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Research article

Rice straw- and rapeseed residue-derived biochars affect the geochemical fractions and phytoavailability of Cu and Pb to maize in a contaminated soil under different moisture content

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A B S T R A C T

Management of toxic elements contaminated upland and wetland soils using biochar is of great concern from both agricultural and environmental points of view. The impact of rice straw- and rapeseed residue-derived biochars produced under 300 °C and 550 °C (added to the soil at 2% and 5%; w/w) on the geochemical fractions, phytoavailability, and uptake of Cu and Pb in a contaminated mining soil under different moisture contents (80%, 60%, and 40% of soil field capacity) was investigated in a greenhouse pot experiment using maize. The higher rate of rice straw-derived biochar pyrolyzed at 550 °C caused a significant reduction in the mobile (soluble + exchangeable) fraction of Cu (59.42%) and Pb (75.4%) and increased the residual fractions of Cu (37.8%) and Pb (54.7%) in the treated soil under the highest moisture content (80%) as compared to the untreated soil. Therefore, this biochar significantly decreased the phytoavailability ($CaCl_2$-extractable form) of Cu by 59.5% and Pb by 67.6% under the highest moisture content. Also, at the same moisture level (80%), the higher rate of rapeseed residue-derived biochar pyrolyzed at 550 °C decreased significantly the phytoavailability of Cu by 46.5% and Pb by 60.52% as compared to the untreated soil. The 5% rate of the higher temperature pyrolyzed rice straw and rapeseed biochars decreased the uptake of Cu and Pb by the roots and shoots of maize up to 51% for Cu and 45% for Pb. Immobilization of Cu and Pb in the biochar-treated soil at 80% moisture content may possibly due to the associated increase of soil pH and poorly-crystalline Fe oxides content, and/or the metals precipitation with sulfides. These results indicated that application of high temperature pyrolyzed rice straw- and rapeseed residue-derived biochars at 5% could immobilize Cu and Pb and decrease their uptake by maize under high levels of moisture content; consequently, they can be used for phyto-management of Cu and Pb contaminated wetland soils.

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1. Introduction

Soil pollution by potentially toxic elements (PTEs) including copper (Cu) and lead (Pb) can cause a potential risk on humans, plants, and animals (Antoniadis et al., 2017). Therefore, remediation approaches are introduced to reduce the bioavailability, mobility, and subsequent decrease the levels of these toxic metals in the food chain.

Chemical stabilization of PTEs in soil using various organic and inorganic amendments is one of the remediation strategies that reduce the mobility and bioavailability of PTEs by precipitation, sorption, or complexation (Shaheen et al., 2017a). Biochar (BC) has been used as a soil conditioner and as an immobilizing agent for PTEs, and C sequestration in recent years (El-Naggar et al., 2018a). Presence of ample functional groups, micro-porous structure, high pH, cation exchange capacity (CEC), surface area, and mineral components have made BC a promising material for immobilization and sorption of PTEs in soils and water (Shaheen et al., 2018a). Various studies have shown that BC has the potential to remediate and phytostabilize PTEs and organic compounds in contaminated soils (Ahmad et al., 2016; Khan et al., 2015; El-Naggar et al., 2018b).

Release, bioavailability, and redistribution of PTEs among their geochemical fractions in soils are influenced by several factors including metal species, pH, moisture content, redox potential (*Eh*), organic matter, leaching, and microbial activity (Kashem and Singh, 2001; Rinklebe and Shaheen, 2017b; Shaheen et al., 2018a,b). Soil moisture is a key factor for controlling soil physical, chemical, and biological properties of soil (Rinklebe et al., 2016a). Geochemical fractions of PTEs and their release and potential availability may change based on the moisture regimes and organic matter addition, which may affect PTEs transformation and phytoavailability in upland and wetland soils (Shaheen et al., 2017b, 2019b). Since the moisture distribution is not uniform during a specific period and season, metal redistribution and uptake by the plants under different moisture levels may also vary; which needs to be addressed properly. So far, limited studies focused on the influence of moisture variations on the PTEs immobilization and metal accumulation.

The efficiency of BC such as rice straw- and rapeseed residue-derived BCs to immobilize Cu and Pb in highly contaminated soils under different moisture content has not been studied up to date. Furthermore, comparative reports regarding Pb and Cu immobilization by rapeseed residue and rice straw BCs is still lacking. Additionally, the use of plants, which are not for direct food consumption and of high economic value, e.g. bioenergy crops such as corn, as test crop in this metal-contaminated soil is an issue worth evaluating. Also, we used corn in this study because it can grow at the different moisture contents we examined (40–80% of soil field capacity).

We hypothesized that redistribution of Pb and Cu among their geochemical fractions and thus their phytoavailability and uptake by maize (*Zea mays* L.) may vary after adding BCs under different moisture levels in naturally contaminated soil. Therefore, the aim of this research was to study the impact of rice straw- and rapeseed residue-derived BCs produced at 300 °C and 550 °C (added to the soil at 2% and 5%; w/w) on the geochemical fractions, mobilization, phytoavailability, and uptake of Cu and Pb in a contaminated mining soil (742.4 mg Pb kg^{-1} soil and 149.6 mg Cu kg^{-1} soil) under different moisture contents (80%, 60%, and 40% of soil field capacity) in a greenhouse pot experiment using maize. The results of this experiment are expected to provide a base for further investigation of Pb and Cu stabilization, and plant uptake under specific moisture levels.

2. Materials and methods

2.1. Sampling and characterization of the studied soil

Composite surface (0–20 cm) soil sample was collected from a paddy field near lead mining site located in Linxiang City, Hunan province, China (30° 19′ N, 117° 47′ E). Rice and rapeseed were rotationally cultivated in the soil. Soil was air-dried and passed through a 2-mm sieve. The basic physicochemical characteristics of the selected soil were determined according to the Soil Science Society of China SSSC (1999) procedures. Soil cation exchange capacity (CEC) was determined by NH_4OAC (pH 7.0) (Hendershot et al., 2008) method. The soil contained 48% silt, 36% sand, and 16% clay. The soil is a weakly acidic non-saline soil with pH value of 6.01 and has an electrical conductivity (EC) of 0.36 dS m^{-1}. The soil has low CEC (8.65 (cmol $_{(+)}$ kg^{-1}), and also has low organic matter content (21.7 g kg^{-1}). The soil is rich in available phosphorus (41.7 mg kg^{-1}) as determined by Olsen method. The pseudo-total content of Pb and Cu in the studied soil was 742.4 mg kg^{-1}, and Cu 149.6 mg kg^{-1}, respectively, which is above the permissible limits for Chinese farmland soils.

