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Original Research

Effect of Biochar Application on Heavy Metal Mobility in Soils Impacted by Copper Smelting Processes

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Abstract

Biochar seems to be a very promising material for remediation, reducing heavy metal mobility in contaminated sites. However, the effect of its application on soil depends on biochar origin, pyrolysis condition, soil type and properties like initial pH or cation exchange capacity, and also on metal form and interactions. This makes prediction about successful remediation with biochar more difficult and a lot of attention should be paid to choose the proper material appropriate to soil conditions. The aim of our study was to evaluate wheat straw biochar application on multi-contaminated soil, to decrease their mobility and minimize the risk of heavy metal occurrence in the area impacted by copper smelting processes. The results of this study indicate that wheat straw biochar application can potentially reduce Cu, Pb, Zn or Cd mobility only in sandy or acidified soils due to the liming effect. In alkaline soils the effect of biochar application on metal immobilization was imperceptible. The effect of wheat straw biochar on heavy metal immobilization in multi-contaminated soils is more complex and cannot be defined as all-purpose material in remediation procedures.

Keywords: soil pollution, heavy metal, biochar, remediation

Introduction

Heavy metals are naturally present in soils but may be enhanced due to anthropogenic activities such as metal ore mining and smelting processes. Poland is one of the biggest copper producers, contributing 3.6% of the global copper market. More than 70 years of copper industry development in SW Poland has resulted in significant pollution of soils in the vicinity of mining and smelting sites. Initially high acidification of soils due to high emissions of sulfur dioxide from smelting and secondary mobilization of heavy metals such as lead (Pb), copper (Cu), cadmium (Cd), zinc (Zn) or arsenic (As) has led to serious chemical degradation of soils and the exclusion of large areas from agricultural use. Even if the scale of these activities is local, it may cause widespread environmental pollution and should be considered as sources of environmental and health risks associated with the transfer of heavy metals to the food chain and human exposure. To reduce the risk, the bioavailability of heavy metals can be modified, leading to the decrease of their accumulation and toxicity in

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the food chain. Like activated carbon, biochar is a solid material obtained in an oxygen-limited environment through the thermochemical transformation (pyrolysis) of biomass [1], but the source materials are generally limited to a large variety of biological residues, e.g., wood, municipal green waste, crop residues, sewage sludge [2, 3] and not commonly activated or further treated before application to soils. Biochars, depending on feedstock type and conditions of pyrolysis, consist of different proportions of carbonized and amorphous organic matter [4, 5]. Typically, most biochars have a large surface area [6], a microporous structure [7], active organic functional groups [5, 8] contain dissolved organic carbon [9] and have high pH [10], which makes this material a strong and effective sorbent for both organic and inorganic soil pollutants [11]. Numerous studies have shown that biochar has the potential to remediate soils contaminated with heavy metals and seems to be an attractive alternative to standard materials used in *in situ* soil remediation [4, 12-15]. One of the main properties controlling metal fate and mobility in contaminated sites is soil pH. The primary mechanisms of metal immobilization by biochar in soils include an increase of soil pH [16], ion exchange with acidic functional groups [17], physical sorption [18] and precipitation [13]. Mechanisms of pH-dependent heavy metal immobilization differs under soil conditions. Adsorption reactions dominate in acidic conditions, while precipitation or the formation of hydroxide complexes, phosphates or carbonates [6] occur at alkaline pH. Secondary mechanisms of element sorption/desorption processes are influenced by particle size distribution and properties of soil sorption complex (cation exchange capacity, organic matter and clay minerals content). In sandy soils metals are present mainly in soil solution, while in loamy or heavy clay soils they are immobilized on soil constituents. In multi-contaminated soils metal competition for binding sites should also be considered [19]. Understanding the extractability and therefore availability of metals in biochar-amended soils is important when using biochar for remediation purposes. Recently, the effects of biochar on heavy metal mobility have been widely reported, both in the field and under laboratory conditions, mainly via column leaching test [16, 20-23]. Published results give very opposite feedback of biochar potential in heavy metal immobilization. Most studies have focused on flooded paddy soils, while mechanisms may vary in more arid soils due to different redox conditions, different organic matter content or lower solubility of elements. Also, knowledge about zinc immobilization by organic sorbents is very limited. As an essential nutrient for living organisms, it is not usually considered as a toxic element. However, an excess supply of this element, that can take place in soils impacted by multi-elemental emissions from smelting processes can become toxic to plants and soil microorganisms. Probably an all-purpose remediation method with biochar is too difficult to achieve, as different biochars, depending on feedstock type or pyrolysis temperature, will have very diverse sorption properties.

