

RESEARCH PAPER

Phosphorus availability from magnesium-modified P-enriched Douglas fir biochar as a controlled release fertilizer

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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 unfavourable. 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 modified P-enriched 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. Aboveground biomass dry weight yield ($R^2 = .7$) and plant height ($R^2 = .86$) improved with P contents. After harvest, residual soil P for the FC treatment was significantly greater than all other treatments (p -value = 1.7848 E-6, $R^2 = .8$). Plant height and aboveground dry weight biomass were 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

nutrient management, P availability, P-enriched Douglas fir biochar, soil amendment, sustainability

1 | 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 because of many factors including low soil P mineral content, and soil properties which influence adsorption mechanisms such as CaCO₃, Al and Fe oxide contents (Malhotra et al., 2018). P fixation involves the conversion

of soluble phosphate into insoluble form, which inhibit its accessibility by plants (Shen et al., 2011). In acidic soils (pH < 5.5), P fixation occurs when soluble P reacts with Fe³⁺ and Al³⁺ oxides and hydroxides to form minerals strengite (FePO₄·2H₂O) and variscite (AlPO₄·2H₂O), respectively. In calcareous soils (pH ≥ 7.5), soluble P can react with the Ca²⁺ ion, forming dicalcium phosphate (CaHPO₄) and sequentially to a less soluble form such as octacalcium phosphate {Ca₈H₂(PO₄)₆·5H₂O}. The resulting

compounds are relatively insoluble substances that limit plant labile soil P (Nierves & Salas, 2015). 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 uptake may be restricted (Bomans et al., 2005).

Many studies have related low crop productivity and yield to insufficient supply of soil P (Arif et al., 2017; Grant et al., 2005), not only because of its role in plant nutrition but it also lowers the efficiency to uptake and utilization of other essential plant nutrients (IPNI, 1998). Synthetic fertilizer or manure is 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 (Withers et al., 2014; Yin et al., 2017). 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 (Withers et al., 2014). Therefore, to realize the UN Sustainable Development Goals (SDGs) 2, 3, 6, 12, 13 and 15 (Hou et al., 2020), stakeholders and policymakers need to find more holistic approaches to soil management challenges (Hou, 2021).

Recent studies have shown biochar's contributions to sustainable soil management (Hou, 2021) because of its unique properties including large specific surface area, internal porosity and rich polar and nonpolar surface sites (Chen, Lan, et al., 2018; Chen, Alim, et al., 2018). Biochar, a by-product of biomass pyrolysis under limited oxygen conditions, has a porous carbonaceous structure with various functional groups (Ding et al., 2016). Biochar can hold nutrients, improve soil water-holding capacity, sequester greenhouse gases, enhance soil cation exchange capacity (CEC), reduce nutrient leaching (Bruun et al., 2017) and improve microbial activity (Ding et al., 2016). However, pyrolysis temperature, treatment methods and treatment cations may alter biochar surface functional groups, pore structure, P sorption capacity and releases (Peng, Sun, Fan, et al., 2021; Peng, Sun, Hanif, et al., 2021). Akgül et al. (2019) reported that tea biochar activated with Mg^{2+} had greater PO_4^{3-} sorption capacity than Fe^{3+} , Al^{3+} and Mn^{2+} ion-treated biochar. Similarly, Yang et al. (2019) used biochar-layered double hydroxide (BC-LDH) composites derived from fabricating corn straw with Mg/Al, Ni/Fe and Zn/Al, respectively. They 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 differences in P sorption capacities were ascribed to the variation in electronegativity ($Mg < Al < Zn < Ni \approx Fe$) resulting in increased electric repulsion between the BC-LDH ($Ni/Fe > Zn/Al > Mg/Al$) and phosphate (HPO_4^{2-} , HPO_4^-) ions. Peng, Sun, Fan, et al. (2021) and Peng, Sun, Hanif, et al. (2021) obtained maximum P sorption capacity

