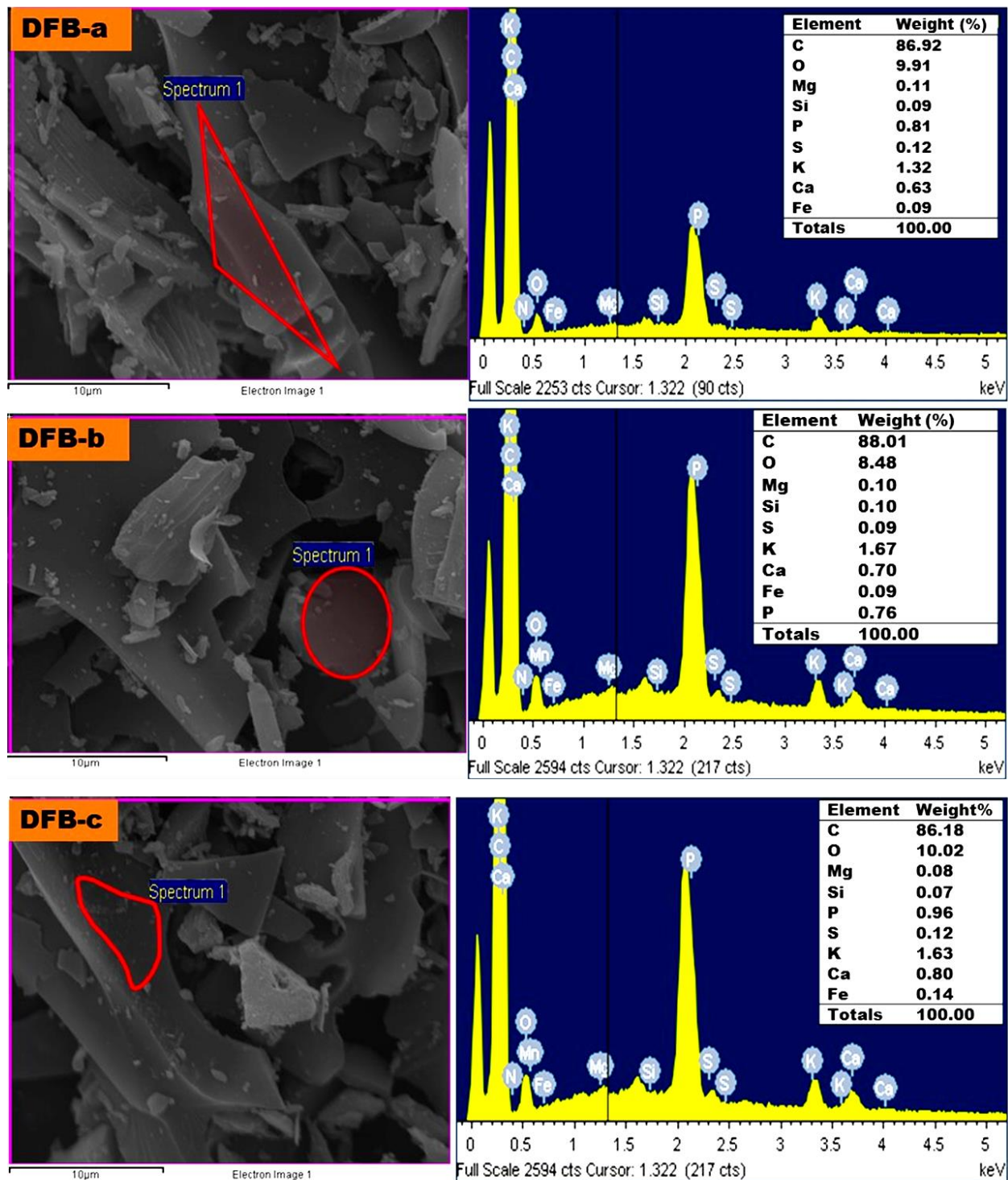


Figure D.2 SEM-EDX spectra of DFB before and after modifying to CAPP, MSPP and CCPP taken from different locations

