

## Article

# Açaí Biochar and Compost Affect the Phosphorus Sorption, Nutrient Availability, and Growth of *Dioclea apurensis* in Iron Mining Soil

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**Abstract:** Organic materials, such as biochar and organic compost, can reduce P sorption mechanisms and improve soil fertility, benefiting the reclamation of areas impacted by mining. This study evaluated how the chemical properties of Fe mining soil, the adsorption of P onto this substrate, and the growth of the native plant *Dioclea apurensis*, were affected by the application of açaí biochar (BC), organic compost (OC), and different P doses. Substrate collected from mining soil piles was incubated for 30 days with BC or OC. Each mining substrate with or without the addition of BC or OC received five doses of P (0, 40, 80, 120, and 240 mg·kg<sup>-1</sup> P). The addition of BC or OC promoted an increase in pH and nutrient availability (P, K, Ca, and B) in Fe mining soil. However, plants grown in the unamended mining soil (W) showed higher growth. The maximum P adsorption capacity decreased as a function of the addition of BC. We conclude that the application of BC reduced P sorption, while the application of either OC or BC altered the chemical properties of the soil and caused contrasting effects on P dynamics in Fe mining soil, and these treatments also affected plant growth.

**Keywords:** P isotherm; phosphate fertilization; soil rehabilitation

## 1. Introduction

The Carajás Mineral Province (CMP) is one of the largest mineral provinces in the world, and open-cast mining activities reshape the landscape, generating large mining pits and extensive waste piles [1,2]. These waste piles are formed by material with low fertility, little organic matter (OM), and limited phosphorus (P) availability; thus, interventions such as OM management and soil fertilization are required to mitigate these limitations and promote the reclamation of the affected land. With these interventions, the growth of plants, as well as the availability of nutrients, is increased because the soil condition (initially very poor) is improved [3].

Soil conditioning with organic materials has been recommended as one of the main ways to enhance physical, biological, and chemical soil properties, accelerating reclamation [4]. Materials such as biochar and organic compost are among the most commonly used materials for this purpose [5] because these materials have the capacity to retain the P applied via fertilizer and release slowly to the soil, maintaining the supply of the element in the soil [6]. Composted organic material results from decomposing organic materials into simpler organic and inorganic compounds by (aerobic) microorganisms and is generally

very active, so it can rapidly provide nutrients to the soil, thus favouring soil microbiota growth. In addition, this material has a high retention capacity and has the potential for large-scale production for use in extensive areas [7,8]. Biochar, resulting from anaerobic pyrolysis derived from organic wastes, which often have no proper disposal destination, is a more recalcitrant material with substantial amounts of surface nutrients and high nutrient retention capacity [9].

The conversion of organic waste into biochar or compost has been widely used due to the multifunctional capacity of these materials for agricultural and environmental applications [10]. The addition of biochar and organic compost can improve the available P in the soil [11,12]; low P availability may constrain plant development in soils rich in Fe and Al oxides and hydroxides, as observed in Fe mining areas [3]. Therefore, the application of compost and biochar may be useful in restoring soil fertility, although their effects on P sorption in mined substrates are little known. Another organic material with potential use in soil is açai (*Euterpe oleracea*) biochar, which is produced from seeds extracted after pulp processing. Açai seeds applied in the form of biochar promote improvements in the chemical properties of cultivated soils [13], but changes in soil P adsorption and P availability parameters have been little explored. In addition, açai production generates tons of organic waste daily in urban areas of the Amazon and has potential use in improving soil fertility and physical properties [13].

Methods for reclaiming mined areas usually include revegetation using commercial and native species, as well as soil management by applying mineral and organic fertilizers [2,14]. Phosphate fertilization in the presence of different organic soil conditioners can improve soil chemical functionality, increase P availability, and favour revegetation [15]. Among the native plants of the CMP, the species *Dioclea apurensis* has potential use in revegetation because it is adapted to edaphoclimatic conditions, produces large amounts of seeds, grows rapidly, and provides substantial matter inputs [16]. For greater efficiency of reclamation practices, it is necessary to evaluate the growth of this species under different management conditions to determine its ideal development conditions.

We assume as hypotheses that the application of biochar and compost may be alternatives that can reduce P sorption mechanisms in mining substrates, increase the efficiency of the use of phosphate fertilizers, and promote greater *D. apurensis* growth in iron mining soil in Carajás. The objective of the present study was to investigate changes in the chemical properties of Fe mining soil after the addition of açai biochar and organic compost, as well as to evaluate their effects on P adsorption and the growth of *D. apurensis*, which is native to Carajás.

## 2. Materials and Methods

### 2.1. Sampling of Fe Mining Soil

The substrate used in this study was Fe mining soil collected in the CMP, located in the Eastern Amazon. Samples were taken at 10 equidistant points (100 m) from the slopes of waste piles, in newly piled areas not yet managed by planting species for revegetation, which had a height of 25 m and an extension of 1000 m. After collection, the entire substrate was sieved (<4 mm) and kept in a well-ventilated environment protected from sunlight and rain until the beginning of the experiment.

### 2.2. Production and Characterization of Biochar and Compost

Two types of organic products were used for the treatment of mining soil whose chemical characterization is shown in Table 1. The first was a commercial organic compost widely used in revegetation activities in Carajás. This material is the result of the composting by aerobic fermentation of organic plant matter from various species, including woody and nonwoody species (approximately 20% and 35%, respectively), mixed with sandy loam soil (30% approximately) (the exact composition of the compost is the intellectual property of the Agropecuária Vila Verde company). The other material used was biochar produced from açai (*Euterpe oleracea*) seeds (pulp extraction waste) from fruit collected

in urban farmers' markets in the city of Belém, Pará, Brazil, in the Eastern Amazon. To produce the biochar, the seeds were washed three times in distilled water and then dried in an oven at 50 °C for 24 h. The pyrolysis temperature was 400 °C for 4 h in a muffle furnace (Quimis, model Q318 M24, Diadema, Brazil) with a heating rate of 3.3 °C·min<sup>-1</sup>, and the final temperature was held for 1 h. The material was slowly cooled inside the muffle for subsequent weighing. After the pyrolysis process, the biochar was macerated in a porcelain crucible and passed through a 2-mm mesh sieve.