of $286.2 \text{ mg/PO}_4^{3-} \text{ g}$ and $215.8 \text{ mg/PO}_4^{3-} \text{ g}$ at $pH = 6.0$ with the AMOST (950-Mg/Al-A) and conventional (950-Mg/Al) methods, respectively. They used Mg/Al-layered double hydroxides biochar produced from corn straw waste at 350, 550, 750 and 950°C . The greater P sorption attained with AMOST (950-Mg/Al-A) compared with the conventional (950-Mg/Al) method was attributed to its larger BET surface area and exposed sorption sites. Despite the disparities in their P sorption capacities and releases, P-enriched biochar slows labile P releases into soil (Takaya et al., 2016; Yao et al., 2013) which can enhance P use efficiency and lower fertilizers cost, application rates (Peng, Sun, Fan, et al., 2021; Peng, Sun, Hanif, et al., 2021) and water pollution risk.

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} (Karunanayake et al., 2019) 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 Mg^{2+} -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 Mg^{2+} -modified Douglas enriched with P, by looking at relationships between plant tissue P concentrations, residual extractable soil P and overall plant growth.

2 | MATERIALS AND METHODS

2.1 | Soil collection and preparation

A Stough fine sandy loam (coarse-loamy, siliceous, semi-active, thermic Fragiatic 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 flowing crushing and sieving through a 1-cm mesh was analysed for selected chemical properties at the Mississippi State University extension service plant and soil testing laboratory (Table S1).

2.2 | 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 Bombuwala et al. (2018). 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) with constant stirring to form a uniform slurry. To the slurry, 200 ml 2 M solution of KOH was added and the mixture stirred at a speed of (500 rpm) with a magnetic stirrer for 2 h, followed by ageing 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 | 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.

2.4 | Determining available (extractable) potassium, magnesium and phosphorus concentrations of biochar

The available (extractable) K and Mg concentrations of UDB, B, B50, B100 and B150 were determined by the method described by Marta et al. (2017). Briefly, 1 g (W) of air-dried samples of UDB, B, B50, B100 and B150 was 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 ($< 2 \text{ mm}$) 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 min to allow for thorough wetting of the biochar (Marta et al., 2017). The samples were then shaken in a reciprocating shaker for 30 min at 25°C . The tubes were centrifuged at $\sim 2500 \text{ g}$ for 10 min 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 $P = \frac{C_p \times V}{W \times 10^3}$.

2.5 | Analyses of surface morphology and elemental composition of biochar

The morphology and elemental composition of UDB, B and modified P-enriched Douglas fir biochar (MPB) were analysed 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 analysed as a representative.

2.6 | Greenhouse experiment

The experiment was conducted in a glasshouse 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 $\times$ 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 were homogenized, air-dried, crushed to pass a 10-mesh sieve and tested for pH (2:1 di H₂O: soil) using a Fisher Scientific Model 25 Accumet pH meter (Denver, CO) following the method described by Thompson and Varco (2002), and extractable nutrients (P, K⁺, Mg²⁺ and Ca²⁺) were determined using the Mississippi State Extension Service Soil Test Method (Cox, 2001; Oldham, 2012) using an Avio 200 ICP-OES (Perkin Elmer) to determine nutrient concentrations in the extracted solution.

2.7 | Plant and soil analyses

Whole plants were harvested 31 days 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

to detect differences among treatment means using OriginPro-8 software. Also, Pearson correlation coefficients were determined.

3 | RESULTS

3.1 | Available potassium (K), magnesium (Mg) and phosphorus (P) 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 mg P L⁻¹ > 100 mg P L⁻¹ > 50 mg P L⁻¹ (Figure 1).

Similarly, per cent yield of available P improved in the order B150 > B100 > B50 (Table 1). However, the per cent available yield for both K and Mg were comparable across B, B50, B100 and B150 treatment. The per cent yield was calculated using the expression:

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

recorded, and then, oven-dried plants were ground to pass through a 40-mesh sieve. Plant tissue was analysed using a modified dry ashing procedure (Jones, 2001) with nutrient elements quantified using an Avio 200 ICP-OES (Perkin Elmer). Plant nutrient content was calculated using plant tissue nutrient concentration and dry matter weight.