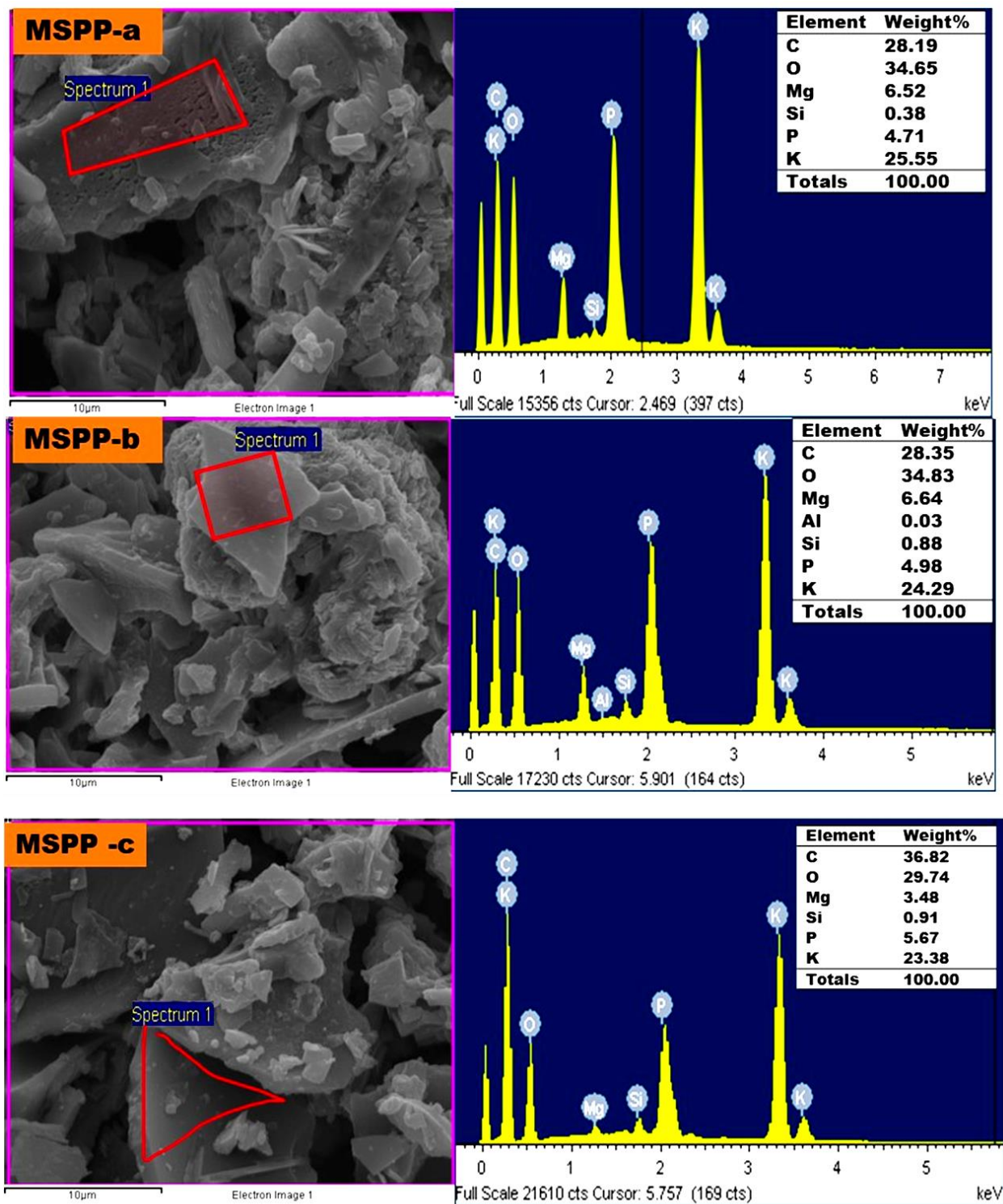


Fig. D.2 (continued)

