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Determination of Heavy Metals Immobilization by Chemical Fractions in Contaminated Soil Amended with Biochar

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Abstract: Biochar is a promising tool to immobilize heavy metals (HMs) in the soil. Biochar's effect on HMs immobilization into acidic soil (pH < 5) and the interaction of plants have been investigated. Three types of feedstocks were used for biochar development via pyrolysis at two temperatures and then applied as soil amendments. A vegetative experiment has been carried out with buckwheat and white mustard to determine the effect of biochar as an HMs immobilizing agent in the presence of sewage sludge. The results show promising biochar properties to immobilize heavy metals and reduce their availability for plants. Biochar incorporation increased soil pH and reduced heavy metal forms available to plants. A sequential extraction procedure was applied to investigate five different forms of six heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) and evaluate their distribution after plants' cultivation. The proportion of the residual fraction (RES) of HMs varied widely and differed from metal to metal and from plant species. RES in the soil after treatment with biochar and buckwheat harvest varied between 68.14 and 96.40% for Zn, 42.39 and 59.48% (Cu), 75.89 and 93.11% (Cr), 81.85 and 92.83% (Ni), and 98.94 and 99.20% (Pb). In comparison, a slightly opposite trend was found in the soil after white mustard cultivation. The proportion of RES was: 0.82–53.44% for Zn, 0.99–52.93% (Cu), 48.87–76.41% (Cr), 10.22–72.63% (Ni), and 98.31–99.32% (Pb). HMs immobilization efficiency in the soil after biochar treatment followed the order Ni > Cr > Pb > Cu > Zn and Ni > Pb > Zn > Cr > Cu after buckwheat and white mustard cultivation, respectively.

Keywords: biochar; sewage sludge; heavy metals; soil improvement; contaminants' immobilization; potential ecological risk

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1. Introduction

Rapidly growing agriculture and metal industries, improper waste disposal, fertilizers, and pesticides contaminate our environment, including water, soils, and the atmosphere. Soil pollution of heavy metals (HMs) is increasingly becoming a problem due to huge, contaminated areas reducing the size of the cultivation land each year. Sources of HMs in the soils are natural or anthropogenic [1]. Elements with an atomic number greater than 20 and an atomic density above 5 g/m^3 are addressed as HMs [2]. They are undegradable, toxic, and possess cancerogenic properties, and they enter into the soil and stay there for a long time. Due to the different interactions with soil's clay and mineral particles, soil physicochemical properties HMs could be trapped in the soil or exist in the soil solution and taken by plants. HMs resist chemical and microbiological degradation [3]. They can migrate in the plant–soil–groundwater system depending on their form, mobility, cultivated plants, and soil properties [4,5]. As plants absorb HMs from the soil, they can enter the human food chain. The mechanism of the ability of various plants to accumulate HMs is examined and

described in previously published works [6–9]. The continuous accumulation of hazardous substances in the soil can endanger living organisms, including soil microorganisms [10], and deteriorate the chemical and microbiological properties of the soil [11]. For these reasons, it is necessary constantly monitor the concentration of HMs in the fertilization products in the soil to determine the relationship between soil physicochemical indicators such as pH, electrical conductivity, amount of nutrients, and heavy metals.

One of the most critical factors determining the hazards of metal is bioavailability [12]. The incorporation of various organic and inorganic amendments to the soil improves its physicochemical properties and microbiological activity and increases the fertilizing value [13]. In addition, depending on the type of soil amendment used and the properties of the soil, the added materials can increase or decrease the mobility of HMs in the soil [14].

Biochar is charcoal from bio-organic waste by pyrolysis [15]. Biochar incorporation into the soil improves long-term carbon sequestration and soil productivity, increases pH, absorbs pollutants of various origins [16], and increases the water-holding capacity of the soil [17]. Moreover, biochar shows the ability to stabilize HMs in soil [18] and significantly impacts the bioavailability of HMs. Several mechanisms describe the stabilization of HMs in soil using biochar: (i) electrostatic attraction; (ii) ion exchange of heavy metals with Ca^{2+}, Mg^{2+} and other cations associated with biochar, attributed to leaching, forming complex internal compounds with humic substances and mineral oxides of biochar; (iii) interaction of HMs with various functional groups, surface complex compounds, and inner-sphere complexes with the free hydroxyl radical of mineral oxides; (iv) precipitation; and (v) indirect interactions between biochar and HMs in soils [19].