Regression analysis was performed for plant height, dry matter yield, plant P content and extractable soil nutrient levels using Microsoft Excel. Analysis of variance (ANOVA) and Fisher's protested least significant difference (LSD) at a 95% confidence limit were performed

where y and z are concentrations of nutrient in untreated biochar and the treatment solution, respectively.

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

3.2 | Surface morphology and structural chemical composition

Scanning electron microscopy (SEM) micrographs and energy dispersive spectroscopy (SEM/EDS) spectra for

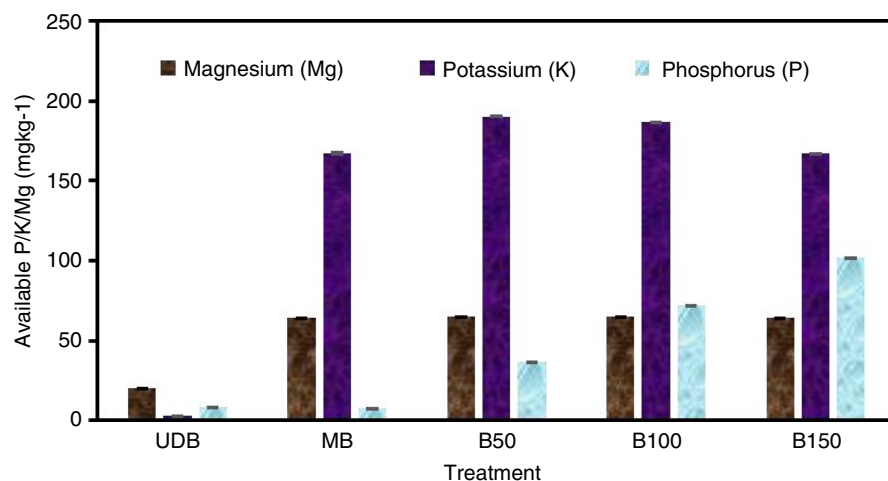


FIGURE 1 Available K, P and Mg in unmodified Douglas fir biochar (UDB), modified Douglas fir biochar (B) and modified P-enriched Douglas fir biochar (B50, B100 and B150). Error bars represented as the standard error of the mean of three replicates

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 and 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.

The peaks from X-ray diffraction techniques (Figure 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 because of graphite diffraction (Siburian et al., 2018). Additional sharp peaks were identified as mixed inorganic components including calcite (Ishizawa et al., 2013), brucite, dolomite, quartz and periclase (not shown) (Dehkhoda et al., 2014). New peaks emerged in B providing evidence for the presence of MgO at $2\theta = 28.46^\circ, 44.05^\circ, 60.79^\circ, 43.88^\circ$ (Yi & Chen, 2018) and $\text{Mg}(\text{OH})_2$ at $2\theta = 37.93^\circ, 50.17^\circ, 58.67^\circ$ and 73.8° (Nagai et al., 2000; Xie et al., 2013; Zhang et al., 2016). Furthermore, additional peaks emerged in MPB because of hydrated $\text{Mg}_3(\text{PO}_4)_2$ at $2\theta = 4.65^\circ, 6.16^\circ, 31.9^\circ, 53.23^\circ$ and MgHPO_4 at $2\theta = 4.65^\circ, 5.73^\circ, 6.80^\circ, 13.18^\circ, 16.51^\circ$ (Chen, Lan, et al., 2018; Chen, Alim, et al., 2018; Qian et al., 2016; Schroeder & Methew, 1978).

TABLE 1 Per cent (%) 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	13.170	0.130	0.170
B100	33.907	0.129	0.167
B150	45.552	0.128	0.149

B = $\text{MgCl}_2 + \text{KOH}$ -treated Douglas fir biochar, B50, B100 and B150 were B treated with 50, 100 and 150 mg P L^{-1} solution of KH_2PO_4 , respectively.

3.3 | Crop response to biochar P loadings

Treatments B150 and the control (C) had the tallest and shortest plant heights, respectively (Figure S1). 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 (Figure S2).