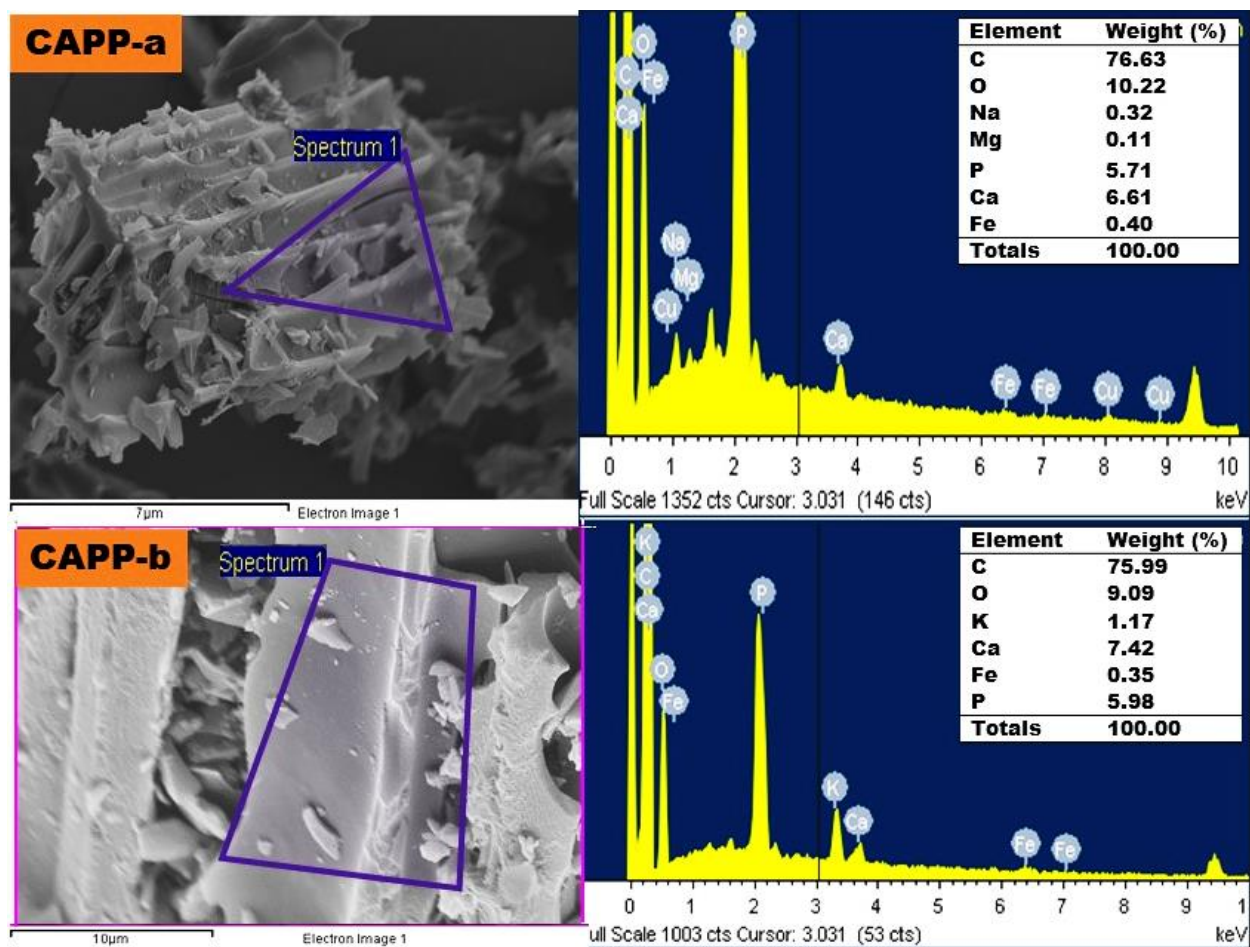


Fig. D.2 (continued)