Most data declare that biochar incorporation into the soil decreases the HMs' bioavailability and changes in bioavailable fractions [20–22]. On the other hand, it is not clear enough how biochar incorporation will affect HMs immobilization into acidic soil (pH < 5), while in this case, metals are more bioavailable and demonstrate higher accessibility by plants. Moreover, there is a lack of studies on how biochar interacts with buckwheat and white mustard plants. Buckwheat was chosen as a model plant due to its capability to accumulate higher amounts of HMs in its morphological parts [23], while white mustard was used due to its properties to accumulate and stabilize higher amounts of HMs in its root [24]. This paper hypothesizes that white mustard interaction with biochar could enhance HMs' phytostabilization.

The aim of the research was to study the influence of biochar raw materials on its properties to immobilize heavy metals in the soil, as well as the influence of the cultivation of certain crops (buckwheat and white mustard) on the efficiency of HM immobilization and the potential ecological risk for the environment. Moreover, the distribution of HMs fractions after introducing biochar obtained from three types of biomasses into acidic soil (pH < 5) was analyzed.

2. Material and Methods

2.1. Pot Experiment Description

A pot experiment was installed at the Lithuanian Research Centre for Agriculture and Forestry Vėžaičiai branch vegetation experiment site under natural climate conditions. Plastic 6.12 l volume and 19.50 cm height pots whose upper and bottom diameters were equal to 20.0 cm were used in the experiment. The growing medium for the vegetation experiments was prepared as follows: The soil was mixed with sewage sludge and different origin biochar, respectively. The detailed experiment scheme is presented in Table 1. There are a total of fifteen treatments, including soil without any amendments, soil with sewage sludge, and soil with sewage sludge and biochar, and this growing medium was tested with two plants, buckwheat and white mustard (denoted by I and II, respectively, in the experiment scheme in Table 1). Sewage sludge used for the pot experiment was obtained from JSC "Klaipėdos vanduo." Experimental plants (buckwheat and white mustard) were sown into each pot. Seeds were incorporated into a growing medium at 1 cm depth at equal distances. The pot experiment was conducted under local environmental conditions,

meaning there was no possibility of controlling climate factors such as light, temperature, or humidity. Experimental pots were additionally watered manually according to meteorological conditions. Each treatment was performed in three replicates.

Table 1. Experiment scheme. Note: I—buckwheat plant; II—white mustard plant; S—soil; SS—sewage sludge; $RBch_{450}$—rapeseed biochar at 450 °C; $CBch_{450}$—corn stalk biochar at 450 °C; $DBch_{450}$—digestate biochar at 450 °C; $RBch_{700}$—rapeseed biochar at 700 °C; $CBch_{700}$—corn stalk biochar at 700 °C; $DBch_{700}$—digestate biochar at 700 °C; MixBch—mixed biochar was obtained by mixing an equal amount of each biochar origin.

Num.	Treatment Abbreviation	Amount of Soil, g	Amount of Sewage Sludge, g	Amount of Biochar, g	Cultivated Plants
1.	I-S	7000	0	0	Buckwheat
2.	I-SS	6882.4	117.6	0	Buckwheat
3.	I-SS+$RBch_{450}$	6672.4	117.6	210	Buckwheat
4.	I-SS+$CBch_{450}$	6672.4	117.6	210	Buckwheat
5.	I-SS+$RBch_{700}$	6672.4	117.6	210	Buckwheat
6.	I-SS+$DBch_{700}$	6672.4	117.6	210	Buckwheat
7.	I-SS+$DBch_{450}$	6672.4	117.6	210	Buckwheat
8.	I-SS+MixBch	6777.4	117.6	105	Buckwheat
9.	II-S	7000	0	0	White mustard
10.	II-SS	6882.4	117.6	0	White mustard
11.	II-SS+$RBch_{450}$	6672.4	117.6	210	White mustard
12.	II-SS+$DBch_{450}$	6672.4	117.6	210	White mustard
13.	II-SS+$DBch_{700}$	6672.4	117.6	210	White mustard
14.	II-SS+$RBch_{700}$	6672.4	117.6	210	White mustard
15.	II-SS+$CBch_{700}$	6672.4	117.6	210	White mustard

2.2. Quality of Soil Used for Pot Experiment

The following soil parameters were determined before the installation of the pot experiment and are given in Table 2. PH_{KCl} was determined using the potentiometric method according to LST ISO 10390:2005; plant-available amounts of phosphorus (P_2O_5) and potassium (K_2O) were determined using the Egner–Riehm–Domingo (A–L) method. Total nitrogen concentration was determined by the Kjeldahl nitrogen distiller (Shimadzu, Kyoto, Japan) following the standard EN 13654-1:2012. Soil total carbon content was analyzed using the total carbon analyzer "Liqui TOC II" (Elementar, Langenselbold, Germany).