An analysis of variance ($\alpha = 0.05$) indicated significant differences in plant heights between treatments ($R^2 = .5$, p -value = .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 $\text{P}_2\text{O}_5\%$ biochar treatments ($R^2 = .88$, p -value = .01). This indicated that plants performed better with increasing rates of P loaded onto biochar even though P application rates were equal (Table 2). 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 ($R^2 = .86$, p -value = .007) between average plant heights and mean P content (Figure S3 A1). Similarly, there was a significant positive relationship ($R^2 = .7$, p -value = .03) between average plant P content and mean dry weight yield (Figure S3 A2).

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 with 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 ($R^2 = .6$, p -value = .002) in soil pH compared with both C and FC treatments (Figure 5). 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 because of high concentrations of basic cations (calcium, potassium and

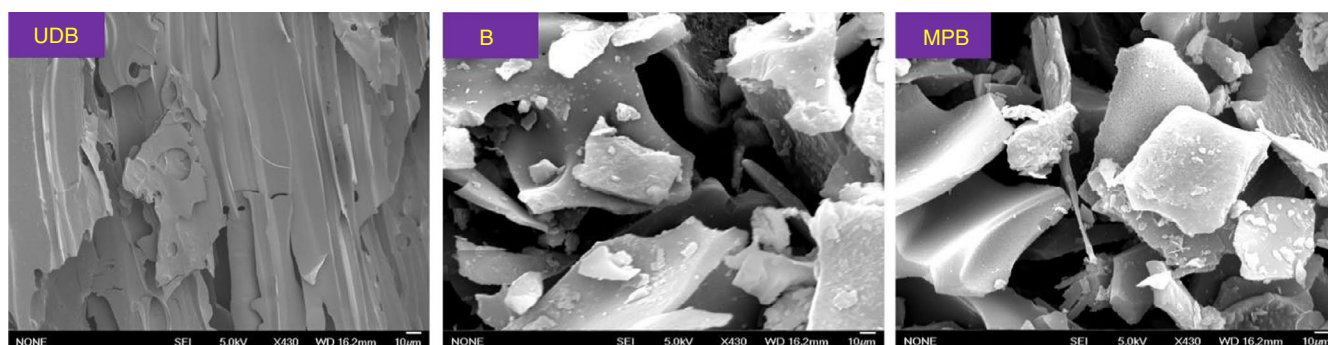


FIGURE 2 Scanning electron microscope (SEM) images for unmodified Douglas fir (UDB), modified Douglas fir biochar (B) and modified p-enriched Douglas fir biochar (MPB)