Therefore, this study was conducted to evaluate changes in Cu, Zn, Pb and Cd mobility in two contrasting soils impacted by copper smelting emissions after wheat straw biochar application. The results presented in the study will provide a useful reference for developing new strategies of soil remediation and protection – especially in areas under agricultural use.

Experimental

Soil Sampling and Analysis

Soils for the incubation experiment were collected from the copper smelting area in SW Poland (16°01'40" N, 51°45'09"E), in two open afforested spots 2.45 km southeast (sampling point 1) and 2.75 km northeast (sampling point 2) of the smelter. These areas are a former protection zone of the copper smelter established in the early 1990s. Despite the smelter operator reducing heavy metal emissions up to 97% during the last decades, there are still elevated concentrations of Cu, Pb, Zn, Cd, As and Hg that can be determined in surface soil layers.

Bulk soil samples were collected from 0-20 cm depth and air dried at room temperature for 14 days. Dry samples were homogenized and sieved (<2 mm). Basic properties of soils and total contents of Cu, Zn, Pb and Cd are presented in Table 1. Particle size distribution in soil samples was performed using the aerometric method [24]. In soil samples, pH was measured in distilled water at a ratio of 1:25 (w/v) biochar/water with a Mettler-Toledo SevenMulti dual pH/conductivity meter. Cation exchange capacity (CEC) and base saturation of tested soil was estimated from equation between 1M KCl exchangeable acidity and exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} measured at pH 7 with 1 M ammonium acetate [24] on an MP-AES 4200 microwave plasma atomic emission spectrometer (Agilent Technologies). Organic carbon content was measured on a Shimadzu TOC analyzer. Semi-total contents of elements after microwave digestion with 10 ml of HNO_3 (method EPA 3051A) were measured on an Agilent Technologies MP-AES 4200. To avoid analytical errors, standard solutions (from LGC Standards Ltd.) for MP-AES 4200 were used for calibration, and certified reference materials (ERM-CC1136a and CRM052) were analyzed with every sample set. Each sample analyzed on the MP-AES 4200 was measured as an average from triplicate with the standard deviation, calculated by MP Expert Software Agilent Technologies.

Biochar Production and Analysis

Wheat-straw-derived biochar (WSBC) was produced at the treatment temperature of 550ºC using a fast

pyrolysis method under limited oxygen supply, and remaining time in the reactor of 30 s. For chemical characterization of WSBC (Table 1) the pH (H_2O) was measured. Elemental composition (CHN) was determined by elemental analyzer (CE Instruments). The ash content was determined by dry combustion in 550ºC [24]. The specific surface area (SSA) was obtained by N_2-BET method using a TrisStar II 3020 surface area analyzer. Oxygen content and atomic ratios C:N, H:C, and O:C were calculated to IBI standards in order to estimate aromaticity and polarity of biochar. All analyses were performed in six replicates.

Pot Experiment Set-Up

Twenty-four pots of 4 L volume, holding approx. 3 kg of soil were prepared. Six pots were set as controls without biochar amendment, and six with one dose of BC (5.0% w/v) for both soil types. The dose was chosen based on previous wheat straw biochar experiments as the lowest effective dose. To create the treatments, soil and BC were mixed and homogenized in pots for 72 h. Soil mixtures were incubated for two years with the humidity of the pots maintained at 60% of maximum water-holding capacity by weighing the pots weekly and adding water as required. No mineral or organic fertilizer was applied.

Analysis of Speciation of Heavy Metals in Soil

To investigate the effects of wheat straw biochar on metal speciation and mobility in tested soils the BCR sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) was performed. The BCR method is viewed as one of the most widely applicable extraction procedures for metal speciation in soils, and four sequential extraction steps were performed to obtain four different fractions of metals [25]. The obtained extracts were analyzed for heavy metals by the MP-AES 4200 microwave plasma atomic emission spectrometer (Agilent Technologies).