Table 2. Experimental soil parameters.

pH_{KCl}	P_2O_5, mg/kg	N_{total}, mg/kg	K_2O, mg/kg	C_{total}, g/kg
4.50	88	1.26	191	12.5

2.3. Amendments Used for the Pot Experiment Characterization

Sewage sludge and biochar were used as soil amendments in the pot experiment. Biochar was produced using three different raw materials at two combustion temperatures (450 °C and 700 °C). To determine the CHN amount in biochar, ~10 mg of the homogenized sample was weighed into a tin capsule. The capsule with the sample was folded and placed in a CHNS-O (ECS 4010—Elemental Combustion System) elemental analyzer equipped with an autosampler. The sample was burned of helium (He) gas combustion. The flow rate was 110 ml/min, and the left furnace temperature was set to 1020 °C; the right furnace—800 °C. The results were processed using the "Elemental analysis software" program, and results were estimated using acetanilide, an external standard for calibration. A 25 ml volume measurement flask was filled with biochar to determine the bulk density and dried at 80 °C overnight. After, the flask was shaken for 1 min to compress the biochar. The density was calculated as a dry material expression

of volume (cm^3) and mass (g). The pH in biochar and sewage sludge samples was measured using a pH-meter Orion Star™ A211 Benchtop (Thermo Fisher Scientific, Waltham, MA, USA). The biochar and deionized water ratio were 1:40, and the sample was stirred for 24 h before registering the pH value. P in sewage sludge sample was measured after 1 h of sample and deionized water stirring at a ratio of 1:5. To investigate the total amount of phosphorous in the digested sample, the same procedure as for heavy metals analysis was used. The total amount of phosphorous was measured by means ICP-MS instrument (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an automated Cetac ASX-520 (Teledyne Technologies, Thousand Oaks, CA, USA) autosampler. The phosphorous calibration curve was set at the interval of 500–2000 µg/L. Organic carbon content in biochar was determined by the dry combustion method using the Liqui TOC II instrument (Elementar, Langenselbold, Germany). Twenty milligrams of biochar were pre-treated with HCl to remove the inorganic carbon fraction. After the sample was combusted at 900 °C and released, carbon dioxide was measured by an infrared detector. The characterization of biochar and sewage sludge used in the experiment are presented in Tables 3 and 4, respectively.

Table 3. Biochar used in the experiment characteristics.

Raw Material	Combustion Temp., ° C	Parameters						
		pH	Bulk Density, g/cm^3	N, %	C, %	C_{org}, %	H, %	P, %
Digestate	450	8.49	0.574	1.30	38.96	31.24	0.75	1.31
	700	9.27	0.529	2.11	57.55	52.60	0.83	1.77
Waste of biodiesel production from rapeseed	450	9.25	0.744	0.08	36.81	32.76	0.28	0.80
	700	10.23	0.735	0.13	43.38	40.12	0.39	0.76
Corn stalk	450	9.53	0.197	1.07	42.77	38.95	1.26	0.053
	700	9.75	0.186	1.16	58.96	53.05	1.62	0.050

Table 4. Sewage sludge used in the experiment characteristics.

Parameters pH	Organic Matter, %	Dry Matter, %	N, %	P, %
7.10	66.10	94.20	5.52	2.61

2.4. Samples Digestion by CEM MARS 6

To determine the total amount of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in soil, biochar and sewage sludge samples, microwave-assisted extraction (MAE) was carried out using an automated CEM MARS 6®(Matthews, NC, USA) digestion system equipped with 100 mL Teflon vessel and described elsewhere [25]. Approximately 0.3 g of the homogenized and dried sample was accurately weighed into a Teflon vessel and digested using nitric (HNO_3) (≥65%, Sigma–Aldrich Corporation (Taufkirchen, Germany)) and hydrochloric (HCl) (≥37%, Sigma–Aldrich Corporation (Taufkirchen, Germany)) acids mixture (5:1). Digestion was performed under the following conditions: temperature—180 °C; pressure—800 psi; ramp time—20 min; hold time—20 min; microwave power—800 W. Then, the digested sample was cooled down and thoroughly transferred into a 100 mL volumetric flask and diluted using bidistilled water till the mark. Each sample was prepared in triplicate, and the blank sample was included in each digestion run.

