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Uptake of Phosphorus from Modified P-Enriched Douglas Fir Biochar and Its Effects on Crop Growth and P Use Efficiency

Beatrice Arwenyo[1,2], **Jac J. Varco**[3], **Andrew Dygert**[3], **Jaime Berry**[1], **Julianna Mills**[1], **Dinesh Mohan**[4], **Charles U. Pittman Jr.**[1], **Todd Mlsna**[1]*

[1]Department of Chemistry, Mississippi State University, Mississippi State, USA
[2]Department of Chemistry, Gulu University, Gulu, Uganda
[3]Department of Plant and Soil Science, Mississippi State University, Mississippi State, USA
[4]School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India
Email: *TMlsna@chemistry.msstate.edu

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, $r^2 > 0.9$) and SPF (p value < 0.0058, $r^2 > 0.9$) treatments. More studies at field scale are needed to demonstrate the practicability of using modified P enriched Douglas fir biochar for soil amendments.

Keywords

Macronutrients, Dry Matter Yield, Micronutrients, Application Rate

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1. Introduction

The world's population is constantly growing and so are the demands for food, fiber, and biofuel (Burgess & Morris, 2012; Werner et al., 2018). Sustainable agricultural productivity is an inevitable requirement if we are to provide these essentials to future generations. Despite improved crop varieties, machinery, pesticides and better nutrient management strategies to improve crop yields (Chuan et al., 2016), smaller than expected yields are often realized in many agricultural soils due to insufficient phosphorus (Plunkett & Wall, 2019). 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 occur (Baligar et al., 2001), which increases expense and subsequently, presents significant eutrophication risks affecting both social and economic development (Allsopp & Tirado, 2012; Withers et al., 2014). Therefore, more environmentally sustainable crop production practices remain an indispensable goal.

Recently, research has demonstrated that, P use efficiency can be improved through the adoption of the 4Rs (Right fertilization sources, Right rate, Right timing, and Right placement) management strategies (Grant & Flaten, 2019). The 4Rs management system integrates practices which optimize crop yield and agronomic efficiency while limiting undesirable environmental impacts and conserving P resources. However, nutrient management decisions based on the 4Rs strategies relies on site-specific conditions such a soil type, climate, and cropping history. For example, Grant & Flaten (2019) 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 to increase soil water and nutrient holding capacity, and improved microbial activities and buffering ability (Werner et al., 2018; Yu et al., 2019). Lately, studies have proposed the use of biochar enriched with plant nutrients for sustainable soil fertility and improved nutrient use efficiency (Baskar et al., 2017; Kizito et al., 2019). Biochar activation with reducing/oxidizing agents and metal salts can enhanced biochar sorption capacity for inorganic compounds including PO_4^{3-} (Yang et al., 2019). Akgül et al., (2019) 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 (Millaleo et al., 2010; Rout et al., 2001), Mg^{2+} is an essential nutrient necessary for the maintenance of enzyme activities including polymerases, kinases and H^+-ATPase (Guo et al., 2016). However, biochar's efficacy in agricultural soil is reported to be regulated by many attributes including pyrolysis temperature, feed stock, soil type, climatic condition and biotic interactions (Torabian et al., 2021).

PEB obtained by sequential treatment of Douglas fir biochar, a byproduct from syngas production, with magnesium sulphate, potassium hydroxide and potassium dihydrogen phosphate (KH_2PO_4). It is an ecofriendly, inexpensive soil additive compared to the conventional chemical fertilizers and manures. PEB may offer additional benefits including greater nutrient contents than crop residue biochar and less soil contamination risks versus manure, poultry litter, and biosolids-derived biochars. Nutrient availability from biochar enriched with phosphate has been reported (Baskar et al., 2017; Werner et al., 2018). However, P uptake from PEB and its ultimate influence on crop growth and P use efficiency remains to be explored. The purpose of this study therefore was to investigate P uptake, compare plant growth responses, and predict P use efficiency from soil amended with PEB, triple super phosphate fertilizer {($Ca(H_2PO_4)_2$ [0 46 0]} (SPF) and modified Douglas fir biochar (MB).

2. Materials and Methods

2.1. Biochar Preparation

2.1.1. 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 ~10 - 30 s residence time at a temperature of about 900˚C - 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).

2.1.2. 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 analytical standard grades (Sigma Aldrich).

2.1.3. Treatment of DFB with Magnesium Sulphate Solution

Anhydrous magnesium sulfate (50.15 g) was dissolved in deionized water to make 800 mL of the solution in a clean glass beaker. This solution was slowly added to 200 g of ground and sieved (300 - 250 µm particle size) DFB and stirred to a uniform slurry. This slurry was magnetically stirred (rpm = 500) for 6 h, at ~24˚C to ensure uniform mixing, left to stand for 24 h and then filtered through Whatman no.1 filter paper. The residue was oven-dried at 80˚C to a constant weight. The magnesium sulphate treated biochar was then stored in a closed container after cooling to room temperature (~24˚C).

2.1.4. Treatment of Magnesium Sulphate Modified Biochar with Potassium Hydroxide Solution

A potassium hydroxide solution was prepared by dissolving 280.5 g of potassium hydroxide pellets in 1000 mL of deionized water in a volumetric flask. To the previously prepared magnesium sulfate modified biochar, 800 mL of 5 M potassium hydroxide solution was slowly added while stirring to form a uniform slurry. This slurry stirred (rpm = 500) for 6 h at ~24˚C, filtered and oven-dried at 80˚C to constant weight. The product (MB) was kept in a closed container after cooling to ~24˚C before use.

2.1.5. Preparation of P Enriched Modified-Douglas Fir Biochar (PEB)

A potassium dihydrogen phosphate solution was prepared by dissolving 219.7 g of KH_2PO_4 in deionized water bringing the total 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 dihydrogen phosphate in a beaker while stirring to form a homogeneous slurry. The slurry was stirred magnetically (rpm = 500) at ~24˚C for 6 h, left to stand for 24 h at ~24˚C filtered and then oven-dried to constant weight at 80˚C (Figure 1). The final product was cooled to ~24˚C and kept in closed containers until use.

2.2. DFB, MB and PEB Characterization

2.2.1. Surface Area, Pore Size and Pore Volume Analysis

PEB, MB and DFB surface area, pore volume and pore size were determined based on N_2 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 TriStar II Plus Version 2.03.