2.2. Biochar preparation and characterization

Rapeseed residue (straw, leaves, and pods) and rice straw were used to produce BC at two temperatures 300 °C and 550 °C, respectively. Both materials were collected from the Huazhong Agricultural University Campus, Wuhan, China (30° 28′ N, 114° 21′ E). The original biomass was milled prior to biochar production. The pyrolysis device was a muffle furnace fitted with a digital temperature regulator and was heated in the absence of oxygen. The temperature was gradually increased to 300 °C and 550 °C at a rate of 20 °C min^{-1}. After heating, the BC samples were cooled down. The BCs produced from rice straw at 300 °C and 550 °C were named as RS300 and RS550 for the rice straw BC and as RP300 and RP550 for the rapeseed BC.

The pH values of the studied BCs were determined in 1:10 solid/water (w/v). CEC was determined using the ammonium acetate (pH 7.0) method (Hendershot et al., 2008). The elemental composition of the BCs was determined by an elemental analyzer (EA3000, Italy). The mobile matter and ash contents were determined at 450 °C in a covered crucible for 1 h, and at 750 °C in an open-top crucible for 1 h, respectively. The moisture content was determined by heating 1.00 g sample at 105 °C in the oven for 24 h. The yield of BC was estimated by the following equation: Production rate (%) = $(M_{\text{Biochar}}/M_{\text{Straw}}) \times 100$, where M_{Biochar} and M_{Straw} are the mass of the BC and its feedstock, respectively. The specific surface areas of the BCs were determined by the BET-N_2 method with a surface area analyzer (Quantachrome instrument, USA). A brief characterization of BC is given in supporting information (Appendix A).

2.3. Experimental setup

The experiment was conducted in greenhouse by thoroughly mixing 1.5 kg of air-dried sieved soil with the BCs in plastic pots. A total of nine treatments were used in the study with each treatment performed in three replicates, labeled as T1 (control), T2 (2% RS300), T3 (5% RS300), T4 (2% RS550), T5 (5% RS550), T6 (2% RP300), T7 (5% RP300), T8 (2% RP550), and T9 (5% RP550). All the pots then received water, so that moisture contents would equal to 80%, 60% and 40% of water holding capacity (WHC). The amended pots were then incubated for one month to equilibrate soil mixtures prior to sowing, and the weights of the pots were recorded. Throughout the experiment, the mixtures were wetted with deionized water (DI) to attain the required levels of moisture by weighing the pots every 3 days. After one month of initial incubation, ten seeds of maize (*Zea mays* L.) were planted in each pot, which were later thinned to 5 plants per pot. After a growth period of 80 days, the plants were harvested, and the control and amended soils were air-dried and sieved again for further analysis. The harvested plants were divided into roots and shoots and were washed first with tape water and then distilled water to remove the soil particles. Roots and shoots were then dried in the oven at 60 °C for 48 h and were crushed to powder by electric grinding machine. The powdered materials (0.5 g) were digested with a mixture of $HNO_3 - HClO_4$ (3:1), for measuring the plant Pb and Cu contents by flame atomic absorption spectrophotometer (Varian AA240FS).

2.4. Fractionation and phytoavailability of Cu and Pb

Among many sequential extraction protocols, the sequential extraction procedure of the Community Bureau of Reference (BCR) has the advantage that it is well standardized (Bacon and Davidson, 2008; Sutherland, 2010). It is a widely used technique and the results can be interpreted as 'operational fractionations' according to the definition of Ure et al. (1993). A modified European community bureau of reference (BCR) sequential extraction method (Rauret et al., 1999) was applied to study Pb and Cu fractionation, as described in details by Jiang et al. (2012) and proposed recently by Rinklebe and Shaheen (2017). Fractions classified in this procedure are acid soluble extracted by 0.11 M acetic acid, reducible (bound to Fe/Mn) extracted with hydroxylamine hydrochloride, the oxidizable (bound to organic matter and sulfides) extracted with H_2O_2 and NH_4OAc, and the residual fraction was digested with $HCl–HNO_3–HClO_4$. The potential phytoavailability test of Pb and Cu was conducted using $CaCl_2$ in a 50 mL centrifuge tube by mixing 2.00 g of soil with 20 mL of 0.01 M $CaCl_2$ extracting solution as proposed by (Houba et al., 2000). The concentrations of Pb and Cu in the filtrates were determined by AAS (Varian AA240FS).

2.5. Statistical analysis

Means and standard deviations (SD) of the studied parameters were calculated by Microsoft Excel (2013), while analysis of variance (ANOVA) and Duncan multiple range test at ($p < 0.05$) were performed to analyze the data using SPSS (22.0). The figures were carried out using Origin Pro 8.5G (OriginLab Corporation, Northampton, USA).

3. Results and discussion

3.1. Impact of biochars on soil properties under different moisture content

Application of the rice straw and rapeseed BCs increased soil pH as compared to the untreated soil (Fig. 1). The RS550-5% showed the highest increasing rate of soil pH, followed by the RP550-5% at the three moisture contents. Both BCs produced under high pyrolysis temperature (550 °C) increased soil pH higher than the same BCs produced under low pyrolysis temperature (300 °C). Soil pH was increased after the addition of BCs in the three moisture levels as compared to control. A significant increase in pH (7.42) was recorded in the RS550-5% treatment at 80% FC, followed by 7.08 in the RP550-5% treatment, whereas, in 60% FC, the highest pH recorded was 6.99, as compared to control. During pyrolysis, transformation and dissolution of alkaline and alkaline earth metals present in BCs into oxides, hydroxides, and carbonates tend to increase in pH as suggested by Ahmad et al. (2016). In addition, the liming effect of BCs and high ash content may lead to increase soil pH (El-Naggar et al., 2018a). The surface functional groups such as phenolic, hydroxyl, and carboxyl in BCs and their ability to bind H^+ ion in soil/water may also cause an increase in soil pH (El-Naggar et al., 2018a; Niazi et al., 2018).