2.5. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis

To determine the total amount of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn), the digested samples were analyzed by means of ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA). Inductively coupled plasma mass spectrometry was performed under standard (STD) operation mode. Samples were introduced using an autosampler with ASXpressTM rapid

uptake module (Cetac ASX-520, Teledyne Technologies Inc., Omaha, NE, USA) through a PEEK nebulizer (Burgener Mira Mist, Mississauga, Burgener Research Inc., Mississauga, ON, Canada). Amounts of analyzed heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) were estimated using an external multi-element calibration curve in the range of 20–1000 µg/L. The accuracy and precision of the method were assessed by recovery experiments using SQC001-certificated reference material. Obtained recovery for individual HMs was Cd 89.1 ± 0.10%, Cu 90.5 ± 0.12%, Ni 91.3 ± 0.19%, Pb 91.0 ± 0.03%, Zn 96.7 ± 0.09%, Cr 104.2 ± 0.02%.

2.6. Sequential Leaching

The heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) concentrations of five different fractions in soil samples after plant vegetation were measured according to the method described by Wang et al. [26]. Approximately 1 g of dried and homogenized soil was weighed into 50 mL centrifugal vials. The detailed sequential extraction procedures for heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) determination are given in Table 5. The concentration of various fractions of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) were analyzed using the ICP-MS instrument.

Table 5. Sequential extraction procedures for heavy metals fractions determination.

Fraction Number	Fraction Name	Extraction Conditions	Extraction Solution
I	Exchangeable (EXC)	Oscillation for 2 h at 25 °C, pH = 7	10 mL 1 mol/L $MgCl_2$
II	Bound to carbonates (CAR)	Oscillation for 2 h at 25 °C, pH = 5	10 mL 1 mol/L CH_3COONa
III	Bound to Fe-Mn oxides (OX)	Oscillation for 6 h in the oven at 96 °C, pH = 2	10 mL 0.04 mol/L NH_2OH-HCl and 25% CH_3COOH
IV	Bound to organic matter (OM)	(i) Intermittent oscillation for 2 h in the water bath at 85 °C, pH = 2 (ii) Intermittent oscillation for 3 h in the water bath at 85 °C, pH = 2 (iii) Oscillation for 30 min at 25 °C	(i) 1.5 mL of 0.02 mol/L HNO_3, 2.5 mL 30% of H_2O_2 (ii) 1.5 mL 30% H_2O_2 (iii) 2.5 mL 3.2 mol/L CH_3COONH_4
V	Residual (RES)	Digestion using an automated CEM MARS 6® (Matthews, NC, USA)	HNO_3-HCl (5:1)

2.7. Heavy Metals Immobilization Efficiency and Potential Ecological Risk

The HM immobilization efficiency for the biochar-amended soil (compared to treated with sewage sludge soil) was estimated using the following Equation (1):

$$HM\ immobilization\ efficiency\ (\%) = \frac{C_{SS} - C_{SS+BCh}}{C_{SS}} * 100 \quad (1)$$

where C_{SS} refers to the HM concentration in the treatment where sewage sludge was applied (I-SS and II-SS, respectively, soil after buckwheat and white mustard vegetation), and C_{SS+BCh} is the HM concentration in the biochar-amended soil after buckwheat and white mustard harvest. The concentrations are expressed in $mg \cdot kg^{-1}$ HM residual (RES) fraction, which are non-available for plants. Therefore, for all calculations, heavy metals determined in non-bioavailable residual fractions were used.