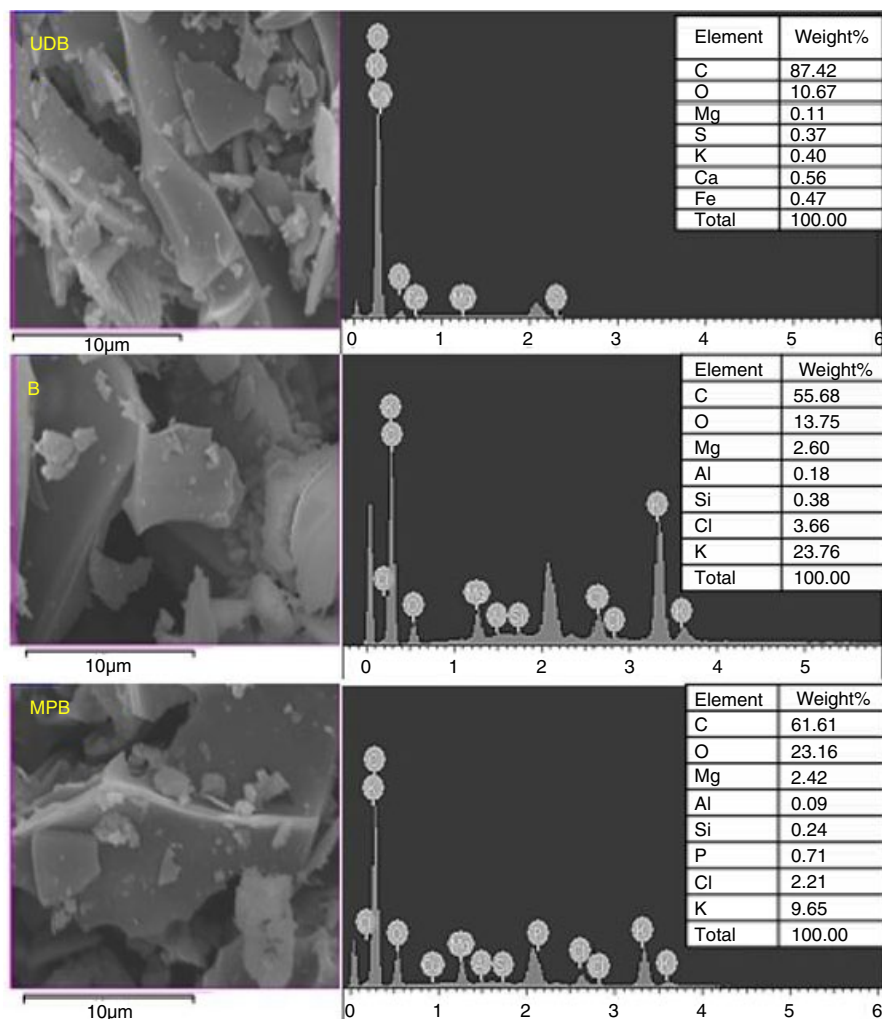


FIGURE 3 Energy-dispersive X-ray (EDX) spectra for unmodified Douglas fir (UDB), modified Douglas fir biochar (B) and modified p-enriched Douglas fir biochar (MPB)

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 (Bedassa, 2020). Organic matters including biochar are also known to absorb Al^{3+} thus reducing potential acidity.

3.4 | 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 (Figure 6). There were weak positive correlations between P plant content and Mg ($r^2 = .3$)/K ($r^2 = .2$) contents.

Analysis of variance showed significant differences in both K ($R^2 = .56$, p -value = .006) and Mg ($R^2 = .7$, p -value = .0001) contents between various treatments. Also, regression analysis showed positive plant growth responses with both soil K/Mg ($R^2 = .54$, p -value = .09)

contents (Figure S4 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 (Figure S4 A₃) showed K content increased with Mg content ($R^2 = .97$, p -value = .0005).

3.5 | 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 (Figure 7).

However, biochar treatments had comparable STP with the C treatment. A Fisher LSD test indicated that STP for the FC treatment differed significantly (p -value = 1.7848E^{-6} , $R^2 = .8$) from both the control and all biochar treatments. Furthermore, the application of both modified Douglas fir biochar and modified P-enriched

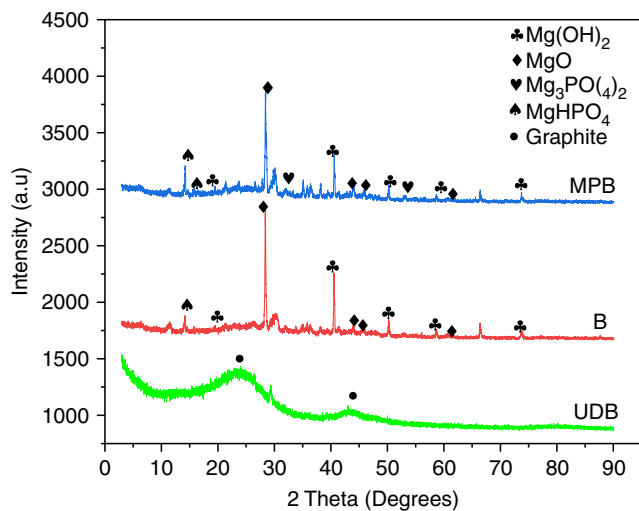


FIGURE 4 XRD spectra for unmodified Douglas fir (UDB), modified Douglas fir biochar (B) and modified p-enriched Douglas fir biochar (MPB)

TABLE 2 Treatment 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 = Aboveground 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 ($p < .05$) among treatments according to Fisher's Protected LSD test.

Douglas fir biochar significantly increased both residual STK (p -value = $4.53876E^{-11}$, $R^2 = .9$) and STMg (p -value = $1.29148E^{-10}$, $R^2 = .9$) levels compared with the control and FC treatment (Figure 7). All biochar treatments had greater STK/Mg levels than the C and FC treatments.