2.2.2. Determination of Surface Morphology and Elemental Compositions

PEB, MB and DFB surface morphologies and elemental compositions were examined using SEM and SEM-EDS. The measurements were done at 5 kV using a JEOL JSM-6500F FE instrument. Structural chemical compositions were investigated by powder X-ray diffraction (XRD) on samples of each biochar 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 Kα radiation (λ = 0.6465944 Å).

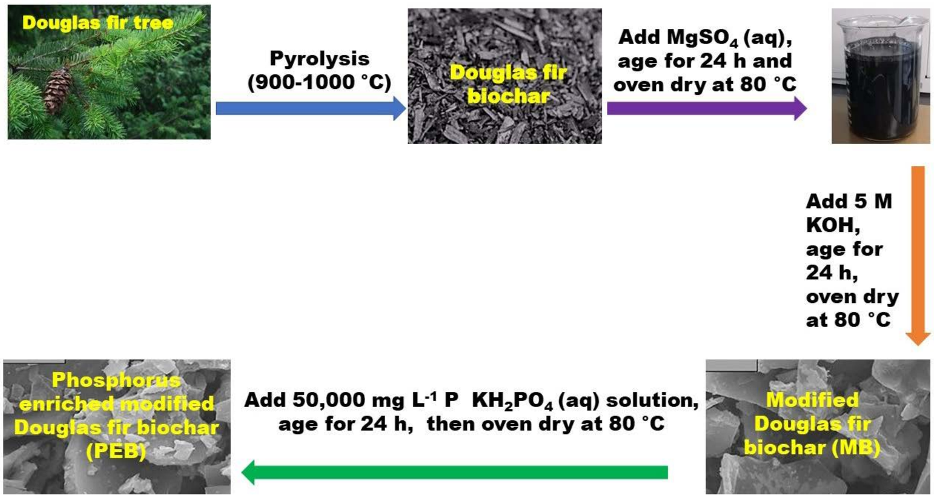

Figure 1. Schematic illustration for the preparation of phosphorus enriched Douglas fir biochar (PEB).

2.2.3. pH, Liming Potential, Ash Content and Total Metal Concentrations Determination

Liming capacity and pH were determined following the procedure described by Singh et al., (2017). Deionized water (50 mL) was added to 5 g of air-dried DFB, PEB and MB samples each in a 100 mL centrifuge tube. These mixtures were shaken on a mechanical shaker for 1 h at room temperature. The suspension pH was recorded using an HI3221 pH meter after 30 min standing.

The liming potential was obtained by weighing 0.5 g of dried PEB, MB, DFB and $CaCO_3$ samples each into a 50 mL polypropylene tube. 1M HCl (10.0 mL) was added to each sample and shaken for 2 h at room temperature, then were left overnight before filtering through Whatman number 1 filter paper. The filtrates were titrated with a 0.5 M sodium hydroxide solution using phenolphthalein as an indicator. Standard calcium carbonate (previously dried at 105˚C) was used as a reference sample, and 1M HCl was used as the blank. The liming capacity was obtained from Equation (1):

$$\%\ \mathrm{CaCO_3\ equivalent} = \frac{M \times (b-a) \times 10^{-3} \times 100.09 \times 100}{2 \times w} \tag{1}$$

where M = Standardized molarity of NaOH (mol/L),

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 ($g \cdot mol^{-1}$) = molar mass of $CaCO_3$ and

2 = Number of H^+ consumed per mole of $CaCO_3$.

Biochar (1.0 g) samples, dried overnight at 105˚C, were ashed in a muffle-furnace at 650˚C for 8 h. After cooling, the remaining ash was weighed, and ash content calculated from Equation (2):

$$\%\ \mathrm{ash} = \frac{\mathrm{Remaining\ mass\ after\ cooling}(\mathrm{g}) \times 100}{\mathrm{Original\ weight}(\mathrm{g})} \tag{2}$$

The ash was then digested at 150˚C in 5.0 mL nitric acid (70% Sigma Aldrich) and 2.0 mL of hydrochloric acid (37% Sigma Aldrich). The digested samples were diluted with deionized water to 100 mL, filtered and analyzed for Mg, Ca, K and P using an Elan DRC II ICP-MS spectrometer.

2.3. Greenhouse Experiment

2.3.1. Soil Sample Collection and Preparation

A Stough fine sandy loam (coarse-loamy, siliceous, semiactive, thermic Fragiaquic 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 S1**) at the Mississippi State University plant and soil testing laboratory (Cox, 2001). This sandy loam soil had very low organic matter. Low organic matter levels have been previously reported in sandy soils (Berns & Knicker, 2014), mainly due to soil texture, drainage, climate and soil management.

2.3.2. Experimental Pots Set up and Management

Experiments were conducted in a greenhouse located at the Mississippi State University campus (33˚27'22"N/88˚47'44"W) in Starkville, between September and November 2019 using corn (*Zea mays* L.) variety DeKalb 67-44. Three treatments; concentrated super phosphate fertilizer (SPF) as a standard, magnesium sulphate plus potassium hydroxide modified biochar (MB) and P enriched MB (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}. The quantity of SPF, MB and PEB corresponding to each application rate was calculated based on its % P concentration (19.8%, 9.6% and 4.2% 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. Treatments were thoroughly mixed with 4.5 kg of air-dried soil/pot. Soil in each pot was limed with 2.3 g of calcium carbonate prior to mixing. Five DeKalb corn Hybrid 67-44 seeds 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.

After harvest, soil from each pot was air-dried, crushed to pass a 10-mesh sieve, and tested for pH (2:1 H_2O:soil) using a Fisher Scientific Model 25 Accumet pH meter (Denver, CO). Extractable nutrients (P, K^+, Mg^{2+} and Ca^{2+}) were determined using the Mississippi State Extension Service Soil Test method (Berns & Knicker, 2014; Cox, 2001; Oldham, 2012) and Avio an 200 ICP-OES (Perkin Elmer, Waltham, MA).

2.3.3. Leave Chlorophyll Concentrations, Plant Heights and Biomass Dry Weight Yields

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 on one side of the midrib around the midpoint of each leaf blade approximately 30 mm apart. 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 to constant weight. Dry matter yield was determined using an analytical balance.