The impact of BCs on soil pH was higher at the 80% moisture content than the 60% and 40% moisture content (Fig. 1). Increasing the moisture content to 80% may decrease soil redox potential (Eh), which may in turn increase soil pH. An inverse trend between Eh and pH has been previously observed in other soils (Rinklebe et al., 2016; Shaheen and Rinklebe, 2015). This is because a decrease in soil Eh leads to an increase in soil pH, which might be due to the consumption of protons in the reduction of other elements such as Mn^{4+} and Fe^{3+} (Shaheen et al., 2018a; El-Naggar et al., 2018b). High pH values at 80% FC could be attributed to the H^+ consumption, as a result of the potential decrease of soil Eh (Kogel-Knabner et al., 2010).

The BC-treated soil exhibited a wider range of pH than the untreated soil under the different moisture contents, which might be explained by the BC composition and redox activity of BC. We assume that BC may increase the soil's capacity to accept and/or donate electrons by controlling electron transfer reactions (Yuan et al., 2017; El-Naggar et al., 2018a), and thus leading to a wider range of Eh in the soil slurry and this the Eh-dependent changes of soil pH (El-Naggar et al., 2018a). The increase of soil pH of the BC-treated soil in comparison to the untreated soil may affect the mobilization and fractions of Pb and Cu at different moisture conditions (section 3.3).

Soil total organic carbon increased after adding BCs, with a higher

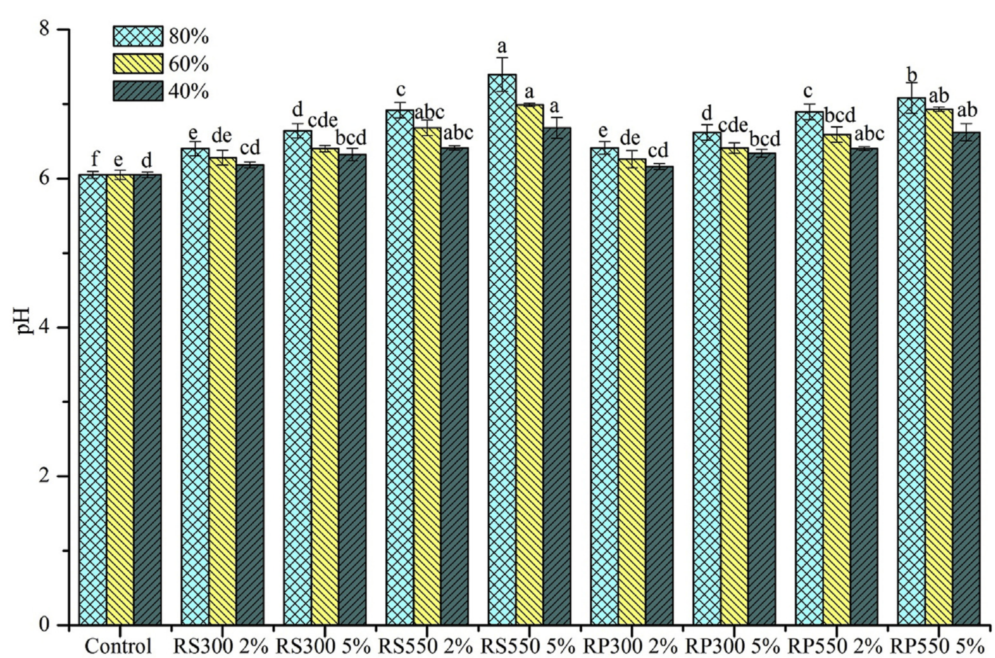

Fig. 1. Effect of biochars on soil pH at different moisture contents. Error bars are the standard deviation of the mean (n = 3). Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$).

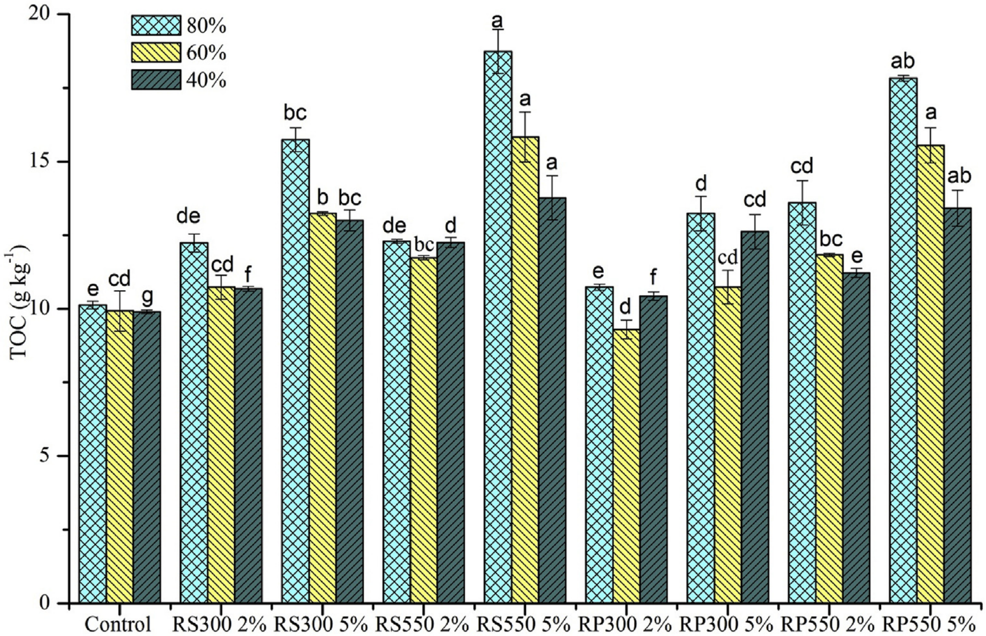

Fig. 2. Effect of the biochars on soil organic carbon at different moisture contents.

increasing rate at the higher moisture content 80% than the lower moisture content 60% and 40% FC (Fig. 2). Values of total organic carbon (TOC) ranged from 10.12 g kg^{-1} in the control to 18.70 g kg^{-1} in the RS550 5% treatment at 80% FC. With increasing moisture content, the rate of decomposition of organic materials decreases consequently results in the organic matter accumulation in the soil. Furthermore, Liu et al. (2016) stated that dissolved organic carbon content in paddy soils tend to increase with increasing the soil moisture content (Shaheen et al., 2018a). Soil organic carbon is an important factor which affects metal redistribution and reduces solubility via complexation and chelation with metals. The increase of soil pH and TOC content of the BC-treated soil in comparison to the untreated-soil may affect the mobilization and fractionation of Pb and Cu under different moisture conditions (section 3.3).