Statistical Analysis

A one-way analysis of variance was undertaken for each treatment to determine significant differences among the treatments at $p<0.05$. Variations in the treatment were determined by calculating the standard deviation (SD). The significant effects for various treatments were detected using t-tests following Fishers Test. The obtained data were compiled using Microsoft Excel 2016 and Statistica Statsoft 13.1. Each value represents the mean from six replicates±SD for soil and biochar samples.

Table 1. Properties of soils and wheat straw biochar.

Properties		Sandy soil	Loamy soil	Biochar
Texture (%)	2.0-0.05mm	73	42	77
	0.05-0.02mm	12	34	10
	0.02-0.002mm	14	20	2
	<0.002mm	1	4	1
pH (in H_2O)		3.9	6.4	9.86
TOC (%)		0.98	1.12	55
CEC (cmol kg^{-1})		5.51	58.4	63
Base saturation (%)		64.9	71.3	100
Ca^{2+}(cmol kg^{-1})		6.5	36.4	7.4
Mg^{2+}(cmol kg^{-1})		1.8	5.1	4.5
K^{+}(cmol kg^{-1})		0.8	8.5	57.0
Na^{+} (cmol kg^{-1})		1.6	8.3	0.59
$CaCO_3$ (%)		-	-	3.36
N_t(%)		0.87	0.94	0.62
H (%)		-	-	1.63
O (%)		-	-	10.3
Ash (%)		-	-	32
C:N		1	1.2	88
H:C		-	-	0.03
O:C		-	-	0.25
SSA (m^2 g^{-1})		-	-	239
Cu_{tot} (mg kg^{-1})		75	210	11
Pb_{tot} (mg kg^{-1})		45	65	2
Zn_{tot} (mg kg^{-1})		29	31	38
Cd_{tot} (mg kg^{-1})		3.6	3.8	<0.01

TOC – total organic carbon, N_t – total nitrogen content, CEC – cation exchange capacity
SSA – specific surface area, tot – total or semi total content of the element. The values are mean of six analyses±SD

Results

Soil Characterization

Soil in sampling point 1 had a silt loam texture and was classified as Cutanic Luvisol (FAO-WRB 2014). Soil in sampling point 2 had a loamy sand texture and was classified as Fulvic Brunic Arenosol (FAO-WRB 2014). Luvisols and Arenosols dominate in the areas impacted by smelting and mining objects in SW Poland but also represent a wide range of soil types characteristic of Eastern and Northern Europe.

In sandy soil (SS), copper exhibited the highest value of 75 mg kg^{-1}, followed by 45 mg kg^{-1}, 15 mg kg^{-1} and 3.6 mg kg^{-1} of Pb, Zn and Cd, respectively. In loamy soil (LS), content of copper was highest and reached 210 mg kg^{-1}, followed by Pb-65mg kg^{-1}. The abundance of Zn and Cd was similar to SS, achieving 31 mg kg^{-1} and 3.8 mg kg^{-1}, respectively. According to Polish law regulation only cadmium content exceeded the soil standards (2 mg kg^{-1} in loamy soils). Contents of all the studied elements were similar to the average (measured in top layers 0-30 cm) for Cutanic Luvisols and Arenosols [26, 27] measured in the past in the same locations.

Biochar Characterization

The properties of biochar depend on the type of feedstock and the pyrolysis conditions. Wheat straw-derived biochar (WSBC) used in the experiment had a very fine "powdery" particle structure. Particle size distribution determined by the progressive dry sewing method showed that over 75% of the material sample had particle diameter <1 mm. The pH of biochar produced at 550ºC was 9.9 as expected and reported in other studies. Material was carbon reach, average C_{tot} was 55%. The elemental composition and atomic ratios are given in Table 1. Low H:C and O:C ratios show high aromaticity and stability of the material [28]. When biochar is applied to soil, the risk of secondary pollution with various elements derived from the material also has to be considered. To verify if the wheat straw biochar is sufficient for soil application, concentrations analyzed in the experiment heavy metals were tested on raw material as well. According to IBI Standards, content of all elements was very low: Cu-11 mg kg^{-1}, Zn-38 mg kg^{-1}, Pb-2 mg kg^{-1}, and Cd<0.01 mg kg^{-1}, and contributions of these elements to total contents of HM in soil were insignificant for Cu, Pb and Cd (Table 1).

