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Pyrolysis temperature influences the capacity of biochar to immobilize copper and arsenic in mining soil remediation

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	the structure of this material and an increase in soil pH and organic matter content. Conversely, As was increased in the soluble fraction for all three types of biochar but in a proportion that lacks relevance. On the whole, given its lower PAH content, higher Cu immobilization ratio, and an almost negligible increase in As availability, biochar obtained at 500 ºC outperformed the other two products with respect to soil recovery. Of note, data on Cu and As availability were doubled-checked using two extraction methodologies. We propose that this operational approach for determining the most suitable pyrolysis temperature will find application in other soil remediation actions
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Pyrolysis temperature influences the capacity of biochar to immobilize copper and arsenic in mining soil remediation

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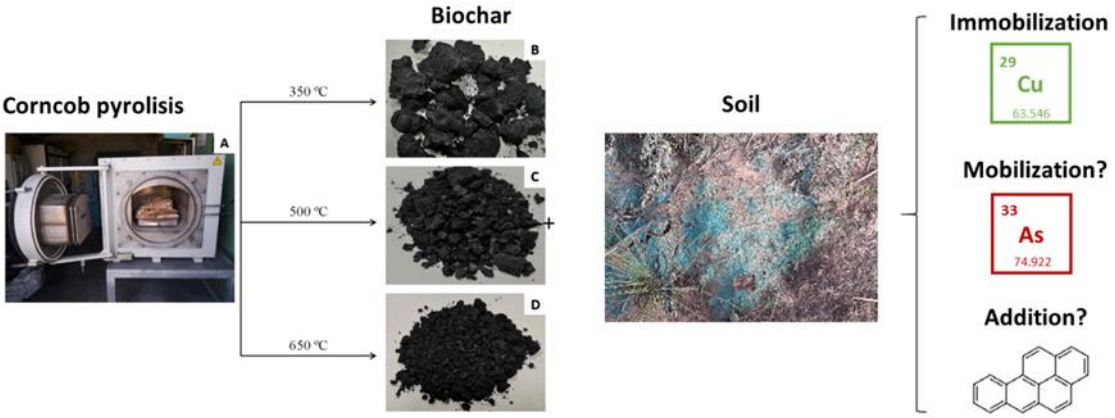
Abstract

Biochar is a promising material used for multiple remediation approaches, mainly in polluted soils. Its properties can differ depending on feedstock and pyrolysis temperature. In this context, we tested the capacity of three biochar products made from corncob, pyrolyzed at different temperatures (350, 500, and 650 ºC), to remediate a mining soil affected by high levels of Cu and As. We performed an exhaustive characterization of the biochar. We found that biochar showed a higher surface area with increasing pyrolysis temperature, whereas high molecular weight PAHs were detected in biochar produced at the maximum temperature, thus indicating potential ecotoxicological risks. After the application of biochar to the soil, Cu was partially immobilized, especially when using that obtained at 500 ºC. This effect is attributed to the structure of this material and an increase in soil pH and organic matter content. Conversely, As was increased in the soluble fraction for all three types of biochar but in a proportion that lacks relevance. On the whole, given its lower PAH content, higher Cu immobilization ratio, and an almost negligible increase in As availability, biochar obtained at 500 ºC outperformed the other two products with respect to soil recovery. Of note, data on Cu and As availability were doubled-checked using two extraction methodologies. We propose that this operational approach for determining the most suitable pyrolysis temperature will find application in other soil remediation actions.

Key words: Biochar, soil remediation, copper, arsenic, Nature-Based Solutions.

Graphical abstract



1. Introduction

One of the main environmental impacts of mining activity is contamination by potentially toxic elements (PTEs) (Akala and Lal, 2000; Shrestha and Lal, 2011; Li et al. 2014). PTEs can promote physical-chemical alterations of mining soils and such changes can extend into areas far from the mine (Ghosh and Maiti 2020). In this context, mining areas affected by pollution usually present a low content of organic matter (OM) and nutrients, decompensated cation exchange capacity (CEC), low water retention capacity, high electrical conductivity, altered pH, little or no vegetation cover, and high available concentrations of PTEs. Such characteristics impair soil ecosystem services (Ussiri and Lal, 2005; Zhou et al. 2015; Pietrzykowski 2019). Open-pit mining in particular causes loss of basic pedological properties. In this context, poor management of settling ponds and tailings can be a major environmental issue. In fact, mine tailings are susceptible to alteration by erosion, leading to increased mobility and leaching of PTEs (Forján et al. 2019), which become a continuous source of long-term contamination until they are stabilized by natural processes. This contamination affects environmental compartments (mainly soil, surface water, and groundwater) close to mine tailings, as well as wider areas, which can lead PTEs to enter the food chain (Mombo et al. 2015; Puga et al. 2016). In this context, and given that the mobility, toxicity, and bioavailability of PTEs do not depend solely on their

concentrations, the examination of chemical speciation is critical to understand contamination by these toxic compounds (Gamboa-Herrera et al. 2021).

Reclamation strategies are required to reduce the incidence of PTE movement into adjacent ecosystems via water and air erosion (Trippe et al. 2021). Soil recovery is currently being promoted through the provision of Nature-Based Solutions (NBS), which are defined as strategies inspired and supported by nature that are cost-effective and simultaneously provide environmental, social, and economic benefits (European Commission, 2017). NBS offer great potential in the field of contaminated soil remediation, including the application of amendments made from by-products such as biochar, a well-known amendment that effectively improves soil characteristics (Yadav and Garg 2011; Wu et al. 2017; Ghosh and Maiti 2020).