3.2. Influence of biochars on the dry biomass yield of maize in the studied soil under different moisture content

Biomass dry weights generally reflect the capability of plants to grow and survive in metal contaminated environments. Dry weights of maize plants increased significantly after BC application as compared to the control and varied considerably among the three moisture levels after the application of BCs (Fig. 3). The highest plant biomass was noted under high soil moisture content (80% FC) which was 36.61 g pot^{-1} in 5% RS550, followed by 32.32 g pot^{-1}in 5% RP500 at the same moisture level. The same treatments showed slight differences in plant biomass at 60% and 40% FC.

Increasing the plant growth in the BC-treated soils as compared to control might be explained by the improved soil physicochemical properties after BC application. The increased biomass of the maize plants at 80% FC in the amended soil could also the result of the decreased metal availability and reduced uptake of Pb and Cu. Plant growth in control treatments under all the three moisture regimes was restricted due to the high concentration of phytoavailable metals as compared to the amended soils as will be discussed in the following sections. The reason for this might be the ultra-cellular structural changes and reduced uptake of nutrients by plant roots in metal stress (Rizwan et al., 2016). These consequences are consistent with the results in section 3.5. Furthermore, the nutrient content such as N, P, K, and S of BC could also improve the plant growth. Increased plant biomass of maize could be attributed to the dependent variations in soil pH and Pb and Cu solubility. Similar results were found by Shaheen et al. (2017b), where they observed a significant increase in biomass yield of sorghum and barnyard grass in wet conditions as compared to dry conditions.

Also, the low yield of the plants in control might be due to its lower soil pH as compared to the BC-treated soil, which might have caused phytotoxicity by increasing the bioavailability and solubility of Cu and Pb (Shaheen et al., 2017a,b, 2019b). Plant growth in the 40% FC was considerably limited, and plants failed to reach the tillering stage, as compared to 80% and 60% FC and control, respectively. Toxicity of metals due to their increased bioavailability might be more prevailed in aerobic conditions as documented by Hu et al. (2015).

3.3. Impact of biochars on the geochemical fractions and mobilization of Pb and Cu under different moisture content

3.3.1. Acid soluble fraction

Sequential extraction results revealed a significant reduction under high moisture content (80% FC) in the acid soluble fraction of Pb from 172.0 mg kg^{-1} in control to 42.3 mg kg^{-1} (75.4%) in the 5% RS550 treatment and to 57.3 mg kg^{-1} (66.4%) in the RP550 treatment (Fig. 4). Likewise, the addition of high-temperature BCs (RS550 and RP550) at the 5% application rate decreased the concentration of Cu in the acid soluble fraction from 52.4 mg kg^{-1} in control to 21.1 mg kg^{-1} (59.4%) and 27 mg kg^{-1} (48.1%), respectively. Therfore, the 5% of the RS550 treatment showed the highest decreasing percentage in the acid soluble fractions of Pb and Cu (Appendix A; Tables S2 and S3). However, the addition of BCs prepared at low temperature, particularly at low application rate (2%), had no significant impact on the concentrations of Pb and Cu in the acid soluble fractions. The reduction rates of acid soluble fractions of Cu and Pb were higher at the highest moisture content (80% FC) than the lower moisture content (60 and 40% FC).

The acid soluble fraction of trace elements including Pb and Cu is considered as a mobile and bioavailable form. The reduction in the acid soluble form, accompanied by an increase in the remaining three fractions (reducible, oxidizable and residual fraction) could be ascribed to the increase in soil pH after BC application as shown in Fig. 1. High pH may decrease Pb and Cu bioavailability through enhanced their precipitation and sorption onto variable-charge colloids as documented

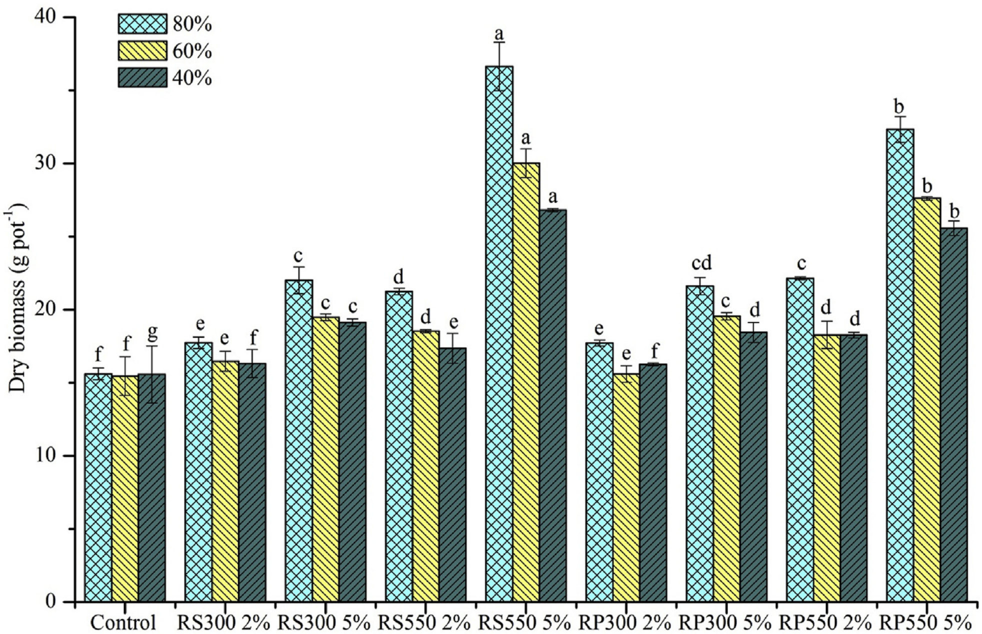

Fig. 3. Effect of biochars on maize dry biomass at different moisture contents.

by Jiang et al. (2012) and Mohamed et al. (2015). Likewise, the activity of free metals ions is higher in low pH environments; therefore, a shift in soil pH may decrease metal concentration in the mobile forms of Pb and Cu. Furthermore, Mohamed et al. (2015) found that high concentration of metal in the acid soluble fraction was due to the low pH of a moderately acidic contaminated soil. The high pH of the BC-treated soil at 80% moisture content might be responsible for the reduction of the acid soluble fraction of Pb and Cu, as compared to the lower moisture content treatments (60% and 40%).