Effects of Biochar on Soil pH and Sorption Properties

Changes in soil pH and CEC after two-year incubation with wheat straw biochar are presented in Fig. 1. pH increased significantly ($p<0.05$) in acidic sandy soil. Compared to the control, the addition of 5% WSBC increased soil pH by 0.85 unit, from pH 3.9 to pH 4.75 in BC soil. In loamy soil with higher pH of 6.4 there was no significant increase of pH after two years of incubation. WSBC application had the opposite effect on CEC values of both tested soils. SS soil saw a significant increase, while in LS a significant decrease of cation exchange was observed after two years from biochar application (Fig. 1). Biochar addition caused a significant ($p<0.05$) increase of base cation saturation from 77% in SS control to 86% in WSBC SS, and a decrease of soil acidity respectively, from 3.1 cmol kg^{-1} to 1.8 cmol kg^{-1}. In LS soil no significant changes of base cation saturation and soil acidity was observed. Wheat straw biochar increased exchangeable K^+, Ca^{2+}, Mg^{2+}, and Na^+, but the change was only significant for K^+ for both tested soils.

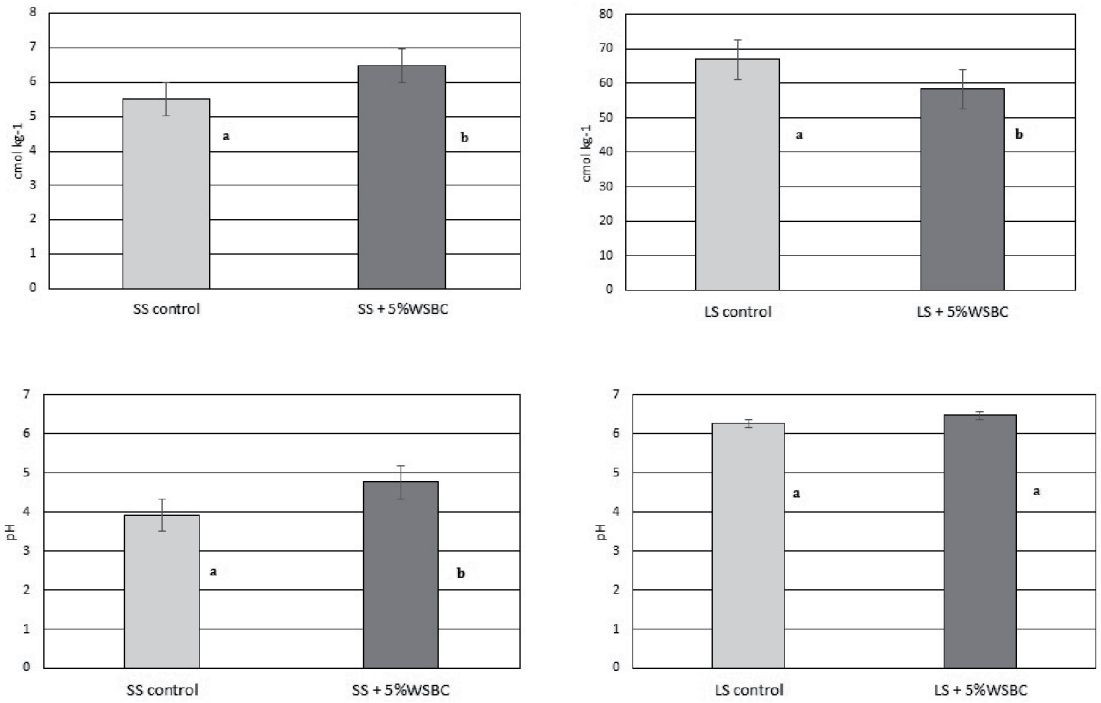

Fig. 1. Effect of wheat straw biochar on soil pH and CEC in tested soil: SS – sandy soil and LS – loamy soil; different letters above the graphs indicate significant ($p<0.05$) differences between treatments.