**Table 1.** Chemical characterization of organic compost and biochar.

Properties	Unit	Biochar	Compost
pH	-	6.7	7.2
N *	%	2.2	0.91
Na *	%	0.02	0.14
K *	%	0.8	0.12
S *	%	0.08	0.21
Ca *	%	0.1	4.34
Mg *	%	0.11	0.28
C *	%	72.2	25.32
P	mg·dm <sup>-3</sup>	2910	1660
B	mg·dm <sup>-3</sup>	10.0	20.0
Cu	mg·dm <sup>-3</sup>	20.9	27.4
Fe	mg·dm <sup>-3</sup>	0.03	3.65
Mn	mg·dm <sup>-3</sup>	524	1320
Zn	mg·dm <sup>-3</sup>	32	52
CEC	cmol <sub>c</sub> ·dm <sup>-3</sup>	785.6	1159.1

\* Values calculated to dry mass.

The total macro- and micronutrient contents in the compost and açai biochar were analysed using the EPA 3050b method and quantified by inductively coupled plasma mass spectrometry (Thermo Scientific, model iCAP PRO XPS, Waltham, MA, USA). The cation exchange capacity (CEC) was measured by ammonium acetate (NH<sub>4</sub>OAC) extraction [17]. Briefly, 40 mL of 1 M NH<sub>4</sub>OAC was added to 0.1 g of biochar or compost (1 g in the case of mining soil) in a 50-mL tube and subsequently stirred (20 min) and filtered. Next, the residue was washed with 30 mL of isopropanol (to remove excess NH<sub>4</sub>) and 40 mL of 1 M KCl (to remove NH<sub>4</sub> from the soil charge). The NH<sub>4</sub><sup>+</sup> contained in the KCl solution was quantified using the salicylate colorimetric method [18], and the CEC (cmol<sub>c</sub>·kg<sup>-1</sup>) was calculated by normalizing the amount of NH<sub>4</sub><sup>+</sup> to the weight of biochar or compost (0.1 g).

### 2.3. Plant Growth in the Greenhouse

The experiment was conducted in a greenhouse, in polyethylene pots with a capacity of 1 dm<sup>3</sup>, at a ratio of 90% mining soil (approximately 0.9 kg) and 10% açai biochar (approximately 0.1 kg), 90% mining soil (approximately 0.9 kg) and 10% organic compost (approximately 0.1 kg) (*w/w*), or 100% mining soil from the waste pile as a control. The pots received five P doses, namely, 0, 40, 80, 120, and 240 mg·kg<sup>-1</sup>, in the form of monoammonium phosphate.

The cultivated species was *D. apurensis*, which is a native species of Carajás widely distributed in the region and therefore has been used in revegetation activities in mined areas. Its seeds were collected in undisturbed areas in the region, transferred to paper bags, and stored in a seed chamber at low temperature and humidity for sowing in the different treatments.

The experimental design used in this study was completely randomized, in a 5 × 3 factorial scheme, with five doses of P and three cultivation substrates (mining soil, mining soil + biochar and mining soil + compost), in five replicates, totaling 75 experimental units. The organic compost and the biochar were homogenized with the mining soil and kept at approximately 60% of field moisture capacity for 30 days for subsequent evaluation.

Before planting, *D. apurensis* seeds were manually scarified with sandpaper to break dormancy and sown directly in the pots at three seeds per pot. After 30 days, thinning was performed, keeping one plant per pot, following the criterion of plant uniformity, and each plant was cultivated for 120 days. The temperature and relative air humidity in the greenhouse were maintained at 28 °C and 88%, respectively. The pots were watered daily with distilled water, maintaining moisture at approximately 60% of field capacity. Each pot received fertilization with macro- and micronutrients in instalments, with the first application 7 days before sowing, the second application at 45 days, and the third application at 90 days. The following P doses were applied 0, 40, 80, 120, and 240 mg·kg<sup>-1</sup> of P by using monoammonium phosphate, and the plants received complementary nitrogen application at rates of 115, 96.5, 78.8, 59.6, and 4.2 mg·kg<sup>-1</sup> of N via urea, respectively, for each P treatment (to provide the need of 115 mg·kg<sup>-1</sup> N). Additionally, 100 mg·kg<sup>-1</sup> K in the form of KCl, 80 mg·kg<sup>-1</sup> Ca in the form of CaCl<sub>2</sub>, and 25 mg·kg<sup>-1</sup> of Mg in the form of MgSO<sub>4</sub> were applied. For the supply of micronutrients, 0.5 mg·kg<sup>-1</sup> of B in the form of H<sub>3</sub>BO<sub>3</sub>, 3.6 mg·kg<sup>-1</sup> of Mn in the form of MnSO<sub>4</sub>, 1.5 mg·kg<sup>-1</sup> of Cu in the form of CuSO<sub>4</sub>, 0.5 mg·kg<sup>-1</sup> of Mo as ammonium molybdate, and 5 mg·kg<sup>-1</sup> of Zn in the form of ZnSO<sub>4</sub> were applied. All fertilizers were diluted with water for application to the mining soil. The doses of P and other nutrients were established according to Novais et al. [19] and Malavolta [20].