Biochar is an amorphous carbonaceous black mass produced by the pyrolytic conversion of organic biomass-a process that yields a porous, low density, carbon-rich material with a large specific surface area (Duwiejuah et al. 2020; Ghosh and Maiti 2020). Biochar has numerous beneficial effects on soil. In this regard, it has been reported to raise soil pH, enhance the OM content and CEC, increase moisture-holding capacity, attract more beneficial fungi and microbes, retain nutrients, and increase carbon sequestration (Beesley et al. 2011; Diacono and Montemurro 2011; Beesley et al. 2014; Forján et al. 2017). Of note, biochar can also reduce the availability of PTEs through metal ion complexation on its surface (Beesley et al. 2010; Beesley and Marmiroli 2011; Beesley et al. 2011; Park et al. 2011). This complexation capacity is explained by the organic functional groups present on the surface of biochar, such as –COOH, –CO–, –OH, and R–COO–R groups, which have a high capacity to take up metal(loid)s from soil (Ahmad et al. 2014, Fellet et al. 2014; Puga et al. 2015; Lomaglio et al. 2017). These effects can be attributed to electrostatic interactions between the negatively charged carbon surface and metal cations, to ionic exchange between metal cations and ionizable protons at the acidic carbon surface, and to sorptive interaction involving delocalized carbon electrons (Sohi et al. 2010). Biochar is more environmentally friendly than active carbon (-0.9 kg CO_2-eq kg^{-1} vs. 6.6 kg CO_2-eq kg^{-1}) and production costs are lower. In this regard, production costs for granular activated carbon and powdered activated carbon were estimated at $6.40 and $1.20-2.00 per kg^{-1}, respectively, whereas

several types of biochar were reported to have an average price of \$0.90 per kg^{-1} (Alhashimi and Aktas 2017; Sizirici et al. 2021).

The behaviour of biochar can differ depending on the anionic or cationic nature of PTEs (Beesley et al. 2011; Park et al. 2011; Manyà 2012; Fellet et al. 2014; Luo et al. 2014; Baragaño et al. 2020). Furthermore, the interaction of biochar with PTEs may also vary in function of its chemical and physical properties (Duwiejuah et al. 2020; Głąb et al. 2021), which are related to the pyrolysis temperature and source material used for its production (Kloss et al. 2012; Chen et al. 2016). The effects of fine-tuning pyrolysis temperature may imply a loss of acidic functional groups and an increase in the amount of ash, as well as variations in the concentration of exchange cations on the surface area, density, and pore diameter (Antal and Grønli 2003; Lin et al. 2008; Budai et al. 2014; Ippolito et al. 2015). In addition, the potential presence of polycyclic aromatic hydrocarbons (PAHs) (Singh et al. 2010; Hale et al. 2012) may also be affected by pyrolysis temperature. Therefore, there is currently controversy regarding the application of biochar to all soil types as some kinds might supply PAHs to this matrix (Xing et al. 2021).

Raw biomass for biochar production usually comes from organic waste, thereby promoting the circular economy (agroforestry biomass, livestock waste, urban or industrial waste, etc.) (Beesley et al. 2011). A good example of such a waste product is corncobs, which are generated in high numbers because maize is one of the most common staple crops worldwide (Szufa et al. 2020). Biochar made from maize waste can remove a large number of contaminants from soil (Lehmann and Joseph 2015; Sizirici et al. 2021).

Given the above considerations, here we comprehensively evaluated the properties of corncob biochar produced at three temperatures and the behaviour of these materials when used to amend mining soil containing metal(loid)s. In particular, we addressed the interaction of the biochar with Copper (Cu, metal) and Arsenic (As, metalloid), both abundant in the mining soil under study.

2. Material and methods

2.1. Soil sampling

Soil affected by As and Cu pollution was sampled in an area close to a metal mine in NW Spain that has been active for decades. Several soil subsamples were taken at a depth of 30 cm. These were then mixed and a 50-kg composite sample was obtained. The composite sample was taken to the laboratory, air-dried, sieved through 2-mm mesh, and homogenized.

2.2. Soil analyses

The pseudo-total concentrations of As and Cu were determined after extraction with aqua regia 1:3 (v/v) (HNO_3 / HCl) in a microwave oven (Milestone ETHOS 1) and analysis by ICP-OES (Perkin-Elmer; Optima 4300 DV). Soil texture data were obtained following Guitián and Carballas (1976) and USDA criteria to determine soil texture (USDA 1982). Clays were qualitatively identified following the procedure described by Brown and Brindley (1980) using X-ray diffraction (XRD) analysis. A powder X-ray diffraction (PXRD) pattern was obtained using a SIEMENS D-5000 diffractometer (with a Cu kα1 radiation source). pH was measured with an electrode in a 1:2.5 ratio of water to sample following the method described by Guitián and Carballas (1976). Total carbon (TC) and total nitrogen (TN) were measured in the solid sample module of a LECO elemental macro-analyzer (CNS2000), while a bidistilled water extraction was carried out to measure dissolved organic carbon (DOC), following Sanchez-Monedero et al. (1996). The Mehlich III method (Mehlich 1984) was used to determine available phosphorus (AP). Organic matter (OM) was measured by weight loss on ignition (LOI: loss on ignition) (Beaudoin 2003). Exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, $Na^{+,}$ and Al^{3+}) were extracted with 0.1M $BaCl_2$ (Hendershot and Duquette 1986) and their concentrations were determined by ICP-OES (Perkin-Elmer; Optima 4300 DV). Cation exchange capacity (CEC) was calculated by adding the total concentrations of exchangeable cations. The concentrations of free oxides of Fe, Al and Mn were determined using the method described by Mehra and Jackson (1960), with subsequent measurement by ICP-OES (Perkin-Elmer; Optima 4300 DV).

2.3. Biochar production and characterization

Three types of biochar were produced using corncobs as raw biomass. The biochar was developed in collaboration with the company Centro de Valorización Ambiental del Norte S.L. (Touro, A Coruña). The furnace used (model HCV_56 CCH) was designed by Forns Hobersal SL. Biochar is usually obtained at temperatures above 250 ºC irrespective of the source of biomass (Lehmann and Joseph 2015; Sizirici et al. 2021). In our case, the pyrolysis temperatures selected were as follows 350 ºC (B350), 500 ºC (B500) and 650 ºC (B650) (Fig. S1A, S1B, S1C Supplementary Material). The raw material was pre-dried so that the starting conditions were the same for all pyrolytic procedures. After pyrolysis, the biochar was air-dried, ground and sieved to 2 mm to homogenize the biochar particles and to equalize them to the soil fraction which is considered below 2 mm. The general pyrolysis times, temperatures, and yields obtained for each biochar product are shown in Table S1 (Supplementary Material). As expected, the yield was lower with increasing pyrolysis temperature due to a greater loss of biomass. These yield data are consistent with those obtained by Szufa et al. (2020) and Das et al. (2021).