Sequential Extraction of Cu, Zn, Pb and Cd

In control sandy soil (SS) with low pH value, readily exchangeable/acid soluble Cu concentrations (fraction F1) were much higher (37%) compared to loamy soil (LS), with higher pH value (8%). In LS most of the copper was already in residual and oxidizable fractions and no effect on Cu fractionation was observed in biochar treatments after an incubation period (Fig. 2). Significant change after biochar application was observed in SS soil, were reduction of F1 by 30% was observed and most Cu was transferred to residual F4 fraction. Content of Cu in residual forms increased by 36% in WSBC sandy soil. There was no significant change in fractions F2 and F3 after the WSBC incorporation and incubation period. Copper in control SS was distributed in the following sequence: F1>F2>F3> F4, while in WSBC SS it was F1=F4>F3>F2 (Fig. 2). Surprisingly, wheat straw biochar had a distinct effect on Zn immobilization in tested soils. In acidic sandy soil the most extractable Zn occurred in the soluble/exchangeable fraction (F1). The application of WSBC caused an increase in Zn mobility and the element was transferred from residual fraction (F4) to exchangeable/acid soluble fraction (F1) and reducible fraction (F2). The opposite was seen in loamy soil with higher pH values as zinc was already in immobile forms, mainly in fraction F2, and biochar application caused Zn to shift to residual forms (F4). The mobility of Pb in tested soil was low compared to Cu, Zn and Cd – not exceeding 3% of total content in sandy soil and 2% in loamy soil. Lead speciation was highly impacted by WSBC application in SS treatment (Fig. 2). However, no effect was observed on Pb speciation in LS treatment