#### 2.4. Chemical Properties

For the chemical evaluation of the substrates, the collected material was dried at room temperature, sieved (<2 mm) and analysed according to Embrapa [21]. The pH was determined in water at a soil:solution ratio of 1:2.5. P and K were extracted with Mehlich-1 solution (0.05 M HCl + 0.0125 M H<sub>2</sub>SO<sub>4</sub>), where K was measured by flame photometry and P was measured by colorimetry according to Murphy and Riley [22]. The exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> were extracted with 1 M KCl, where Ca<sup>2+</sup> and Mg<sup>2+</sup> were measured by atomic-absorption spectrometry and Al<sup>3+</sup> was measured by titration. Potential acidity (H + Al) was determined by extraction with 0.5 M calcium acetate and quantified by titration. The available Fe, Mn, Zn, and Cu contents were extracted in diethylenetriamine-pentaacetic acid (DTPA) solution at pH 7.3 and measured by atomic-absorption spectrometry [23]. The OM content was estimated from the soil organic carbon concentration determined by wet combustion (Walkley-Black method) (where OM = organic C × 1.724) [21]. The crystalline forms of Fe and Al (196.2 and 8.7 g·kg<sup>-1</sup>, respectively) were extracted with dithionite-citrate-sodium bicarbonate and the low-crystalline oxides of Fe and Al (2.7 and 0.8 g·kg<sup>-1</sup>, respectively) with ammonium acid oxalate [24,25]. The CEC in the mining soil, mining soil + biochar, and mining soil + compost samples was determined by extraction in NH<sub>4</sub>OAC according to Song and Guo [17].

#### 2.5. Plant Analyses

After the 120-day cultivation period, the plants were harvested and separated into shoots and roots and immediately washed in running water and distilled water to avoid contamination with the cultivation substrate. Then, the fresh biomass was quantified. The dry biomass in these tissues was determined by drying in a forced-air oven at 65 °C to constant weight, with subsequent weighing and grinding of the dry material.

The N, P, K, Ca, Mg, S, Cu, Fe, Mn, B, and Zn contents were measured in the shoot tissues, while in the roots, only macronutrients were measured. The N content was determined by Kjeldahl digestion followed by distillation [26]. B was extracted by incineration and measured by azomethine colorimetry [26]. For the other elements, the samples were subjected to nitroperchloric digestion in a block digester and determined by inductively coupled plasma-atomic emission spectrometry.

## 2.6. Phosphorus Adsorption

Some of the mining soil samples incubated for 30 days (90% mining soil + 10% biochar or organic compost) were reserved and used in the P adsorption tests to evaluate the P adsorption parameters of the substrates. For this step, 1 g (<2 mm) of each substrate was weighed and added to 30 mL of 0.01 M KCl containing 40, 80, 120, and 240 mg L<sup>-1</sup> P in the form of KH<sub>2</sub>PO<sub>4</sub> at pH 6. The samples were stirred for 24 h at 25 °C. The suspensions were then centrifuged (4000 rpm, 30 min), and the extract was filtered through Whatman 42 paper. The P concentration was determined by colorimetry according to Murphy and Riley [22], and the P adsorption was calculated as the difference between the amount of P added and the amount in the equilibrium solution for the soil weight used.

The parameters of the Langmuir and Freundlich isotherms were estimated by linearization of the hyperbolic model according to Alvarez and Fonseca [27]. With the data obtained, the adsorption isotherms were plotted and fitted to hyperbolic models given by Equations (1) and (2):

$$x/m = K_L C / (\beta_L + K_L C), \text{ Langmuir} \quad (1)$$

$$x/m = K_F C^n, \text{ Freundlich} \quad (2)$$

where  $x/m$  is the amount of P adsorbed in mg g<sup>-1</sup>;  $K_L$  is the Langmuir constant and is related to the binding energy in L mg<sup>-1</sup>;  $C$  is the concentration of P in the equilibrium solution in mg·L<sup>-1</sup>;  $\beta_L$  is the maximum P adsorption capacity in mg·kg<sup>-1</sup>;  $K_F$  is the Freundlich adsorption coefficient in L·mg<sup>-1</sup>; and  $n$  is a dimensionless parameter reflecting the sorption intensity.

## 2.7. Statistical Analysis

All variables were normally distributed, as confirmed by the Shapiro-Wilk test, and were compared by analysis of variance. When a significant difference was observed, the individual means were compared by the Scott-Knott test ( $p < 0.05$ ). The variables were also subjected to regression analysis as a function of P dose and were compared by significance levels. Statistical analysis was performed in the R environment, version 3.2.4 [28]. Principal component analysis of the nutrient contents in the plant parts was performed in scaled and normalized form using the “prcomp” function of the “vegan” package.

