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# Soil mineralogy-controlled phosphorus availability in soils mixed with phosphate fertiliser and biochar

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## ABSTRACT

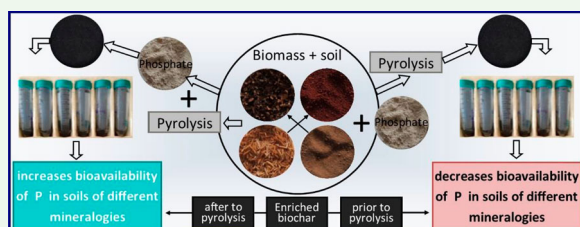
The biochar amendment to soil proved to be beneficial to improve soil quality and provide nutrients. However, the effect of biochar on the availability of P is still controversial. We aim to study the effect of adding phosphate fertiliser and biochar on the P bioavailability in soils of different mineralogies. Eight biochars derived from biomass (rice husk and coffee husk), soil (sandy and clayey), and phosphate fertiliser (triple superphosphate) were produced. The biochar enrichment process with superphosphate was carried out before and after pyrolysis. Thus, we tested two biochar groups: (1) enriched biochars prior to pyrolysis; (2) enriched biochars after pyrolysis. These biochars were tested as P sources in soils of three mineralogies (kaolinite/oxide, kaolinite, and smectite). Batch sorption-desorption experiments were conducted. The sorbed P was fractionated to examine the factors controlling the retention of applied P. In the three soil mineralogies the use of enriched biochars prior to pyrolysis results in lower availability of P. In contrast, the enriched biochars after pyrolysis increase the bioavailability of P. The coffee husk biochar is more suitable than rice husk biochar to protect P from soil retention reactions. The use of sandy soil rather than clayey soil in enriched biochars compositions results in higher P content availability when applied to soils. The factor that controls the retention of P is the reaction between P, organic compounds, and Fe and Al compounds. The greater the relationship between biochar and soluble P in the fertiliser, the higher the increase of P retention.

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## KEYWORDS

Biochar; enriched biochar; organo-mineral associations; phosphorus availability; soil mineralogy




## 1. Introduction

The use of biochar; which consists of a solid material rich in recalcitrant carbon (C), obtained by biomass pyrolysis; as soil amendment has agronomic and environmental benefits that have been widely proven, among which we can highlight the improvement of physical-hydric conditions and soil fertility, the increase in productivity of agricultural crops, the carbon sequestration and greenhouse gas emission reduction [1,2]. Regarding

soil fertility, one of the benefits of biochar is the possibility of reducing phosphate retention reactions and, consequently, increasing phosphorus (P) bioavailability [3,4].

Phosphate retention is defined as the conversion of labile to non-labile P, and occurs through two simultaneous processes, precipitation, and phosphate sorption [5,6]. This phenomenon consists in one of the main problems in relation to the fertility of most

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cultivated land, which provides overfertilization, causing financial and environmental losses, such as increase in production costs and reduction of available P sources (phosphate rocks) [7]. It is estimated that up to 85% of the soluble P applied to soil takes forms that are unavailable to plants in the first 60 days [8].

The dynamics of P in soil is complex, and the main edaphic factors that influence it are pH, mineralogy, clay content, content and composition of organic matter, and the interaction of P with other elements [8–10]. The increase in soil organic carbon content tends to decrease phosphate retention due to the reactions of competitive sorption between organic acids and P for soil sorption sites, metal complexation (mainly Fe and Al), and increase in the negative charge on the soil [11]. However, the form of carbon added to the soil affects P availability in different ways, with raw residues with a high C/P ratio (e.g. wheat straw, sawdust, and corn stalks) increasing phosphate retention, while biochars produced from these same residues, decreasing the p retention process and increasing P availability in the soil [12].

There are three mechanisms by which biochar can increase the bioavailability of P in the soil: (1) the content of P available in the biochar can increase the activity of P in the soil solution [12–14]; (2) the addition of biochar can increase the soil pH and, consequently, decrease the phosphate reactions with iron (Fe) and aluminium (Al) compounds [4,12,15,16]; (3) the organic surface acids of the biochar can complex Fe, Al, and calcium (Ca) ions active in the soil solution and also bind to phosphate sorption sites, such as clay minerals and Fe and Al oxyhydroxides [13,16].

Schneider and Haderlein [13] estimated that biochar application (with marginal affinity for P) in a proportion of 10% (v/v), if the concentration of P solution remains constant, can reduce P retention by 10%. These authors also verified that the effect of biochar in protecting P from goethite retention reactions occurs mainly at acidic pH. Ghodszad et al [12]. also found an increase in P availability in acidic soils with the incorporation of alkaline biochar. On the other hand, Xu et al [16]. found that the application of 10% of alkaline biochar (without the ability to sorb P) in the soil, increased the maximum capacity of P sorption in acidic soils and decreased in alkaline soil. Thus, we see that the effect of biochar on the bioavailability of P in the soils is variable. Ghodszad et al [12]. found that phosphorus sorption and desorption characteristics of soils were impacted by soil characteristics, biochar properties, application rates, and initial P concentration.

Another gap in knowledge about P, soil, and biochar dynamics is the fact that the research has been carried

out, mainly, in biochar-amendment soils [15,13,16] and not with the use of biochar as a source of P. However, the concentration of P in the biochar has been pointed out as one of the factors that affect the process [13,16]. In addition, recent experiments have presented biochars enriched with mineral compounds (enhanced biochar) to use them as a fertiliser and not just as a soil conditioner [3,17]. Given this, and the complexity of the reactions between P and organic and mineral compounds in the soil, experiments on the effect of adding biochar to the soil as a source of P in different edaphic contexts are justified.

Biochar enrichment (enhancement) mechanism can be classified into five categories: metal-biochar composites, mineral-biochar composites, layered doublehydroxide (LDH)-biochar composites, carbonaceous engineering nanocomposites, and microorganism-biochar composites [18]. The main methods to produce mineral-biochar composites are co-pyrolysis, mixing mineral suspension with biochar, and co-precipitation of mineral compounds directly onto biochar [3,18–20]. According to Wang et al. [18] co-pyrolysis stands out as a facile synthesis method, that is suitable for largescale applications.

Compared with the unenriched biochars, enriched biochars have shown excellent performances in various environmental applications [18], among which, we highlight: higher nutrient content, higher content of surface oxygen groups, higher carbon retention in the biochar [17,19–21].

We worked with mineral-biochar composites produced and characterised by Matoso et al. [17]. These enriched biochars were obtained through different combinations of biomasses (rice and coffee husks), soils (sandy and clayey), and phosphate fertiliser (triple superphosphate), obtaining P rich biochars, without the ability to adsorb phosphate and acidic pH. However, these biochars present different concentrations of labile, moderately labile, and non-labile forms of P. Thus, our study proposes that the application of enriched biochar as a source of P increases the availability of this element in the soil, due to the higher concentration of P in solution associated to less conversion of labile P to non-labile forms, and that the magnitude of this process can be affected by the properties of biochars. To support our hypothesis, we conducted experiments of P sorption and desorption in soils of different mineralogies using a reference source ( $\text{KH}_2\text{PO}_4$ ) and eight enriched biochars. The sorbed P was fractionated to examine the factors that control P retention in these soils. Thus, we present the novelty of testing enriched biochars as sources of P and not just as a soil conditioner.

## 2. Material and methods

### 2.1. Enriched biochars

Details about the process for obtaining and characterising the enriched biochar are found in Matoso et al. [17] and Supplemental material, since four biochars were obtained by the pyrolysis of two agricultural residues (rice husks and coffee husks) mixed with soil of two textures (sandy and clayey) and phosphate fertiliser (triple superphosphate).

The biomasses (rice and coffee husks) were selected due to their high availability and worldwide distribution. The use of soil to compose enriched biochars proved to be effective in increasing the degree of aromaticity and thermal stability of biochars, while resulting in greater carbon retention during pyrolysis [21]. It is important to note that the soils used to compose the enriched biochars are not the same ones used in the experimental phase. The triple superphosphate is a typical phosphate fertiliser used as a source of P in agriculture.

