**Article**

**Effect of Biochar and Hydrochar on Forms of Aluminium in an Acidic Soil**

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**Abstract:** Biochars and hydrochars have a significant effect on soil properties linked to fertility or to carbon cycling and have been proposed as an amendment to increase soil productivity, particularly in acidic soils. Phytotoxic forms of aluminium (Al) are relatively abundant in acidic soils and, for a long period of time, liming has been used to correct this. Ca(OH)_{2}, a pig manure (PM) and two biochars and two hydrochars prepared from pig manure were studied for their effects on Al fractions. Biochars were prepared at 450 °C (BPC450) and 600 °C (BPC600) and hydrochars were obtained using a pig manure solution (ratio 30:70) that was heated at 200 °C (HPC200) and 240 °C (HPC240). A treatment with an amount of Ca(OH)_{2} necessary to increase soil pH to the same pH value as the average in the treatments BPC450, BPC600, HPC200, HPC240 and PM was used for comparison. The fractionation of Al was studied, with the liming treatment allowing the differentiation between changes in fractionation driven by pH changes from other mechanisms. In relation to the control, all soil amendments presented high capacity of controlling toxic Al, similar to a traditional liming product (Ca(OH)_{2}) and decreased the exchangeable Al extracted by NH_{4}Cl. Both types of materials (biochars and hydrochars) lead to the formation of an increased number of organo-aluminium complexes (OAC). Biochars lead to the formation of OAC of low to medium stability, while hydrochars promoted the formation of OAC of high stability.

**Keywords:** biochar; hydrochar; aluminium; manure

**1. Introduction**

Aluminium (Al) is a natural constituent of all soils, comprising approximately 8% of the total soil inorganic fraction content. Soils in Galicia (NW Spain) and in many other humid regions in the world are acidic as a consequence of the high precipitation, grossly exceeding evapotranspiration. Acidic soils are considered to occupy approximately 30% of the Earth’s ice-free surface [1]. Aluminium has a complex chemistry and its speciation is of utmost importance in acidic soils. In this type of soils, the occurrence of aluminium in the soil solution, which increases at pH values below 6, and its toxicity to plants can lead to decreased plant yields. In fact, aluminium toxicity is considered to be the most limiting factor for productivity in acidic soils [1]. Most soil Al is bound to the soil mineral structure with only a relatively small proportion released to soil solution. It has been commonly accepted that the Al^{3+} ion and monomeric hydroxyaluminium complexes are the most toxic species of this element [2].
Organocomplexes of Al or combinations with fluoride and sulphate pose lesser concern in regard to phytotoxicity [3]. In Galicia, soils have medium to high exchangeable Al content [4]. Generally, liming agents are added to soils in humid regions with the aim to neutralize the pH. This leads to a decrease of aluminium in the soil solution and in the exchange complex through the formation of organo-mineral complexes or precipitation [5]. Thus, exchangeable Al is rapidly neutralized by lime, while non-exchangeable Al (organo-aluminium complexes, hydroxyaluminium compounds, polymers) react slower.

In the last years, an increasing amount of research has been conducted with the aim to add value to waste and incorporate it to the soil system. Biochar is the solid product produced from the pyrolysis, a thermal process in the absence of oxygen, of waste at moderated temperatures and intended for soil amendment. While the initial focus on biochar research was as a geoengineering approach to increase carbon sequestration [6], a multifaceted research literature has emerged in the last years. Biochars are able to sorb multiple contaminants and can be used in the remediation of organic and inorganic polluted areas [7,8]. The addition of biochars to soil can result in an improved nutrient cycling [9].

Finally, it is reasonably well established that biochar can be used to increase crop yields, particularly in acidic soils [10,11]. The reason for this is that biochars tend to be alkaline and part of their benefits in soils, including both, agronomic productivity and soil remediation, has been associated with an amelioration of soil pH [11]. Alkalinity is one of the most important chemical characteristics of biochars. Total biochar alkalinity is comprised of different compartments such as bicarbonate and carbonate (HCO$^-$_3 and CO$_3^{2-}$), organic and other inorganic (non-carbonate) alkalinity [12]. As a consequence of the alkalinity promoted by the biochar application, changes may occur in acidic soils, such as an increase in the concentration of available nutrients (especially P), in the cation exchange capacity, as well as in reducing Al toxicity. Hydrothermal carbonization has been explored in the last years as a methodology to transform wet waste biomass into a potential soil amendment named hydrochar. The production of this material can be more cost-effective than biochar, depending on the intrinsic water content of the samples. To date, few articles have attempted to compare the characteristics of hydrochar and biochar (see for example [13,14]) or its effect upon soil addition [15].