At the higher high moisture content, the possible decrease in soil Eh and thus the Eh-dependent increase in soil pH may cause an increase in negative charges on organic matter surfaces and soil clay colloids, which would consequently decrease the acid soluble (exchangeable) fractions of Pb and Cu in the current study. Due to its surface negativity, BC could improve electrostatic attraction of cationic metals, thereby immobilized Pb and Cu as reported by Ahmad et al. (2016). The π-π electron donor-acceptor interaction between π-electron-rich-graphene-surface of BC and π-electron-deficient charged-cationic metal is expected to be enhanced (Shaheen et al., 2018a). Furthermore, the decreased concentration of Pb and Cu in acid soluble fraction might be the result of metal complexation with BC via ligand exchange with hydroxyl functional groups as suggested by Rinklebe et al. (2016). Formation of metal complexes with soil organic matter (SOM) could also contribute in reducing metal solubility. BC produced at higher pyrolysis temperature, particularly the rice straw BC, was more effective than the low-temperature produced BCs, which might be due to the pyrolysis conditions and feedstock composition. The effectiveness of high-temperature rice straw BC has been documented in many studies (Salam et al., 2018, 2019; Jiang et al., 2012).

3.3.2. Reducible fraction

Application of BC significantly increased the reducible fraction of Pb up to 397.5 mg kg^{-1} (21.3%) and 386.7 mg kg^{-1} (14.0%) in the 5% RS550 and RP550 treatments when compared with control (332.4 mg kg^{-1}). Similarly, this fraction of Cu increased from 46.2 mg kg^{-1} in control to 74 mg kg^{-1} (32.68%) in the 5% of RS550 treatment at the higher moisture content (Fig. 4). (Appendix A; Tables S2 and S3). Reducible fractions of Pb and Cu were higher at 80% FC than those at 60% and 40% FC.

A concomitant increase in the reducible portion of Pb and Cu could be related to the Fe content of BCs, which may act as an adsorbent in specific adsorption, as well as free Fe oxides that act as an adsorbent in non-electrostatic adsorption (Jiang et al., 2012). Under reduced conditions (increased moisture), the pH-dependent metal sorption and dissolution of Fe-Mn hydroxides might have controlled the mobility of Pb and Cu in the acidic soil as stated by Rinklebe et al. (2016). Organic matter (OM) and hydrous Fe and Mn oxides could decrease the activity of metals in soil solution through metal complexation and adsorption (Kandpal et al., 2004). Overall, the increase in the reducible fraction at 80% FC might be the result of Pb and Cu fixation with Fe-Mn oxy-hydroxides onto the BC surface. Similar results were reported by Kashem and Singh (2004) who found that the adsorption of trace metals on Fe and Mn oxides was mainly responsible for the reduced metal mobility and solubility in increased moisture condition.

3.3.3. Oxidizable fraction

The oxidizable fractions of Pb and Cu were substantially increased following the addition of BCs, particularly the 5% of RS550 and RP550, respectively (Fig. 4). When compared to control (172.80 mg kg^{-1}), the concentration of Pb in oxidizable fraction was increased to a maximum of 197 mg kg^{-1} (12.15%) in the soil amended with the 5% of RS550. Likewise, the oxidizable fraction of Cu increased from 13.3 mg kg^{-1} in the control to 29.7 mg kg^{-1} (55.3%) in the 5% RS550 treatment (Fig. 4). Similarly, the addition of the 5% RP550 increased the oxidizable fraction of Pb and Cu by 11.7% and 43.7%, respectively (Appendix A; Tables S2 and S3). The maximum increase in the oxidizable fractions was noticed at the highest moisture level, followed by 60% and 40% FC, respectively.

Increase in the oxidizable fraction could be ascribed to the formation of Pb and Cu complexes with organic functional groups present in the BC, as mentioned by Kim et al. (2015), and Jiang et al. (2012). Soil organic matter could dissociate Fe and Mn from the oxidizable portion, and hence the increased negative sites would absorb metals in this fraction (Kashem and Singh, 2001). The application of alkaline material such as BC to the soil not only increase the soil pH but also increase the concentration of sulfides, which might have caused Pb and Cu precipitation as sulfides as reported by Sumi et al. (2014). The same authors also pointed out that metal affinity towards alkaline materials for sulfides vary, probably due to which the increased activity of Pb and Cu in oxidizable fraction was more in 80% FC in this study. The response of