The biomass was mixed with soil in a 3:2:2 ratio (45 g of biomass: 30 g of soil: 30 g of fertiliser) and placed in closed aluminium containers (159 mL) to create a CO<sub>2</sub> rich atmosphere. Then pyrolysis was carried out in an EDG muffle furnace equipped with a microprocessed controller, at 350°C for 2 h. This group of biochars was called enriched biochars prior to pyrolysis, and each product was named as follows:

- P-RiS: biochar derived from rice husks, sandy soil, and triple superphosphate;
- P-RiC: biochar derived from rice husks, clayey soil, and triple superphosphate;
- P-CfS: biochar derived from coffee husks, sandy soil, and triple superphosphate;
- P-CfC: biochar derived from coffee husks, clayey soil, and triple superphosphate.

We produced four other biochars through the same combination of biomasses and soils and the same pyrolysis method, but the addition of phosphate fertiliser to the biochars was carried out after the pyrolysis process, in a proportion of 65 g of soil-enriched biochar to 35 g of fertiliser. This group of biochars was called enriched biochars after pyrolysis and each product was designated as follows:

- RiS + P: biochar derived from rice husk and sandy soil, with triple superphosphate added after pyrolysis;
- RiC + P: biochar derived from rice husk and clayey soil, with triple superphosphate added after pyrolysis;
- CfS + P: biochar derived from coffee husk and sandy soil, with triple superphosphate added after pyrolysis;

- CfC + P: biochar derived from coffee husk and clayey soil, with triple superphosphate added after pyrolysis.

### 2.2. Soils of different mineralogies

The enriched biochars were tested on samples of B horizon of soils of three distinct mineralogies. These soil samples were obtained in the form of air-dried soil (< 2,0 mm), from the Collection of Reference Soils of the State of Pernambuco, from the Federal Rural University of Pernambuco (UFRPE), and are classified as Nitisol, Ferralsol, and Vertisol [22].

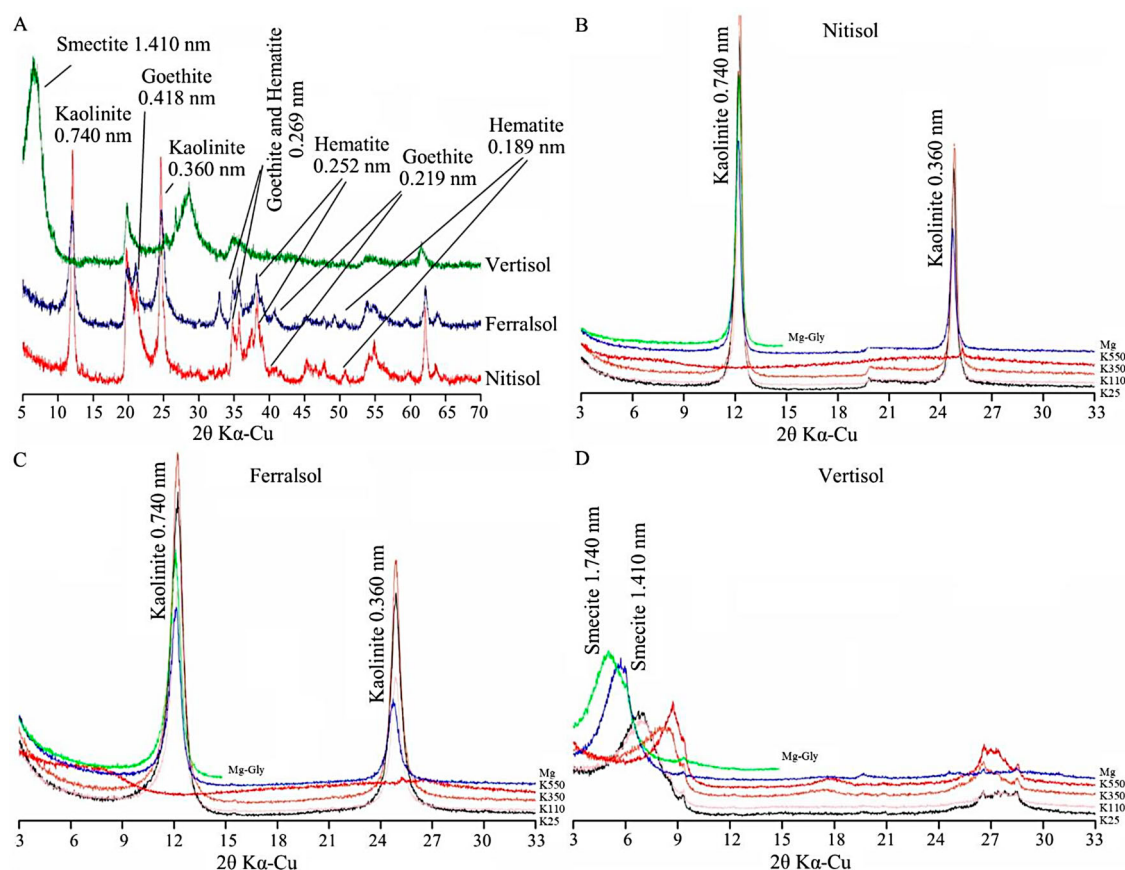
The soils were selected to obtain different magnitudes of phosphate retention, since mineralogy is a factor that has a high influence on this phenomenon [8,9]. The clay fraction of the samples was characterised in terms of its mineralogy (Figure 1), qualitatively, by X-ray diffraction (XRD) using a Shimadzu XRD 6000 diffractometer operated with Cu K $\alpha$  at 40 kV and 30 mA and a graphite monochromator.

The samples in the form of unoriented powder were analyzed at a speed of 1° min 2 $\theta$  and registered in the range of 5–70° (2 $\theta$ ). Then the samples were pre-treated to eliminate cementing agents, carbonates, organic matter, and iron oxides, using 1 mol L<sup>-1</sup> sodium acetate at pH 5.0, 15% v/v hydrogen peroxide, and dithionite-citrate-bicarbonate (DCB) solution, respectively [23]. To better identify the presence of minerals, including expandable minerals, the samples underwent different saturation and heat treatments [23], and were analyzed in the form of microaggregates oriented on a glass slide. The K-saturated samples (KCl 1 mol L<sup>-1</sup>) were analyzed after successive heat treatments, 25, 110, 350, and 550 °C (K25, K110, K350, and K550) at a speed of 1° min 2 $\theta$  and registered in the range of 3–35° (2 $\theta$ ). The Mg-saturated samples (MgCl<sub>2</sub> 1 mol L<sup>-1</sup>) were analyzed at room temperature, solvated with glycerol (Mg, and Mg-Gly) at a speed of 1° min 2 $\theta$  and registered in the range of 3–15° (2 $\theta$ ).

Smectite rich Vertisol was characterised by an alkaline pH, a high content of available P, and a high cation exchange capacity, mainly occupied by Ca<sup>2+</sup>, and Mg<sup>2+</sup> (Table 1). Haematite rich Nitisol and kaolinite rich Ferralsol had an acidic pH, low P content available, and low cation exchange capacity, mainly occupied by H<sup>+</sup> and Al<sup>3+</sup> (Table 1). Nitisol was also characterised by a higher total content of Fe and Al and of Ox-Fe and Ox-Al, when compared to other soils (Table 1).

### 2.3. Phosphorus sorption and desorption

2 g of each soil (Nitisol, Ferralsol, and Vertisol) were placed in 50 ml centrifuge tubes, in duplicate, adding



**Figure 1.** X-ray diffraction patterns of the clay fractions (<2 μm) of B horizon samples from a Vertisol, Ferralsol, and Nitisol. (A) diffractograms of the samples in the form of unoriented powder; (B, C, and D) diffractograms of the samples in the form of microaggregates oriented on a glass slide.

