


Article

Biochar-Ca and Biochar-Al/-Fe-Mediated Phosphate Exchange Capacity are Main Drivers of the Different Biochar Effects on Plants in Acidic and Alkaline Soils

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Abstract: Because of the low consistency of the results obtained in the field, the use of biochar as a soil amendment is controversial. Thus, in general, in acidic soils, results are positive, while in alkaline soils, they are non-significant or even negative. The results regarding biochar action in acidic soils have been related to a lime-like effect due to its alkaline pH and the high doses normally used. However, the causes of biochar effects in alkaline soils remain unknown. Our objective was to explore the chemical mechanism of biochar interaction in acidic and alkaline soils. We used well-characterized biochar as a component of two complex N and PK granulated fertilizers at two different doses (1% and 5%). These fertilizers were applied to wheat cultivated in pots containing an alkaline soil and grown for 60 days. No effect was shown for the N-biochar fertilizer application. However, the PK-biochar fertilizer application caused a decrease in crop yield. In addition, the adsorption isotherms of Al, Fe, Mo, Mn, and Phosphate (Pi) in biochar were also studied. The results showed that Fe and Al were rapidly adsorbed in biochar, while Pi was only adsorbed on the Fe-, Al-biochar complex. Desorption experiments showed that P and Fe/Al were not desorbed from the P-Fe/Al-biochar complex by water or the Olsen reagent, while partial desorption was observed when HCl 0.1 M was used. This blockage of Fe/Al and P through Fe/Al bridges in biochar could partially explain the negative effects in alkaline soils. After these studies, soil solution sorption experiments were carried out in both acidic and alkaline soils and were complemented with a greenhouse trial using tomato plants. The results showed that biochar enhanced foliar Ca and N content, as well as growth in acidic soil only, and the possible mechanism of the failure in alkaline soils.

Keywords: biochar; liming; phosphate blockage; acidic and alkaline soils

1. Introduction

Amazonian *terra preta* soils have been the inspiration of biochar addition to soils [1]. In these soils, fertility is improved in comparison to adjacent soils, which have had no organic C added. Similarly, biochar has been extensively applied as an amendment to fields to increase the organic C content as well as the C sequestration level in soils [2]. Biochar technology, either in production or agronomic, from an environmental point of view, has been extensively investigated [3]. However, there is still a lack of knowledge involving the total energy balance of biochar production. Moreover, agronomic yields results in crops treated with biochar amendments are controversial [4,5]. More controversial are its collateral effects on decreasing soil microbial biomass, influencing soil physical properties or processes affecting the mobility and loss of biochar in the soil profile, or influencing soil organic matter dynamics [4]. The biochar use might be considered notable in comparison to the well-known humic

and composted material applications as soil improvers or fertilization enhancers [6,7]. Although biochar application is widespread, some authors have shown an improvement in crop yields for acidic soils, but the opposite for alkaline soils [2,8]. One explanation of this loss of fertilization capacity of biochar in comparison to *terra preta* could be the lower Pi content of biochar in comparison to that of *terra preta*, which is assumed to originate from “Ash from fires, bones from fish and game animals, feces, urine, and turtle shells account for the relatively high levels of phosphorus in black earth” [9]. Biochar and the organic complex involved in *terra preta* soil fertility probably present many and significant differences to each other. Thus, to associate the high fertility of *terra preta* to biochar alone could be doubtful [10]. Biochar could also be used to mitigate climate change and waste accumulation, but as far as the biochar addition to soil is virtually irreversible, we must be careful [1]. Biochar may indeed be applied to soils with management issues, and here could be its place, mitigating salt stress in plants [11], heavy metal adsorbing [12,13], or herbicide sequestration from soil [14].

One of the mineral nutrients affected by biochar addition to soils is phosphorus (P), normally inorganic phosphate (Pi). Pi has shown different chemical behavior in both acidic and alkaline soils but in the same way, chemical blockage. Thus, in acidic soils, Pi is adsorbed in Al/Fe oxides, and in alkaline soils, Pi is precipitated through Ca bond. Different authors have described the effects of biochar on P bioavailability [15,16], the soil P fraction related to P plant availability [17], the efficiency of P use by plants [18], mycorrhizal colonization [19], and indeed, changes in phosphate crystalline structures [20]. Moreover, this effect could be increased by a large number of carboxylic groups and high surface adsorption area that different biochars normally show. In this framework, we hypothesized that the different effects of biochar on acidic and alkaline soils might be caused by biochar interactions with mineral nutrients in soil and fertilizers. To investigate this hypothesis, we studied the effects of fertilizers granulated incorporating biochar [18,21] at different concentrations, as well as of biochar used as an amendment, on plant growth and mineral nutrition. These experiments were complemented by studies on both the adsorption-desorption of different elements (Al, Fe, Mn, Mo, and Pi) in biochar and the effects of biochar on mineral elements in soil solution.