The biochars obtained were subjected to the following determinations. First, the specific surface area (SSA) was measured by CO_2 adsorption at 77 K using an ASAP 2020 Micromeritics analyzer on samples previously outgassed at 373 K for 2 h. Complementarily, pore size distribution was determined following the Dubinin-Stoeckli model. CHN concentrations were measured in a LECO CN-2000 module, oxygen content was calculated by difference. Biochar surface was observed using a JEOL JSM-5600 Scanning Electron Microscope. To obtain information about the presence of ash in the biochar, thermogravimetric curves (TGA) and differential scanning calorimetry (DSC) were achieved from ambient temperature to 1273 K at a heating rate of 283 K min^{-1} in an inert N_2 atmosphere using an SDT Q600 instrument. Finally, to determine PAHs, 5-g representative subsamples were extracted by dichloromethane:acetone (1:1) in a Soxtherm apparatus (Gerhardt), according to a usual protocol (Boente et al. 2020). The 16 priority PAHs were measured after injection into a 7890A GC System coupled to a 5975C Inert XL MSD with a Triple-Axis Detector (Agilent Technologies) and following a modification of EPA method 8272. A capillary column DB-5 ms (5% phenyl and 95% dimethylpolysiloxane) 30 m × 0.25 mm i.d. × 0.25 μm film (Agilent Technologies) was used, with He as carrier gas at a flow rate of 1 mL

164 min^{-1}. The initial oven temperature was 80 °C (held for 2 min), which was ramped up at 15 °C/min
165 to 300 °C (held for 10 min). The GC injector was operated in splitless mode for 2 min at 260 °C.
166 The mass spectrometer was operated in selected ion monitoring mode (SIM), and the m/z ratios
167 for PAHs quantification were 128, 152, 153, 154, 165, 166, 178, 202, 228, 252, 276, and 278I.
168 Calibration mixtures (AccuStandard) were used.
169

170 **2.4. Experimental design and pollutant mobility**

171 The soil (S) was subjected to the following four treatments:

172 - S: Initial mining soil.
173 - SB350: S + corncobs pyrolyzed at 350 ºC (B350).
174 - SB500: S + corncobs pyrolyzed at 500 ºC (B500).
175 - SB650: S + corncobs pyrolyzed at 650 ºC (B650).

176 The samples (100-g, dry weight) with a soil:biochar ratio of 95:5 (w/w) were incubated in 500-
177 mg glass jars in triplicate for 40 days under controlled conditions of darkness, temperature (22 ±
178 2 °C) and water content (maintained around field capacity by adding distilled water periodically).
179 At the end of the experiments, samples were air-dried, passed through a 2-mm sieve, and
180 homogenized prior to analysis. To monitor the available concentrations of As and Cu, these metal
181 and metalloid were extracted with 0.01 M $CaCl_2$ in soil solution (Houba et al. 2000) and their
182 concentrations were determined by ICP-OES (Perkin-Elmer; Optima 4300 DV).
183 Furthermore, and to gain a deeper understanding of pollutant mobility, a sequential extraction
184 was carried out following the procedure described by Salbu et al. (1998), modified from the
185 method of Tessier et al. (1979). The concentrations of As and Cu were fractionated into mobile
186 phases (F1: Water-soluble, F2: Exchangeable, and F3: Bound to carbonates) and less mobile or
187 immobile phases (F4: Bound to iron and manganese oxides, F5: Bound to organic matter, and F6:
188 Residual) by means of extractants of increasing strength from fraction 1 to fraction 6.

189 After each extraction, the samples were centrifuged, and the extracts were clean with syringes
190 with 0.45-µm filters (Sartorius Minisart) into 50-ml glass tubes (using the same syringe and filter

for each of the replicates during the entire process). Each sample residue was washed with 10 ml of bidistilled water (water was added, stirred manually, and centrifuged for another 15 min at 3300 rpm), and the resulting extract was added to the extract obtained in that fraction. The extracts obtained were analyzed by ICP-OES (Perkin-Elmer; Optima 4300 DV).

2.5. Statistical analysis

All analytical determinations were performed in triplicate. The data obtained were processed statistically using the SPSS program for Windows (version 24.0), taking statistical significance with p values <0.05. Normality tests (Kolmogorov-Smirrnov test), Levene's homogeneity of variances, and analysis of variances (ANOVA) were performed. In the case of homogeneity of variances, a post hoc least significant distance (LSD) test was performed, while if there was no homogeneity of variances, Dunnett's T3 test was carried out. In addition, a Pearson's bivariate correlation analysis was also performed.

3. Results and discussion

3.1. General characteristics of the biochar and mining soil

Pseudo-total concentrations of As and Cu in the initial soil were higher than in natural soils, whereas the contents of these PTEs in the three biochar products were almost negligible. Concretely, As concentrations in the three pyrolyzed biochar products remained below the quantification limit (0.001 mg L^{-1}), while soil content was 85.09 mg kg^{-1}. At the same time, Cu concentration in soil was 1124 mg kg^{-1}, while in the biochar products it was below 10 mg kg^{-1}, with slightly increasing values as the pyrolysis temperature increased (Table 1). The chosen soil belongs to a mine tailing, according to the USDA (1982), the initial soil can be classified as loam-sandy-clay. The XRD analysis indicated that the clay fraction consisted mainly of kaolinite, montmorillonite and illite (Fig. S2, Supplementary Material), while other silicates such as quartz were also present (Table S2, Supplementary Material).

Oxide analysis of the initial soil showed high concentrations of Fe oxides and considerable concentrations of Al oxides, while concentrations of Mn oxides were low (Table 1). The initial

soil had an acidic pH while three biochar products were alkaline. Biochar pH values (B350, B500 and B650) increased with pyrolysis temperature, as previously indicated by Duwiejuah et al. (2020). The soil had a lower OM and TC content than the biochar, whereas the increase in pyrolysis temperature caused a slightly decrease in the OM content of the latter, whereas the higher the pyrolysis temperature, the higher the TC content. This result might be due to the yield being lower at 650 ºC and are consistent with those reported by Kim et al. (2021) and Das et al. (2021), who concluded that biochar TC content increases up to 10.14% with pyrolysis temperature. In turn, we observed that the biochar products had a higher DOC content than the soil (Table 1) and that biochar pyrolyzed at higher temperature had a greater DOC content than that produced at 350°C. These data contrast with those obtained by authors such as Luo et al. (2015) and Uchimiya et al. (2013), who concluded that an increase in pyrolysis temperature leads to a decrease in DOC content. The biochar products showed a higher TN content and available P concentration than soil (Table 1). In this regard, B350 had a higher available P concentration than B500 and B650, whereas TN was almost the same. These results are in line with the conclusions obtained by Mukherjee and Zimmerman (2013). All three biochar products had a higher CEC than the initial soil (Table 1) and, specifically, B500 and B650 had a higher CEC than B350. Remarkably, the high CEC values of the products were due mainly to their high concentrations of K^+. It should also be noted that Al^{3+} was undetectable in these amendments, and thus the base saturation values (V) were 100% in all three cases; however, the Al^{3+} concentration in soil was 11.60 $cmol_{(+)}kg^{-1}$.