20 ml of 0.01 M KCl solution, containing 0, 15, 30, 60, 120, 180, and 240 mg L<sup>-1</sup> of P in the form of monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>). The samples were shaken for 24 h, centrifuged at 3200 units of gravity for 10 min and filtered through a membrane filter of ± 0.45 μm. The P content remaining in the extracts was determined by the colorimetric method with absorbance measured at

880 nm, according to Murphy and Riley [24], modified by Drummond and Maher [25], using a JASCO model V630 spectrophotometer.

The sorbed P was obtained by the difference between the initial concentration of P in the solution and the concentration of P remaining in the equilibrium solution. The content of sorbed P in each dose was adjusted by the equations of Langmuir (1) and Freundlich (2). The results were presented and discussed for the equation that presented the best fit, verified by the highest determination coefficient (R<sup>2</sup>).

$$Q = (K_L \times Q_{max} \times C_{eq}) / [1 + (K_L \times C_{eq})] \quad (1)$$

$$Q = K_F \times C_{eq}^{1/n} \quad (2)$$

where Q represents the total amount of sorbed P (mg kg<sup>-1</sup>), K<sub>L</sub> is a constant related to the element sorption energy (L mg<sup>-1</sup>), Q<sub>max</sub> is maximum sorption capacity (mg kg<sup>-1</sup>), C<sub>eq</sub> is the concentration of P remaining in the equilibrium solution after 24 h (mg L<sup>-1</sup>), K<sub>F</sub> is the Freundlich constant, and 1/n is the linearity coefficient.

For the study of P desorption, samples of the three soils, in duplicate, were treated, as previously described,

**Table 1.** Chemical and granulometric properties of soils of different mineralogies.

Properties	Nitisol	Ferralsol	Vertisol
pH (H <sub>2</sub> O)	4.6	4.7	7.6
pH (KCl)	3.9	4.2	5.5
Organic C (g kg <sup>-1</sup> )	1.33	4.23	5.57
Available P (mg kg <sup>-1</sup> )	1.47	1.20	210.00
Available K (cmol <sub>c</sub> kg <sup>-1</sup> )	0.04	0.01	0.11
Ca <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	3.19	0.02	18.30
Mg <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	1.32	0.46	26.54
H <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	5.29	2.53	0.70
Al <sup>3+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	5.88	0.59	0.00
Total Al (g kg <sup>-1</sup> )	30.81	21.07	25.19
Ox-Al (g kg <sup>-1</sup> )	1.46	0.98	0.83
Total Fe (g kg <sup>-1</sup> )	125.52	13.28	34.11
Ox-Fe (g kg <sup>-1</sup> )	1.10	0.56	0.75
Sand (g kg <sup>-1</sup> )	61.0	335.5	257.8
Silt (g kg <sup>-1</sup> )	339.0	14.5	417.2
Clay (g kg <sup>-1</sup> )	600.0	650.0	325.0

with three levels of P (30, 120, and 240 mg L<sup>-1</sup>) and, after checking the pH of the equilibrium solutions (pH<sub>eq</sub>), the supernatants from the sorption assay were discarded. The residual material was then added with 20 ml of 0.01 M KCl solution, and the tubes were shaken for 24 h. Then the supernatant was separated by centrifugation and filtration and the P content in the equilibration solution was determined. This process was repeated three times, always checking the amount of P. The total amount of P desorbed was obtained by adding the P content in the three equilibrium solutions.

To investigate the effect of enriched biochars on the phosphate sorption and desorption capacity in soils of different mineralogies, the methodology described was adapted, replacing the source of soluble P (KH<sub>2</sub>PO<sub>4</sub>) with the eight enriched biochars. Based on the content of P soluble in neutral ammonium citrate + water (NAC + water) [26], the necessary mass (g) of each source was estimated to reach doses of 0, 15, 30, 60, 120, 180, and 240 mg L<sup>-1</sup>. For the enriched biochars prior to pyrolysis, the dose of 480 mg L<sup>-1</sup> was also estimated. These doses were measured on an analytical balance with a precision of 0.1 mg, packed in centrifuge tubes containing 2 g of soil and added with 20 mL of 0.01 M KCl solution. As they were measured from the mass, the doses varied up to 4 mg L<sup>-1</sup> of P. Thereafter, the described methodology was followed to determine the sorption and desorption capacity of P.

The available P content in the soil was calculated by comparing the values of sorbed P and desorbed P in relation to the added P, according to Xu et al. [16].

#### 2.4. Sequential phosphorus fractionation

Three soils were stored in centrifuge tubes, in quadruplicate, and treated with three levels of P (30, 120, and 240 mg L<sup>-1</sup>) from the reference source (KH<sub>2</sub>PO<sub>4</sub>); from the sources RiS + P and CfS + P, which represent the group of enriched biochars after pyrolysis; and P-CfC, which represents the group of enriched biochars prior to pyrolysis. After stirring for 24 h, the equilibrium solution was separated by centrifugation (10,000 units of gravity) and discarded. The samples were then separated into two duplicates, one of which was used to determine the total P content contained in the soil after equilibrium and the other to perform the sequential fractionation of P.

The total P content was extracted by acid digestion at 90 °C, using nitric acid, hydrogen peroxide and hydrochloric acid (5:3:5) [27]. The P content was determined by a colorimetric method with absorbance measured at 880 nm, according to Murphy and Riley [24],

modified by Drummond and Maher [25], using a JASCO model V630 spectrophotometer.

The sequential fractionation of P was performed by the method described by Ruttenberg [28], with adaptations. Soil samples treated with KH<sub>2</sub>PO<sub>4</sub>, RiS + P, CfS + P, and P-CfC (0.5 g) were extracted step by step, using [1] MgCl<sub>2</sub> (1 M), [2] NaHCO<sub>3</sub> (0.11 M) + Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (0.11 M), [3] NaOH (0.1 M), and [4] HCl (0.5 M). Then, the P content in each extract was determined by colorimetric method and measured in spectrophotometry at 880 nm, obtaining [1] P poorly sorbed and soluble (labile P), [2] P associated with Fe oxyhydroxides (Fe-P), [3] P associated with clay minerals and Al hydroxides (Al-P) and [4] P bound to calcium (Ca-P).

The extracts from step [3] were acidified with H<sub>2</sub>SO<sub>4</sub> diluted in water (1:5) until reaching pH ≈ 1, and after 16 h of decanting they were filtered through a membrane filter of ± 0.45 mm, with the filters calcined (520 °C for 2 h) and digested in 1 M HCl (90 °C for 6 h) for the determination of P associated with humic substances (HS-P). The P associated with black carbon (BC-P) was obtained by calcination (520 °C for 2 h) and digestion in 1 M HCl (90 °C for 6 h) of residual soil samples, after all extractions. The difference between the total content of P (P contained in the soil after the sorption test) and the sum of all determined fractions was considered a form of occluded P.

#### 2.5. Selective fractionation of phosphorus, iron, and aluminium

Fractions of P, Fe, and Al were determined by extractions, in duplicate, with ammonium oxalate and sodium pyrophosphate [26]. Fe, Al, and P associated with organic matter and amorphous and/or low crystallized material were extracted with ammonium oxalate solution (pH 3.0). Fe and Al bound to organic matter were extracted with sodium pyrophosphate solution (0.1 M), and called Py-Fe and Py-Al, respectively. As the extractions were not carried out sequentially, the content of Fe and Al associated only with amorphous and/or low crystallized material (Ox-Fe and Ox-Al) was obtained by subtracting the contents of Py-Fe and Py-Al. For P, as the extraction with pyrophosphate was not carried out, the Ox-P fraction represents the P associated with amorphous and low crystallinity and organic compounds.

These extractions were carried out in the three soils treated with 0 and 120 mg L<sup>-1</sup> of P (stirring for 24 h) in the forms of KH<sub>2</sub>PO<sub>4</sub>, RiS + P, CfS + P, and P-CfC. The levels of Ox-Fe, Ox-Al, Py-Fe, and Py-Al were determined by atomic absorption spectroscopy and Ox-P was measured by inductively coupled plasma optical emission

spectrometry (ICP\_OES PerkinElmer, model Optima 4300 DV, with PerkinElmer AS93-plus autosampler).