2.3.4. Plant Nutrient Uptake

Oven-dried plants were ground to pass through a 40-mesh sieve. Nutrients (P, K, Mg, Ca, Fe, Zn, B, Mn and Cu) in plant tissue were determined with an Avio

200 ICP-OES (Perkin Elmer, Waltham, MA) following a modified dry ashing procedure (Jones, 2001). Plant nutrient uptake was calculated from plant tissue nutrient concentrations and dry matter weight as shown in Equation (3).

$$\text{Plant nutrient uptake} = \frac{\%\ \text{nutrient}\left(\text{P}/\text{Mg}/\text{K}/\text{Ca}\right) \times \text{Dry weight}\left(\text{g}\cdot\text{pot}^{-1}\right)}{100} \quad (3)$$

2.3.5. P use Efficiency

The Agronomic P use Efficiency (AGE) in ($\text{kg}\cdot\text{kg}^{-1}$) was obtained from Equation (4) as described by Chuan et al. (2016).

$$\text{AGE} = \frac{Y - Y_0}{F} \quad (4)$$

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.

2.4. Statistical Analysis

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

3. Results and Discussions

3.1. Biochar Characterization

3.1.1. Surface Area, Pore Size and Pore Volume

Surface area analysis indicated that biochar modification 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 $\text{m}^2\cdot\text{g}^{-1}$ to 14.640 $\text{m}^2\cdot\text{g}^{-1}$ (~97%) while pore volume reduced from 0.192 $\text{cm}^3\cdot\text{g}^{-1}$ to 0.005 $\text{cm}^3\cdot\text{g}^{-1}$ (>97%). P enrichment of the modified Douglas fir biochar reduced the surface area even further (**Table S2**). The blockage and partial loading of pores by modification agents and their aggregate reduced the surface area following modification of DFB. Blockage obstructs the passage of N_2 to micropores. According to Kose et al. (2016), the micropores are the primary determinant of the surface area, and the amount of nitrogen volume adsorbed by biochar corresponds to its pore volume and surface area. Similar observations were reported previously (Yakout et al., 2015).

3.1.2. Surface Morphology and Elemental Compositions

The surface morphology of DFB, MB and PEB were determined by SEM (**Figure S1**). DFB had a smoother surface with honeycomb structures ascribed to fibrous structure from plant cells. DFB had the greatest BET surface area recorded. The MB and PEB surfaces showed wide irregular shaped structures with crystal particles bound to their surfaces due to the deposited modifications. These crystal particles block DFB pores, explaining 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 to a depth of ~5.3 µm. The corresponding peaks and the atomic percentage of each element are shown in **Figure S2**. Generally, biomass derived biochar samples surfaces 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% to 2.24% and 0.43% to 23.52%, respectively. Although P enrichment of MB did not show substantial effect on K% weight 23.52% to 23.38%, it did significantly reduce the weight percent of surface region Mg, 2.24 to 0.9, in PEB.

The structural composition of samples the structure region was studied using X-ray diffraction from which probed to a depth of about 40 µm (**Figure 2**). The XRD patterns for DBF showed two broad peaks similar to that of graphene between 2θ = 20˚ to 30˚ and 40˚ to 50˚ (Dehkhoda et al., 2014; Siburian et al., 2018). These peaks are ascribed to graphite diffraction. Other sharp peaks showed mixed inorganic components mostly calcite ($CaCO_3$) at 2θ = 12.24˚ (1 0 4) (Ondrus et al., 2003), brucite [$Mg(OH)_2$] at 2θ = 7.96˚ (0 0 1) (Nagai et al., 2000) and dolomite [$CaMg(CO_3)_2$] 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 2θ = 38˚ (1 1 1), 42˚ (200), 67˚ (3 1 1) (Nemade & Waghuley, 2014) and $Mg(OH)_2$ at 2θ = 7.80˚ (0 0 1), 15.78˚ (1 0 −1), 20.85˚ (1 0 −2), 45.01˚ (3 0 2) (Aminoff et al., 1021). Furthermore, additional peaks in PEB matched $MgHPO_4$ at 2θ = 4.16˚ (2 0 0) (Qian et al., 2016), and $Mg_3(PO_4)_2$ at 2θ = 9.68˚ (1 2 0) (Berthet et al., 1972).

3.1.3. The pH, Liming Capacity, Ash Content and Total Metal Concentrations

Modified Douglas fir biochar (MB) had the highest pH (11.8) and liming capacity

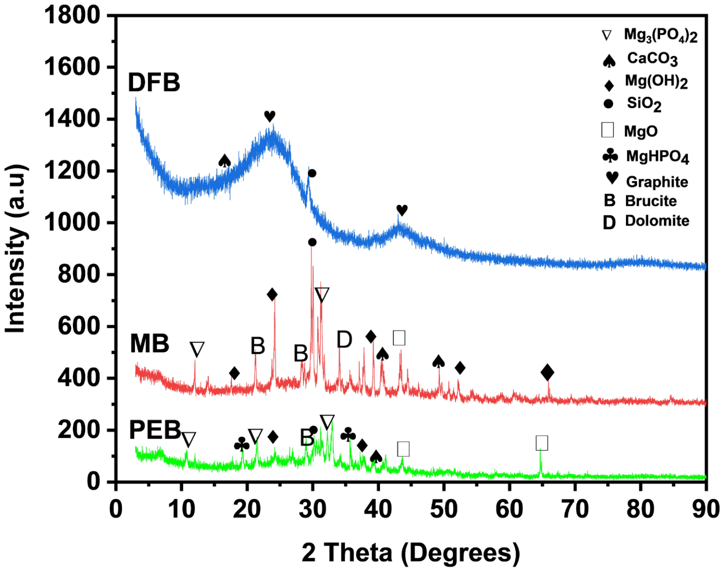

Figure 2. XRD pattern for Douglas fir biochar (DFB), Douglas fir biochar treated with $MgSO_4$ + KOH (MB) and MB treated with potassium dihydrogen phosphate (PEB).

(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 (Figure 3). Liming potential and pH were positively correlated (r = 0.9) indicating their interdependency.

Activation of DFB with $MgSO_4$ and KOH significantly increased both ash content and total metal concentrations (Table S3). 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 of MB can be explained by the greater concentrations of magnesium and potassium deposited on MB as revealed by EDX and total metal concentrations.