2. Materials and Methods

Biochar used in the experiments was obtained from holm oak (*Quercus ilex*) trunks and chips and manufactured by pyrolysis at a temperature of 450 °C for 6 h by Piroeco Bioenergy, S.L. company (Malaga, Spain).

2.1. Nutrients Content in Biochar

The nutrient contents in biochar were measured by Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in a previously digested sample in a microwave oven with a mixture of 2 mL of H₂O₂ and 6 mL of HNO₃ and diluted to 25 mL with deionized water.

2.2. Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy

The ATR-FTIR spectrum was recorded over the 4000–650 cm^{−1} range with a resolution of 2 cm^{−1} in a Thermo Scientific Nicolet iS10 (Madison, WI, USA).

2.3. Nuclear Magnetic Resonance Spectroscopies

The ¹H-NMR experiment was measured at 11.7 T in a Bruker Advance XDR-500 spectrometer (Karlsruhe, Germany) operating at 500 MHz.

The ¹³C-NMR spectrum was obtained using the cross-polarization magic angle spinning technique on a Varian Unity spectrometer (Varian Inc., Palo Alto, CA) operating at 75.429 MHz with a spinning speed of 5 kHz, 90° pulse width, 1 ms contact time, 69 ms acquisition time, and 1.0 s delay.

All the NMR spectra were processed, and the signals were assigned with MestreNova software v10.0. For each NMR experiment, the area of each type of structure was divided by the total area of the integrated spectrum and was expressed as a percentage of the total area.

2.4. Scanning Electron Microscopy (SEM)

Images were taken in an FE-SEM from the Carl Zeiss Ultra-Plus model with a nominal resolution of 1 nm. At an energy of 3.00 kV, the magnification and scale were indicated on each image.

2.5. Biochar Integration on Granulated Fertilizers and Growth Chamber Experiment

Two PK (0-8-12) granulated fertilizers were carried out—the first one with a 1% (P-CHAR1) and the second one with a 5% (P-CHAR5) of biochar in w/w (Figure S1). A PK (0-8-12) without biochar was also prepared for controls. The different fertilizers were obtained by granulating the different raw materials using a granulator disc. The final P content in fertilizers was determined by ICP-OES.

These two biochar fertilizers were used in a growth chamber plant experiment:

Six wheat plant seedlings (*Triticum aestivum* cv Ippon R1) were transplanted to plastic pots in perlite/alkaline soil (10/90; w/w) and irrigated at field capacity, and five replications for the treatment were carried out. Soil (Typic Calcixerepts) analysis results are available in Table S1; as wheat was fertilized with different P sources, a soil poor in Pi (B deep horizon) was chosen for a better observation of possible growth differences. Growth chamber conditions were 25/21 °C day/night temperature, 70–75% of relative humidity, and 15/9 h day/night photoperiod (irradiance: 250 $\mu\text{mol m}^{-2} \text{s}^{-1}$). Plants received the same amount of mineral nutrients but used different fertilizers depending on the treatment. Harvest was carried out after 60 days. Once the fresh matter production was analyzed, shoots were dried in an oven at 40 °C for 3 days to determine the dry matter (Figure S2).

2.6. Biochar Adsorption Isotherm Kinetics

Adsorption isotherm kinetics were carried out in aqueous solution under continuous stirring. Biochar at 5% and all mineral nutrients (Al, Fe, Mn, Mo, and Pi) at 1000 mg L⁻¹ were added in separated experiments. Element concentrations were measured at 5, 15, 30, 60, and 240 min. Pi adsorption in Al/Fe-biochar was carried out using previously prepared Al- and Fe-biochar composites.