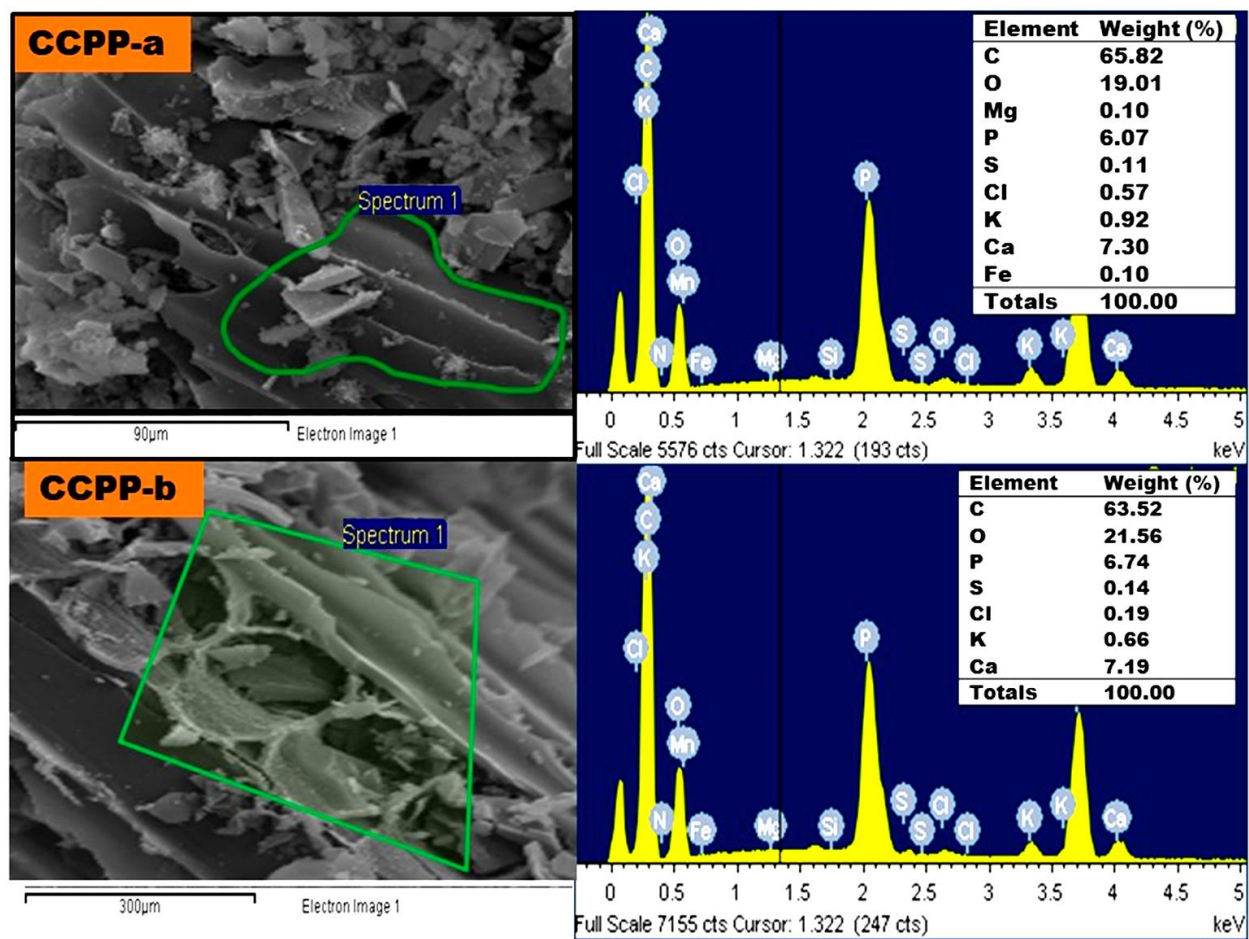


Fig. D.2 (continued)

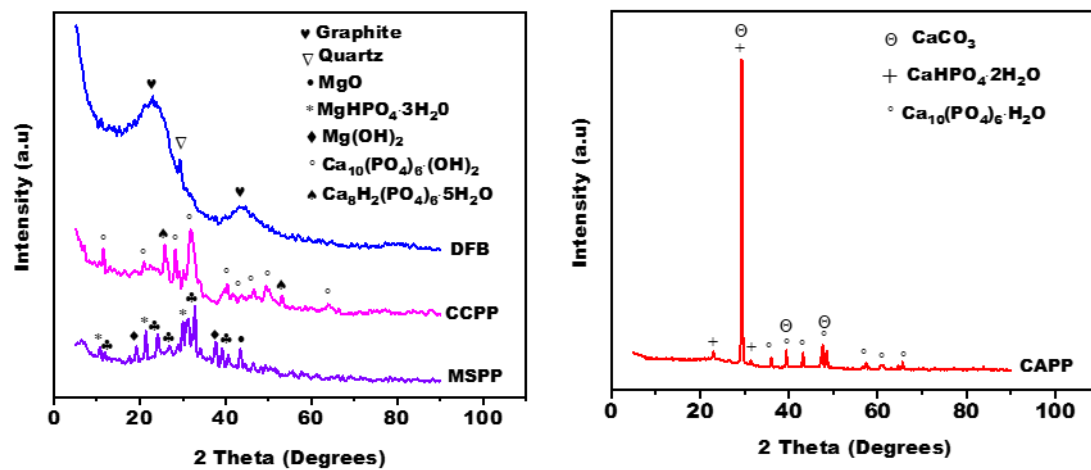


Figure D.3 XRD spectra for DFB before and after modifying to CCPP, CAPP and MSPP.