## 2.6. Statistical analysis

The principal component analysis (PCA) procedure was performed using as variables  $Q_{max}$ ,  $K_L$ ,  $pH_{eq}$ , sorbed P and desorbed P in the doses of 30, 120, and 240 mg  $L^{-1}$  for Nitisol and Ferralsol. For Vertisol, we replaced  $Q_{max}$  and  $K_L$  with  $K_F$  and  $n$ , respectively. Statistical analysis was performed in the Xlstat software [29].

## 3. Results and discussion

### 3.1. The biochar composition affects the availability of P on the soil

Analyzing the available P content of Nitisol, Ferralsol, and Vertisol, after batch sorption-desorption experiments we verified an effect mainly of the type of soil used to compose the enriched biochars (Table 3). The use of enriched biochars composed with sand soil, in comparison to the clayey soil-enriched biochars, resulted in a higher content of available P in all three soils, mainly in the dose of 120 mg  $L^{-1}$  of added P (Table 3). Matoso et al. [17] studied the precursor biochars (RiS, CfS, RiC, and CfC) of the enriched biochars used in this study. The presence of clayey soil in biochars resulted in a higher specific surface than sandy soil [21]. The specific surface of biochars is a characteristic positively correlated with the ability to adsorb P and other elements [1]. The type (texture) of soil used in the composition of the biochars also affected the distribution of the forms of P of biochar [17]. The biochars composed of biomass and clayey soil (RiC and CfC) were characterised by less labile forms of P, when compared to the biochars that contained sandy soil in their composition (RiS and CfS) [17]. This property explains the fact that enriched biochars composed with clayey soil reduced the availability of P when compared to enriched biochars composed with sandy soil.

The type of biomass used in the composition of the biochars also affected the availability of P in the soils, and the coffee husk was superior to rice husk, mainly in Nitisol, with values of 64.7 and 45.5%, in the doses of 120 and 240 mg  $L^{-1}$  of added P, respectively. In other soils, the increase in available P content ranged from 22 to 43% (Table 3). Matoso et al. [17] verified that rice husk had less ability to protect P from forming bonds with Fe and Al compounds in the biochar than the coffee husk. Matoso et al. [21] demonstrated that biochars derived from coffee husks had a higher negative surface charge than biochars derived

from rice husks. According to Guppy et al. [11] the increase in the negative charge on the soil is one of the factors that decrease phosphate retention.

### 3.2. Biochar enrichment method affects P availability on the soil

When using enriched biochars prior to pyrolysis as a source of P, we obtained high rates of retention of this element, associated with low desorption power, in all three soil mineralogies, in relation to the reference source ( $KH_2PO_4$ ) (Table 3). Matoso et al. [17] found that the heating of the phosphate fertiliser during pyrolysis results in a higher degree of crystallinity of the phosphates and a lower available P content in the biochars. We observed, therefore, that the use of enriched biochar prior to pyrolysis is not a good strategy to convey P in the soil and make it available to plants. However, these biochars can be studied as an alternative for soils with high potential for loss of P, such as flooded or sandy soils, since the recalcitrant P fractions contained in the biochar can be sources of P over time [13].

On the other hand, the use of enriched biochars after pyrolysis, mainly RiS + P and CfS + P, reduced the retention and increased the desorption of P in haematite rich Nitisol and kaolinite rich Ferralsol, resulting in a higher P availability. We found, therefore, that the use of enriched biochars after pyrolysis is an alternative to increase the bioavailability of P in highly weathered soil. Similar results are reported in the literature, but with the use of alkaline biochars [12,13,15]. We found that even acid-reacting biochars, caused by the presence of fertiliser, can increase P availability in the soil. This can bear implications for further studies on biochar utilisation and soil P sorption and desorption characteristics.

In smectite rich Vertisol, despite increasing P sorption, the use of enriched biochars after pyrolysis increased desorption, which resulted in greater P availability when compared to data from the reference source (Table 3). Our results demonstrate the possibility of using biochars combined with triple superphosphate (provided the phosphate fertiliser does not go through the pyrolysis process) to increase P availability in smectite soils. However, this practice should be carefully studied in these soils, evaluating in long-term experiments various combinations between doses of biochar and doses of P.

### 3.3. Factors controlling the retention of applied P

#### 3.3.1. Kaolinitic and oxic soils

For Nitisol, the isotherm data obtained from the nine P sources had a good fit by the Langmuir equation, with

a coefficient of determination ( $R^2$ ) ranging from 0.98 to 1.00 (Table 2). Considering the  $\text{KH}_2\text{PO}_4$  source as reference, we observed that P sorption was enhanced along with the increase of initial P concentration in all soil samples, resulting in an elevated  $Q_{\text{max}}$  of P ( $2000\text{mg kg}^{-1}$ ) with  $K_L$  of  $0.25\text{ L mg}^{-1}$  (Table 2). We also verified that the ability to desorb P was null in the lowest applied dose ( $30\text{ mg L}^{-1}$ ) and low in the highest doses, 120 and  $240\text{ mg L}^{-1}$ , solubilising approximately 0.5 and 17% of the P retained in the soil, respectively (Table 3). These results were consistent with previous studies [15,12,13,16].

Ferralsol also obtained a satisfactory adjustment of sorption isotherms through the Langmuir model, with  $R^2$  ranging from 0.92 to 0.99. From the isotherm data generated with  $\text{KH}_2\text{PO}_4$ , we found lower  $Q_{\text{max}}$  ( $909\text{ mg kg}^{-1}$ ) and  $K_L$  ( $0.28\text{ L mg}^{-1}$ ) than in Nitisol (Table 2). In contrast, the capacity to desorb P was greater, reaching 15 and 30% at doses of 120 and  $240\text{ mg L}^{-1}$ , which in absolute values resulted in 119 and  $330\text{ mg kg}^{-1}$ , respectively (Table 3).

Clay fraction of Nitisol was dominated by kaolinite and iron-oxide minerals (mainly haematite), while the clay fraction of Ferralsol was essentially dominated by kaolinite (Figure 1). Thus, the higher  $Q_{\text{max}}$  of P measured with the use of the soluble P source ( $\text{KH}_2\text{PO}_4$ ) observed in Nitisol, followed by Ferralsol (Table 2), is explained by the content of Fe and Al oxyhydroxides in these soils (Table 4), because the  $Q_{\text{max}}$  of P has a positive correlation with these fractions [8,9].

The F1 and F2 axes of the ordering diagram derived from the PCA accumulated 74.67% of the information from the original matrix for the Nitisol (Figure 2(A)) and 67% for the Ferralsol (Figure 2B). Due to the distribution observed in the F1 axis on both soils, the biochars were divided into two groups, which coincided with the way of obtaining enriched biochars. The first, was composed of enriched biochars prior to pyrolysis (P-RiS, P-RiC, P-CfS, and P-CfC), being defined by the high  $Q_{\text{max}}$

of P and the high levels of sorbed P even with high doses of P applied ( $120$  and  $240\text{ mg L}^{-1}$ ). The second group was influenced mainly by the greater capacity to desorb phosphate and was composed of enriched biochars after pyrolysis (RiS + P, RiC + P, CfS + P, and CfC + P). Considering the data from the F2 axis, the  $\text{KH}_2\text{PO}_4$  source showed a different behaviour from biochars, being influenced by the higher  $\text{pH}_{\text{eq}}$  (Figure 2(A, B)).

One risk of applying high doses of biochars to the soil is to destabilise the mineral phase. Both the acidic pH of enriched biochars and the addition of organic acids in the soil can result in the dissolution of Fe and Al of the crystalline and low-crystalline structure of soil minerals, by different mechanisms [30,11,31] and, therefore, raise the  $Q_{\text{max}}$  of P of both Nitisol and Ferralsol. However, as there was no difference in the levels of Ox-Fe and Ox-Al, comparing the samples of these soils without the addition of P, with those treated with different P sources (Table 4), we found that there was no destabilisation of the mineral phase of these soils, even at the highest doses of P and, consequently, biochar.