Desorption experiments were carried out on Pi-Al-biochar and Pi-Fe-biochar samples by applying different extractants: deionized water, Olsen Pi extraction method, 0.1 M HCl, and 1.0 M ammonium citrate at pH 7. The composite:extractant ratio was 1.5 g:15 mL of extractant. Al or Fe, as well as Pi, was determined by ICP-OES.

2.7. Biochar-Soil Solution Interactions

Due to the importance of adsorption isotherm studies completed with the desorption data, a biochar-soil solution interaction study was carried out. In this study, two acidic (Eugi, Ultic Hapludalfs; Girona, Udertic Haplustepts) and two alkaline (Zizur, Typic Calcicusteps; Marcilla Typic Calcixerepts) soils were amended with biochar and compared to the same four soils that were not amended with biochar. In the soil solution interaction experiment, the A horizon of the four soils was chosen because roots are principally developed in the first soil centimeters. Biochar was applied as an amendment at 5% (w/w). Soils with or without biochar were irrigated at field capacity and incubated at 25 °C. Three replications were carried out, combining each soil and treatment. The nutrient content was analyzed after 7 and 15 days in water-soil extracts. Briefly, water-soil extracts in a 10:1 ratio were shaken and later centrifuged at 5000 g after filtration samples were measured by ICP-OES.

2.8. Greenhouse Experiment

The greenhouse experiment was carried out in both acidic (Ultic Hapludalfs) and alkaline (Typic Calcixerepts) soils, under controlled temperature (20/14 °C day/night), natural lighting conditions, and relative humidity of 40–60%. Five replications of each treatment—Control – (without Pi), Control + (with Pi), and biochar (with Pi + 1% biochar)—were carried out in a mixture of perlite/soil (10/90), fertilization covered as N as well K nutritional requirements. As plants were fertilized with different P treatments, a soil poor in Pi (B deep horizon) was chosen for a better observation of

possible growth differences. Soil analysis results are available in Tables S2 and S3. Finally, one tomato (*Solanum Lycopersicon*) seedling was planted in each pot. Harvest was carried out after 30 days of growth, and once analyzed for fresh matter, shoots were dried in an oven at 40 °C for 3 days to determine the dry matter. Next, the dry shoots were homogenized in a mill, and subsamples attacked with HNO₃ and H₂O₂ and digested in a microwave oven. Briefly, 0.25 g of shoot materials were digested in 5 mL of HNO₃ and 2 mL of H₂O₂, later diluted to 25 mL, and the nutrient content was determined by ICP-OES.

2.9. Statistical Analysis

Statistical analyses: ANOVA ($p < 0.05$) and principal components analysis (PCA) were performed using the STATISTICAL software version 10.01011.0 (Stat Soft. Inc., Tulsa, OK 74104, USA).

3. Results

3.1. Biochar Characterization

The structural characterization showed a C-based disposition in aromatic blocks with both alkyl and O-alkyl C, completing this structure with carboxylic groups (10.2%) but mainly substituted as ¹H-NMR indicated (3.75% unsubstituted), as shown in Table 1 and Figure S1.

Table 1. ¹³C- and ¹H NMR of biochar. Principal structural areas by each spectroscopic technique.

¹³ C-NMR Spectroscopy (%)					¹ H-NMR Spectroscopy (%)			
Alkyl C	O-alkyl C	Arom. C	Phen. C	Carbox. C	Alkyl H	O-alkyl H	Arom. H ¹	Carbox. H
19.8	30.9	28.2	10.9	10.2	40.3	24.9	30.05(6.65)	3.75

¹ Only 6.65% is Aromatic-H, up to 30.05% is double bond-H.

In addition to this structural disposition, the elemental composition of biochar used (Table 2) indicated that Ca was the predominant element in a ratio close to 9 times larger to the next elements (K and Na). This implied that biochar had an alkaline nature with carboxylic, phenolic, catechol, phthalic, and other chelating groups substituted mainly by Ca and secondarily by K and Na.

Table 2. Elemental composition of biochar.

mg kg ⁻¹												
Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	S	Zn
1092	70.8	58,492	26.5	953	6601	6459	678	<0.1	1005	1981	663	70.8

The temperature of manufacturing biochar was 450 °C, which was relevant because the functionalization and the binding capacity were related to the carboxylic groups in biochar. The more is the temperature, the less the carboxylic groups and then the less binding capacity [22,23]. SEM showed a granular structure at 10 µm but porous at 2 µm, and at 1 µm—200 nm, we observed structures with high surface adsorption area (Figure S2).