The potential ecological risk index (RI) was used to determine the potential contamination risks of heavy metals in the soil after organic amendments incorporation. The RI was originally proposed by Hakanson [27] and later widely applied [28–31]. The calculation was made according to the Formulas (2)–(4) presented by [29]:

$$C_f^i = C_D^i / C_R^i \quad (2)$$

$$E_r^i = T_r^i \times C_f^i \quad (3)$$

$$RI = \sum_{i=1}^{m} E_r^i \quad (4)$$

RI—potential ecological risk index to the environment; E_r^i—the ecological risk of a single metal; C_f^i – contamination index for individual heavy metals; C_D^i—the determined concentration of heavy metal in the soil after plants harvest in bioavailable fractions (EXC+CAR+OX+OM); C_R^i—the determined concentration of heavy metal in the soil after plants harvest in non-bioavailable fraction (RES); T_r^i—a toxic response factor for a given heavy metal, where T_r^i(Ni = Pb = Cu) = 5; T_r^i (Zn) = 1; T_r^i(Cr) = 2 [27]. Evaluation criteria for single heavy metal contamination (C_f^i), potential ecological risk of the environment (RI), and ecological risk of a single metal (E_r^i) are given in Table 6 and previously used by Chabukdhara and Nema [29,32,33].

Table 6. Heavy metals risk evaluation for E_r^i, C_f^i, and RI by [33].

C_f^i	Pollution Degree	E_r^i	RI Value	Grade of Potential Ecological Risk of Environment
$C_f^i < 1$	Clean	≤ 15 E_r^i	≥ 50 RI	Low risk
$1 \leq C_f^i < 3$	Low	$15 \leq E_r^i < 30$	$50 \leq$ RI < 100	Moderate risk
$3 \leq C_f^i < 6$	Moderate	$30 \leq E_r^i < 60$	$100 \leq$ RI < 200	Considerable risk
$6 \leq C_f^i < 9$	Considerable	$60 \leq E_r^i < 120$	RI > 200	High risk
$C_f^i > 9$	High	$E_r^i > 120$		Very high risk

2.8. Statistical Analysis

Results were presented as an arithmetic mean of three replicates ± standard deviation calculated using MS Excel 2018 software.

3. Results and Discussion

Number of heavy metals in soil amendments. The bars of Figure 1 show the initial concentration of HMs in organic soil amendments. The highest HMs concentration was determined in sewage sludge, followed by biochar produced from digestate, then biochar produced from rapeseed waste, and biochar from corn stalks residue. It was obtained that the higher temperature used for biochar production reduces the total amount of HMs, except in the treatment where corn stalk residues were used as raw material. On the other hand, this kind of biochar possesses the lowest number of HMs of all investigated. The temperature effect on the reduction of HMs could be based on previous findings that at high temperatures (>600 °C), HMs volatilize [34]. The organic amendments incorporated into the soil will increase the number of HMs due to their existence in the raw materials and the decomposition of organic matter during pyrolysis [21,35–37]. Moreover, it was investigated before that biochar integration into the soil decreases the bioavailability of HMs and their plant uptake [38].

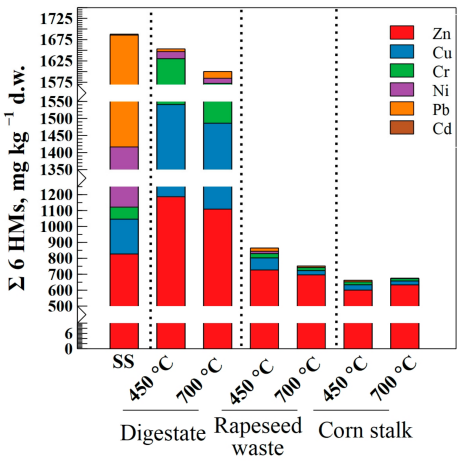

Figure 1. Distribution of heavy metals in soil amendments: SS—sewage sludge and different origin biochar.

Effect of organic soil amendments on soil pH. The biochar incorporation into the soil increases the soil's pH. Changes in soil pH after the plants' vegetation are shown in Figure 2. Biochar incorporation into the soil increases soil pH due to certain alkaline substances in their composition, which process neutralizing properties of acidic soil [39]. Soil interaction with biochar causes changes in soil physicochemical properties such as pH, cation exchange capacity, porosity, and electrical conductivity [40]. Hydrogen and aluminum exchangeable ions replaced by less acidic ions from biochar, for example, calcium, magnesium, etc., increases soil pH [41]. The highest increase in pH was determined after incorporating biochar produced from digestate (Figure 2) into the soil, with Δ pH values of 1.17 ± 0.1 and 1.04 ± 0.09 after growing buckwheat and white mustard, respectively. Lucchini et al. [42] demonstrated that the increase in soil pH was lower after a higher rate of incorporation of biochar than in our study. These findings depend on soil and biochar individual properties, cation exchange capacity (CEC), soil acidity, and biochar feedstock.