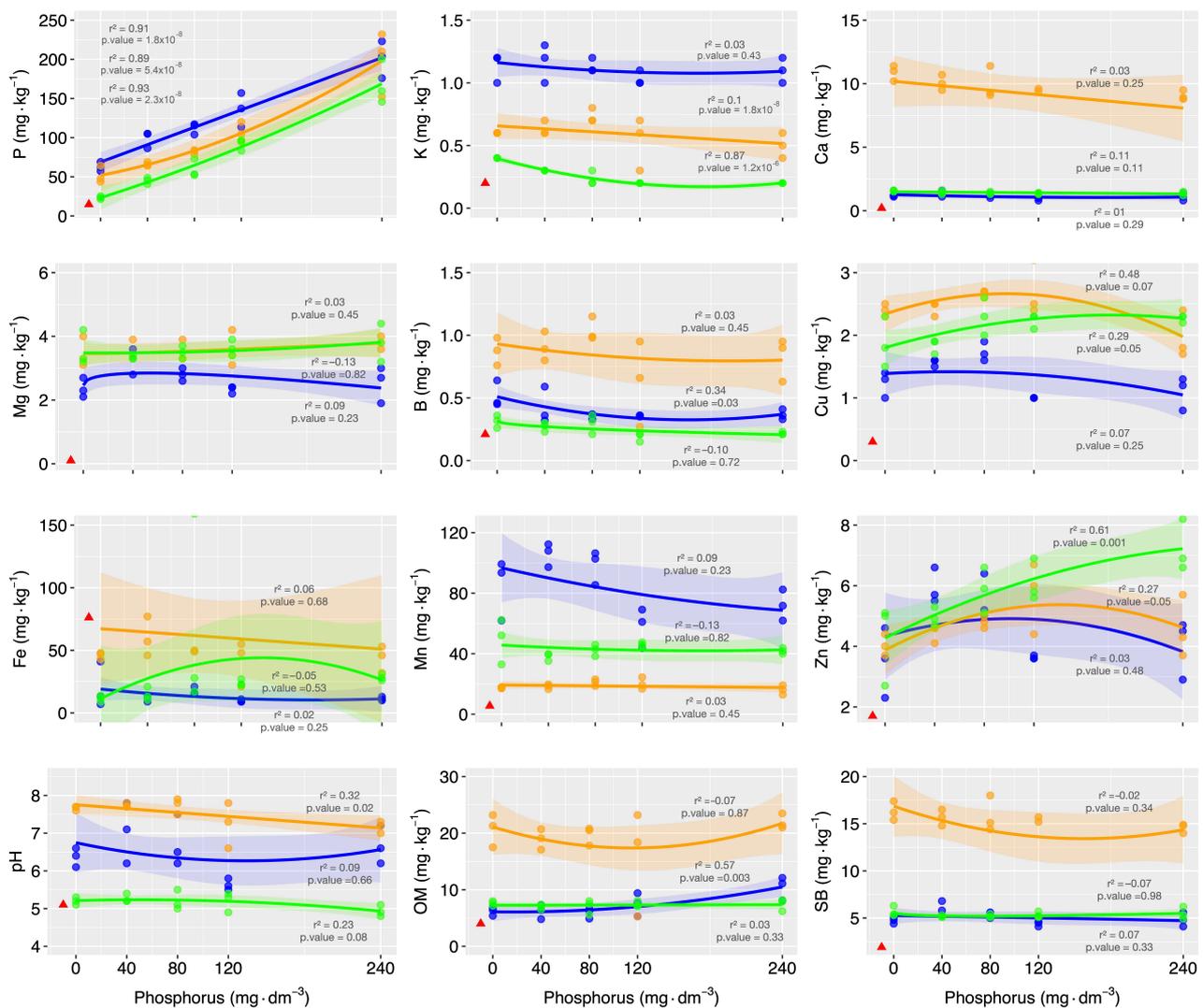
## 3. Results

### 3.1. Changes in Mining Soil Properties

The chemical properties of the mining soil before and after the application of açai biochar or compost and subsequent cultivation with *D. apurensis* are shown in Figure 1. The application of compost increased the K, Ca, and B availability, while biochar increased the K and P availability, in the Fe mining soil during the cultivation of *D. apurensis*.

The acidity of the mining soil cultivated with *D. apurensis* was highest without the application of biochar or compost at all P doses. Conversely, the application of compost promoted lower acidity in the Fe mining soil but tended to reduce the pH as the P dose in this substrate increased, whereas the application of biochar promoted intermediate pH values in the mining soil, which did not vary as a function of P dose.

When applied, biochar and compost promoted greater P availability in the waste, and the highest values were obtained when biochar was used. The application of this product also led to lower Mg and Cu contents and kept the sum of bases (SB) low, similar to that of the mining soil without treatment. Biochar also promoted greater availability of K and Mn for the cultivation of *D. apurensis*, although there was no change in the level of either element as a function of P dose or before vs. after cultivation. The application of compost increased the levels of Ca, OM, B, and SB at all P doses, while at the initial P doses, the Cu content in the mining soil also increased. In general, the Fe contents at all P doses and the Zn content at the initial P doses were not influenced by the addition of biochar or compost during *D. apurensis* cultivation.



**Figure 1.** Properties of the Fe mining soil as a function of the application of biochar (blue) or compost (orange) and without the application of biochar or compost (green). The red triangle represents the Fe mining soil properties before *D. apurensis* cultivation and before incubation.

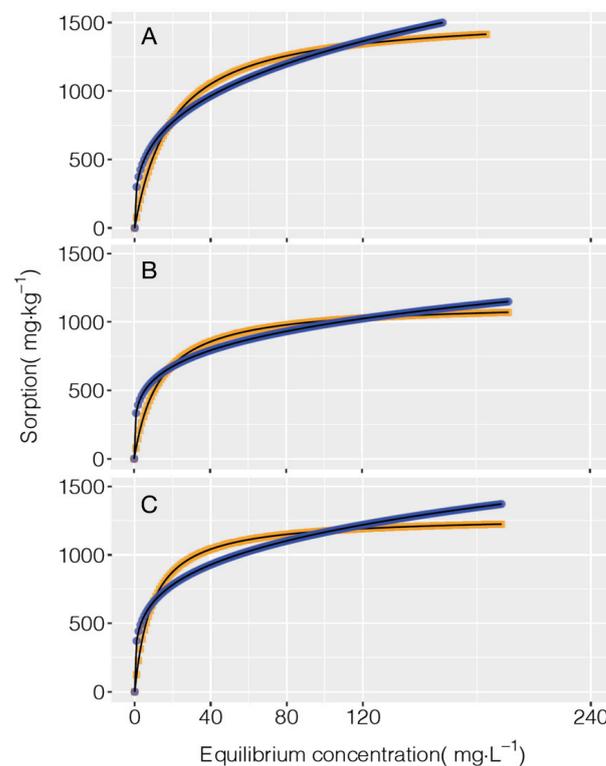
### 3.2. Effect of Açai Biochar and Compost on P Adsorption

The P adsorption isotherms describe similar behaviour between the mining soil samples treated and not treated with açai biochar and organic compost, characterizing substrates with high affinity for P. The best fit was obtained with the Langmuir model (Table 2 and Figure 2). The Freundlich model predicted an increase in the adsorption capacity ( $K_F$ ), as well as in the intensity of this process ( $1/n$ ), from the addition of biochar to the mining soil. However, the Langmuir model estimated that the maximum P adsorption capacity decreased with the application of biochar, along with the binding energy ( $K_L$ ) with which P was retained.

**Table 2.** Goodness of fit and parameters of the Langmuir and Freundlich equations observed for P adsorption in mining soil without organic amendments (W), with biochar (BC), and with organic compost (OC).