To our knowledge, the potential alleviation of aluminium toxicity and the concomitant changes in the forms of aluminium by biochar or hydrochar has seldom been studied. Qian et al. [16] investigated aluminium phytotoxicity in a hydroponic system using a single biochar. They found that inhibition of plant growth by Al was significantly reduced, chiefly due to Al species being converted to the monomers Al(OH)$_2^+$ and Al(OH)$_3^+$, strongly adsorbed by the biochar, while Al$_3^+$ was transformed to less toxic Al(OH)$_3$ and Al(OH)$_4^-$ . Qian et al. [17,18] used batch adsorption experiments to explore the interactive mechanisms of biochar with Al in aqueous solutions. These studies further elucidated the mechanisms for biochar adsorption of Al. In particular, it was found that both, the complexation of Al with organic hydroxyl and carboxyl groups and the surface adsorption and coprecipitation of Al with silicate particles (as KAlSi$_3$O$_8$) contributed to Al adsorption [17]. Biochar aging introduced carboxylic functional groups on the biochar surfaces, which acted as additional binding sites for Al$^{3+}$ [18]. In general, there is a lack of studies conducted in soil. Studies in soil have aimed to unravel the effect of biochar amendment on Al phytotoxicity [19] or to compare the effects of biochar with lime amendments on Al phytotoxicity during soil re-acidification [20]. These studies [19,20] have so far only considered the effect of biochar in KCl-extractable Al, but not on other fractions. Considering that (i) there are several forms of alkalinity generated by thermal processes, and that (ii) these forms are dependent on the feedstock and the temperature used, it is possible that biochars and hydrochars act on specific aluminium fractions in the soil.

The objective of this study was to investigate the influence of biochar and hydrochar on the chemistry of aluminium in an acidic soil. We aimed to compare these more novel amendments with a traditional material, Ca(OH)$_2$, used by farmers in the region for liming. Thus, similarly to previous experiments with biochars using liming controls [20,21], Ca(OH)$_2$ was used to increase the pH of the
soil to a value which was the average of all other treatments, allowing to differentiate changes in Al fractionation caused by pH changes from those generated by other mechanisms.

2. Material and Methods

2.1. Site Description and Soil Characteristics

Two kg of the A horizon of a control soil (C) were sampled in the vicinity of Sesamo, Culleredo (43°16’40” N 8°24’43” O). The climate of the region is Csb (warm-summer Mediterranean climate) according to Köppen’s classification [22], with an average temperature of 14 °C and an average annual precipitation of 1073 mm. The soil, a Haplic Umbrisol [23] was sampled at an altitude of 100 m above sea level in 2016. The soil was developed over granites and under a vegetation dominated by Eucaliptus and Ulex. The soil is very strongly acidic, according to the descriptive range for pH in soils [24], with a pH value of 4.7. The soil was a loam, with a 47% sand content and a 22% clay content. Organic carbon, organic nitrogen and cation exchange capacity (CEC) were measured using well established methods [25–27]. The carbon content of the soil was high (11.5%) and the organic nitrogen content was 0.51%. The CEC was 11.82 cmolc kg⁻¹.

2.2. Biochar and Hydrochar Preparation

Hydrochar and biochar were produced from pig manure (PM) supplied by a pig farm located at Santa María del Arroyo (Ávila, Spain). Details on hydrochar and biochar production methods and characteristics were comprehensively explained in Gasco et al. [14]. Briefly, hydrochars were prepared as follows: PM samples (1 L with a solid content of 30%) were heated at 200 and 240 °C and the final temperature was maintaining during 2 h under autogenous pressures leading to HPC200 and HPC240. The pressure inside the reactor was 14 bars for HPC200 and 24 bars for HPC240. Biochars were prepared as follows: PM samples were introduced in a 2 L steel reactor. Samples were heated at 3 °C min⁻¹ until 450 and 600 °C leading to BPC450 and BPC600, respectively. The final temperature was maintained during 1 h. For both biochars a N₂ flow of 0.5 L min⁻¹ was used to exclude oxygen from the reactor. Later, biochars and hydrochars were sieved below 5 mm.