4 | DISCUSSIONS

4.1 | Available potassium (K), magnesium (Mg) and phosphorus (P) concentrations of Biochar

While available K and Mg concentrations increased following modification of biochar, there was a small decline in available P concentration (Figure 1). However, the concentration of available P significantly increased after treatment with different potassium dihydrogen phosphate

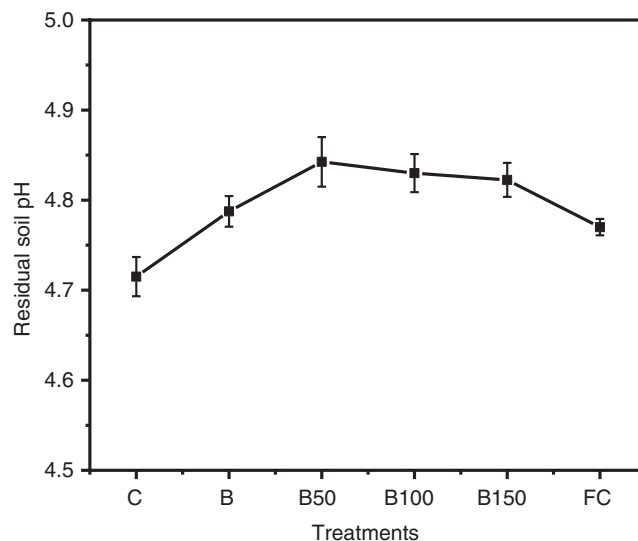


FIGURE 5 The effect of C, B, B50, B100, B150 and FC treatments on residual soil pH. Errors bars shown as the standard error of the mean ($n = 4$)

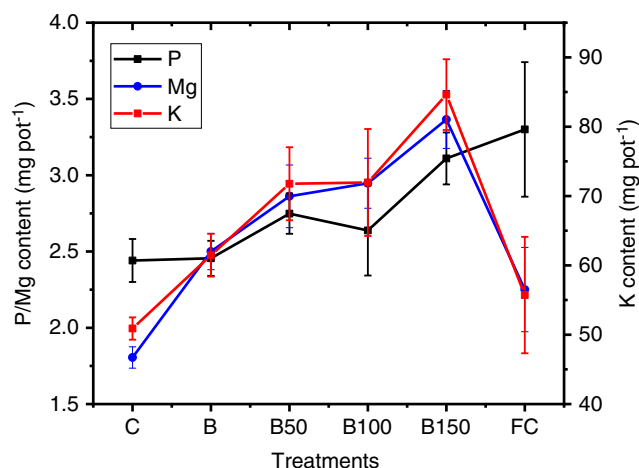
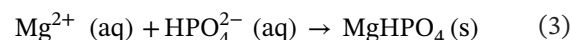
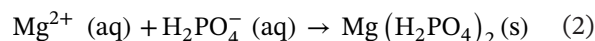
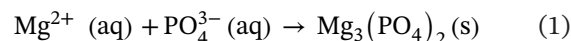


FIGURE 6 The effect of biochar enrichment rate on nutrient contents of corn plants as compared to an untreated biochar and a commercial fertilizer. Errors bars shown as the standard error of the mean of four replicates

solution concentrations. The decrease in P concentration following the modification of biochar may be because of the reaction of Mg ions from the modification solution with biochar phosphate forming less soluble compounds such as $Mg_3(PO_4)_2$, $Mg(H_2PO_4)_2$ and $MgHPO_4$ (Equations 1–3).



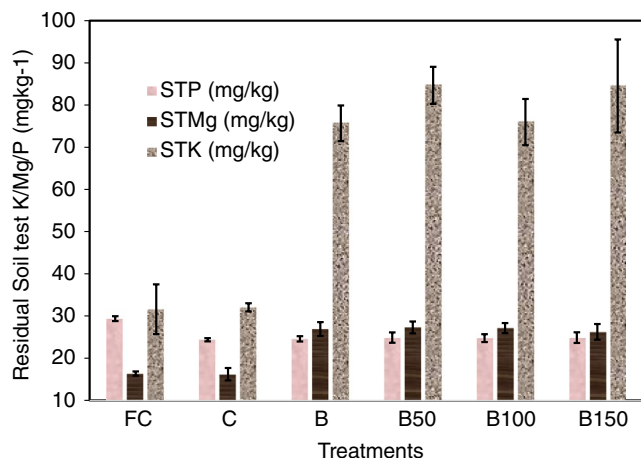
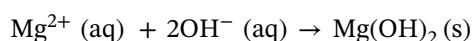