Some studies [13,16] raised the hypothesis that the surface acid functional groups present in the biochar, such as hydroxyls (-OH) and carboxylic acids (-COOH), may decrease the phosphate sorption and precipitation by binding to clay minerals and Al hydroxides, or complexing Fe and Al active in solution, competing for phosphate retention sites. The CfS + P and RiS + P biochars reduced the  $Q_{\text{max}}$  of P from Nitisol and Ferralsol (Table 2) without decreasing the concentration of the Fe-P and Al-P fractions, when compared to the reference source ( $\text{KH}_2\text{PO}_4$ ) (Figure 3). Thus, the role of biochar surface acid functional groups was not clear in the occupation of these phosphate retention sites.

The content of soluble P added in any form was sorbed to the active sites present in the two soils. However, the CfS + P and RiS + P biochars increased the P desorption and the content of P available in

**Table 2.** P sorption parameters of the isotherms described by Langmuir and Freundlich equation for soils of different mineralogies treated with different sources and doses of P.

P sources	Nitisol			Ferralsol			Vertisol		
	$R^2$	$Q_{\text{max}}$	$K_L$	$R^2$	$Q_{\text{max}}$	$K_L$	$R^2$	$K_F$	$n$
$\text{KH}_2\text{PO}_4$	0.99	2,000	0.24	0.95	909	0.28	0.76	2.96	0.70
RiS + P	0.99	1,667	0.67	0.97	909	0.21	0.93	3.05	0.70
RiC + P	0.99	2,000	0.71	0.98	1,250	0.20	0.99	4.26	0.69
CfS + P	1.00	1,111	1.29	0.96	1,000	0.14	0.96	5.21	1.00
CfC + P	1.00	2,000	0.45	0.96	1,428	0.08	0.95	6.48	0.83
P-RiS	0.98	3,333	0.25	0.98	2,000	0.22	0.98	6.86	0.69
P-RiC	0.98	5,000	0.13	0.99	2,000	0.36	0.99	7.08	0.64
P-CfS	0.98	3,333	0.30	0.92	3,333	0.07	0.99	7.69	0.65
P-CfC	0.98	5,000	0.22	0.94	2,500	0.15	0.99	6.06	0.53

The abbreviations of the enriched biochars correspond to their composition. Ri: rice husk; Cf: coffee husk; S: sandy soil; C: clayey soil; P-: triple superphosphate added prior to pyrolysis; +P: triple superphosphate added after to pyrolysis.



**Table 3.** Equilibrium pH and amount (mg kg<sup>-1</sup>) of adsorbed P (ads P), desorbed P (des P), and available P (av P) on soils when the samples were loaded with solutions contained 30, 120, and 240 mg L<sup>-1</sup> of P from different sources.

Soil	Added P		KH <sub>2</sub> PO <sub>4</sub>	RiS + P	RiC + P	CfS + P	CfC + P	P-RiS	P-RiC	P-CfS	P-CfC
Nitisol	30	pH <sub>eq</sub>	5.0	5.0	4.9	4.7	4.9	4.8	4.8	4.9	4.7
		Ads P	321	321	317	319	317	310	310	309	310
		Des P	0	0	0	0	0	0	0	0	0
		Av P	-21	-21	-17	-19	-17	-10	-10	-10	-9
	120	pH <sub>eq</sub>	4.9	4.5	4.5	4.6	4.7	4.5	4.6	4.9	4.6
		Ads P	1157	1144	1183	1134	1172	1199	1206	1203	1207
		Des P	5	38	0	43	0	0	0	0	0
		Av P	48	94	17	109	28	1	-6	-3	-7
	240	pH <sub>eq</sub>	4.9	4.5	4.4	4.6	4.6	4.3	4.4	4.7	4.6
		Ads P	1780	1764	2031	1741	1761	2243	2322	2326	2300
		Des P	296	358	273	361	295	128	67	61	38
		Av P	916	994	642	1020	934	285	145	135	138
Ferralsol	30	pH <sub>eq</sub>	5.4	4.9	4.9	4.9	5.0	4.8	4.8	5.0	5.0
		Ads P	315	317	317	315	314	309	308	308	310
		Des P	5	5	5	5	5	5	5	5	5
		Av P	-10	-12	-12	-10	-9	-4	-3	-3	-3
	120	pH <sub>eq</sub>	5.3	5.1	4.9	5.1	5.2	5.0	5.0	5.1	5.1
		Ads P	774	765	902	763	770	1091	1147	1128	1140
		Des P	119	188	123	188	174	51	22	35	32
		Av P	545	623	421	625	604	160	75	107	92
	240	pH <sub>eq</sub>	5.2	4.9	4.9	5.1	5.2	4.8	5.0	5.1	5.7
		Ads P	1082	1123	1409	1242	1120	1903	2072	2082	2012
		Des P	330	483	365	553	483	198	159	188	169
		Av P	1648	1760	1356	1711	1763	695	487	506	557
Vertisol	30	pH <sub>eq</sub>	6.0	5.9	6.0	6.0	6.1	5.9	6.0	6.1	6.1
		Ads P	120	133	151	138	147	247	262	259	271
		Des P	7	36	20	42	28	0	1	0	0
		Av P	187	203	169	204	181	53	39	41	29
	120	pH <sub>eq</sub>	5.8	5.8	5.8	5.9	5.9	5.6	5.6	5.8	6.0
		Ads P	257	317	495	407	339	804	970	939	1.017
		Des P	142	255	213	292	259	114	81	99	47
		Av P	1085	1138	918	1085	1120	510	311	360	230
	240	pH <sub>eq</sub>	5.6	5.5	5.7	5.7	5.7	5.4	5.3	5.6	5.6
		Ads P	670	734	1032	940	567	1573	1913	1846	2161
		Des P	285	532	421	636	590	226	163	213	164
		Av P	2015	2198	1789	2096	2423	1053	650	767	403

The abbreviations of the enriched biochars correspond to their composition. Ri: rice husk; Cf: coffee husk; S: sandy soil; C: clayey soil; P-: triple superphosphate added prior to pyrolysis; +P: triple superphosphate added after to pyrolysis. pH<sub>eq</sub>: pH measured in the equilibrium solution; Ads P: sorbed phosphorus; Des P: desorbed phosphorus; Av P: available phosphorus.