2.3. Pot Experiments

Soil (350 g per pot) was placed in pots with a 500 mL volume. Soil was amended with hydrochars, biochar and feedstock at a 5% dose (w:w). Soil was amended with biochar prepared at 450 and 600 °C (BPC450 and BPC600), hydrochars prepared at 200 and 240 °C (HPC200 and HPC240) and with pig manure (PM). A liming control was prepared, using the control soil and the necessary amount of Ca(OH)₂ to increase soil pH to the same value (6.4) as the average in the treatments BPC450, BPC600, HPC200, HPC240 and PM.

Soils were incubated at constant temperature (25 °C) and humidity (60% water holding capacity) for two months. After this period, soils were collected and analysed. All treatments were undertaken in triplicate.

2.4. Forms of Aluminium

The forms of aluminium extracted and the method can be found in Table 1. Several fractions of aluminium were extracted from the soil solid fraction using different reagents. Aluminium was extracted with acid ammonium oxalate (Al₀) as an estimate of total non-crystalline Al [28]; sodium pyrophosphate [29] estimates the organically bound Al (Alₚ), while 0.5 M CuCl₂ estimates the organo-aluminium complexes of low and medium stability (Alₙ). Moreover, the difference between Alₚ and Alₙ was used as an estimate of the Al forming high-stability complexes with organic matter [30], while the difference between Al₀ and Alₚ was used as an estimation of the inorganic, non-crystalline Al [31]. Exchangeable aluminium was extracted by NH₄Cl [32] and CaCl₂ [33].
Table 1. Forms of aluminium (Al) extracted and methods.

| Extractant            | Fraction                                      | Method     |
|-----------------------|-----------------------------------------------|------------|
| CaCl₂                 | Exchangeable Al                               | [33]       |
| NH₄Cl                 | Exchangeable Al                               | [32]       |
| Acid ammonium oxalate (Al₀) | Total non-crystalline Al                    | [28]       |
| Sodium pyrophosphate (Alₚ) | Organically bound Al                      | [29]       |
| CuCl₂ (Al₉Cu₆)        | Organo-aluminium complexes of low and medium stability | [34]       |
| Sodium pyrophosphate (Alₚ)-CuCl₂ (Al₉Cu₆)| Al that forms high-stability complexes with organic matter | [30]       |
| Acid oxalate (Al₀)-Sodium pyrophosphate (Alₚ) | Inorganic non-crystalline Al             | [31]       |

For the extractions of Al, the following procedures were used:

(i) Extraction with acid ammonium oxalate (Al₀): The Al extracted with acid ammonium oxalate (Al₀) (ratio soil: extractant 1:100, with 4 h shaking in the dark).

(ii) Extraction with sodium pyrophosphate (Alₚ): Extraction with 0.1 M Na–pyrophosphate (pH 10) with soil:solution ratio 1:100; shaking for 16 h. Suspension was centrifuged (15 min at 2500 rpm, with three drops of “superfloc”) [29] and the supernatant filtered as previously described.

(iii) Extraction with CuCl₂ (Al₉Cu₆): 5 g of soil was shaken for 5 min with 50 mL of 0.5 M CuCl₂ (pH 2.8); then the suspension was allowed to equilibrate for 12 h and was shaken again for 30 min, filtered through acid-washed paper and the soil in the filter washed with CuCl₂ to a volume of 100 mL [34].

(iv) Extraction with NH₄Cl: The exchangeable Al was extracted with unbuffered NH₄Cl with ratio soil:extractant 1:20, and contact time of 12 h [32].

(v) Extraction with CaCl₂: 10 g of air-dried soil was shaken with 20 mL of 0.02M CaCl₂ in an end-over-end shaker for 1 h, centrifuged (9000 rpm for 5 min) and filtered (Whatman no. 42 filter paper). The resulting solution was analysed using by atomic absorption spectrophotometry.