3.2. Growth Chamber Experiment

The PK fertilizers were combined with the biochar in order to be applied to a growth chamber experiment in wheat. The two PK fertilizers were based on a conventional NPK (0-8-12) fertilizer with 1% biochar (P-CHAR1) and 5% biochar (P-CHAR5). No further amounts of biochar could be added without negatively affecting the granule stability and integrity (Figure S3). After 60 days of growth under a complete nutrition plan and in controlled temperature, humidity, and light conditions, plants were harvested (Figure S4). P-CHAR5 treatment showed a statistically significant decrease in mass

production (Figure 1). The decrease was observed for both fresh and dried weight. Due to the alkaline nature of biochar, we hypothesized that the Pi was retained inside the fertilizer granule.

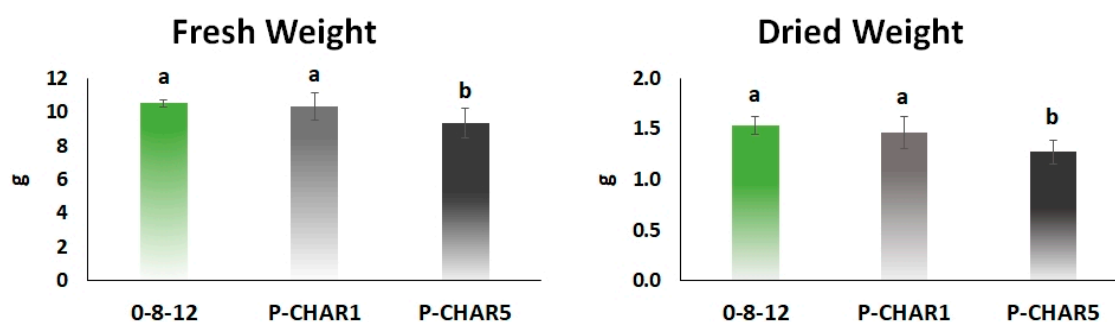


Figure 1. Fresh and dried weight of wheat plants supplied with 0-8-12 conventional NKP fertilizer, P-CHAR1, and P-CHAR5. Different letters indicate significant differences among treatments.

3.3. Biochar-Nutrients Adsorption Isotherm Kinetics

To study the potential interactions between biochar and mineral nutrients, several adsorption isotherms were carried out involving Mn, Mo, Al, Fe, and Pi. As we could see in Figure 2, neither Mo, Mn, or Pi could be bound by biochar, while Al and Fe were bound. The two cations were adsorbed—Al adsorbed at 60 min but Fe more rapidly at 5 min. While Pi directly was not adsorbed, it was following Al and Fe adsorption. Pi was adsorbed, as it could be observed in Figure 2. Moreover, Pi was more rapidly adsorbed on Al-biochar, totally at 5 min ($\text{Al}/\text{PO}_4\text{H}_2^-$ in Figure 2), whereas in Fe-biochar, it was totally at 240 min ($\text{Fe}/\text{PO}_4\text{H}_2^-$ in Figure 2). Besides, this last Pi adsorption isotherm more closely followed a Reciprocal mathematical model more than a Freundlich or Langmuir in the case of $\text{Al}/\text{PO}_4\text{H}_2^-$, but Reciprocal or Langmuir in the case of $\text{Fe}/\text{PO}_4\text{H}_2^-$ (Figure S5). These particular results indicated that all the groups involved in biochar-Al/Fe binding were homogeneous, equivalents, and the binding energy was independent of the adsorption process.

The desorption behavior of biochar- $\text{Al}/\text{PO}_4\text{H}_2^-$ and biochar- $\text{Fe}/\text{PO}_4\text{H}_2^-$ demonstrated the physiochemical nature of nutrient-biochar interactions. Two different interactions might be seen through desorption kinetics (Figure 3). On the one hand, Pi was mainly desorbed by 0.1 M HCl in both Al- and Fe-biochar-mediated complexes, indicating that acid hydrolysis was the preferred chemical detachment mechanism to release Pi—and in a significantly higher quantity for Fe—in comparison to Al-biochar-mediated complexes.