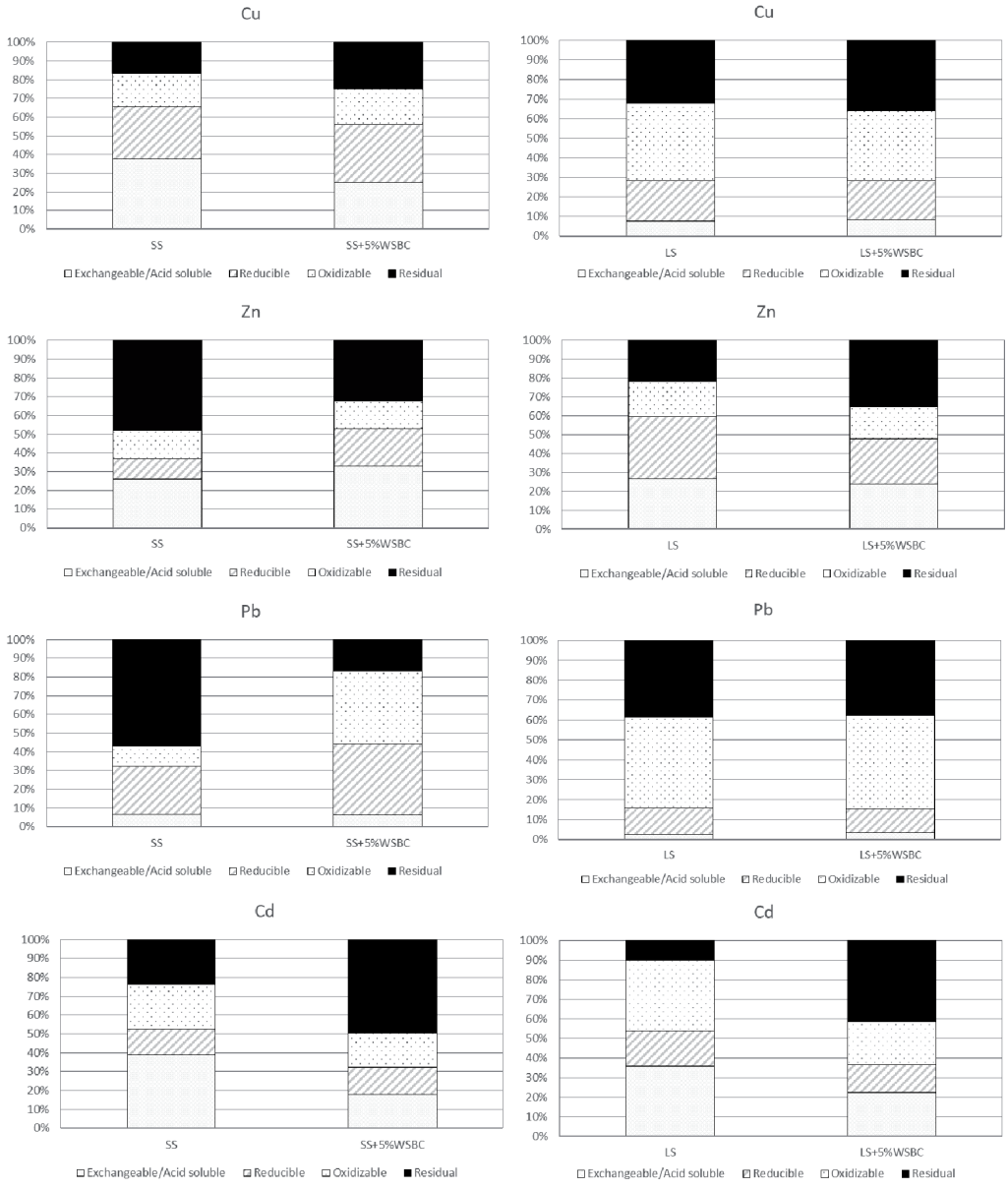

Fig. 2. Variation of Cu, Zn, Pb and Cd species in soils after wheat straw application: SS – sandy soil control, SS+5%WSBC – sandy soil with 5% wheat straw biochar, LS- loamy soil control, and LS-5%WSBC – loamy soil with 5% wheat straw biochar.

(Fig. 4). Biochar application in SS caused a shift from residual fraction to oxidizable (bonded with organic matter) F3 and reducible F2 fraction. An increase in F3 was statistically significant in SS+5%WSBC treatment ($p<0,05$) compared with control SS, at 39% and 11%, respectively. The chemical fractionation results of smelter-impacted soils showed that wheat straw biochar application significantly reduced the mobility of Cd in both tested soils. The greatest change was observed for exchangeable and acid-soluble fractions (F1). The content of Cd in fraction F1 decreased from 39% in control SS to 18% in SS+5%WSBC treatment, and from 36% to 22% in LS+5%WSBC treatment. Most of the cadmium forms were shifted to residual fraction F4, resulting in Cd immobilization, from 23% to 49% in SS+5%WSBC treatment, and from 10% to 42% in LS+5%WSBC treatment.

Discussion

Wheat straw biochar used in the experiment had high ash content and high specific sorption, which can be attributed to feedstock type and high pyrolysis temperature (550ºC). With increasing temperature of the process also surface area and charge density on the BC surface increase, which makes high temperature biochars more sufficient as sorbents. Compared to other biochars made from different feedstock types like rice straw (45 cmol kg^{-1}) or bamboo (15 cmol kg^{-1}) [22], CEC of wheat straw biochar was higher (Table 1). Another important property of material affecting sorption behavior and the potential for soil alkalization is ash content. Wheat straw biochar had high ash content (Table 1) and as a result, more effective precipitation and immobilization of metals can be expected. Alkaline pH of biochar and high CEC affected basic soil properties significantly in cases of sandy soil, while in loamy soil with higher pH and better sorption properties the effect was less significant. Observed increases of soil pH after biochar application to sandy soil is in agreement with Bian et al. [29] or Yang et al. [30]. Similar results for BC amendment soil were described by Masud et al. [31]. The potential of H^+ dissociation [5] in alkaline pH that can occur in biochar-amended soils can be important information for predicting biochar ability for heavy metal sorption, which is due to the process of H^+ exchange for metal cations and the increase of negative load of BC. The decrease in soil acidity induced by the biochar amendment responds with the increase of BC soil pH mentioned above. Biochars can also comprise ample oxygen-containing functional groups that can form surface complexes with Al^{3+} [32]. This process also contributes to the decrease of soil acidity and is similar to the one that occurs when organic matter is applied to the acidic soil [33].