3.2. Plant Growth and Nutrient Uptake

3.2.1. Nutrient Content

Macronutrient content was affected by application rates across all treatments (Figure 4). Significant variations in nutrient recovery were observed in both PEB ($r^2 \geq 0.8$, p-value ≤ 0.03) and SPF ($r^2 \geq 0.9$, p-value ≤ 0.01) treatments. However, no significant differences were recorded in MB treatment ($r^2 \leq 0.6$, p-value ≥ 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 the nutrient contents 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 based on its very low initial P soil test value (Table S1). Soil, P plays plant growth and development

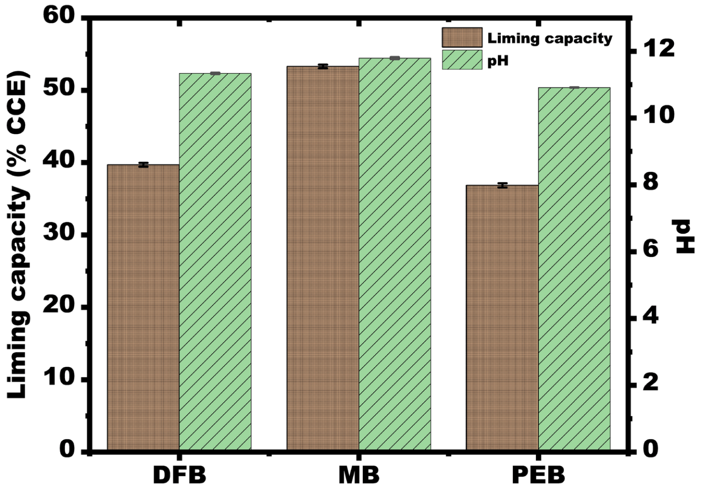

Figure 3. pH and liming capacity of Douglas fir biochar (DFB), Douglas fir biochar treated with $MgSO_4$ + KOH (MB) and MB treated with potassium dihydrogen phosphate (PEB). CCE = Calcium carbonate equivalence, (Values used are mean of three replicates, errors bars shown as standard deviation).

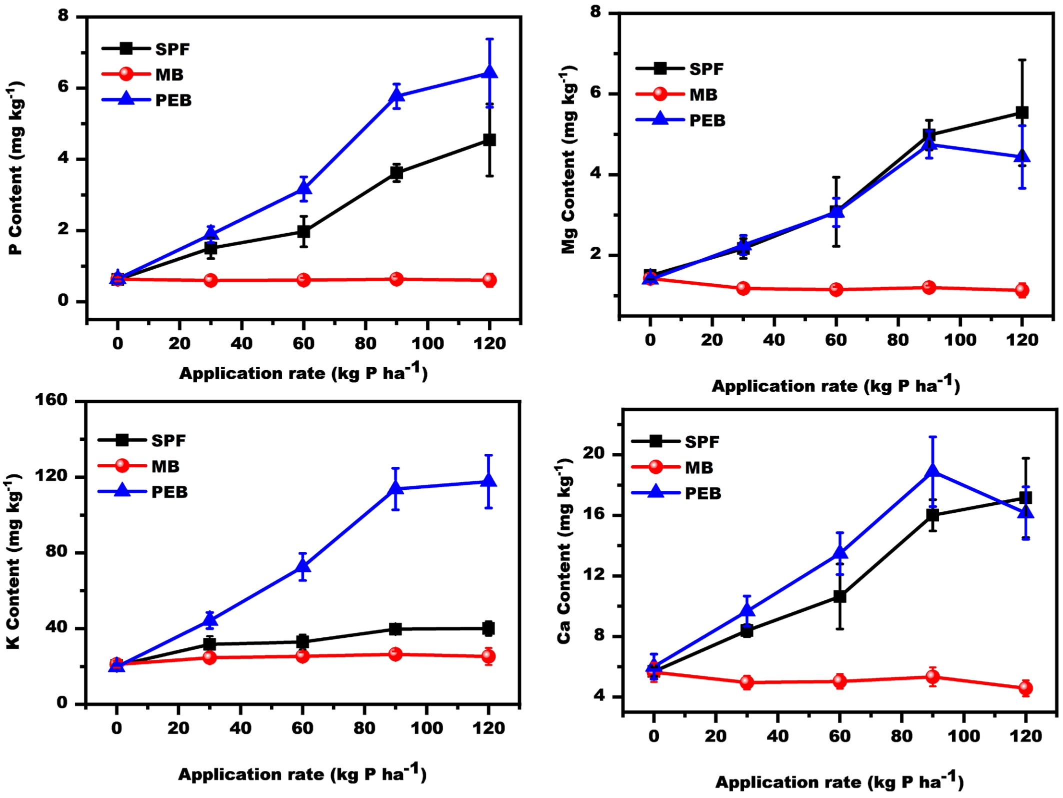

Figure 4. Variations of P, Mg, K and Ca contents with application rates of triple super phosphate fertilizer (SPF), modified P enriched biochar (PEB) and modified biochar (MB), (plotted values are mean of four replicates with standard deviation as error bars).

roles including energy storage and production, reproduction and enhancing shoot and root growth (Fageria & Moreira, 2011; Malhotra et al., 2018; Mollier & Pellerin, 1999). Reduced root growth and development, limits nutrient uptake, water use efficiency and subsequently, plant growth. The lower nutrient content observed here upon MB treatment is likely due to its inability to release available phosphate. This subsequently affected the uptake of Ca, Mg and K despite their availability in soil. Plant P, K, Ca, and Mg contents increased with increasing PEB and SPF treatments. However, a greater increase was observed upon PEB treatment due to its ability to replenish P, K, Mg, Ca for plant growth. The increased nutrient content observed for PEB and SPF treatments suggests that P facilitates the uptake of Mg, K and Ca. Increased Mg, K and Ca contents following P fertilization was previously reported (Fageria et al., 2014; IPNI, 1999).

For the MB treatment, plant uptake of P, Mg, K and Ca 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 the Control (0 kg p ha^{-1}) did not vary significantly with those of the MB treatment regardless of the application rates. In addition, increasing levels of extractable K, Mg and Ca associated with the MB treatment appeared in residual soil tests. Therefore, the low level of available P from the MB treatment could have affected root development, reducing contents of K, Mg and Ca. Besides, the observed K content reduction with increasing Mg and Ca could be due to antagonistic effects where high Mg and Ca concentrations reduce K content. Several studies have reported antagonistic plant removal effects between magnesium, calcium and potassium (IPNI, 1999; Stevens, 1970).