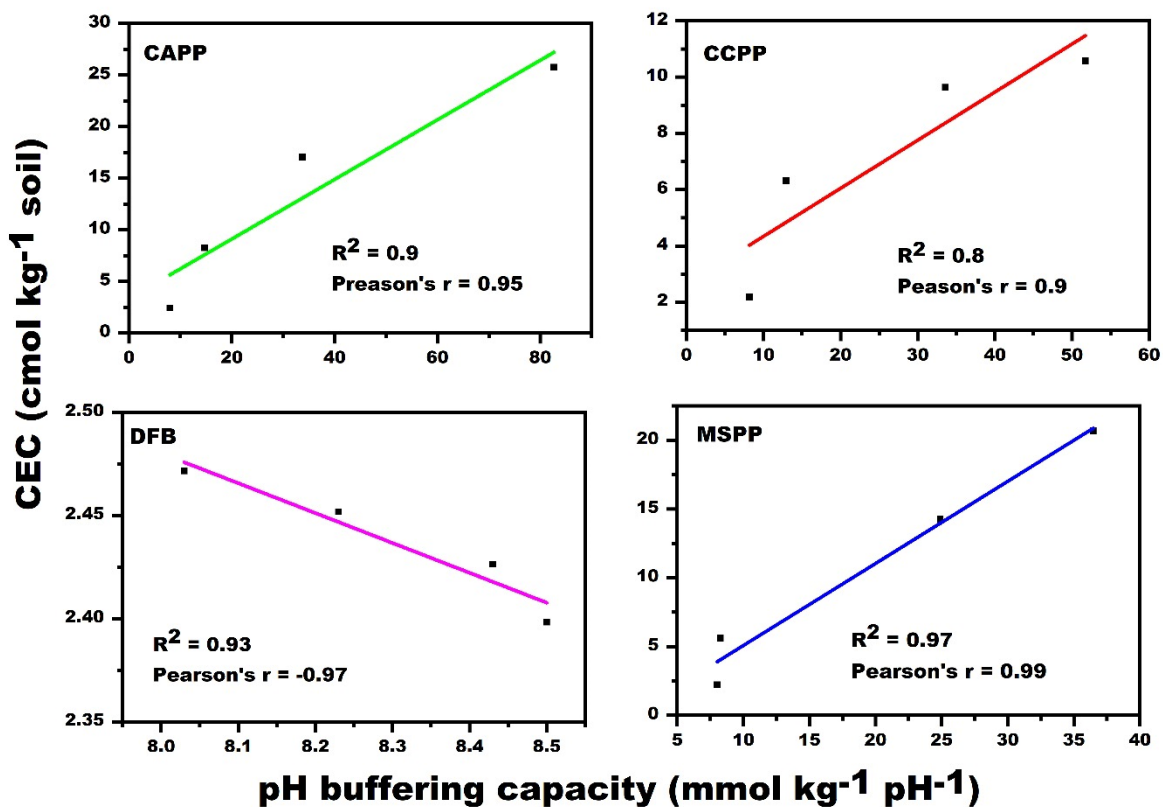


Figure D.4 Cation exchange capacity (CEC) vs pH buffering capacity for acidic soil after a 30-d incubation with 0% (nothing added to soil), 10%, 30% and 50% wt./wt. (biochar /soil). DFB- untreated Douglas fir biochar, CCPP-Douglas fir biochar plus anhydrous calcium chloride plus potassium dihydrogen phosphate, CAPP-Douglas fir biochar plus calcium carbonate plus diammonium phosphate and MSPP-Douglas fir biochar plus magnesium sulphate plus potassium hydroxide plus potassium dihydrogen phosphate