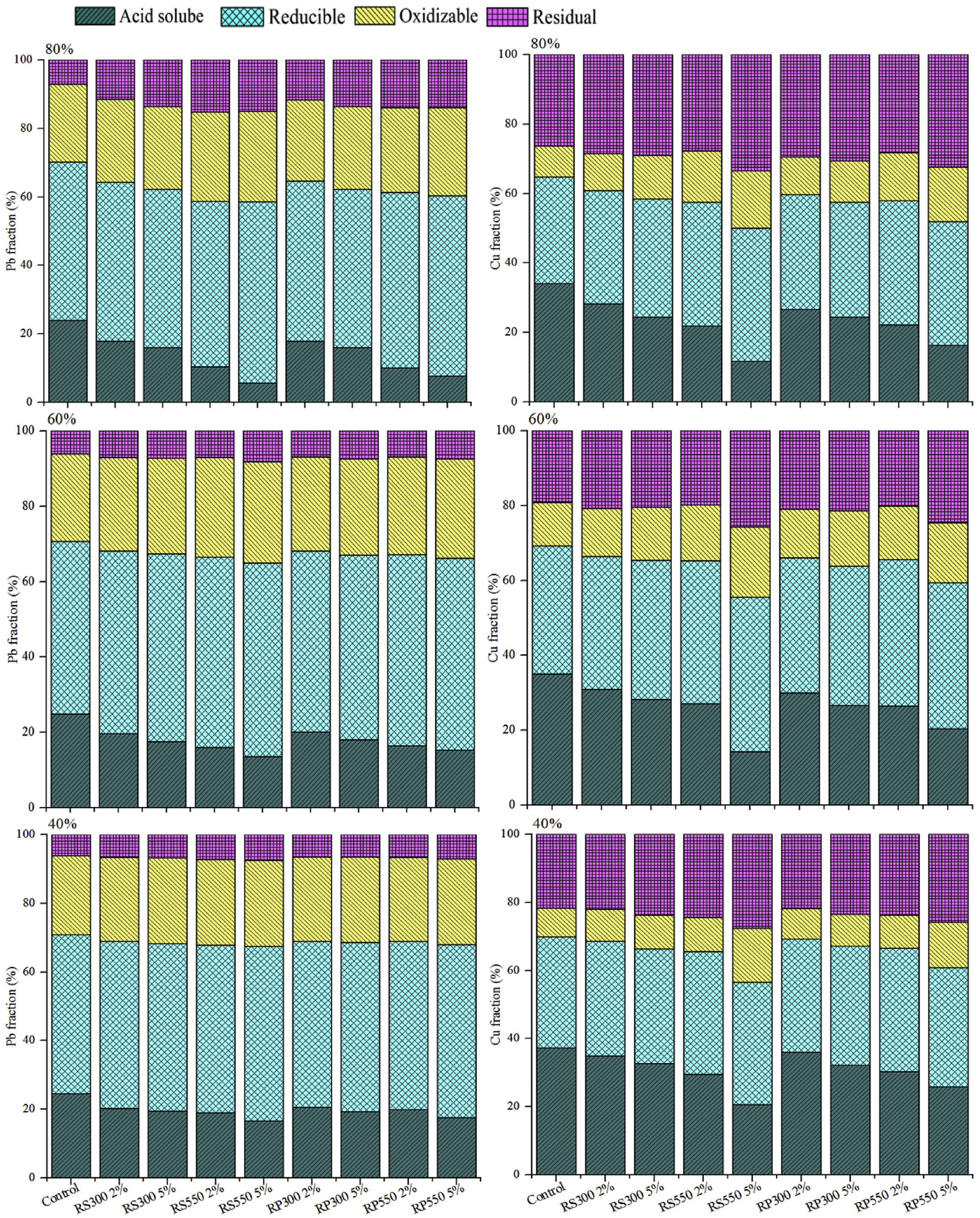

Fig. 4. Influence of biochars on the geochemical fractions of Cu and Pb in soil at different moisture contents.

the oxidizable fraction of Pb to the amendments and moisture level was more apparent than Cu, more probably due to the role of organic material role in Pb and Cu binding in the oxidizable fraction by forming organo-metallic complexes, whose magnitude was higher at increased moisture level.

3.3.4. Residual fraction

The applied BC effectively increased the concentration of Pb and Cu in their residual fractions (Fig. 4). Highest increase in the residual fraction of Pb was 112.06 mg kg^{-1} (54.76%) and 102.73 mg kg^{-1} (53.36%) in the 5% RS550 and the 2% RS550 treatments respectivley as compared to control (50.93 mg kg^{-1}). Similarly, the residual fraction of Cu increased from 40.24 mg kg^{-1} in control to 55.41 mg kg^{-1} (37.82%) and 51 mg kg^{-1} (33.77%) in the soil amended with the 5% RS550 and the RP550 respectivley (Appendix A; Tables S2 and S3). Overall, metal concentration in different fractions of Pb and Cu at the three moisture levels followed the order 80% FC > 60% FC > 40% FC.

The results of Pb and Cu fractions show that the application of BCs caused a considerable shift in the available and potential mobile fractions of Pb and Cu to the residual fractions. The residual portion is recognized as stable and is not released into the soil water system, because of its existence in the soil silicate crystalline structure (Liu et al., 2016; Rinklebe and Shaheen, 2017a). This increase in the residual fractions of Pb and Cu under high moisture level (at 80% FC) could be attributed to the enhanced metal hydrolysis on the surface of aluminosilicate layer minerals with associated release of protons, shifting the adsorbed metals into a less mobile form as concluded by Kandpal et al. (2004). Therefore, the additions of RS550 and RP550 at 5% were more effective in transforming the mobile forms of Pb and Cu to residual forms and could be considered a potential candidate for stabilizing Pb and Cu in soil under different environments.

As discussed earlier, application of BC altered soil properties such as pH and organic carbon (OC) which might have affected the metal redistribution pattern, thereby immobilized Pb and Cu as reported by Yin et al. (2016). Due to its organic matter content, BC can accomplish metal stability and fixation by interacting with PTEs. Moreover, change in pH could develop a more negative charge on soil fraction, which enhance Pb and Cu adsorption and subsequently reduce their solubility (Jiang et al., 2012). The influence of moisture level and the amendments on the transformation and redistribution of Pb and Cu was more apparent in the high moisture regime. The reduced Cu mobility under wet conditions might be due to the precipitation of Cu with sulfides as reported by Shaheen et al. (2018a), and Rinklebe et al. (2016). We assume that changing the moisture level from 80% FC to 60% and 40% FC may cause a decrease in soil pH and TOC values, thereby may affect the distribution of Pb and Cu among their fractions. On the other hand, low soil pH could assist the release of carbonate-bound metals to soil solution.

3.4. Biochar reduced metal phytoavailability under different moisture levels

Phytoavailability of Cu and Pb exhibited different behavior under all moisture levels (Fig. 5). BCs decreased significantly the phytoavailability of Cu and Pb as compared to control. The decrease in the concentration of Pb was observed under all moisture levels, while the reduction in the Cu availability was more obvious at 80% FC and 60% FC, respectively. Addition the 5% RS550 decreased the phytoavailability of Pb from 7.98 mg kg^{-1} in the control to 1.85 mg kg^{-1} (67.6%), and also decreased the phytoavailable Cu from 4.0 mg kg^{-1} in the control to 1.6 mg kg^{-1} (59.50%) at 80% FC (Appendix A; Tables S4 and S5). This showed the effectiveness of BCs in decreasing the Pb and Cu phytoavailability. These results are in agreement with Liu et al. (2016), as they observed similar reduction in the concentration of $CaCl_2$ extractable metals in wet and dry conditions, respectively.