Different mechanisms of heavy metal immobilization can be observed after biochar application. First, biochar can influence soil properties determining element mobility like pH or cation exchange capacity. Secondly, biochar can support soil sorption complexes and accomplish trace element immobilization by several mechanisms, including metal exchange, complexation with different functional groups on biochar [12], and specific and nonspecific adsorption [28], which can be partly determined during sequential extraction procedure. Depending on initial pH values of soil, element mobility and biochar properties (ash content, specific sorption area, functional groups, etc.) the effect of biochar application may vary between soil types. Arenosols and Luvisols represent soils with very distinct properties and different effects on heavy metal immobilization/mobilization was observed after biochar application. In general, in acidic sandy soil low pH values determined higher initial mobility of tested trace elements, and pH increase was the dominant mechanism of their immobilization after WSBC application. In loamy soil with pH above 6.0, the increase of pH after biochar application was insignificant and precipitation and surface complexation reactions dominate biochar's remediation capacity [19], causing a shift of metals between fractions, but not resulting in significant changes in their mobility. It is also likely that increases of soil pH after biochar application to tested sandy soil promoted heavy metal adsorption and precipitation processes [29, 34, 35]. Wheat straw biochar had high ash content and most of the mineral elements were in the forms of carbonates and bicarbonates (Table 1) or oxides and orthophosphates [23]. These compounds are alkaline after dissolving in water and contribute to short-term amelioration [10, 36], as well as promote the formation of hydroxide complexes, phosphates or carbonates [6], Cd as $CdCO_3$, Cu as $Cu(OH)_2$ and Pb as $Pb_5(PO_4)_3OH$ [12, 22], which was observed after sequential extraction of heavy metals from tested soils. The immobilization effect varied between elements, showing different sensitivities to pH change or different affinity to biochar. Copper was sensitive to pH change and the effect of immobilization was only observed in SS treatment. Similar findings were observed by Moore et al. [37], where biochar application to Cu-contaminated soil in the vicinity of the Vantanas Cu smelter in Chile increased soil pH and decreased the Cu exchangeable fraction by 5 and 10 times by increasing the Cu bound in organic matter and residual fractions. Concurrently, an increase of CEC in sandy soil suggests that biochar can support sorption capacity for cations like Cu^{2+}. Tong et al. [38] determined that Cu(II) can be adsorbed specifically through the formation of surface complexes with -COOH and phenolic hydroxyl groups on biochar surfaces. Zinc in alkaline soils is immobile, which can explain the shift to residual forms in LS+ 5%WSBC treatment, were pH increased from slightly acidic to alkaline. In sandy acidic soil, increases of exchangeable/soluble faction F1 were observed. Ippolito et al. [39] showed that with increasing application rates of biochar, zinc tended to decrease in the residual fraction and increase in the soluble/exchangeable/carbonate fraction.

Wheat straw biochar could be a donor of easily soluble forms of Zn and caused enrichment of this element in tested soil (Table 1). To verify this thesis, soluble forms of Zn were determined in biochar after extraction with 0.11 M acetic acid as per BCR protocol. Compared with amounts of Zn determined as a soluble fraction (F1) in control soil and BC soil (3.6 mg kg^{-1} and 5.9 mg kg^{-1}, respectively) the content of 0.11 M HOAc-extractable Zn in biochar was high (3.0 mg kg^{-1}) and might contribute to the content of exchangeable/acid soluble fraction extracted from soil + BC mix during BCR sequential extraction, giving a false result of element shift. The increase of F1 fraction could also be explained by Zn complexation by acetate [40]. The application of biochar increased soil alkalinity, which can cause Zn^{2+} hydrolysis and promote the formation of easily soluble salts like $Zn(OAc)_2$, which can explain the changes in Zn mobility in tested sandy soil. Xu et al. [41] suggested that the probable mechanism of Zn immobilization behavior depends on the ash content in biochar and the occurrence of easily soluble minerals like PO_4^{3-} and CO_3^{2-}. They were probably released from biochar and could react with $Zn^{2+}$to form easily soluble Zn phosphates and Zn carbonates, increasing amounts of fraction F1 during the first step of BCR extraction. Also, increases in F2 fraction in SS were observed after biochar application, which can be explained by chemical precipitation processes occurring on wheat straw biochar surface upon the formation of oxides. Qian et al. [42] suggested that high-temperature biochars contain higher amounts of OH^-, $CO_3^{2-}$and Si species or other sorption sites like oxygen-containing functional groups. We suggest that the formation of oxide Zn species on high temperature wheat straw biochar surface caused an increase of reduced Zn forms in fraction F2 during the BCR sequential extraction procedure. Some Zn^{2+} could also be occluded on Mn, Al, and Fe oxides formed on biochar and soil constituent surfaces. As Zn has a lower affinity to be complexed with Mn and Fe oxides compared to the other metals like Pb or Cd, it is probable that it can be a secondary mechanism of Zn immobilization in tested soils. We postulate that LS alkaline conditions after WSBC treatment could promote the formation of $Zn(OH)_2$, and amorphous hemimorphite could occur. This can explain the increase of Zn residual fraction, which was also found by Qian et al. [42] for wheat straw biochar produced at 550ºC.