3.2. Specific biochar characterization

The specific surface area (SSA) of the biochar products increased progressively with pyrolysis temperature (Table 1), in agreement with Zhang et al. (2011), who deduced an increase in aromatic C content and the progressive destruction of –OH groups, ester C=O bonds, aliphatic -CH_2, and C–O groups shielding the aromatic core as the pyrolytic temperature rises, i.e., the increase in aromatic C content enlarges the SA. Furthermore, this higher SSA is possibly due to a decrease in pore size as pyrolysis temperature rises (Sizirici et al. 2021). In this regard, the

largest difference in pore size was found between B350 and the other two amendments (B500 and B650) (Fig. S3, Supplementary Material); these differences also coincide with differences in SSA. In addition, it is possible to observe this using SEM, as it is revealed in Fig. S1 (Supplementary Material). C/H and C/O ratios indicate degree of aromaticity and polarity, respectively, which are critical properties to evaluate the carbon structure of this material (Xing et al., 2021). The molar H/C ratio is important as it gives an indication of the degree of carbonization of biochar (Das et al., 2021; Mohan et al., 2018). In our case, contrary to what might be expected, B350 and B650 showed identical degrees of carbonization (Table 1). In turn, authors such as Mohan et al. (2018) and Das et al. (2021) took the C/O molar ratio as an indicator of the hydrophilicity of the biochar surface because it reflects the content of polar groups derived mainly from carbohydrates. We found that the value of the C/O ratio followed the sequence B500 > B650 > B350 (Table 1), thereby suggesting that biochar produced at 500 ºC is the most hydrophilic.

The thermogravimetric analysis (TGA) curve (Fig. S3, Supplementary Material) of the three biochar products revealed that B350 lost more mass (weight %) and more rapidly than B500 and B650. Higher losses at lower temperatures could be explained by moisture as the mass loss from 0 ºC to 250 ºC was due to the release of water (volatilization), together with the formation and release of volatile gaseous products such as CO, CO_2, CH_3COOH, and other organic compounds (Szufa et al., 2020; Das et al., 2021). The mass loss from 250 ºC to 600 ºC was caused by thermal decomposition of the biomass and decomposition of lignocellulosic substances (Cao and Harris 2010; Das et al. 2021). In this regard, corncob has three main components, namely hemicellulose, cellulose, and lignin, and these compounds pyrolyze at different temperatures and thus influence the TGA curve of each biochar product (Ouyang et al. 2015). The mass loss from 600 ºC and above could be attributable to, among other factors, the decomposition of calcium phosphate and inorganic minerals such as calcite ($CaCO_3$) (Das et al. 2021). Regarding the PAH content of each biochar product, quantitative data are shown in Table 2. In our case, biochar pyrolyzed at the lowest temperature had a higher content of low molecular weight PAHs (2-3 aromatic rings), whereas the highest temperature promoted an abundance of heavy molecular weight PAHs (4 or more aromatic rings). Of note, the total concentration of PAHs was the lowest at the intermediate

temperature (500 ºC) and thus this material emerges as the best option as a soil amendment in terms of reducing potential toxicity.

3.3. Biochar treatments of polluted soil.

3.3.1. pH, organic matter, and dissolve organic carbon evolution.

The three treatments applied caused a moderate but significant ($p<0.05$) increase in soil pH (Fig. 1A). However, in all cases, the soil treated with biochar continued to maintain an acidic pH. The increase in pH observed is consistent with previous work on biochar treatment of mining soils (Zhao et al. 2015; Rodríguez-Vila et al. 2017). This increase is probably caused mainly by the association of H^+ ions with the biochar and subsequent decarboxylation processes (Solaiman et al. 2015). The SB500 treatment led to the greatest increase in pH (Fig. 1A), possibly because this amendment had a greater CEC due to its higher content of the basic cation K^+ (Table 1). In this regard, high CEC and %K are often correlated with high pH values (Canet et al. 2007; Alvarenga et al. 2008; Forján et al. 2018). The increase in pH after soil treatment with biochar was lower than expected, possibly due to a low buffering capacity of the soil, a common effect in acidic soil such as that found in and around mines (Baileys and Blankenhord 1982, Beesley et al. 2014, Budai et al. 2014, Forján et al. 2018). Regarding potential acidity (pH_{KCl}), in the control soil, this parameter was less than 3.4, and a significant increase ($p <0.05$) was observed after the addition of biochar, reaching a maximum of 4.3 in SB500. On the whole, an increase in pH, although restrained in our case, may influence other soil properties and thereby mobilize metalloids (Ahmad et al. 2014; Duwiejuah et al. 2020).

The addition of B350, B500, and B650 to the mining soil caused an increase in OM content. This increase was more notable with biochar produced at higher pyrolysis temperatures (Fig. 1B), conversely to what could be expected since, for instance, B350 had a higher OM content than B650. Therefore, and also taking into account (Fatima et al. 2021) that the amendment of soil with biochar can reduce the decomposition of soil OM, we conclude that the increase in pyrolysis temperature improves the capacity of biochar to retain organic matter by mechanisms such as adsorption (Duwiejuah et al. 2020, Xing et al. 2021),. In turn, the increase in OM caused a

significant increase in DOC in all treatments (Fig. 1C), i.e., a remarkable positive correlation was observed between OM and DOC (0.94, $p < 0.01$). A greater increase in DOC content was expected in the SB500 and SB650 treatments since the biochar prepared at 500 ºC and 650 ºC had a much higher initial DOC content than B350 (Table 1). However, the greatest increase in soil DOC was induced by B350, which is in agreement with Li et al. (2018), who observed that biochar pyrolyzed at low temperatures leads to a greater increase in this parameter than that produced at higher temperatures.