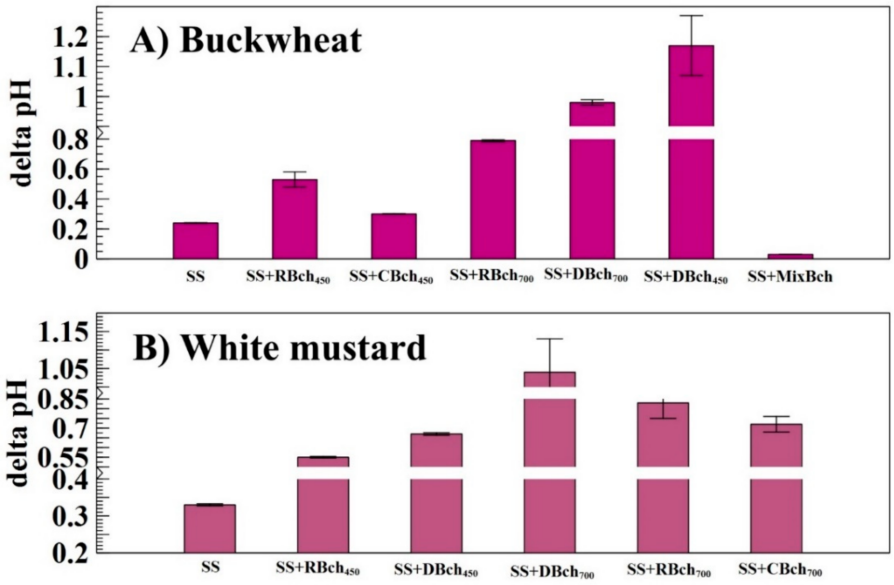

Figure 2. Δ pH in the soil after (**A**) buckwheat and (**B**) white mustard vegetation.

Effect of biochar additive on heavy metals bioavailability in the soil after buckwheat cultivation. Overall, five HMs fractions of six different HMs were investigated after a pot experiment where buckwheat was growing. Distribution of different HMs fractions in the soil after buckwheat harvest is presented in Figure 3. Due to the low amount in the initial soil and organic amendments (sewage sludge and biochar), the Cd amount was determined below the limit of quantification (0.007 mg kg^{-1}) in all investigated fractions. After analyzing different fractions, it was determined that the predominant fraction was residual in all treatments and HMs (Cr, Ni, Pb, Cu, Zn). The residual fraction is determined after sample digestion in concentrated acids (HNO_3:HCl) at a ratio of 1:5 [25]. Such aggressive acidic conditions do not exist in the natural environment, which means that in the soil are predominant, not bioavailable, forms of HMs. Biochar incorporation increased the amount of Cr, Ni, Cu, and Zn bonded to organic matter. Other scientists who determined that biochar increased Ni bonded to organic matter amount [26] obtained similar findings previously. In addition, a slightly increased amount of Ni was found in the ion exchange fraction, compared to the control (soil without additives), but only in the treatment where biochar produced from rapeseed waste at 700 °C was used. For example, Cu and Pb were not detected in the ion exchange fraction in any of the investigated treatments. Other researchers who determined that biochar additives do not increase Cu ion exchange fraction in the soil [43] also confirmed these findings. The results reveal that the input of the organic amendments (sewage sludge and biochar) does not affect Pb immobilization because the percentage distribution was very similar among all investigated treatments. Pb fractions

in the soil after buckwheat vegetation were distributed as follows: CAR > OX > RES. Yang et al. [39] have demonstrated that biochar significantly reduces the Pb amount in leachate but does not affect Zn and Cd amounts. These findings are attributed to the higher affinity of Pb to biochar than Zn and Cd. Sewage sludge integration into the soil slightly increased Cu content bonded to Mn and Fe oxides. Moreover, Zn fractions distinguish from other metals in the highest changes (Figure 3) after organic amendments incorporation. In the soil (I-S), after plants vegetation, the predominant Zn fraction was bonded to Fe and Mn oxides, and only 20% of Zn was determined in the residual fraction. Organic amendments (sewage sludge and biochar) additive increased Zn bonded to organic matter and residual fractions. Compared to Cu or Pb, Zn is a rather mobile metal, and changing its bioavailability is much easier [44]. P, Ca, Al, Mn, and Fe oxides and organic matter content in the soil [45] could change Zn bioavailability in plants. Basta et al. [46] have demonstrated that soil pH < 6 increase Zn bioavailability. The bioavailability of HMs is distributed in the following descending order: EXC > CAR > OX > OM > RES, implying that increasing HMs into the OM fraction does not pose a high risk for plant uptake [47].