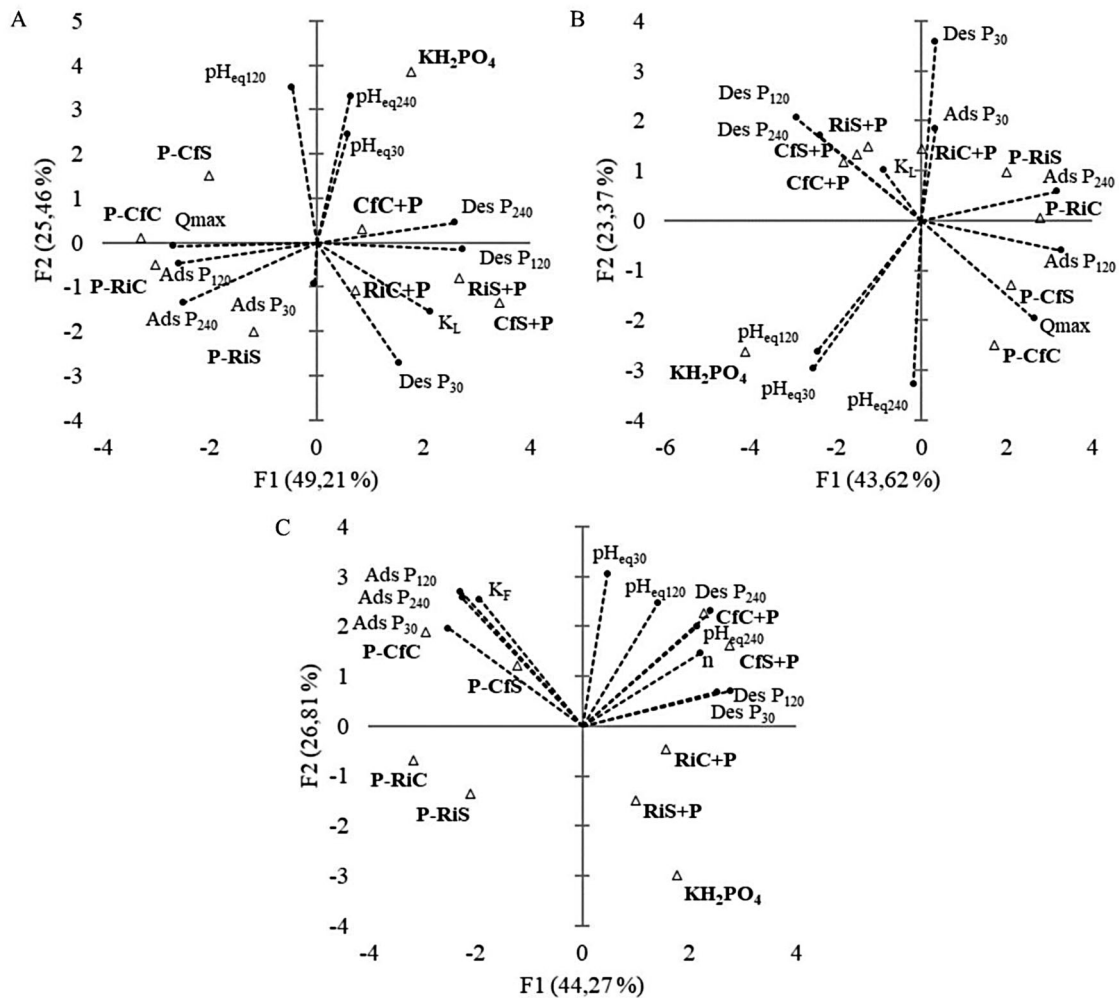
Nitisol and Ferralsol (Table 3), and these results were accompanied by a higher concentration of the Py-Fe and Py-Al fractions in relation to the Ox-Fe and Ox-Al fractions, mainly in Ferralsol (Table 4). This implies

that the organic fraction of the enriched biochars after pyrolysis was able to decrease the formation of highly stable complexes between phosphate and the mineral fraction of soils, but it was not possible to specify the

**Table 4.** Fractions of iron (Fe), aluminium (Al), and phosphorus (P) (mg kg<sup>-1</sup>) extractable in ammonium oxalate and sodium pyrophosphate on soils when the samples were loaded with solutions contained 0 and 120 mg L<sup>-1</sup> of P from different sources.

Soil	Added P	P source	Ox-Fe	Py-Fe	Ox-Al	Py-Al	Ox-P
Nitisol	0	KH <sub>2</sub> PO <sub>4</sub>	1163.50	36.00	1056.50	500.00	2.09
			1153.00	32.00	1285.00	590.00	178.82
	120	RiS + P	1190.50	34.50	1040.00	545.00	164.88
		CfS + P	1180.50	34.50	1020.00	530.00	183.66
		P-CfC	1064.50	110.50	945.00	675.00	287.62
Ferralsol	0	KH <sub>2</sub> PO <sub>4</sub>	238.50	420.00	716.00	365.00	1.16
			40.00	590.00	555.00	565.00	106.17
	120	RiS + P	60.00	605.00	570.00	580.00	122.94
		CfS + P	80.00	585.00	630.00	530.00	123.52
		P-CfC	55.00	725.00	725.00	475.00	291.90
Vertisol	0	KH <sub>2</sub> PO <sub>4</sub>	235.00	1215.00	126.00	1400.00	35.87
			1140.00	2100.00	445.00	2540.00	4214.93
	120	RiS + P	1235.00	1910.00	500.00	2550.00	4328.60
		CfS + P	1005.00	2140.00	540.00	2555.00	4379.15
		P-CfC	1310.00	2050.00	675.00	2870.00	4618.07

The abbreviations of the enriched biochars correspond to their composition. Ri: rice husk; Cf: coffee husk; S: sandy soil; C: clayey soil; P-: triple superphosphate added prior to pyrolysis; +P: triple superphosphate added after to pyrolysis.



**Figure 2.** Ordering diagram derived from the principal component analysis of the soils of different mineralogies treated with different sources and doses of P. (A) Nitisol; (B) Ferralsol; (C) Vertisol. The abbreviations of the enriched biochars correspond to their composition. Ri: rice husk; Cf: coffee husk; S: sandy soil; C: clayey soil; P-: triple superphosphate added prior to pyrolysis; +P: triple superphosphate added after pyrolysis. Qmax: sorption maximum;  $K_L$ : binding strength;  $pH_{eq}$ : pH measured in the equilibrium solution; Ads P: sorbed phosphorus; Des P: desorbed phosphorus; 30, 120, 240: P loadings of 30, 120, and 240 mg L<sup>-1</sup>, respectively.

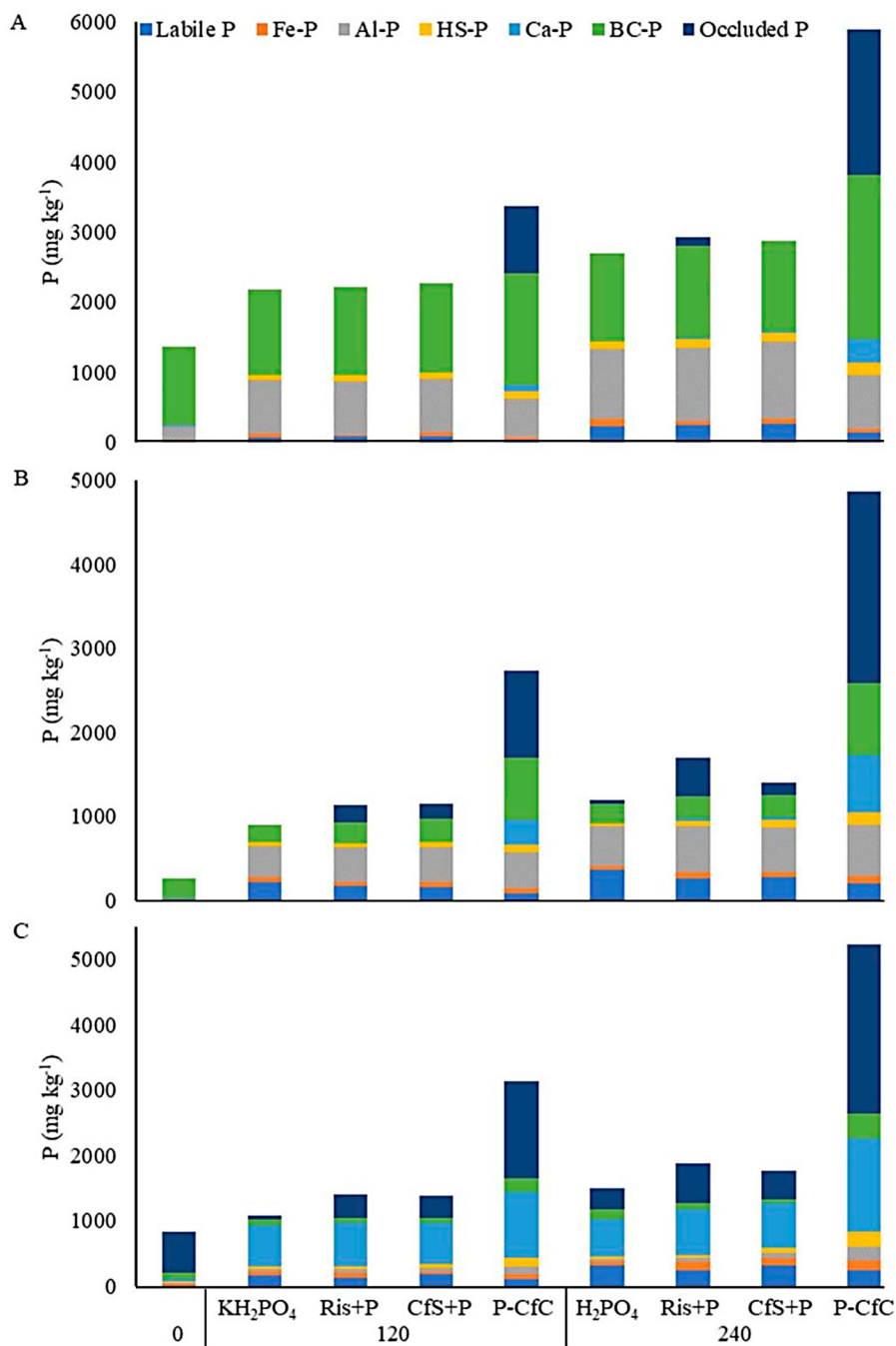
mechanism involved, requiring studies with speciation techniques with greater detail to understand these results.