Results from micronutrient analyses indicated plant nutrient contents increased with application rates for both SPF and PEB (**Figure 5**). Regression analysis showed significant variations in micronutrient 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. Only the Cu content varied insignificantly with application rate for the PEB treatment (p-value < 0.057, $r^2 > 0.75$). Micronutrient content variations for MB treatments (**Figure 5**), 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 exhibit 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 ($r > 0.9$). Except for K

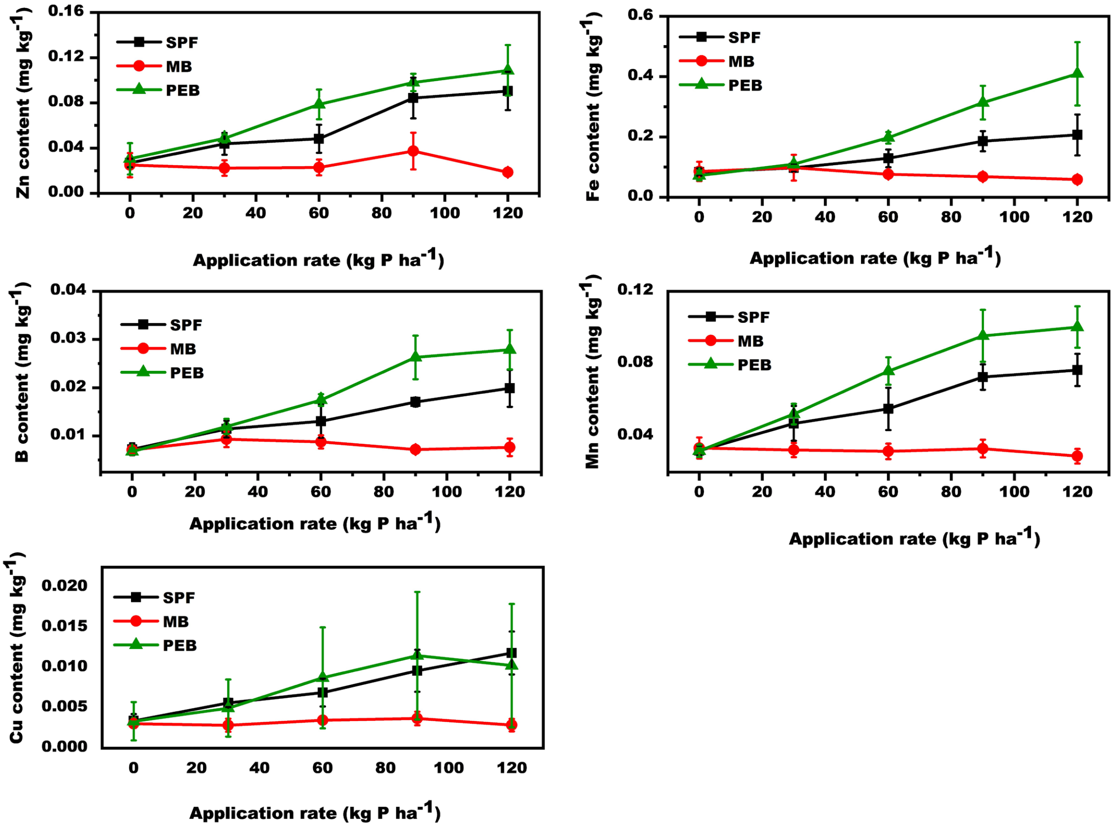

Figure 5. Variations of application rates with micronutrient contents (Fe, Cu, B, Mn and Zn) in super phosphate fertilizer, (SPF); modified P enriched biochar, (PEB); and modified biochar, (MB) treatments. Values shown are average of four replications, error bars shown as standard deviation).

(r = 0.8), Zn (r = 0.05) and Cu (r = 0.17) which had positive correlations with MB application rates, P (r = 0.49), Mg (r = 0.72), B (r = 0.12) and Mn (r = 0.7) were negatively correlated.

Plants require micronutrients for optimum growth and yield (Taghi Tavakoli et al., 2014). The soil serves as the major source for micronutrients (Tripathi et al., 2015). Availability of soil micronutrients are greatly influenced by soil pH. Except for Mo, availability of micronutrients drops with a rise soil pH. Deficiencies rarely occur in soil with pH values less than 6.5 (Hart et al., 1999). In our work, pH caused micronutrient deficiencies were 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 be explained due to enhanced P availability and plant growth. The decreased plant nutrient contents for the MB treatment was likely due to deficiency of available P and less dry matter yield. Increased plant Zn, Mn, Cu and Fe content with P fertilization has been previously reported by (Fageria et al., 2014).

3.2.2. Leaves Chlorophyll Concentrations and Dry Weight Yields

Treatments with P fertilizer exhibited significantly greater levels of leaf chlorophyll as indicated by SPAD readings. SPAD readings were greatest for the SPF treatments irrespective of application rates (Figure 6). The increase in chlorophyll

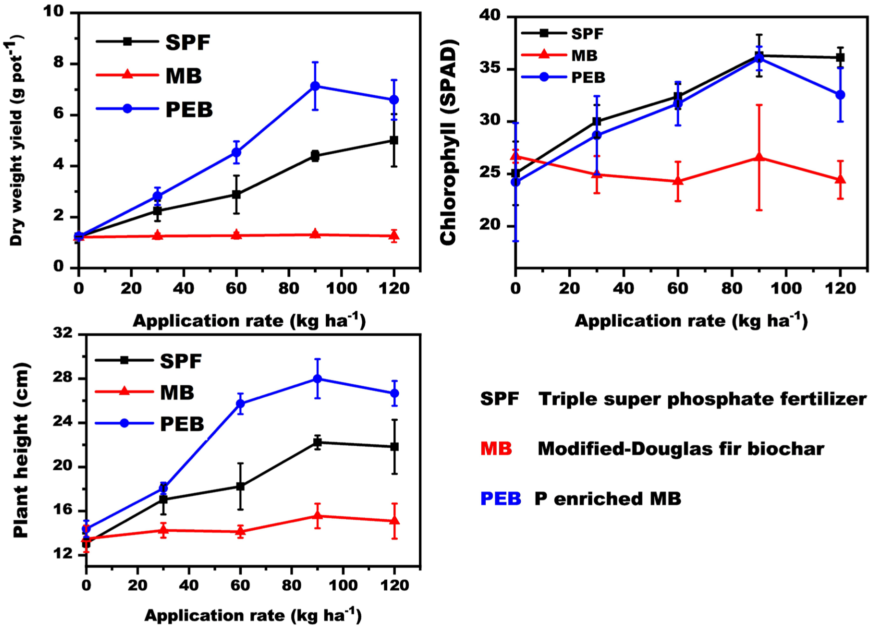

Figure 6. Variations of dry weight yields, plant heights and plant leaf SPAD readings versus application rate, (Values shown are average of four replicates, error bars indicated as standard error of the Mean).