In all cases, aluminium was determined in the extracts with a Perkin Elmer Analyst 400 Atomic Absorption Spectrophotometer. Forms of aluminium extracted and the method can be seen in Table 1.

2.5. Statistical Analysis

Data were analysed using a one-way ANOVA. The normality and homoscedasticity of the residues were assessed by the Lilliefors and Cochran tests, respectively. Means were compared by Tukey’s HSD test ($p < 0.05$) as a post-hoc method to detect statistically significant differences among all treatments. To illustrate the relationship between Al fractions and the other chemical properties of hydrochars and biochars, the variables together were subjected to a principal component analysis (PCA). All statistical analyses were performed using XLSTAT 2013 software [35].

3. Results and Discussion

3.1. Soil Chemical Properties

Soil pH increased after the addition of different material, from a value of 4.7 in the control to values ranging from 6.0 (HPC240) to 6.7 (BPC600). Values after amendment with other materials were 6.5 for HPC200, 6.5 for BPC450 and 6.2 for PM. In general, the results followed the same trend than the ones reported for the original pH of the materials (see Supplementary Table S1).
3.2. Soil Aluminium Fractions

3.2.1. Exchangeable Al Extracted by NH$_4$Cl and by CaCl$_2$

Figure 1 shows the concentrations of exchangeable Al extracted by NH$_4$Cl (Figure 1a) and by CaCl$_2$ (Figure 1b) in response to application of soil amendments. The concentration of Al-NH$_4$Cl was higher in the control than in the other treatments ($p < 0.05$). On average, the Al-NH$_4$Cl contents decreased approximately 4 times after soil amendments addition compared to the control. All soil amendments led to similar concentrations of Al-NH$_4$Cl with values ranging from 16.37 mg kg$^{-1}$ in PM to 21.1 mg kg$^{-1}$ in HPC240. The materials obtained by thermal treatment (biochar and hydrochar), regardless of the temperature, resulted a content of Al-NH$_4$Cl in the soil similar to Ca(OH)$_2$ which is a traditional material used for liming. Exchangeable Al (Al$^{3+}$) is considered the most toxic Al and might have high values in soils with pH $< 5.5$. In the present study, it could be assumed that pH changes are driving the reported alterations of NH$_4$Cl-extractable Al, as the values shown by the chars were similar to those exhibited by the lime control. While the ability of biochar to reduce extractable Al was already reported [19], this is the first time that a similar fact is witnessed for hydrochar amendment. Al extracted by CaCl$_2$ is considered as the exchangeable Al in soils with the best correlation with plant available Al for a selected number of plant species [33]. Surprisingly, in the present work, the concentrations of exchangeable Al extracted by CaCl$_2$ (Al-CaCl$_2$) were not reduced after soil amendments application (Figure 1b). When produced in a higher temperature both biochar (BPC600) and hydrochar (HPC240) increased the Al-CaCl$_2$ contents compared to the other treatments. Therefore, the results show that the temperature adopted in the thermal process is a key factor to determine the effect of biochars and hydrochars on the Al-CaCl$_2$ concentration in the soil.

![Figure 1](image-url)

**Figure 1.** Exchangeable Al extracted by NH$_4$Cl (a) and CaCl$_2$ (b). Means followed by the same letter are not significantly different ($p < 0.05$) using Tukey’s HSD test.

3.2.2. Al Extracted by Acid Ammonium Oxalate (Al$_0$) and by Sodium Pyrophosphate (Al$_p$)

Aluminium extracted by acid ammonium oxalate (Al$_0$), by sodium pyrophosphate (Al$_p$), and inorganic non-crystalline Al (Al$_{0-p}$) in the soil are shown in Figure 2a–c, respectively. The concentration of Al$_0$ ranged from 163 to 182 mg kg$^{-1}$ (Figure 2a) and it was significantly higher in the soil amended with slaked lime than in soils after chars (biochar and hydrochar) application. Possibly, slaked lime promoted the formation of non-crystalline Al (Al$_0$) from exchangeable Al (NH$_4$Cl) [36]. On the other hand, char addition transformed the soil non-crystalline Al into organo-aluminium complexes as it will be shown in the following sections. No significant differences were observed among the other treatments ($p > 0.05$).
In the present study, Al$_p$ was not affected by soil amendments (Figure 2b). On average, the concentration of Al$_p$ was 25% lower than the Al$_0$ concentration. As Al$_0$ represents the total non-crystalline Al and Al$_p$ is the total organo-aluminium complexes [37], Al$_0$-Al$_p$ has been considered an indicator of inorganic non-crystalline Al [31]. In the present study, both biochar and hydrochar, regardless of the temperature of preparation, had similar concentration of inorganic non-crystalline Al (Figure 2c). In addition, PM promoted higher concentration of inorganic non-crystalline Al than the hydrochars ($p < 0.05$).