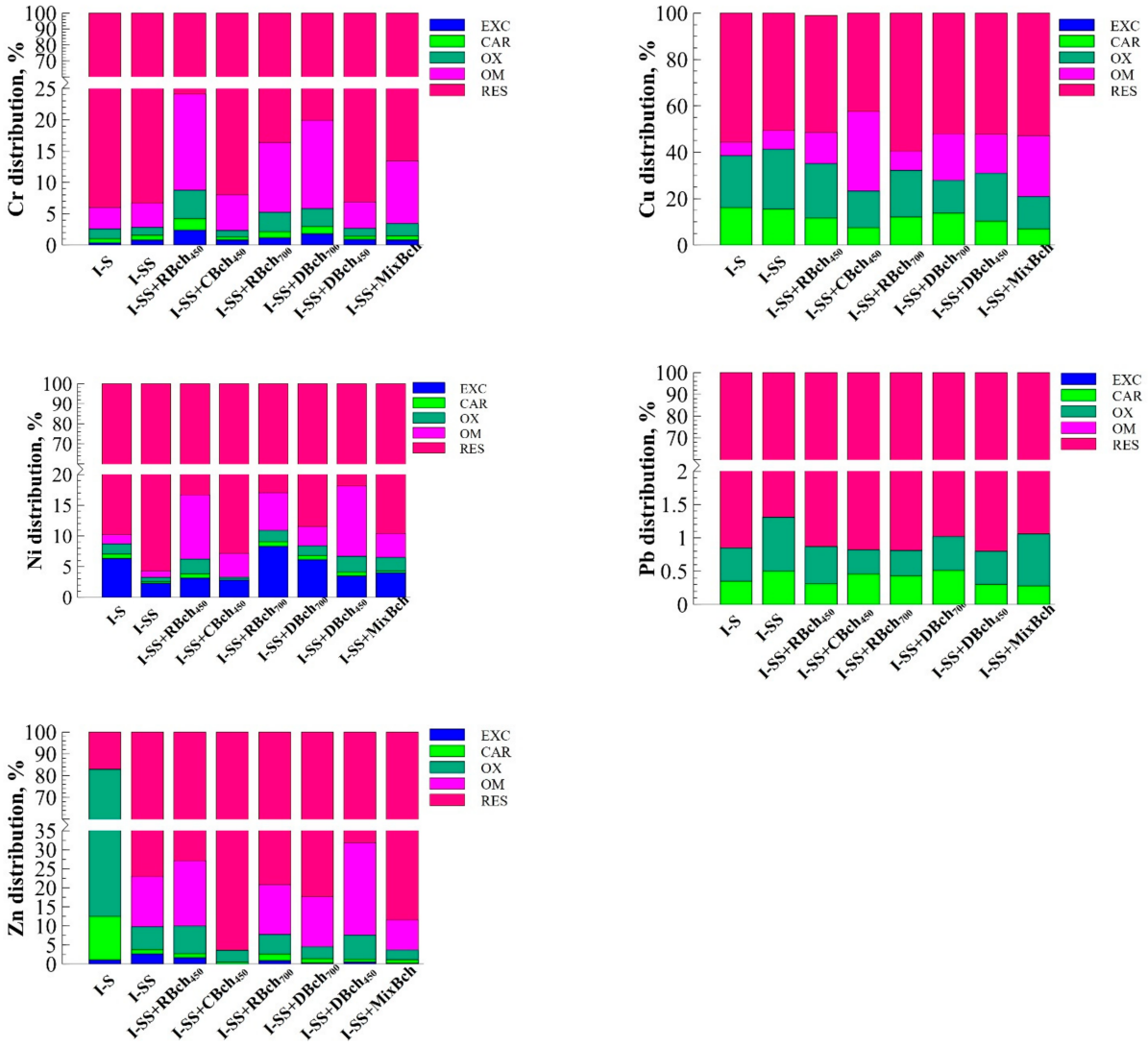

Figure 3. Distribution of heavy metals fractions in the soil after buckwheat vegetation. Note: I—buckwheat plant; I-S—soil; I-SS—sewage sludge; I-SS+RBch450—sewage sludge + rapeseed biochar at 450 °C; I-SS+CBch450—sewage sludge + corn stalk biochar at 450 °C; I-SS+DBch450—sewage sludge + digestate biochar at 450 °C; I-SS+RBch700—sewage sludge + rapeseed biochar at 700 °C; I-SS+DBch700—sewage sludge + digestate biochar at 700 °C; I-SS+MixBch—sewage sludge + mixed biochar was obtained by mixing an equal amount of each biochar origin.