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 produced dropping 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 ($r > 0.8$). SPAD readings for the PEB and SPF treatments had positive correlations ($r > 0.9$). MB recorded weak negative correlations with both PEB ($r = 0.2$) and SPF ($r = 0.3$) treatments.

The contents of other nutrients increased with P fertilization because it influenced plant removal of other nutrients. The effects of plant P removal on chlorophyll content however seems to be indirect and complex. Chlorophyll regulates photosynthesis, respiration, cell division and protein formation. Therefore, increased chlorophyll levels induced by SPF and PEB treatments can be ascribed to P supplied by SPF and PEB which then aided the recovery of other essential nutrients responsible for corn's chlorophyll formation (**Figure 4** and **Figure 5**, respectively). This increase in chlorophyll agrees with that observed in rice with increasing P application (Rietra et al., 2017). Also, Jawale et al., (2017) reported that uptake of other essential nutrients such as Mg, N and Fe Influence corn plant chlorophyll formation.

PEB and SPF applications resulted in a greater total aboveground corn biomass yield compared to the MB treatments (**Figure S3** and **Figure S4**, respectively). Simple regression analysis indicated the rise in dry weight yield versus application rates was significant for both PEB (p value = 1.7×10^{-9}, $r^2 = 0.90$) and SPF (p value = 1.2×10^{-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 (**Figure 6**). Maximum dry weight yield corresponded to an application rate of 90 kg P ha^{-1} for PEB (3488 $kg \cdot ha^{-1}$) and MB (639 $kg \cdot ha^{-1}$) and 120 P $kg \cdot ha^{-1}$ for SPF (2449 $kg \cdot ha^{-1}$) treatments. Similar observations were recorded for plants heights (**Figure 6**).

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 rate from the biochar or mineralization (Sial et al., 2019). Multiple variables have been cited for the effects of biochar on increasing crop yield. Such variables include liming effects, increased water-holding capacity, structural soil improvement, increased surface area for nutrient adsorption, and improved microbial activities (Kätterer et al., 2019; Major et al., 2010; Van Zwieten et al., 2010). Biomass dry weight yield at 0 kg P ha^{-1} was comparable for all treatments (602.6 $kg \cdot ha^{-1}$, 592.8 $kg \cdot ha^{-1}$ and 605 $kg \cdot ha^{-1}$ for SPF, MB and PEB, respectively) in this study. Yield response was mainly influenced by the source's nutrient content and availability. Furthermore, since adequate nitrogen was added to all treatments, any growth variation should have been minimal unless adsorption or immobilization of 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 sulfate and potassium hydroxide. Although all treatments had phosphate, the % P in MB (4.16) treatment was much lower compared to PEB (9.57) and SPF (19.78). Therefore, the lower biomass yield observed for the SPF treatment than the PEB treatment, despite the greater % P concentration of SPF, may have been partially due to an inadequacy of Mg and K. Biochar's increased K, Mg and P concentrations because of PEB 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. However, the low % P concentration and recovery with MB may have affected uptake of both K and Mg regardless of their availability, hence reducing the growth response. Improved plant growth with nutrient uptake has been reported (Sial et al., 2019).

3.2.3. P Use Efficiency

Phosphorus use efficiency (PUE) can be defined as a yield increase per kg P fertilizer added (Lovelock et al., 2012). It is related to P sources, environmental factors, soil chemical properties, and crop management (Mosaic, 2012). There are many ways of calculating P use efficiency. In this study, the agronomic P use efficiency was applied because the objective was to compare P use efficiency associated with SPF, MB and PEB treatments at different application rates. The agronomic P use efficiency (AGE) is as a short-term indicator of the applied nutrient impact on productivity. It helps determine productivity improvement gained by nutrient inputs and aids identifying the optimal nutrient levels required for improved yield (Martínez et al., 2018). Thus, 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 (**Figure 7**). The largest P use efficiencies corresponded to application rates 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, which correspond to application rates of 76 Kg P ha^{-1} and 81 kg P ha^{-1}. 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 (Mosaic, 2012). PUE was primarily affected by fertilizer formulation in this work. The effect of pH was minimized by liming prior to planting. Other factors were controlled thus were 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.

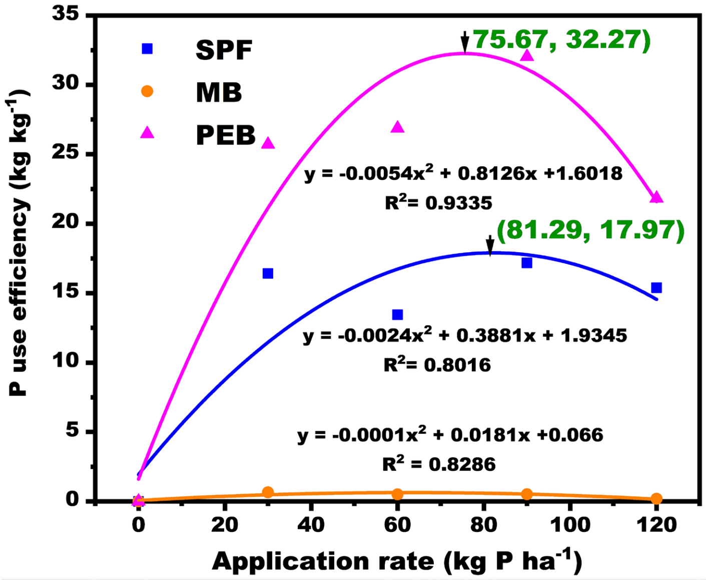

Figure 7. The influence of application rates of P-enriched biochar (PEB), superphosphate fertilizer (SPF) and modified biochar (MB) on agronomic P use efficiency (AGE).