The reduced Pb and Cu availability could be attributed to the high pH of BC, and BC interaction with Pb and Cu under different moisture levels. Trace element sorption and subsequent reduction in their availability as a result of increased pH of the BC is a well-studied phenomenon. Soil pH is generally regarded key factor in decreasing metal solubility and mobility as reported by Wang et al. (2015), thus reducing metal availability. Moreover, the negative surface charge of soil is also linked with pH, and high pH promotes metal sorption onto the BC surface, consequently decreasing their phytoavailability. BC may reduce the phytoavailability of trace elements by forming stable complexes through ligand exchange with hydroxyl functional groups (Rinklebe et al., 2016a), and with soil organic carbon (SOC) as stated by Kim et al. (2015). These mechanisms might have reduced the concentration of phytoavailable Pb and Cu in the current study. Moreover, the SOC content of the applied BCs might also be a factor controlling the availability of Pb and Cu under different moisture conditions as reported by Rinklebe et al. (2016). Concluding, the decrease in $CaCl_2$ extractable Pb and Cu concentration can be explained as being as a result of pH and SOC changes after adding the biochar.

3.5. Effect of the biochar and moisture on Pb and Cu uptake

Concentrations of Cu and Pb in the roots and shoots of corn plants were significantly decreased in the treatment of 5% RS550 at 80% FC, followed by 60% FC and 40% FC over control (Fig. 6). Additions of both the RS550 and the RP550 BC at 5% application rate to the soil under the highest moisture content (80% FC) decreased significantly the concentration of Pb in maize roots from 153.25 mg kg^{-1} in the control to 71 mg kg^{-1} (44.90%) and 82.34 mg kg^{-1} (35.67%), respectively. The Pb concentration in maize shoots decreased to minimum value of 35.30 mg kg^{-1} (39.16%) in 5% RS550, followed by 41.84 mg kg^{-1} (33.94%) in the 5% RP550 treatment as compared to control (80.63 mg kg^{-1}) (Apemdix A; Tables S6 and S7). Likewise, a significant reduction in Cu uptake was observed at 80% FC in the soil amended with 5% of the RS550 which was 11 mg kg^{-1} (51.26%) for roots and 8.22 mg kg^{-1} (37.53%) for shoots, respectively (Apemdix A; Tables S6 and S7). The reduction rates of both Cu and Pb were higher at the high mositure content (80% FC) than the low ones (60 and 40% FC).

The highest decrease in plant metal concentrations at 80% FC was consistent with the reduction in the mobile portion, as we observed a greater reduction in this portion in the sequential extraction. Decreased metal concentration in plants could be chiefly linked with the immobilization of the available metals and dilution effect as a result of increased biomass. Increase in soil pH under increased moisture regime (80% FC) after BCs application led to the reduced concentrations of Pb and Cu, and consequently decreased their translocation to the aboveground plant parts. Due to its porous structure and large surface area, BC could enhance the soil sorption capacity, which might have caused Pb and Cu retention in the amended soils and thus reduced metal uptake. Furthermore, the reduction in the concentration of phytoavailable Pb and Cu was the reason for reduced uptake, which is consistent with the $CaCl_2$ extraction results. Similarly, the addition of organic materials is known to increase the capability of soil to adsorb trace metals.

The decrease in the concentration of Pb and Cu in shoots could be explained by the declined upward transfer of the metals from roots to shoots, and the reduced uptake by roots due to the decreasing metal availability following the addition of BCs. Concentrations of Cu and Pb in plant shoots and roots at 60% FC was less than that of 80% FC, with the lowest concentration observed in 40% FC. Decreased metal concentration in plants under high moisture conditions could further be ascribed to the metal bioavailability in rhizosphere and dilution effects (Liu et al., 2016; Wang et al., 2015). The increased accumulation of Pb and Cu in maize plants at low moisture content might be due to the associated decrease of soil pH. Furthermore, the more concentrated solution at low pH might be responsible for the high concentration of the metals in the plants under low moisture regimes as stated by Tack (2017). Also, the differences in maize growth at the different treatments can further affect the accumulation of Pb and Cu in roots and shoots.