3.3.2. Evaluation of Cu sequential extraction

The chemical distribution of Cu is shown in Fig. 2. On the whole, and irrespective of the treatment, a similar concentration of immobile Cu (F4 to F6) and mobile Cu (F1 to F3) was found. This behaviour was not observed in the control soil, in which there was a higher concentration of Cu in the mobile than in the immobile phase. This trend was more evident in the case of the SB500 treatment, especially for F1. In the most mobile phases (F1 and F2), the availability of Cu decreased significantly ($p < 0.05$) in all three biochar treatments (Fig. 2A). The maximum reduction was observed in the SB500 treatment (from 234 mg kg^{-1} in the control down to 121 mg kg^{-1} in F1). Similarly, exchangeable Cu in F2 (Fig. 2B) was decreased from 386 mg kg^{-1} in the control down to 302 mg kg^{-1} in SB500. On the contrary, in the fraction bound to carbonates (F3, Fig. 2C), the concentration of Cu was increased, being more significant in treatments SB500 and SB650. Regarding the less mobile fractions, F4 and F5 (Fig. 2D and Fig. 2E), there were only slightly significant differences in F5 between the control and the treatments. Finally, the residual fraction, F6, remained essentially stable irrespective of the biochar used.

As indicated by these results, the most bioavailable fractions (F1 and F2) tended to show immobilization, especially in the SB350 and SB500 treatments. This observation is consistent with the findings of Solaiman et al. (2015) as the two most important factors affecting the bioavailability of toxic metals are the OM content and pH of the soil. In our case, the increase in pH described is expected to have promoted the precipitation of Cu carbonates. In the same sense, negative correlations were found between OM vs. pH and Cu concentrations in F1 and F2, with

329 values of -0.91, -0.95 ($p < 0.01$) and -0.78, -0.80 ($p < 0.01$), respectively. Several authors obtained
330 similar results (a decrease in Cu availability) when pH and OM values were increased (Park et al.
331 2011; Pérez-Esteban et al. 2012; Forján et al. 2016). Also, and according to Sizirici et al. (2021),
332 Cu removal efficiency and sorption capacity increase more in a pH range from 2 to 6 while at
333 higher pH the growth in sorption efficiency is lower. In our case, SB500 caused the greatest
334 increase in pH (from 3.42 to 4.27), becoming the treatment with the highest Cu sorption efficiency
335 in these first two fractions. Complementarily to pH effects, the decrease in Cu concentrations in
336 the most mobile phases (F1 and F2) was significantly negatively correlated with the DOC
337 provided by the treatments (-0.92 and -0.91, $p < 0.01$), thus Cu can also be complexed by DOC
338 and subsequently its concentration decreases (Beesley et al. 2014).

339 The reduction of Cu bioavailability can be explained not only by the chemical effects of biochar
340 amendments but also by the intrinsic properties of the different biochar material used. In this
341 regard, B500 and B650 had higher SSAs and smaller and more homogeneous pores than B350,
342 and these two factors should improve Cu immobilization (Chen et al. 2014; Sizirici et al. 2021).
343 In fact, the functional groups present on the biochar surface confer adsorption potential for toxic
344 compounds such as Cu (Uchimiya et al. 2010; Duwiejuah et al. 2020). In addition, the increase in
345 SA also increases the number of functional groups that interact with pollutants.

346 **3.3.3. Evaluation of As sequential extraction**

347 The results are shown in Fig. 3. Note that only F1, F4, F5, and F6 are shown as F2 and F3 values
348 were below the quantification limit. The initial As availability was very low (F1 close to detection
349 limit, Fig. 3A), whereas the most abundant fractions were F4 and F6 (Fig. 3B and Fig. 3D,
350 respectively). A general effect of biochar amendment was slight mobilization (F1 increase but
351 only up to very low concentrations) for all treatments (Fig. 3A), and this was simultaneous to a
352 slight decrease in As in the residual fraction (F6 reduction, Fig. 3D). Although the pH increased
353 significantly in all treatments, it continued to be acidic, as shown in Fig. 1A, and thus positive
354 charges predominated on the soil adsorption surface, allowing As to remain strongly retained (Lin
355 et al. 2008; Hartley et al. 2009; Tack et al. 2010). Therefore, the increase in pH in the SB350,

SB500 and SB650 treatments was not enough for relevant mobilization of As. On the contrary, the presence of biochar may favour a slight increase in available As, as the negatively charged functional groups present in biochar repel As anions (Arco-Lázaro et al. 2016; Abou et al. 2019). In the same context, an increase in DOC mobilizes available As (Beesley et al. 2010; Guisquiani et al. 1998; Hartley et al. 2010), given that OM is adsorbed preferentially on the soil aggregates instead of As and/or it forms soluble organometallic complexes with As. However, in this experiment, no correlations were obtained between DOC and F1, perhaps because As concentrations were very low. In turn, as shown previously in Table 1, the biochar products showed a significantly higher P content than the initial soil. This might also partially explain the release of some As to the most mobile fraction due to the competitive interaction between As and P for sorption sites given that P can displace and mobilize As (Hartley et al. 2009; Bolan et al. 2013; Fleming et al. 2013; Baragaño et al. 2020). This process occurs most significantly in low pH soils (Xu et al. 2014; Solaiman and Anawar 2015), as occurs in our case (Table 1).

3.3.4. Evaluation of Cu and As availability in $CaCl_2$ extraction.

To corroborate previous results of sequential extraction and to address potential effects on vegetation, an additional extraction with $CaCl_2$ was performed. The treatments applied caused a decrease in available Cu, with SB500 being the most effective (Fig. 4A). This decrease is probably due to the increase in pH and OM, as explained above (Weng et al., 2001; Park et al., 2011). In addition, this relationship between pH and OM with available Cu was reflected by negative Pearson correlations, with values of r=-0.82, r=-0.97 for pH and OM, respectively ($p<0.01$). Again, there was a significantly negative correlation between available Cu and DOC (-0.87, $P<0.01$)—an observation that reinforces the results obtained in the previous section. As regards available As, this was below the quantification limit in the initial soil whereas As availability in $CaCl_2$ increased marginally once the treatments were applied (Fig. 4B), without significant differences between the three biochar products. This behaviour is fully concordant with that of the most mobile fraction of the Tessier extraction described in the previous section.