3.2.3. Organo-Aluminium Complexes of Different Stabilities

Organo-aluminium complexes (OAC) of low and medium stability (Al$_{Cu}$) and OAC of high stability (Al$_p$-Al$_{Cu}$) in soil amended with slaked lime, manure and its biochar and hydrochar are shown in Table 2.

| Soil Amendment | Organo-Aluminium Complexes (OAC) of Low and Medium Stability | OAC of High Stability |
|----------------|---------------------------------------------------------------|-----------------------|
| Control        | Al$_{Cu}$ = 49.00 ± 1.74 b                                    | Al$_p$-Al$_{Cu}$ = 69.00 ± 5.06 cd |
| PM             | 32.26 ± 1.86 c                                               | 76.81 ± 6.93 bc |
| Lime           | 48.25 ± 1.74 b                                               | 88.36 ± 3.46 b |
| BPC450         | 58.92 ± 1.74 a                                               | 54.88 ± 7.80 d |
| BPC600         | 62.34 ± 0.45 a                                               | 66.06 ± 5.99 cd |
| HPC200         | 52.03 ± 0.05 b                                               | 91.27 ± 15.18 b |
| HPC240         | 33.20 ± 3.79 c                                               | 108.35 ± 6.03 a |

Means followed by the same letter in the column are not significantly different ($p < 0.05$) using Tukey’s HSD test.

In general, the concentrations of OAC of high stability were higher than those of low and medium stability. The concentrations of OAC of low, medium and high stability followed the order HPC240 ≈ HPC200 ≈ Lime ≈ BPC600 > Control ≈ BPC450 ≈ PM.

Only the biochars increased the number of organo-aluminium complexes of low and medium stability, when compared to the control soil or to the addition of lime. Slaked lime and hydrochar addition led to an increase in organo-aluminium complexes of high stability. The amendment with HPC240 led to significantly higher amounts of OAC of high stability, compared to any other treatments. The higher amount of OAC of high stability in soils amended with hydrochars could be due to the presence hydroxyl and carboxyl groups, as they are known to complex with Al [17]. The aforementioned functional groups were significantly more abundant in hydrochars compared to biochars [14]. The differences in the type of OAC generated by biochars and hydrochars points to a contrast in the organic matter in biochars and hydrochar, particularly a more condensed aromatic structure.
in the biochars [14]. Biochars produced at different temperatures promoted similar concentrations of OAC in the soil. However, there seems to be a strong influence of the hydrothermal temperature, controlling the amount of OAC of high stability formed in the soil. Compared to biochar, hydrochars had higher easily oxidizable carbon (OC) content and less stable carbon structures [15]. The lower recalcitrance of the carbon in hydrochar, compared to biochars, seems to impact hydrochars’ ability to form OAC in the soil. Interestingly, slaked lime did not alter any OAC in the soil compared to the control. In fact, there is no general agreement about the effect of liming on the forms of non-extractable Al [23]. These results suggest that pH changes are not one of the main mechanisms involved in the formation of OAC upon char addition to the soil.