Sample	Langmuir			Freundlich		
	$K_L$	$Ads_{max}$	$R^2$	$K_F$	$1/n$	$R^2$
W	0.05b	1452.5a	0.99	309.4a	3.46a	0.93
OC	0.05b	1564.7a	0.90	299.4a	3.16a	0.78
BC	0.07a	1144.2b	0.99	333.6b	4.27b	0.87

$Ads_{max}$ : Maximum adsorption capacity ( $mg \cdot kg^{-1}$ );  $K_L$ : Langmuir constant related to the binding energy;  $K_F$  and  $1/n$ : Freundlich constants related to adsorption capacity and intensity, respectively;  $R^2$ : Model goodness of fit. Means followed by the same letter in the column are not significantly different ( $p < 0.05$ ) by the Scott-Knott test.



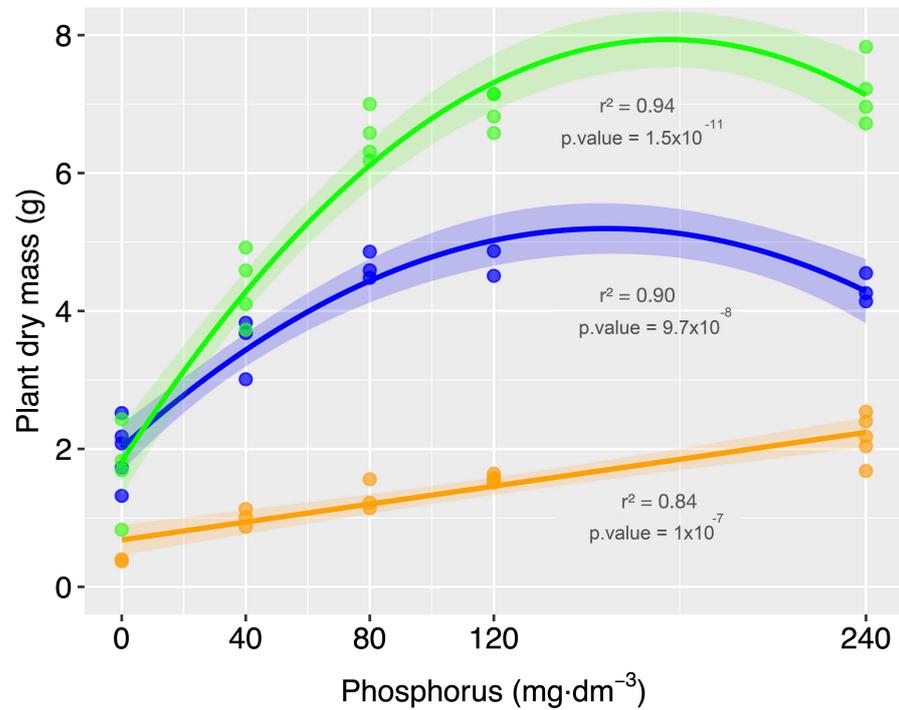
**Figure 2.** P adsorption isotherms fitted to the Langmuir (yellow) and Freundlich models (blue) in mining soil without the addition of organic amendments (A), with compost (B), and with biochar (C).

### 3.3. *Dioclea apurensis* Growth

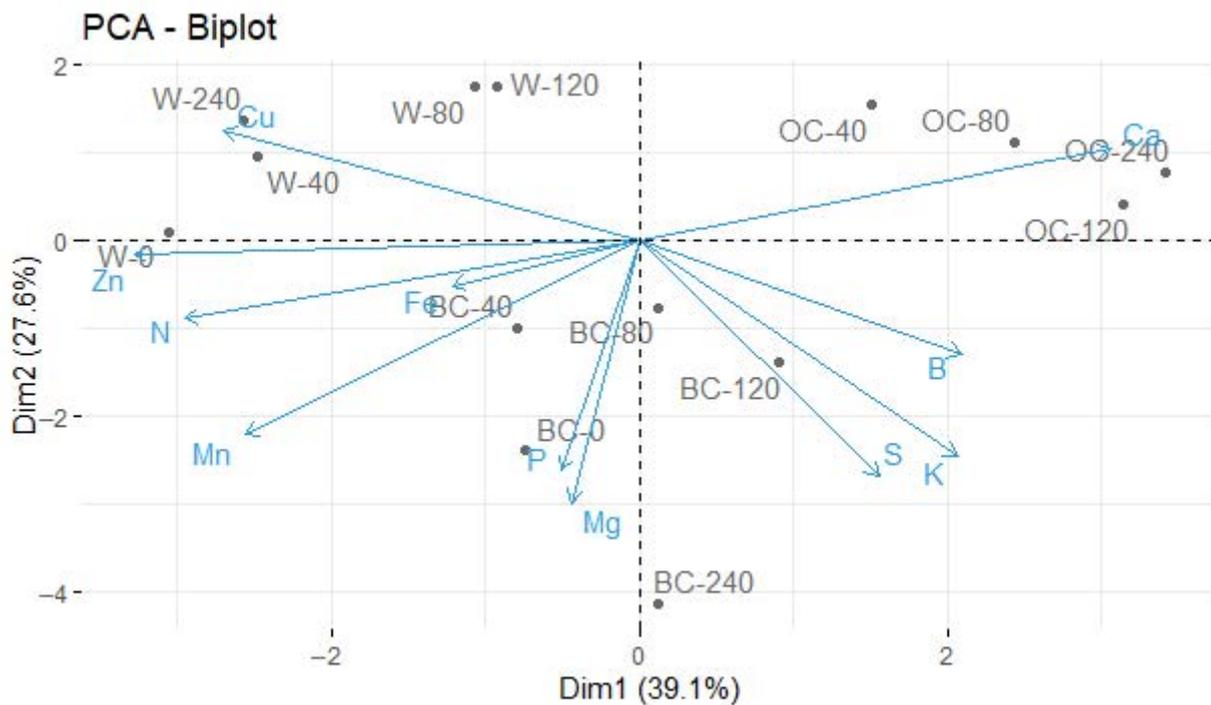
The total biomass production of *D. apurensis* was significantly influenced by the P dose and by the addition of biochar or compost (Figure 3). A greater P dose promoted greater biomass of *D. apurensis*, and the highest production was obtained without the addition of biochar or compost. The application of compost led to a linear response and lower total biomass production of this species. However, the addition of biochar promoted intermediate biomass production in *D. apurensis*, showing no effect on the growth of this plant species at doses of  $\geq 80 \text{ mg} \cdot \text{dm}^{-3}$  P in the Fe mining soil.