4. Conclusion

The results reported herein indicate that the use of biochar as an amendment led to an improvement in the physical-chemical characteristics of the mining soil, such as an increase in OM content and pH in all cases, irrespective of the pyrolysis temperature used to prepare the biochar. However, biochar produced at higher pyrolysis temperatures (350 ºC > 500 ºC > 650ºC) showed a higher specific surface area, which is related to Cu immobilization. The SB500 and SB650 treatments were more effective at immobilizing Cu than SB300. Of note, B500 emerges as the amendment of choice as it showed lower concentrations of PAHs and less energy was required for its production. All the biochar treatments led to a slight mobilization of As. However, the very low As availability observed, these changes are not significant enough to cause a relevant effect. The different behaviour of Cu and As in response to biochar amendment were concordant in a sequential extraction procedure and a $CaCl_2$ extraction, thereby demonstrating the feasibility of using biochar to immobilize metals without remobilizing metalloids. In addition, pyrolysis temperature emerges as a critical parameter to take into account when preparing biochar for remediation purposes.

Author contribution Sandra Rúa-Díaz: Conceptualization, Investigation, Formal analysis, Writing. Manoel Lago-Vila: Investigation. Beatriz Cerqueira: Investigation, Supervision. Elena Arco-Lázaro: Conceptualization, Investigation. Purificación Marcet: Supervision, Funding acquisition. Rubén Forjan: Investigation, Formal analysis, Writing. Diego Baragaño: Investigation, Formal analysis, Writing. José Luis R. Gallego: Supervision, Project administration, Funding acquisition. Emma F. Covelo: Conceptualization, Supervision, Project administration, Funding acquisition.

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Data availability All the experimental data in this paper are obtained through three experiments, and the data are reliable. The materials are derived from daily life and are simple and easy to obtain

Declarations

Ethics approval This article does not involve human and animal research. The authors of this paper all participated in the research work of the paper. All authors agree to participate in the writing of the paper and agree to publish this article.

Consent for publication Not applicable.

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Figure 1

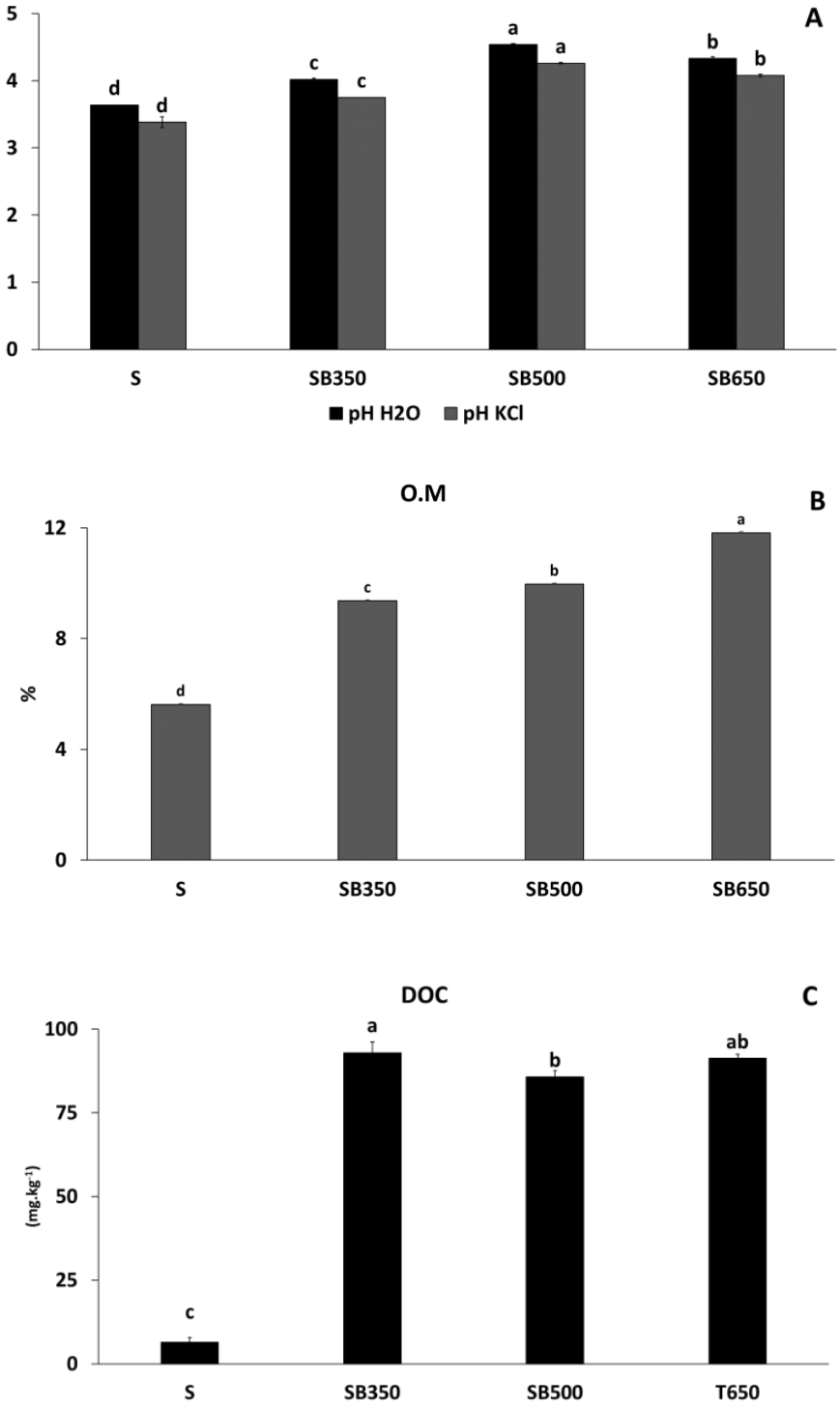

Fig. 1. pH_{H20} and pH_{KCl} (A), organic matter (OM) (B), and dissolved organic carbon (DOC) (C) in the control soil and in the different treatments after 40 days.