3.3. Relationship between Soil Aluminium Fractions and Chemical Properties of Manure and Its Biochars and Hydrochars

A principal component analysis (PCA) was conducted to determine the relationships between the chemical properties of soil amendments (Table S1) and soil Al fractions. The two main components (PC1 and PC2) of PCA explained 81% of the total variation in the properties evaluated (Figure 3). Considering all variables together and based on eigenvectors and correlation coefficients (Table 3), it is possible to separate three distinct groups comprised of PM, biochars (BPC450 and BPC600), and hydrochars (HPC200 and HPC240). Overall, according to the PCA results, it was possible to conclude that the thermal processes promoted chemical changes in PM and, consequently, in its interaction with the soil Al. Furthermore, products obtained by distinct thermal processes (pyrolysis and hydrothermal carbonization) act on specific fractions of Al in the soil. The PCA results showed that PM was statistically associated with the soil total (Al₀) and inorganic non-crystalline Al (Al₀-Alₚ). EC in PM was strongly related to the presence of non-crystalline Al in the soil. In general, EC in PM, Al₀ and Al₀-Alₚ had the most positive correlation coefficients with PC1 (Table 3), leading to stark contrasts between PM and its biochars and both hydrochars. Hydrochars showed a relationship with the soil exchangeable Al (Al-NH₄Cl and Al-CaCl₂), probably associated with high CEC in hydrochars, mainly in the one produced at the highest temperature (HPC240). Furthermore, the high OC values in the hydrochars [15] were also related to the presence of organically bound Al (Alₚ) in the soil. As previously shown (Table 2), the soil amended with hydrochars presented the highest concentrations of OAC of high stability. From the PCA results it is also possible to surmise that pH and carbonate content were the properties of biochar that contributed the most to the OAC of low and medium stability accumulation in the soil. In general, biochar pH measured in water increases with increasing total alkalinity. Although it varies widely according to the feedstock, pyrolysis temperature, and other pyrolysis conditions, generally the total alkalinity of biochars is composed mostly of carbonates [6]. Overall, the results of the PCA seem to suggest that there are different mechanisms underpinning the observed changes in Al fractions upon the addition of biochar, hydrochar or manure. These mechanisms are likely to include pH, EC, the amount and form of organic matter and the presence of different anions and cations introduced with the amendments.
The addition of manure or their biochars and hydrochars increased the pH value of the soil with respect to the control soil from a value of 4.7 to values between 6.0 and 6.7. The amendments modified the aluminium chemistry of the soil. In general, products obtained by different thermo-chemical processes (pyrolysis and hydrocarbonization) affected specific fractions of Al in the soil. Biochars and hydrochars formed organo-aluminium complexes of different stability in the soil. Whereas PM and lime transformed exchangeable Al into inorganic non-crystalline Al. The results of the PCA seem to imply that the mechanisms responsible for changes in Al fractionation differ for manure, biochar and hydrochar. Further studies would be required to elucidate the exact mechanisms underpinning the observed transformations. All thermal amendments were capable of replacing slaked lime to reduce the soil exchangeable Al extracted by NH$_4$Cl to a value of less than one fourth of that in the control soil.

**Figure 3.** Principal component analysis for soil aluminium fractions and chemical properties of manure (PM) and its biochars (BPC450 and BPC600) and hydrochars (HPC200 and HPC240).

**Table 3.** Eigenvectors and correlation coefficients between principal components (PC1 and PC2) and variables (soil Al fractions and chemical properties of the amendments).

| Variable     | Eigenvectors | Correlation Coefficient | PC1 | PC2 | PC1 | PC2 |
|--------------|--------------|--------------------------|-----|-----|-----|-----|
| Al-CaCl$_2$  | -0.277       | 0.131                    | -0.658 | 0.264 |
| Al-NH$_4$Cl  | -0.363       | 0.191                    | -0.864 | 0.386 |
| Al$_{ox}$    | 0.374        | 0.079                    | 0.891  | 0.159 |
| Al$_p$       | -0.298       | 0.306                    | -0.708 | 0.618 |
| Al$_{Cu}$    | -0.233       | -0.385                   | -0.554 | -0.777 |
| Al$_p$-$Al_{Cu}$ | -0.064       | 0.488                    | -0.151 | 0.985 |
| Al$_{ox}$-$Al_p$ | 0.357        | -0.193                   | 0.849  | -0.390 |
| pH           | -0.317       | -0.131                   | -0.754 | -0.265 |
| EC           | 0.394        | 0.048                    | 0.938  | 0.096 |
| CEC          | -0.010       | 0.399                    | -0.024 | 0.805 |
| OC           | 0.058        | 0.405                    | 0.138  | 0.817 |
| Carbonates   | -0.343       | -0.285                   | -0.816 | -0.576 |

4. Conclusions
Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/21/7843/s1, Table S1: Main properties of pig manure, biochars and hydrochars.

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