Principal component analysis was performed for the nutrient contents in the plant shoot and root, whose first two components explained 66.7% and 79.7% of the data variability, respectively (Figure 4). In the shoot, the N, Zn, and Fe contents showed a negative correlation with the presence of organic compost; thus, the shoot presented a lower content of these nutrients after organic amendments application. The P content increased the most at the dose of  $240 \text{ mg} \cdot \text{kg}^{-1}$  P in the presence of açai biochar. In addition, the K, S, and Mg contents were higher in the presence of biochar. Similarly, the Ca content in the shoot

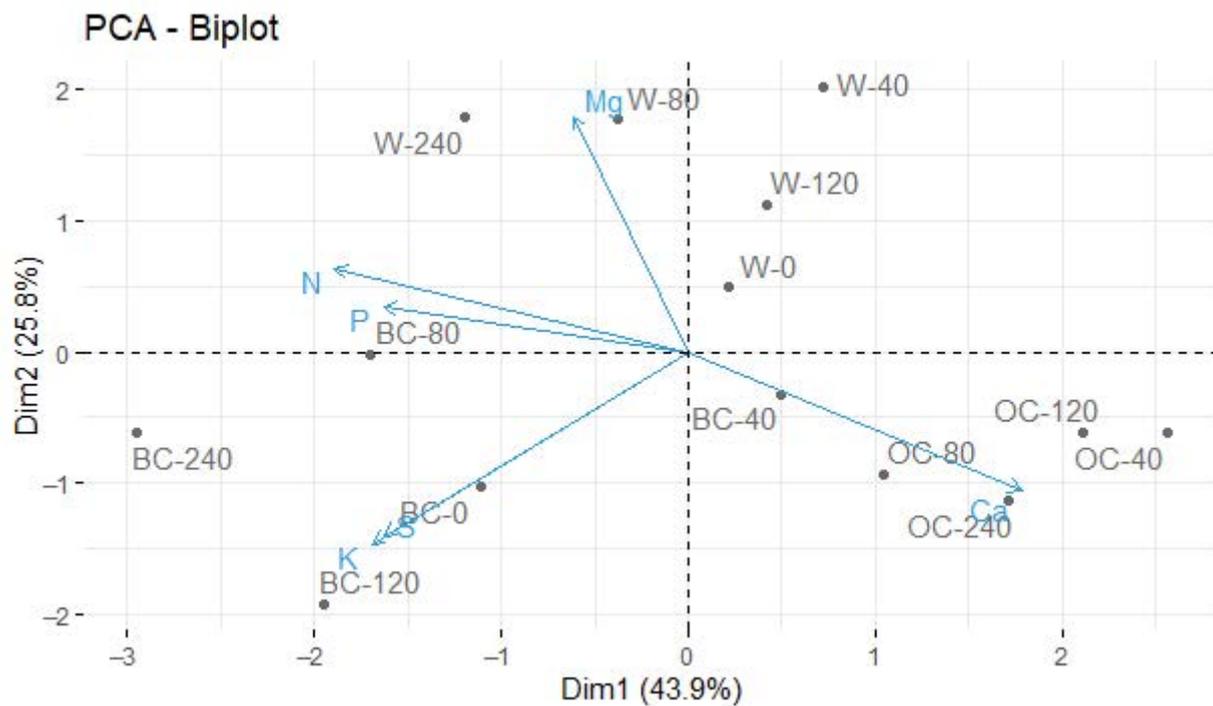
was higher when compost was added for *D. apurensis* cultivation (Figure 4), an effect also observed in the root (Figure 5 and Table 3).



**Figure 3.** Total dry biomass of *D. apurensis* in response to P dose without the application of organic amendments (green), with açai biochar (blue), and with compost (orange).



**Figure 4.** Principal component analysis of the macro- and micronutrient contents in the shoots of *D. apurensis* as a function of P dose in waste without organic amendments (W), with biochar (BC), and with organic compost (OC).



**Figure 5.** Principal component analysis of the macronutrient contents in the roots of *D. apurensis* as a function of P dose in waste without organic amendments (W), with biochar (BC), and with organic compost (OC).

**Table 3.** Content of macronutrients and micronutrients in the aerial part and roots of *D. apurensis* as a function of doses of P without organic amendments (W) with biochar (BC) and with organic compost (OC).