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. The 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 was also observed. Previous researchers suggested that fertilizer nutrient use efficiency could be improved if a fertilizer was formulated such that antagonistic effects among nutrients were minimized (Rietra et al., 2017). Our residual soil test results indicated synergetic interactions occurred between P and the other nutrients in both PEB and SPF treatments. These results confirmed that application of either PEB or SPF facilitated plant uptake of K, Mg, Ca, Fe, Zn, B, Mn and Cu. This was further verified by positive correlations between P content and K, Mg, Ca, Fe, Zn, B, Mn, and Cu contents for both SPF and PEB treatments ($r > 0.9$).

3.3. Soil Residual P, K, Mg and Ca

Following harvest, soil residual nutrients were tested. Across all treatments (**Figure 8**). Regression results showed an increase in soil residual P (p value ≤ 0.04). In addition, residual soil K and Mg test concentrations were significantly increased by treating with 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).

P uptake did not respond to rate of MB treatment, only a slight increase in soil residual P resulted, indicating MB could hold some fixed P which was unavailable for plant uptake. Conversely, PEB and SPF treatments increased residual P upon higher application rates. This may indicate their ability to release available

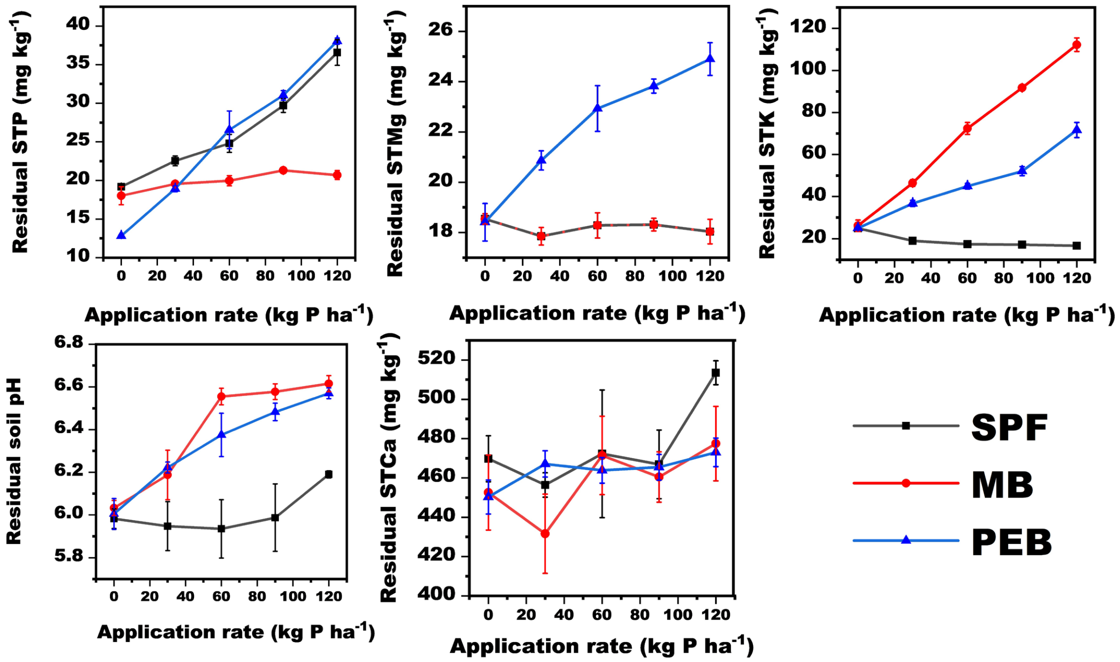

Figure 8. Variations of residual soil test pH and macronutrients versus application rates of modified P enriched Douglas fir biochar, (PEB); modified Douglas fir biochar, (MB) and super phosphate fertilizer (SPF) treatments (Values shown are mean of four replicates, error bars shown as SEM).

P for plant uptake. 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}.

No substantial variation in soil Ca test response was noted across all treatments. Ca deficiency is not commonly encountered in soil environments which are limed as was the case in this study (Fageria & Moreira, 2011). 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.

The decline in soil test K and Mg levels during SPF treatment indicated that, as more P was added to the soil, plant demand for K and Mg also increased. Since no external replenishment for either K or Mg was possible with SPF treatment, the soil was the only Mg and K source. EDX studies revealed K and Mg concentrations rose following MB and PEB treatments, and as application rates increased, more K and Mg were released and accumulated in the soil. Clearly, application of P facilitated removal of other nutrients as previously noted.

4. Conclusion

P recovery from PEB and MB, its impact on plant growth and P use efficiency was investigated versus use of 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.

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 achieved under controlled growth conditions and 35 d of growth. Further research under field conditions is now needed to validate P availability from PEB, plant growth responses and P use efficiency to establish practicability.

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Conflicts of Interest

The authors declare no conflict of interest.

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Supporting Information

Table S1. 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

[a]Cation exchange capacity (centimole per kg of soil).

Table S2. 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

[a]DFB = untreated Douglas fir biochar, MB = DFB treated with $MgSO_4$ + KOH, PEB = MB treated with KH_2PO_4.

Table S3. 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).