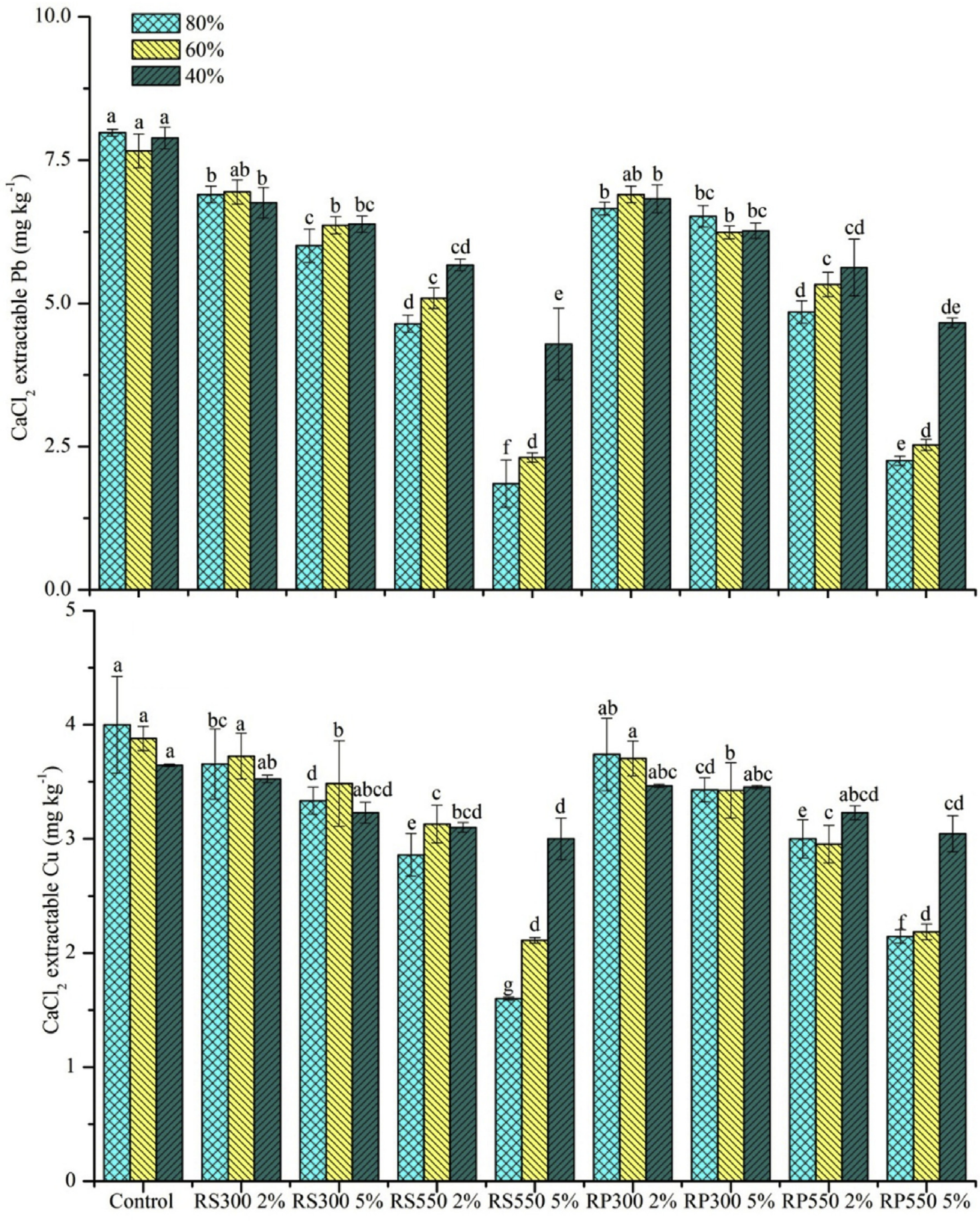

Fig. 5. Effect of biochars on the concentrations of $CaCl_2$ extractable Cu and Pb at different moisture contents.

4. Conclusions

The impact of rice straw- and rapeseed residue-derived BCs produced at low (300 °C) and high (550 °C) pyrolysis temperatures on the geochemical fractions, mobilization, and phytoavailability of Cu and Pb in a contaminated mining soil under different moisture contents (80%, 60%, and 40% of soil field capacity) was investigated in a greenhouse pot experiment using maize. The high temperature produced rice straw- and rapeseed residue-derived BCs were able to reduce the mobility of Cu and Pb, redistribute them among their more stable geochemical fractions, and decrease their phytoavailbility and uptake by maize, in particular under the highest moisture content. We conclude that high temperature pyrolyzed rice straw- and rapeseed residue-derived BCs could be suitable candidates for remediation and management of Cu and Pb contaminated wetland soils. These results should be verified under the field conditions. Also, in future, the use of spectroscopic techniques, combined with sequential extraction, could provide insights into the mechanism of (im)mobilization processes which the BC may cause in the soil under different moisture contents.

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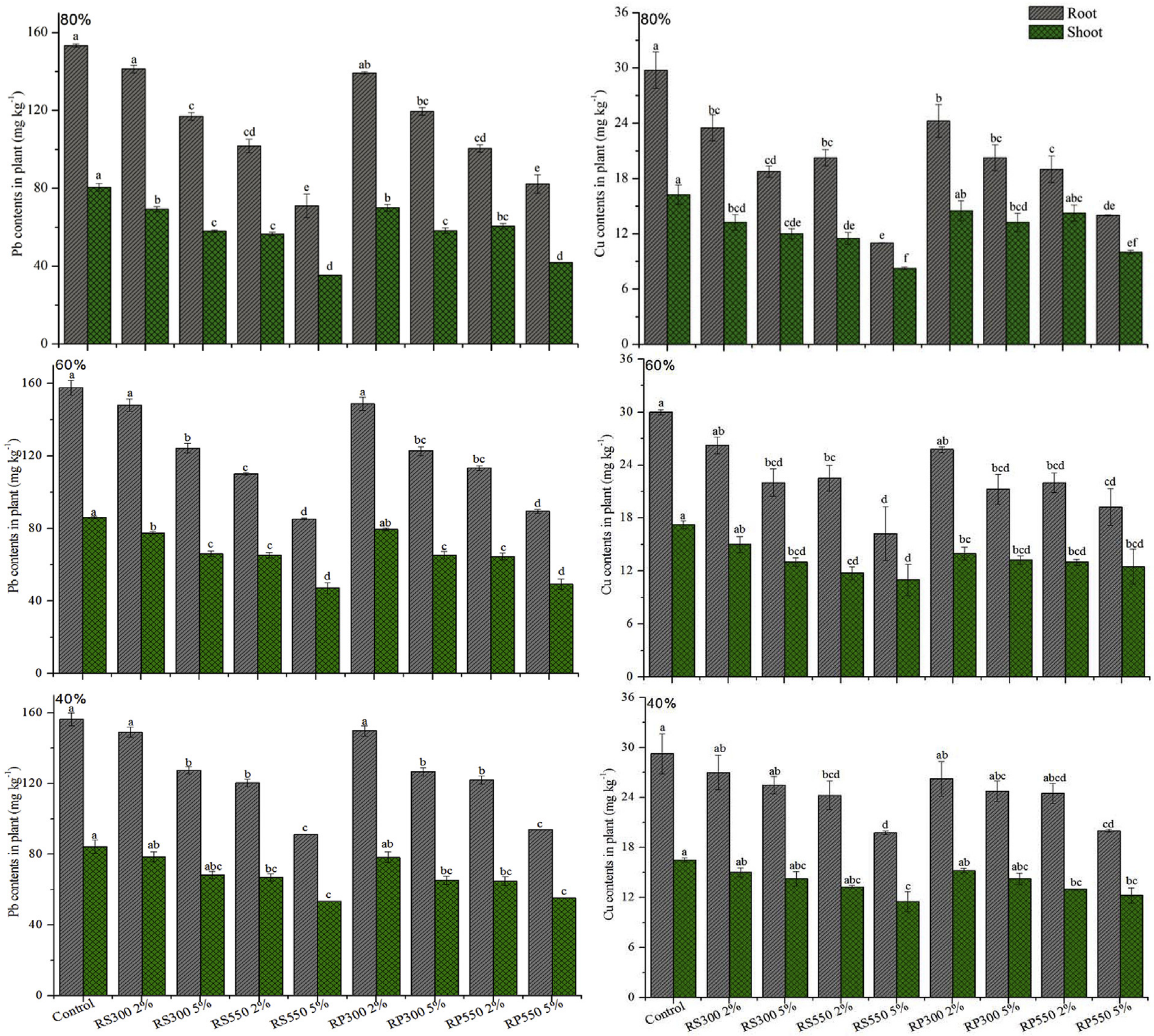

Fig. 6. Effect of biochars on the concentrations of Cu and Pb in the shoots and roots of maize at different moisture contents.

(2015BAD05B02).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.02.047.

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