Treatments	N	P	K	Ca	Mg	S	B *	Cu *	Fe *	Mn *	Zn *
	g · kg <sup>-1</sup>						mg · kg <sup>-1</sup>				
<b>Aerial part</b>											
OC-0	-	-	-	-	-	-	-	-	-	-	-
BC-0	21.3 a	1.0 b	17.8 a	9.1 b	5.6 a	2.2 a	37.9 a	2.3 b	251.5 a	812.3 a	36.4 a
W-0	24.2 a	0.6 b	13.8 a	8.7 b	4.7 a	1.4 b	39.3 a	5.9 a	213.8 a	855.7 a	43.7 a
OC-40	18.8 a	0.5 b	18.1 a	17.5 a	3.2 b	1.8 a	35.3 a	2.6 b	229.1 a	86.3 c	30.5 a
BC-40	20.5 a	0.7 b	21.6 a	7.8 b	4.9 a	1.5 b	39.0 a	2.8 b	307.3 a	646.1 b	32.4 a
W-40	21.4 a	0.7 b	12.1 b	7.8 b	4.1 a	1.3 b	39.4 a	5.5 a	222.2 a	616.6 b	48.7 a
OC-80	18.3 a	0.6 b	19.6 a	17.1 a	3.5 b	1.7 a	40.4 a	2.4 b	215.4 a	93.4 c	17.4 b
BC-80	19.8 a	0.9 b	22.0 a	7.8 b	4.3 a	1.5 b	42.3 a	3.2 b	198.2 a	761.4 a	24.3 b
W-80	18.6 a	0.8 b	9.9 b	8.4 b	3.1 b	1.3 b	37.9 a	3.8 b	219.6 a	536.6 b	40.5 a
OC-120	18.0 a	0.5 b	18.9 a	18.3 a	4.4 a	1.8 a	47.4 a	2.4 b	224.7 a	92.5 c	11.2 b
BC-120	19.3 a	1.0 b	21.9 a	9.1 b	4.2 a	1.9 a	40.5 a	1.5 b	192.4 a	777.5 a	25.9 b
W-120	20.0 a	0.8 b	9.0 b	7.1 b	3.3 b	1.3 b	34.6 a	3.2 b	181.1 a	490.0 b	29.5 a
OC-240	18.9 a	0.8 b	18.5 b	17.8 a	3.4 b	1.9 a	43.2 a	1.8 b	152.9 a	72.4 c	7.0 b
BC-240	21.3 a	2.1 a	23.4 a	7.7 b	5.0 a	2.5 a	42.5 a	2.1 b	201.3 a	833.7 a	32.4 a
W-240	22.8 a	1.1 b	8.1 b	6.2 b	2.9 b	1.6 b	24.9 b	3.4 b	235.3 a	513.0 b	35.1 a

Values with the same letter do not represent a significant difference ( $p < 0.05$ ) between treatments by the Scott-Knott test. \* In root, micronutrients were not analyzed.

Table 3. Cont.

Treatments	N	P	K	Ca	Mg	S	B *	Cu *	Fe *	Mn *	Zn *
	g·kg <sup>-1</sup>						mg·kg <sup>-1</sup>				
Root											
OC-0	-	-	-	-	-	-	-	-	-	-	-
BC-0	24.0 a	0.9 c	16.9 c	3.5 d	3.4 a	2.8 b					
W-0	25.2 a	0.9 c	8.1 e	3.9 d	3.3 a	2.1 d					
OC-40	19.3 c	0.7 c	8.4 e	9.0 c	3.3 a	1.9 e					
BC-40	21.2 b	1.0 c	14.4 d	3.6 d	3.2 a	1.9 e					
W-40	20.2 b	1.1 c	7.8 e	3.2 d	4.6 a	1.9 e					
OC-80	18.9 c	1.0 c	11.1 e	7.9 b	3.9 a	2.8 b					
BC-80	23.7 a	1.6 b	19.1 b	3.5 d	4.3 a	2.7 b					
W-80	23.7 a	1.6 b	9.3 e	3.1 d	4.4 a	2.1 d					
OC-120	17.3 c	0.8 c	9.6 e	7.5 a	3.6 a	2.2 c					
BC-120	21.6 b	1.8 b	21.9 a	3.6 d	3.6 a	3.3 a					
W-120	20.4 b	1.4 b	7.7 e	3.6 d	4.2 a	2.3 c					
OC-240	17.7 c	1.7 b	9.8 e	8.8 a	3.5 a	2.5 c					
BC-240	24.6 a	4.5 a	17.4 c	3.5 d	3.7 a	3.1 a					
W-240	23.3 a	3.8 a	8.7 e	4.1 d	4.6 a	2.4 c					

Values with the same letter do not represent a significant difference ( $p < 0.05$ ) between treatments by the Scott-Knott test. \* In root, micronutrients were not analyzed.

#### 4. Discussion

##### 4.1. Effects of Açai Biochar and Compost on the Properties of Fe Mining Soil

The application of biochar and compost led to an increase in the pH of the substrate, which may be related to the high pH of the biochar, the greater amount of surface charge, and the high retention capacity of H<sup>+</sup> ions of the organic materials used [29]. A higher soil pH is reported as one of the main benefits of the application of organic materials, which can also favour the retention of exchangeable cations or essential anionic elements, such as P and S [30]. Forján et al. [5] tested the effect of the application of biochar and compost to mining soil and observed reductions in soil acidity.

In contrast, phosphate fertilization increased soil acidity, especially in compost treatments, resulting in a lower soil pH as the P dose applied to the waste increased. According to Delgado et al. [31], this effect occurs due to the release of H<sup>+</sup> ions by phosphate molecules in the soil. This finding was confirmed by Bindraban et al. [32], who reported that with the addition of P sources based on H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (such as single or triple superphosphate and monoammonium phosphate), there was an increase in acidity in soils with pH greater than 7.2 due to the dissociation of H<sup>+</sup> from H<sub>2</sub>PO<sub>4</sub> molecules. However, these sources did not alter the acidity of the soil under acidic conditions, which corresponds to the condition of untreated mining soil or biochar treatment in the present experiment.

The application of biochar increased the availability of K, which, according to Zhao et al. [33], may be associated with the gradual release of the nutrients retained on the surface of the biochar, which tends to favour the absorption of this element by cultivated plants. Similarly, greater availability of other elements, such as P, B, and Mn, was observed in the mining soil, possibly due to the release of these nutrients from the structure or surface of the organic materials used [34]. According to Prasad et al. [35], biochar can contain high amounts of available Mn and P, which are readily released to the soil. The results corroborate the study by Safaei Khorrām et al. [36], who reported that the application of biochar increased the availability of K and P, benefitting plant growth. It is also possible that biochar reduces the availability of elements that are already low in the soil, such as Mg and Cu [37,38]. In the present study, biochar promoted lower availability of Mg, Cu, Fe, and Zn, while lower Mn contents were found in the presence of compost. Other functions of biochar or organic compost are the capture of metallic elements from the soil, which react strongly with the surface charges of these materials and may reduce their availability to plants [39]. This beneficial and extremely useful effect for the remediation of contaminated

areas requires closer attention in areas where the rapid establishment of vegetation cover is the main goal.