On the other hand, Al, as well as Fe, was preferably released by 1.0 M neutral ammonium citrate, a notable chelating agent [24–26].

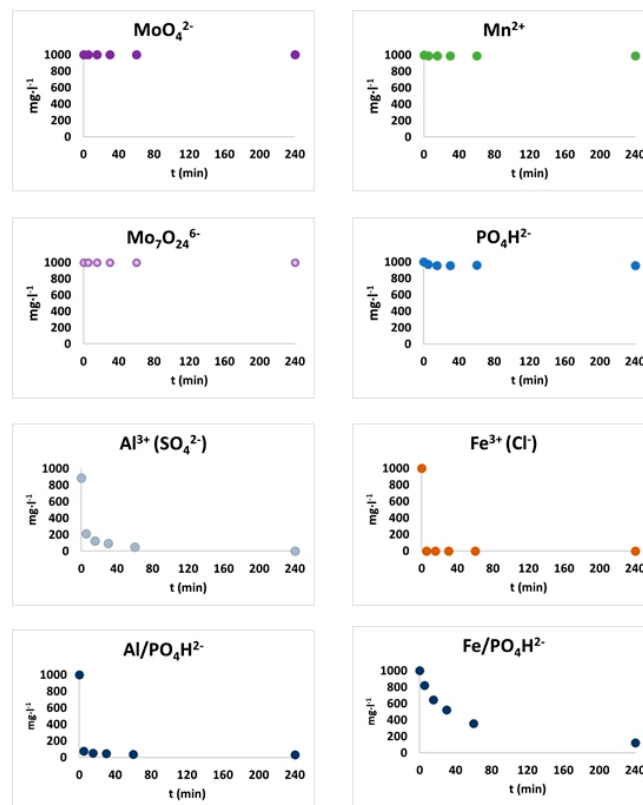


Figure 2. Nutrients-biochar adsorption isotherms.

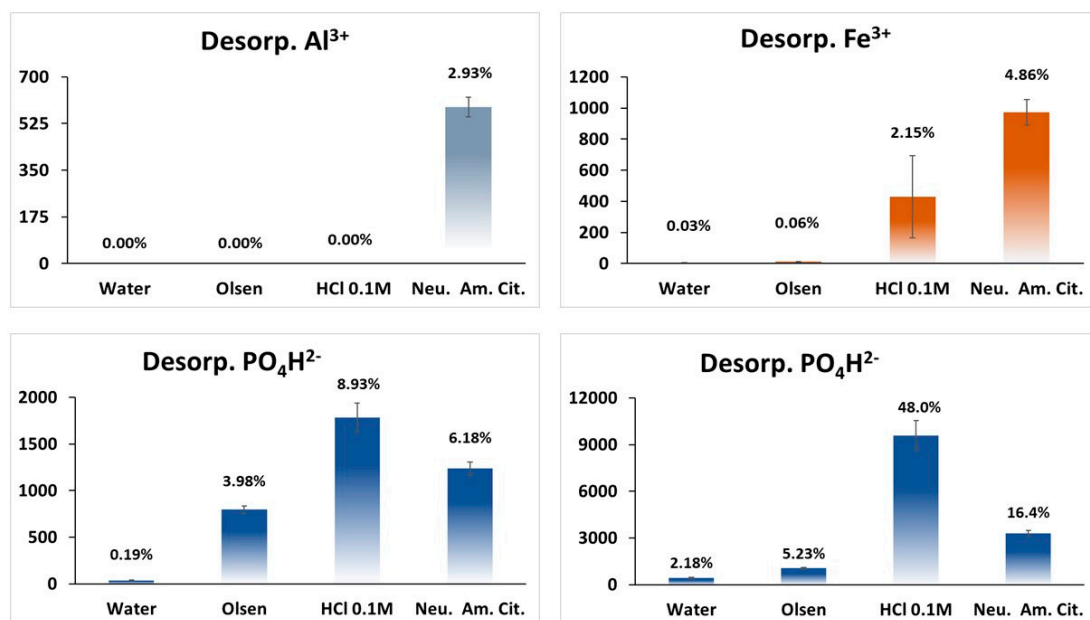


Figure 3. Desorption data for Pi-Al-biochar and Pi-Fe-biochar complexes. Al, Fe, and Pi percentages were relative to the 1000 mg L^{-1} of each element added.