In this sense, studies that have investigated the factors that control P retention in biochar-amended soils have yielded quite variable results. Schneider and Haderlein [13] found that biochar can release dissolved organic matter, which competes for the P sorption sites in Fe hydroxides (goethite), mainly at acidic pH (5.0). Xu et al. [16] observed an increase in P sorption and a reduction in desorption in acidic soils and observed that these results were related to an increase in the Ca-P fraction. Zhou et al. [4] found evidence that the addition of biochar to the soil inactivated  $Al^{3+}$  ions in the solution but had no effect on the activity of  $Fe^{3+}$  and  $Ca^{2+}$  ions.

From the results of the sequential fractionation in the samples treated with P-CfC (Figure 3(A,B)), we observed

that the highest Qmax correlated with the Ca-P, BC-P, and occluded P fractions in Nitisol and Ferralsol. The increase in the Ca-P fraction was also observed by Xu et al. [16], however it is not considered common in highly weathered soil, of acid reaction and with low Ca activity in the solution (Table 1), since in these conditions the preferential route is precipitation in the form of Fe and Al phosphates or sorption in low crystallinity compounds, due to the high specific surface and P affinity of these minerals [9]. Therefore, these results are best explained by the presence of non-solubilized Ca phosphates from the phosphate fertiliser itself, as found by Matoso et al. [17].

BC-P and occluded P are the most recalcitrant fractions determined in sequential fractionation [28], thus explaining the low P desorption with the use of P-CfC. The higher levels of Py-Fe and Py-Al with the use of P-



**Figure 3.** Phosphorus fractions ( $\text{mg kg}^{-1}$ ) on soils when the samples were loaded with solutions contained 30, 120, and 240  $\text{mg L}^{-1}$  of P from different sources. (A) Nitisol; (B) Ferralsol; (C) Vertisol. The abbreviations of the enriched biochars correspond to their composition. Ri: rice husk; Cf: coffee husk; S: sandy soil; C: clayey soil; P-: triple superphosphate added prior to pyrolysis; +P: triple superphosphate added after to pyrolysis.

CfC in relation to the other sources and to the soil without the addition of P indicate that there was Fe and Al complexation by the organic fraction of the biochar and the formation of bridges resulting in an increase in  $Q_{\text{max}}$  of P. This effect has been described for soil organic matter [11] and occurred with the use of this biochar due to its lower content of P soluble in NAC + water (Supplemental material) and, consequently,

a greater amount of product added to achieve the added doses of P. These results can be extrapolated to the biochars P-RiS, P-RiC, and P-CfS and explain the high  $Q_{\text{max}}$  of P with the use of these sources in Nitisol (3333–5000  $\text{mg kg}^{-1}$ ) and Ferralsol (2000–3333  $\text{mg kg}^{-1}$ ) (Table 2).

Xu et al. [16] indicated that the increase in the dose of biochar in soil with a high content of soluble P increases

the sorption of P, with a lower desorption rate of the element and that the greater protection effect of the conversion reactions from labile P to not labile occurred at a concentration of  $100 \text{ mg L}^{-1}$  of P in solution with a biochar application rate in the soil of 1%. Schneider and Haderlein [13] observed similar results, emphasising that the dissolved organic matter in the biochar competes for the P sorption sites, depending on the concentration of the organic fraction in relation to the concentration of P in solution. Similar results were found by Bornø et al. [15]. Thus, future studies using enriched biochar as a source of P should focus on the relationship between soluble P and biochar.

### 3.3.2. Smectitic soil

In Vertisol P retention was better described by the Freundlich model (Table 2), which indicates that the reactions occurred in multiple layers, with the interaction between the adsorbate molecules [15,32]. The format of the sorption isotherms demonstrated that the energetically active sites increased according to the dose of P added, regardless of the source used (Figure 4). The most active sorption sites in Vertisol were Ca ions, clay minerals and Al hydroxides, and black carbon (Figure 3(C)). These results are consistent with the chemical and mineralogical characterisation of this soil (Table 1; Figure 1(A,D)) and with previous studies [9,15].

All enriched biochars increased P retention in Vertisol, when compared to the reference source  $\text{KH}_2\text{PO}_4$  (Table 2). These results were indicated by the higher  $K_F$  values, a parameter related to the sorption capacity of P, and of  $n$ , which has a qualitative relationship with the distribution of energy sorption sites in soils [33]. By the value of  $n$ , it was also identified that sorption energy can be considered low with the use of all P sources ( $n < 1.0$ ) (Table 2).

This effect can also be verified by the sorbed P content, which for the  $\text{KH}_2\text{PO}_4$  source was 120, 257, and  $670 \text{ mg kg}^{-1}$  with the application of 30, 120, and  $240 \text{ mg L}^{-1}$  of P, respectively (Table 3). Enriched biochars after pyrolysis increased the sorbed P content by up to 26, 93, and 54%, respectively. Enriched biochars prior to pyrolysis increased P sorption by 126, 296, and 223%, respectively.