Figure 2

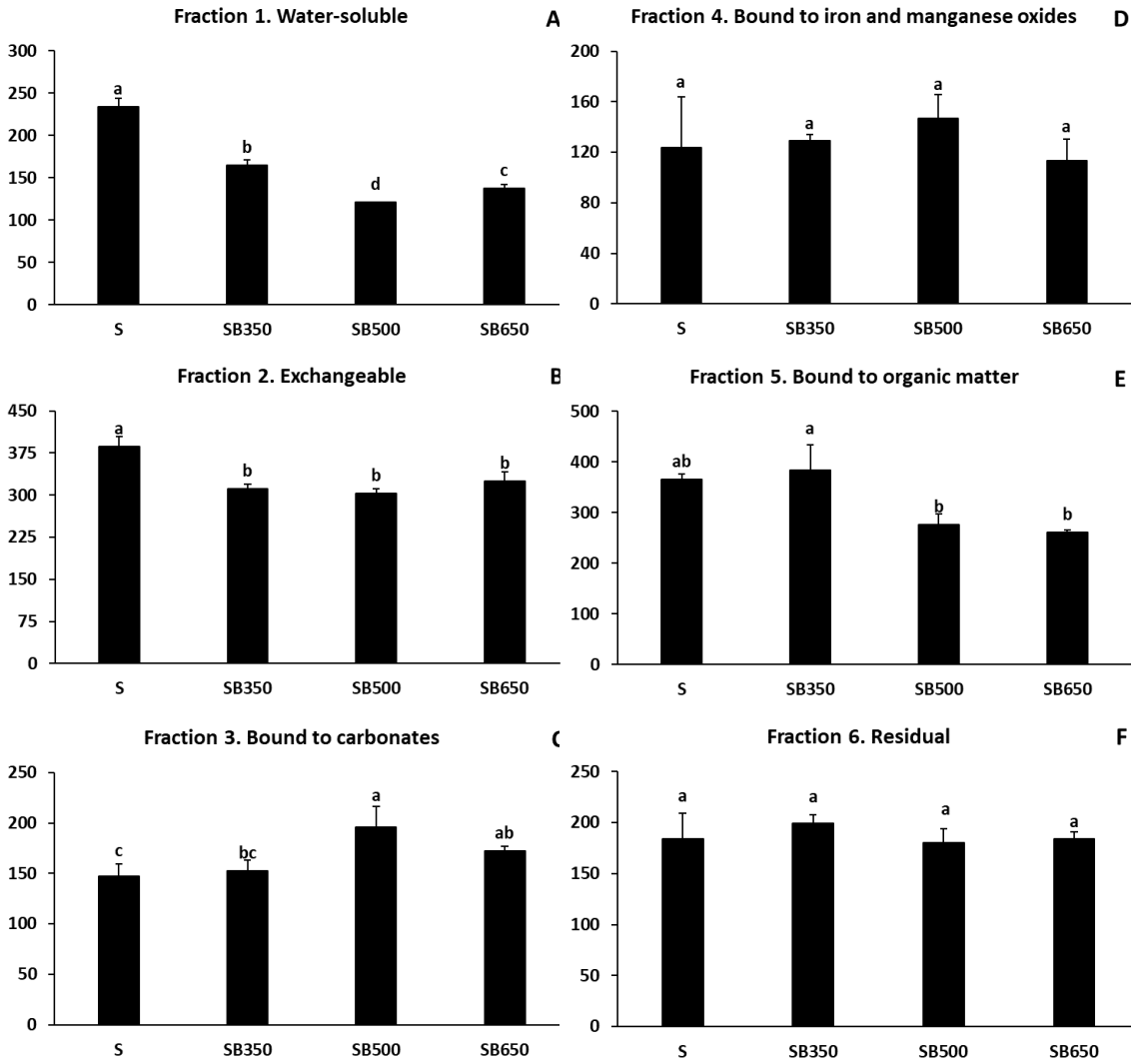

Fig. 2. Evaluation of sequential copper extraction (mg kg^{-1}) where the fractions measured are observed: A (F1), B (F2), C (F3), D (F4), E (F5), F (F6).

Figure 3

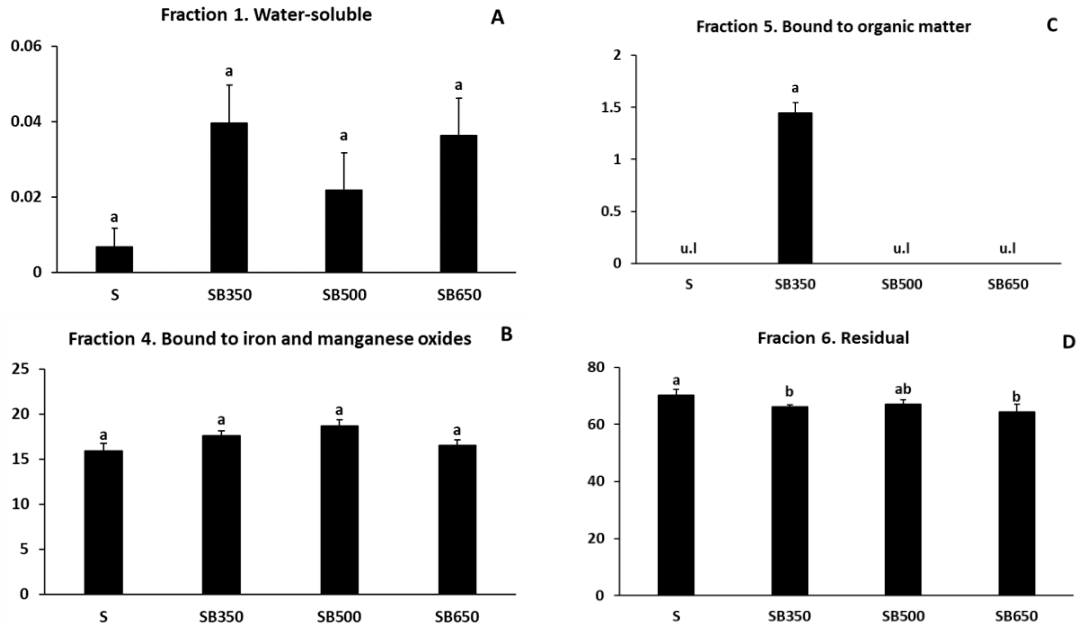

Fig. 3. Concentrations (mg kg^{-1}) of As in F1 (A), F4(B) F5 (C) and F6 (D) from each treatment.