3.4. Biochar-Soil Solution Interactions

The water extraction yielded an interesting perspective of what happens when biochar is applied to the soil. As shown in Figure 4, all micronutrients (Al, Fe, Mn, Mo, and Zn) and Pi were less available

over 15 days in all soils, but Ca and Mg were more available in acidic soils. Note that Figure 4 only shows the relative difference of nutrients measured between soil + biochar and soil.

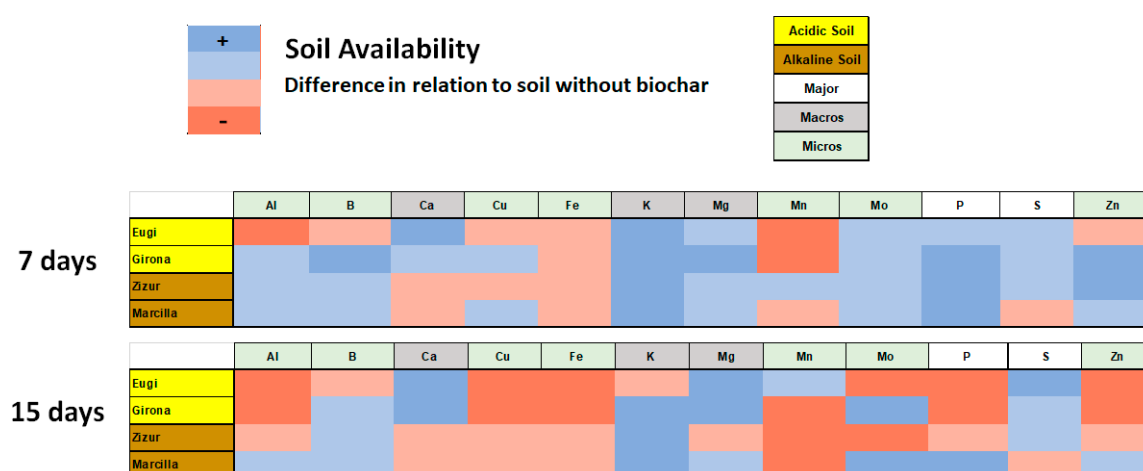


Figure 4. Nutrients availability over 7 and 15 days in soil solution by biochar effect.

Principal components analysis (PCA) (Figure S6) of Al, Zn, and Pi at 7 days evolved to a new grouping of Al, Cu, Fe, Zn, and Pi at 15 days. At 7 days, Ca was opposed to micronutrients and Pi, and at 15 days, Ca and Mg were opposed to micronutrients and Pi. Thus, PCA results showed two opposite behaviors—the first, including micros and Pi, and the second one, Ca and Mg.

3.5. Greenhouse Experiment

The greenhouse experiment carried out in both acidic and alkaline soils (Figure S7) yielded statistically significant differences among Control - and Control + treatments (Figure 5). However, only in acidic soil biochar treatment, at both tomato fresh and dried weight, there were statistically significant differences in Control + treatments (Figure 5).