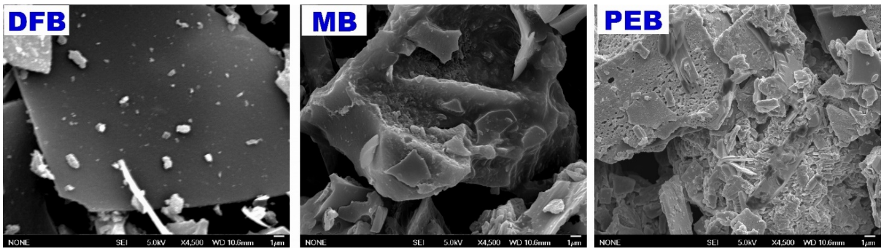
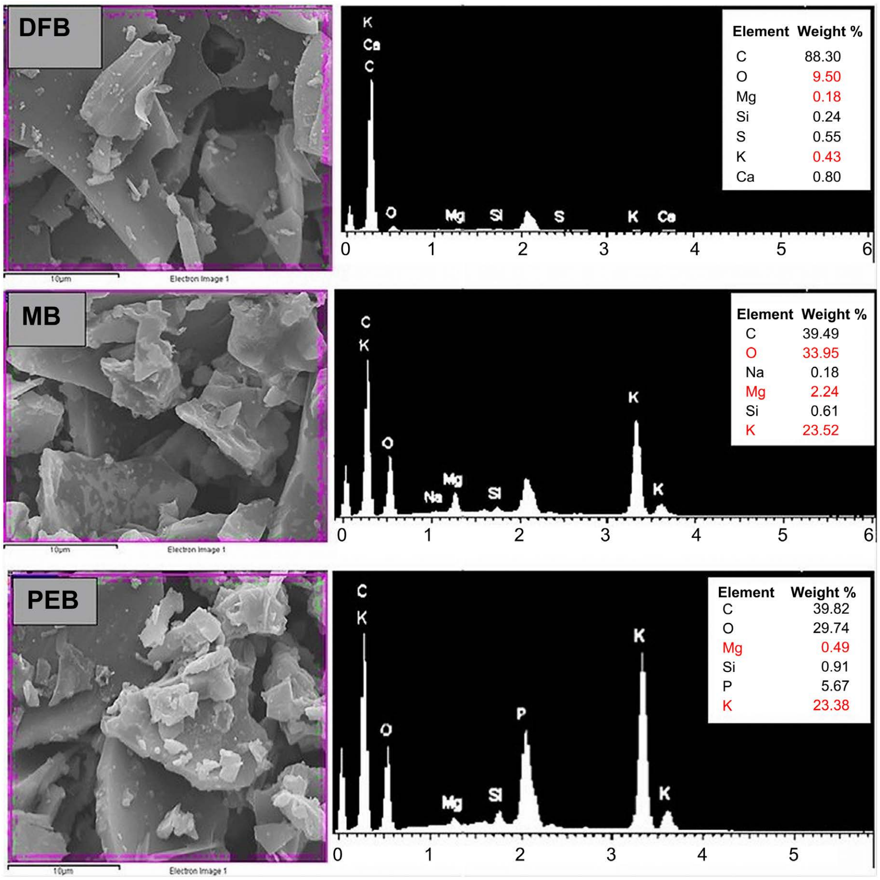


Figure S1. Scanning electronic microscopy (SEM) of biochar before modification (DFB), after modification (MB) and after enrichment with phosphate (PEB).



Element	Weight %
C	88.30
O	9.50
Mg	0.18
Si	0.24
S	0.55
K	0.43
Ca	0.80

Element	Weight %
C	39.49
O	33.95
Na	0.18
Mg	2.24
Si	0.61
K	23.52

Element	Weight %
C	39.82
O	29.74
Mg	0.49
Si	0.91
P	5.67
K	23.38

Figure S2. Energy-dispersion X-ray spectroscopy (EDS) images of biochar before modification (DFB), after modification (MB) and after enrichment with phosphate (PEB).

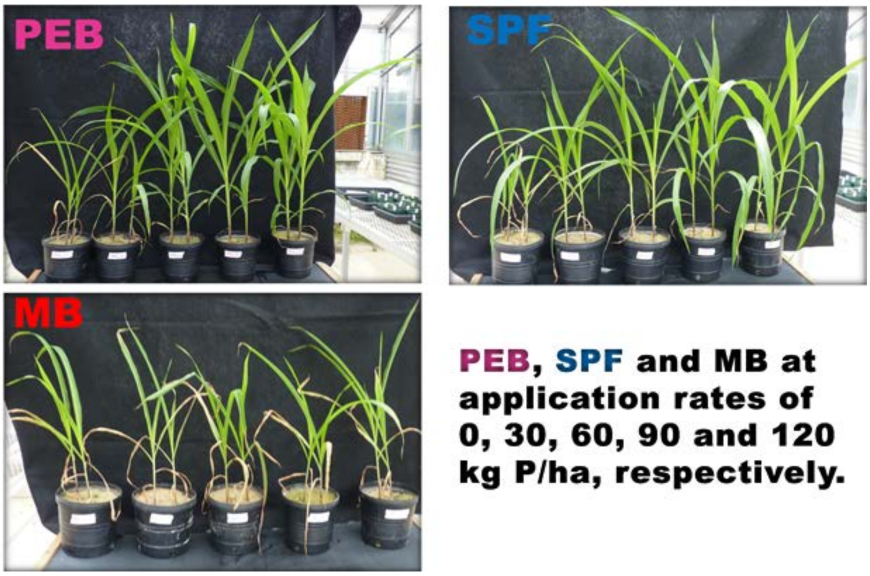


Figure S3. Plant growth at different application rates of Triple super phosphate fertilizer (SPF), MB treated with potassium dihydrogen phosphate (PEB), and Douglas fir biochar treated with $MgSO_4$ + KOH (MB).

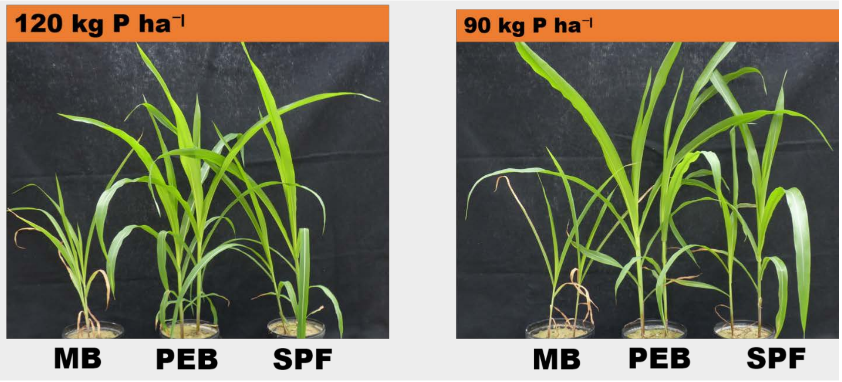


Figure S4. Plant growth at 120 kg P ha^{-1} (left) and 90 kg P ha^{-1} (right) application rates after amendment with Triple super phosphate fertilizer (SPF), MB treated with potassium dihydrogen phosphate (PEB), and Douglas fir biochar treated with $MgSO_4$ + KOH (MB).