A positive effect of the application of organic compost is the increase in Ca, OM, B, Cu, and SB contents in the mining soil. Therefore, the application of compost in mining areas under reclamation can be highly important, since these are key properties for more efficient soil management in ferruginous substrates, especially where there is low OM content, which controls a set of other soil characteristics such as nutrient availability and microbial activity, helping to restore soil ecological processes [40,41].

The results of the present study show that the use of açai biochar and organic compost improves the chemical properties/fertility of the Fe mine substrate for plant cultivation. However, these materials have different effects. An increase in some soil properties seemed to be correlated with a reduction in others when biochar or organic compost was applied. Compost increased the SB, K, Ca, B, and OM contents while it decreased Mn and Zn availability. Similarly, biochar increased P and K availability and soil pH while it decreased Mg, Cu, and Zn availability, a finding also observed by Mensah and Frimpong [29] and Safaei Khorram et al. [36].

#### 4.2. Phosphorus Sorption

The fits found for P adsorption to the Langmuir and Freundlich models describe a high affinity (with sorption above  $1000 \text{ mg}\cdot\text{kg}^{-1}$ ) between the Fe mining substrate and phosphate ions, which can generate low P availability in this material. The high affinity of P to the substrate occurred due to a set of factors, such as the high content of Fe oxides, both in the crystalline and in the low-crystalline form. According to Gérard [42], the low-crystalline forms of Fe and Al oxides have higher surface charge since they have little-consolidated crystalline structures; however, the crystalline forms are highly important due to their higher proportion in the soil. In addition, it is important to consider the strong presence of clay minerals observed in the substrate, which have a strong ability to interact with phosphate [43].

Despite the increased adsorption estimated by the Freundlich model, the Langmuir model was better fitted and estimated a reduction in the maximum P adsorption capacity and energy as a function of the addition of açai biochar. A reduction in adsorption capacity is observed less frequently when analysing materials such as biochar given its high adsorptive potential [44]. However, the possible changes that biochar causes in the soil, such as pH elevation, release of organic substances with high surface charge, and the presence of other ions in high concentration, in addition to the release of the P contained in the biochar, decrease the maximum adsorption capacity and increase P availability [45].

The increase in P availability and the decrease in P adsorption capacity as a function of biochar application were also observed by Soinne et al. [46] and Han et al. [47], who attributed this finding to the increase in soil pH promoted by the use of this material. The pH elevation increases the formation of negative charges on the surface of soil particles, increasing repulsive forces and reducing P adsorption, in addition to reducing the formation of  $\text{H}_2\text{PO}_4^-$ , a chemical species that preferentially adsorbs onto soil colloids [45,48]. Importantly, the increased P availability and reduced  $\text{Ads}_{\text{max}}$  promoted by the application of biochar do not necessarily imply better development conditions for plants since the addition of biochar can reduce the availability of other nutrients [6]. Similarly, the use of organic compost, even without an effect on  $\text{Ads}_{\text{max}}$ , may be important for other fundamental soil characteristics, such as structure, CEC, and pH, because this material presents high CEC and pH, in addition to favoring soil aggregation [49]. Rodríguez-Vila et al. [50] observed that the application of organic compost, even with a short incubation time, was sufficient to raise the pH of high-acidity mining soil, highlighting the importance of using organic compost for the rehabilitation of degraded areas.

### 4.3. *Dioclea apurensis* Growth

*D. apurensis* is a native species of the ferruginous cangas of Carajás and is known to be tolerant to the edaphic conditions of this environment [51], which include acidic soils and low nutrient availability [52]. The results found in this study show that the growth of *D. apurensis* was altered by the application of biochar and organic compost, which could have been due to the change in the pH of the cultivation substrate by the application of both materials. The addition of compost promoted a higher increase in the pH of the cultivation substrate, which resulted in lower *D. apurensis* growth, while the addition of biochar promoted an intermediate increase in the soil pH and growth of *D. apurensis*. Conversely, the non-addition of both organic products did not increase the pH of the Fe mining soil, which favored greater growth of *D. apurensis*. This result corroborates that found by Ramos et al. [16], who observed that *D. apurensis* growth was favored by the addition of nutrients without increasing the pH of the cultivation soil.

The increase in P content in the shoot was directly related to the increase in P availability promoted by the biochar. There was a similar effect on other elements, such as Mg, K, and S. These factors are correlated because the plant's need for macronutrients naturally increases the levels of these elements in the shoot to support its development; however, nutrient absorption may be conditioned on the availability promoted by the soil organic matter [16]. Similarly, the Ca content in the shoots and roots was strongly influenced by the high content of this element in the compost, which acted as the main source of Ca for cultivation. According to Manca et al. [53], organic compost may have a high concentration of Ca and increase its availability in the soil as well as its content in leaves and roots. However, the excess sodium contained in the compost may have caused salt stress in the plant, generating a physiological response to reduce nutrient absorption [54]. Perhaps because of this response, the addition of organic compost was not efficient in increasing the N, Zn, and Fe contents in the plant, which may have compromised the growth of *D. apurensis*.

## 5. Conclusions

The application of biochar and organic compost increased the availability of elements such as Ca, Mg, and K, in addition to increasing the pH and OM of the substrates; however, the use of these products also reduced the availability of micronutrients, which can cause nutritional deficiency and low plant development. Thus, it was observed that these forms of biochar and organic compost did not favor the growth of *D. apurensis*, so use of these products is not recommended in operations to recover degraded areas involving the species *D. apurensis* in mine wastes of Carajás because it may increase costs and reduce soil cover, reducing the efficiency of the area recovery process. However, it was found that the application of biochar reduced the adsorption capacity and increased the availability of P in the substrates, contributing to the longer-term availability of P.

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