Lead sorption on biochars is controlled by multiple sorption mechanisms: organic functional groups (e.g., C-H, -COOH,-OH, C=O and C-X), mineral content, ionic content and π-electrons [43] – all of which should be considered in the case of tested soils. A study in single-contaminant systems demonstrated that four different types of biochar (bamboo-, sugarcane bagasse-, hickory wood- and peanut hull-derived) removed Pb^{2+} at 18–35% efficiency. The authors suggested that the adsorption of Pb may be affected by the pore structure [36, 44] directly correlated with the amount of oxygen functional groups on biochars and increase of CEC, which promotes more negative charge and adsorption affinity of soils for Pb^{2+} [33]. We suggest that biochar renewed stock of organic matter played the most important role in cation exchange and sorption/desorption processes. Under acidic conditions biochar released Ca^{2+}, Mg^{2+} and K^+, which was replaced by Pb^{2+} and which can be confirmed by changes in base cation contribution in the sorption complex described above. The transformation of Pb from residual (extractable) to non-residual form after biochar addition, might occur concurrently with the formation of lead phosphate and lead hydroxyapatite-like minerals [45, 46]. This suggests that tested phosphorus reach wheat straw biochar could influence Pb retention by phosphate formation in LS + 5%WSBC treatment.

Fraction F1 from BCR extraction is considered a bioavailable fraction, which is very prone to leaching [47] and wheat straw biochar application reduced significantly the risk of cadmium leaching from copper smelter-impacted soils. In the tested soils changes in oxidizable and bounded with organic (F3) fraction also were observed, with some cadmium forms shifting from fraction F1 to F3. This is possibly due to the precipitation processes on biochar and the formation of insoluble cadmium carbonate hydroxides and organic complexes [19]. The most probable mechanism of cadmium immobilization in tested soils was the increase of soil pH after biochar application. Soil pH is a key factor governing Cd solubility and, therefore, bioavailability. Higher pH affords more negative surface charge, higher density of pH-dependent exchange sites and increased hydrolysis of Cd [48]. Beesley and Marmiroli [33] found that biochar significantly reduced leachate concentrations of Cd, with evidence of surface sorption to biochar [19]. Cadmium sorption mechanism was also suggested by Fellet et al. [49]. Cui et al. [50], Bian et al. [29] and Puga et al. [16], indicating that biochar can be effective in Cd immobilization in the contaminated paddy soil. However, this effect in the presented study case was not well reported.

Conclusions

The effect of biochar application on Cu, Zn, Pb and Cd immobilization depended strongly on initial soil pH and varied between soil types. In acidic soils pH increase after biochar application should be considered as the major factor influencing heavy metal immobilization. On the other hand, in alkaline soil, biochar had no significant effect on pH increase, although the shifts between metal fraction occurred, suggesting that above pH 6.0 adsorption and precipitation processes on biochar surface dominate in trace element immobilization processes. The application of wheat straw biochar was more successful in sandy acidic soil, causing significant reduction of risk related to heavy metal presence in soil impacted by copper smelting and mining processes. Biochar application significantly reduced Cd mobility

in both tested soils, suggesting that the addition of this material can be considered as good management practice in soils contaminated with cadmium. Presented results show that the effect of wheat straw biochar on heavy metal immobilization in multi-contaminated soils is more complex and cannot be defined as all-purpose material in remediation procedures.

Conflict of Interest

The authors declare no conflicts of interest.

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