FIGURE 7 The influence of C, B, B50, B100, B150 and FC treatments on soil residual P (STP), K (STK) & Mg (STMg) test levels. (Errors bars shown as standard errors of the mean, $n = 4$)

According to Akgül et al. (2019), 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.

As expected, the per cent yield of available P increased with increasing P concentration in Biochar (Table 1) and the per cent 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. Results from XRD show that P exists in the form of hydrated $\text{Mg}_3(\text{PO}_4)_2$ and MgHPO_4 (Figure 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 $\text{Mg}_3(\text{PO}_4)_2$ ($\text{pK}_{\text{SP}} = 23.28$) (Recz & Soron, 1968), 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 with B.

In contrast, the low release of Mg could possibly be because of the precipitation of Mg^{2+} in the form of less soluble forms such as $\text{Mg}(\text{OH})_2$ ($\text{pK}_{\text{SP}} = 10.86$) (Ziegenheim et al., 2020) at increased Mg^{2+} and OH^- concentration.



Angst and Sohi (2013) 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.

4.2 | Surface morphology and structural chemical composition

Results from SEM (Figure 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 (Figure 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 because of activation with MgCl_2 and KOH. In addition, MPB had P (0.71%) revealing that modification and enrichment of biochar increased its nutrient contents.

4.3 | Variation of P source with plant heights, dry matter yield and P uptake

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 P_2O_5 (46%) compared with other treatments (Figure S1), 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 were likely because of their inability to release relatively sufficient available P for plant recovery compared with 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 because of 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 solubility and Al solubility. 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 because of 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 in P uptake between the FC and P-enriched Douglas fir biochar treatments, the results suggest 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 (Detpiratmongkol et al., 2014; Khan et al., 2018; Marlina & Zaki, 2017; Muhammad et al., 2017). For example, increased dry weight yield following poultry manure-derived biochar has been shown (Khan et al., 2018). 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 (Detpiratmongkol et al., 2014).

Other studies (Kätterer et al., 2019; Mensah & Frimpong, 2018) 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 (Igalavithana et al., 2016). Researchers (Kätterer et al., 2019; Mensah & Frimpong, 2018) have claimed that biochar's liming ability was the principal reason for enhanced plant growth on acid soils because of a reduction in Al^{3+} and Fe^{3+} activities and hence improved P availability for plant use. For this study, although soil pH was greater for the B, B50, B100 and B150 treatments compared with the C and FC treatments (Figure 5), the soil test P for the FC treatment was the greatest compared with all other treatments. Nevertheless, residual STP for the B, B50, B100 and B150 treatments was comparable to that of C treatment (Figure 7). The low residual STP in B50, B100 and B150 treatments compared with FC could signify that most available P associated with the enriched biochar was released for plant uptake. In addition, the low STP could be an indication for the need for greater P loading while enriching biochar.

4.4 | Variations of K and Mg Contents with treatments

Results showed weak positive correlations between P content and Mg ($r^2 = .3$)/K ($r^2 = .2$) 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. (2001), 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 with the FC and C treatments can be because of 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 suggest 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. (2016). They noted that growth responses to magnesium were 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 (Figure S4 A₃) showed plant K content increased with Mg content ($R^2 = .97$, $p\text{-value} = .0005$). This observation contrasts with the antagonistic effect between K and Mg uptake reported in the literature (Laekemariam et al., 2018; Yan & Hou, 2018). 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.

4.5 | Residual soil test P, K and Mg levels

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 (Figure 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 with 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 with the C and FC treatments.

5 | CONCLUSIONS

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 were greatest for the FC treatment because of 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 was directly correlated with available soil P, suggesting that modified P-enriched 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.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon request.

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SUPPORTING INFORMATION

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