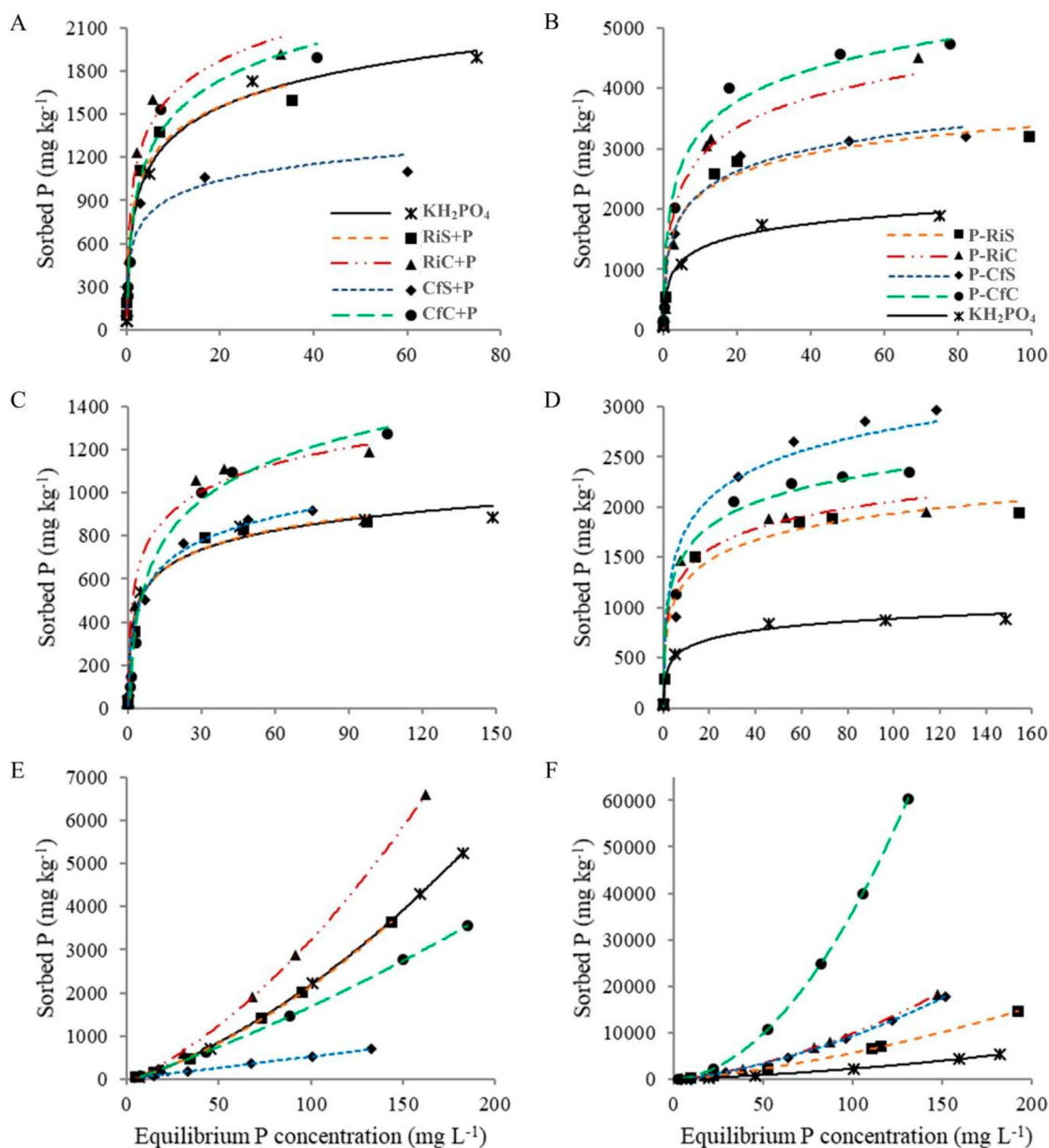
These results are reflected in the F1 axis of PCA, which accumulated 44.27% of data inertia (Figure 2(C)). Thus, the P sources were divided into two groups, to the left of the diagram are the enriched biochars prior to pyrolysis (P-RiS, P-RiC, P-CfS, and P-CfC), which provided high sorption in all the doses of P added, and on the right are the enriched biochars after pyrolysis (RiS + P, RiC + P, CfS + P, and CfC + P) and  $\text{KH}_2\text{PO}_4$ , which showed greater

potential for desorbing P and higher  $\text{pH}_{\text{eq}}$  (Table 3 and Figure 2(C)). The F2 axis (26.81%) removed the sources CfS + P and CfC + P from sources RiS + P, RiSF + P, and  $\text{KH}_2\text{PO}_4$ , due to the higher content of desorbed P in the dose of  $240 \text{ mg L}^{-1}$  obtained with the use of biochar derived from coffee husk (Figure 2(C)).

The fact that enriched biochars have increased the  $Q_{\text{max}}$  of P, cannot be attributed to the sorption capacity of P of the biochar itself, as according to Matoso et al. [17], these biochars did not show the ability to adsorb P. 2:1 minerals (smectite) are less stable under acid reaction conditions [30]. Therefore, it can be inferred that there was a destabilisation of the clay minerals, resulting in the dissolution of Fe and Al. This premise is corroborated by the reduction of the  $\text{pH}_{\text{eq}}$  to values lower than the initial soil pH and the increase in the concentration of the Fe-P and Al-P forms (Table 4). Organic sites have also become more active. This effect was even greater with the use of P-CfC (that represents enriched biochars prior to pyrolysis), which has a lower content of soluble P and, therefore, was added in greater quantity (g) to reach the doses of P used.

Observing the desorbed P content in this soil (Table 3), we found that although the biochars have potentiated the P sorption reactions, the content of P desorbed was higher with the use of enriched biochars after pyrolysis, when compared to  $\text{KH}_2\text{PO}_4$  and enriched biochars prior to pyrolysis. Combining these results with fractionation data, we observed that the use of CfS + P increased the concentrations of the Fe-P and Al-P fractions (Figure 3(C)). These compounds can be formed from reversible (monodentate) bonds, being considered moderately labile forms [5]. Thus, adding the non-sorbed P content to the desorbed P, we found that these biochars obtained the highest available P content (Table 3).

In studies of P dynamics in alkaline soils with high available P content, little effect of biochar addition on P availability has been observed since biochar pH does not generally affect soil pH [15,12]. In our study, as we worked with acidic biochar, there was a reduction in equilibrium pH of Vertisol, which led to a change in the retention sites of P, favouring the sorption with Fe and Al compounds. As the equilibrium pH remained greater than or equal to 5.5, even with the highest doses of P applied in the form of biochar enriched after pyrolysis (Table 3), the formation of P-Fe and P-Al compounds favoured the desorption of P, since P-Ca compounds under alkaline pH conditions are more stable [28]. These results must be further evaluated in studies with long incubation times, because even with high doses of P added to the soil, the longer the incubation time, the lower the recovery of available P [8].



**Figure 4.** Phosphorus sorption isotherms for soils of different mineralogies treated with different sources and doses of P. (A) Nitisol treated with enriched biochars prior to pyrolysis and  $\text{KH}_2\text{PO}_4$ ; (B) Nitisol treated with enriched biochars after to pyrolysis and  $\text{KH}_2\text{PO}_4$ ; (C) Ferralsol treated with enriched biochars prior to pyrolysis and  $\text{KH}_2\text{PO}_4$ ; (D) Ferralsol treated with enriched biochars after to pyrolysis and  $\text{KH}_2\text{PO}_4$ ; (E) Vertisol treated with enriched biochars prior to pyrolysis and  $\text{KH}_2\text{PO}_4$ ; (F) Vertisol treated with enriched biochars after to pyrolysis and  $\text{KH}_2\text{PO}_4$ .

#### 4. Conclusions

The results revealed that the different properties of enriched biochars differently affects the P dynamics in the soils. P sorption and desorption characteristics of soils are impacted by enriched biochar composition, enrichment method, and soil characteristics. Thus, the study provides useful information for optimising the use of enriched biochar in agricultural P management.

The different biomasses tested in the composition of enriched biochars present a greater difference when

applied to the soil of haematite rich Nitisol, and smectite rich Vertisol. The coffee husk is more suitable than rice husk to protect P from retention reactions in the soil. The use of sandy soil in the composition of the enriched biochars, in comparison to the clayey soil, results in a higher content of available P when applied to the soils with different mineralogies.

The procedure of enriching biochar with phosphate fertiliser is the main factor that affects the availability of P in soil. Enriched biochars after pyrolysis are an

alternative to increase the bioavailability of P in the mineralogy of soils with low to high degrees of weathering. Although the greatest effect is observed in highly weathered soils. In this sense, the procedure for preparing enriched biochar that most contributes to increasing the availability of P in soils is biomass (coffee husk) pyrolysis in conjunction with soil (sandy texture), with the addition of phosphate fertiliser after pyrolysis.

The elaboration of biochar with the mixture of biomass, soil and phosphate fertiliser prior to pyrolysis is ineffective as a P source when the intention is to reduce phosphate retention reactions in soils of any mineralogy. However, these enriched biochars can be studied as an alternative for soils with high potential for P loss.

The organic fraction of biochar can reduce the formation of highly stable complexes between the phosphate and the mineral fraction of the soil, especially in soils with a high degree of weathering, of kaolinitic/oxic (Nitisol) and kaolinitic (Ferralsol) mineralogy. However, due to the analytical techniques used, it is not possible to specify the mechanism involved. Studies with more detailed specialised techniques are required to elucidate this process. In the three soil mineralogies, the higher concentration of the organic fraction in relation to the soluble P content in the enriched biochars increases the P sorption capacity and decreases the desorption potential.

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### Disclosure statement

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### Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

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