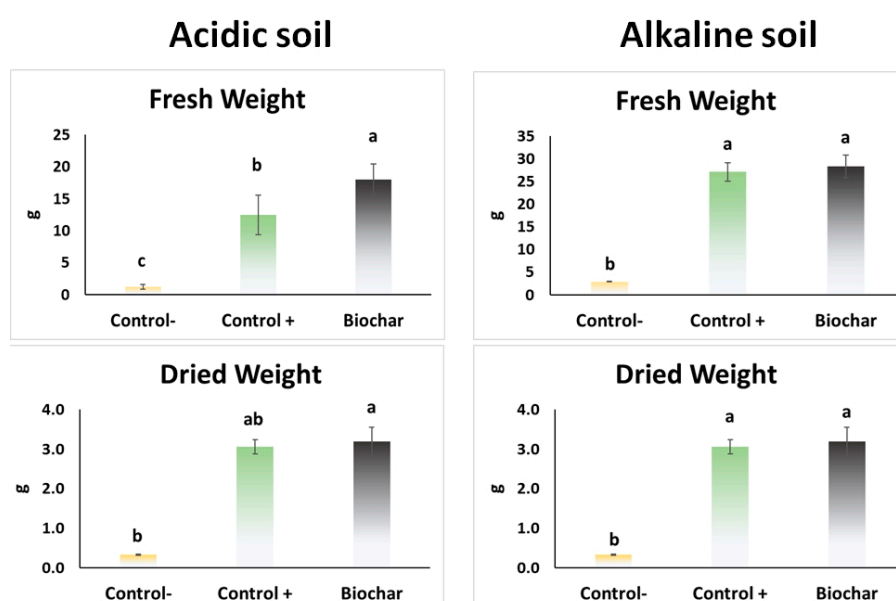


Figure 5. Tomato plants—fresh and dried weight—in both acidic and alkaline soils. Control -, without Pi; Control +, with Pi and biochar, with Pi + biochar as an amendment. Different letters indicate significant differences among treatments.

These same differences were observed in the foliar nitrogen (N) content on tomato plants (Figure 6). There was a statistically higher foliar N content in biochar treatment compared to both Control – and Control +, but only for acidic soils. For alkaline soil, no difference was observed (Figure 6).

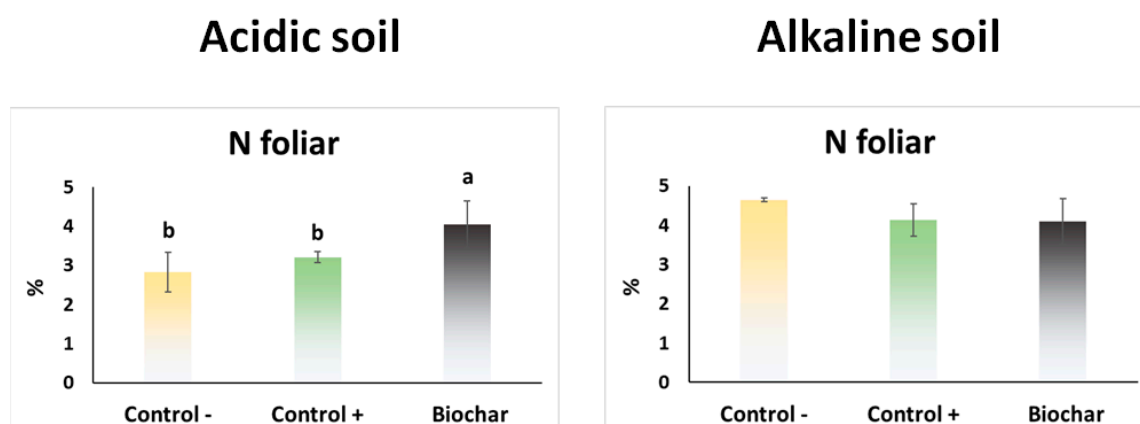


Figure 6. Tomato plant foliar N content in both acidic and alkaline soils. Control –, without Pi; Control +, with Pi and biochar, with Pi + biochar as an amendment. Different letters indicate significant differences among treatments.

For the rest of the nutrients, no statistical differences were observed in both alkaline and acidic soil, among biochar treatment and Control + except for Ca in acidic soils for which biochar treatment showed a higher value (Figure S8). Logically biochar as well as Control + presented statistical and significant differences with Control – on Pi foliar content by the P shortage induced to this last treatment.

4. Discussion

The structure and composition of biochar are of crucial importance because these characteristics establish the mechanism of action in soils. The biochar used in this research consisted of a well-balanced morphological structure. The relevant numbers of carboxylic groups observed by NMR and FTIR were binding structures and were the result of a relatively low manufacturing temperature (400 °C) [22,23]. Besides, there was a high surface adsorption area observed by SEM (Figure S2). Moreover, the dominant element content in biochar was Ca, as revealed by the ICP-OES analysis (Table 2). This fact confers to biochar an evident liming potential [2,27]. This effect, as well as the effects of crop P-use efficiency, has been described in many studies [17,18]. Other studies have suggested that these effects can be mediated by the high adsorption capacity of biochar [15,28].

For this reason, in our study, biochar integration in an NPK fertilizer was performed in a Pi-based fertilizer (Figure S3). However, the growth chamber experiment in wheat (Figure S4) showed a decrease in dry matter production, which indicated an adverse effect of the higher dose of biochar (5%) (Figure 1).