Figure 4

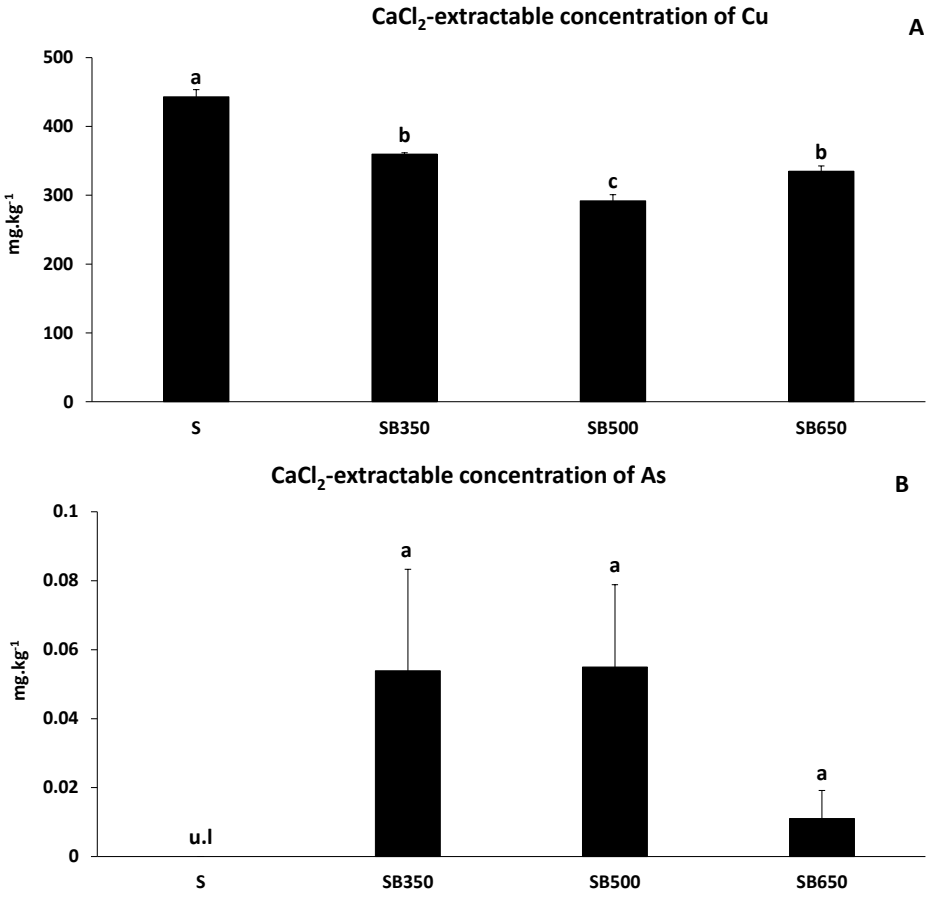

Fig. 4. Graphical representation of $CaCl_2$ extracted Cu (A) and As (B) after 40-day incubation.

Table 1. Soil and biochar characterization.

Parameter		Units	Polluted Soil (S)	Biochar 350 ºC (B350)	Biochar 500 ºC (B500)	Biochar 650 ºC (B650)
pH H_2O		-	3.73 ± 0.01	8.38 ± 0.06	9.95 ± 0.03	10.21 ± 0.02
pH KCl		-	3.49 ± 0.01	7.13 ± 0.01	9.65 ± 0.02	9.91 ± 0.01
SSA D-A		(cm^3/g)	-	170	346	421
SSA D-R			-	171	347	435
C/H			-	0.07	0.11	0.07
C/O			-	0.69	1.11	0.74
Sand		%	49.74	-	-	-
Silt			27.45	-	-	-
Clay			22.81	-	-	-
Iron oxides		($mg\ kg^{-1}$)	3855.65	-	-	-
Aluminum oxides			744.07	-	-	-
Manganese oxides			5.51	-	-	-
OM		%	7.18 ± 0.02	98.18 ± 0.16	96.19 ± 0.15	96.18 ± 0.14
TC		($g\ kg^{-1}$)	0.15 ± 0.02	72.04 ± 0.07	80.4 ± 0.15	83.01 ± 0.09
DOC			0.05±0.01	0.66±0.02	3.75±0.39	3.67±0.06
TN			0.01 ± 0.00	0.69 ± 0.03	0.67 ± 0.02	0.70 ± 0.01
AP			14.45 ± 0.67	232.78 ± 5.10	120.86 ± 2.46	142.19 ± 3.19
Exchangeable cations	Na^+	$cmol_{(+)}kg^{-1}$	1.71 ± 0.38	2.10 ± 0.24	3.56 ± 0.89	5.72 ± 0.05
	K^+		4.09 ± 0.44	147.24 ± 3.46	378.29 ± 4.57	369.32 ± 6.28
	Ca^{2+}		34.13 ± 0.79	3.97 ± 0.59	2.12 ± 0.27	0.33 ± 0.08
	Mg^{2+}		33.29 ± 0.99	10.88 ± 0.95	1.09 ± 0.13	1.69 ± 0.05
	Al^{3+}		11.60 ± 0.14	< 0.001	< 0.001	< 0.001
	CEC		84.82 ± 0.56	164.20 ± 4.04	385.06 ± 5.22	377.05 ± 6.36
	%V	%	86.32	100	100	100
	%Al		13.68	u.l.	u.l.	u.l.

Pseudototal	As	(mg kg^{-1})	85.09 ± 9.94	< 0.001	< 0.001	< 0.001
	Cu		1124.96 ± 10.33	8.50 ± 0.46	4.39 ± 4.06	3.39 ± 5.88

u.l.: undetectable level, BET Surface Area Dubinin- Astakhov (SSA D-A) and Dubinin-Radushkevich (SSA D-R), C/H and C/O ratios, TC: total carbon, TN: total nitrogen, AP: available P, OM: organic matter, DOC: dissolved organic carbon, CEC: cation exchange capacity, %V: base saturation, %Al: aluminium saturation. ±, standard error.

Table 2. Polycyclic aromatic hydrocarbon (PAH) content in the initial soil and the three biochar products.

PAHs (μg·kg^{-1})		Soil	B350	B500	B650
2-3 ring PAHs	Naphthalene	4	611	3	8
	Acenaphthylene	6	53	3	21
	Acenaphthene	5	92	7	9
	Fluorene	u.l.	117	17	35
	Phenanthrene	24	740	171	480
	Anthracene	3	181	76	128
4-6 ring PAHs	Fluoranthene	5	127	87	323
	Pyrene	4	102	79	361
	Benzo[a]anthracene	2	35	49	151
	Chrysene	1	27	35	135
	Benzo[k]fluoranthene	u.l.	u.l.	22	93
	Benzo[b]fluoranthene	u.l.	u.l.	4	22
	Benzo[a]pyrene	u.l.	u.l.	29	80
	Indeno[1,2,3-c,d]pyrene	u.l.	u.l.	29	49
	Dibenzo[a,h]anthracene	u.l.	u.l.	19	21
	Benzo[g,h,i]perylene	2	u.l.	10	34
Sum 16 PAHs		56	2085	641	1951