Different adsorption isotherms were applied with micronutrients and Pi to confirm the hypothesis of Pi blockage in biochar. As we could observe in Figure 2, Mn, Mo, or Pi were not adsorbed onto biochar. However, Al and Fe were adsorbed. According to other studies describing the capacity of humic substances—Al or Fe complexes—to bind Pi [29–31], Pi is supplied for an adsorption experiment on biochar previously treated, on the one hand, with Al and, on the other hand, with Fe. The result was that the Pi was effectively bound through these metals to biochar, as shown in Figure 2. This conclusion was reliable because the Pi-metal chemical bond is hydrolyzed by HCl and metal-biochar chemical bond by neutral ammonium citrate, a well-known metal chelating agent [24–26], principally in the case of Fe. HCl did not noticeably hydrolyze the Pi-Al-biochar complexes, as shown in Figure 3. Moreover, in the same Figure, we could observe that Al-Pi and Al-biochar chemical bonds were stronger than

those involved in Fe-Pi-biochar because the Fe (4.86%) and Pi (48.0%) released from Pi-Fe-biochar material was higher than the Al (2.93%) and Pi (8.93%) released from Pi-Al-biochar.

Moving to conventional conditions of biochar amendments in soil, the Pi reactivity with biochar has been previously cited [15–20], but as shown by the isotherm experiments, some other elements could be involved in this biochar reactivity in soil. This fact might explain the disparity between the results reported by different studies. Thus, many studies have described the capacity of biochar to bind heavy metals [12,13,22,23,32,33], including rare earth [34], and micronutrients. However, the results regarding plant growth have been varied very much, depending on the study [17,35–37].

Our results, which examined biochar-soil interactions, might shed some light on these conflicting results. We observed a decrease in water solubility, which increased from 7 days to 15 days, for metals (Al, B, Cu, Fe, Mn, Mo, Zn) and Pi (Figure 4). On the other hand, Ca was increased weakly, and Mg, K, and S also experienced slight changes. These relationships were statistically reinforced by PCA, which showed two very different groupings, corresponding, on the one hand, to the blockage of Pi through micronutrients bridges and, on the other hand, the potential liming action of Ca and Mg (Figure S6).

These relationships were supported by the results obtained in the greenhouse experiment with tomato (Figure S7), which showed positive results in acidic soils, but any effect in the alkaline soils agreed with the results reported by other studies [2,8] (Figure 5). It is noteworthy that the result obtained for N foliar content in acidic soil increased with biochar treatment (Figure 6). This particular result could be related to the concomitant increase in Ca foliar content, which was also associated with biochar treatment (Figure S8). No differences were appreciated in alkaline soil for any treatment and any nutrient, in agreement with other studies previously published [36].

5. Conclusions

This study showed that the effects of biochar on soil properties and plant growth were greatly influenced by its capacity to bind Fe and Al, as well as Pi through Fe and Al chemical bridges. This capacity was related to the presence of carboxylic groups in the biochar structure and, therefore, most likely affected by the origin and temperature/pyrolysis time conditions of biochar manufacture. As this research revealed, this could be the principal reason for the failure in alkaline soils. Likewise, the high amount of Ca that is commonly fixed in biochar was probably associated with a liming effect in acidic soils reflected in improvements in plant growth, as shown by the experiments.

A possible strategy to resolve the possible blockage of micronutrients and Pi in soils might be the use of humified organic matter mixed with biochar, as proposed by some authors [8,38].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/10/7/968/s1>, Table S1: Analysis of soil used in Growth Chamber experiment, Table S2: Analysis of acidic soil used in Greenhouse experiment, Table S3: Analysis of alkaline soil used in Greenhouse experiment, Figure S1: ^1H -, ^{13}C -NMR and ATR-FTIR spectra. Structural groups are indicated in brackets and in the different spectra, Figure S2: SEM images of biochar. Scale bars and magnification are indicated in the images, Figure S3: Biochar fertilizer manual manufacturing in the rotatory disc, Figure S4: Growth chamber experiment in wheat plants using biochar-based fertilizer, Figure S5: Mathematical models for Pi-Al-biochar and Pi-Fe-biochar adsorption isotherms, Figure S6: PCA for biochar-soil interactions at 7 and 15 days, Figure S7: Greenhouse experiment in tomato plants in both acidic and alkaline soils, Figure S8: Nutrient foliar content in tomato plants in both acidic and alkaline soils.

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