Effect of biochar additive on heavy metals bioavailability in the soil after white mustard cultivation. After harvesting the white mustard plants, the same trend was observed after buckwheat harvesting when Cd was not determined in any investigated treatments. Organic soil amendments (sewage sludge and biochar) incorporation increased bonded to organic matter Cr amount (Figure 4). After the sewage sludge additive, we found a small part of Cr in the exchangeable fraction, while biochar incorporation increased the Cr amount bonded to Fe and Mn oxides. To immobilize Cr in the soil using various alkaline additives, it is recommended not to manifold them because when the soil pH rises above neutral, the Cr (III) oxidation process to Cr (VI) is enhanced, whose bioavailability and toxicity are significantly higher [48,49]. Various origin biochar decreased the Cu bonded to carbonates, while sewage sludge incorporation without biochar additive slightly increased Cu bonded to carbonates. It was determined that biochar produced from rape seed residues and digestate at 450 °C increased bonded to organic matter Cu amount while mixed rape seed biochar, mixed corn stalk biochar, and digestate biochar produced at a higher temperature (700 °C) gave an opposite observation. The application of biochar increased EXC, OX, and OM fractions of Ni in the soil. The ion exchange fraction is directly available to plants, and the changes in Ni indicate an increased bioavailability. Only two fractions of Pb were determined in the soil after the mustard plant was harvested: RES and bounded to Fe and Mn oxides. These two metal fractions are less available for plants, and metals are strongly bound to soil minerals and only could be released at high temperatures. Most of the Zn in all tested variants was found in non-bioavailable fractions (RES) or hard bioavailable fractions (OX, OM). The effect of different feedstock's biochar incorporations into the soil differentially affected the separate heavy metals.

Heavy metals immobilization efficiency and the potential ecological risk evaluation of soil after buckwheat and white mustard cultivation.

Heavy metals immobilization efficiency is presented in Figure 5. The negative values indicate that the number of heavy metals in the residual fraction was higher after biochar treatment than in the soil treated with sewage sludge alone. The heavy metals' existence could explain these findings in the different origins of biochar (Figure 1). On the other hand, predominating residual fraction reveals that metals are trapped in the soil and its amendments particles and do not pose a risk to plants and the environment. Different observations of HMs immobilization into the acid soil (pH < 5) were determined after the buckwheat (Figure 5A) and white mustard (Figure 5B) harvest. HMs immobilization efficiency in the soil after biochar treatment followed the order Ni > Cr > Pb > Cu > Zn and Ni > Pb > Zn > Cr > Cu after buckwheat and white mustard cultivation, respectively. Research on the effectiveness of HMs immobilization after soil treatment with biochar and in the presence of plants was not carried out within the framework of this work.

Soil contamination index C_f^i for individual heavy metals is presented in Table 7. Obtained results indicate that after buckwheat cultivation, the soil remains mostly clean, except Zn indicates low pollution and Cu—moderate pollution in I-SS+RBch$_{700}$ and I-S treatments, respectively. Opposite observations were noticed after the white mustard harvest. Cu and Zn posed the highest risk. Even though Cu and Zn could be either micronutrients or heavy metals depending on the concentration range, the excess of these elements in the soil negatively affects plants' growth and development [50]. Previously performed studies confirm the findings that various by-products (compost, sewage sludge, bio ash, and wastewater) from Lithuania show higher contaminations levels for Cu and Zn than for other metals [28,51–53]. Other authors who used white mustard for heavy metals phytoextraction demonstrated that Cu and Zn accumulation was lower than radish, perennial rye, and green pea [54]. It should be noted that white mustard demonstrated the highest Cu content in roots and determined the worst translocation factor among tested plants [54]. After the white mustard harvest, some thin root parts were mixed with the testing soil, and the obtained results were confirmed by the estimated contamination index C_f^i.

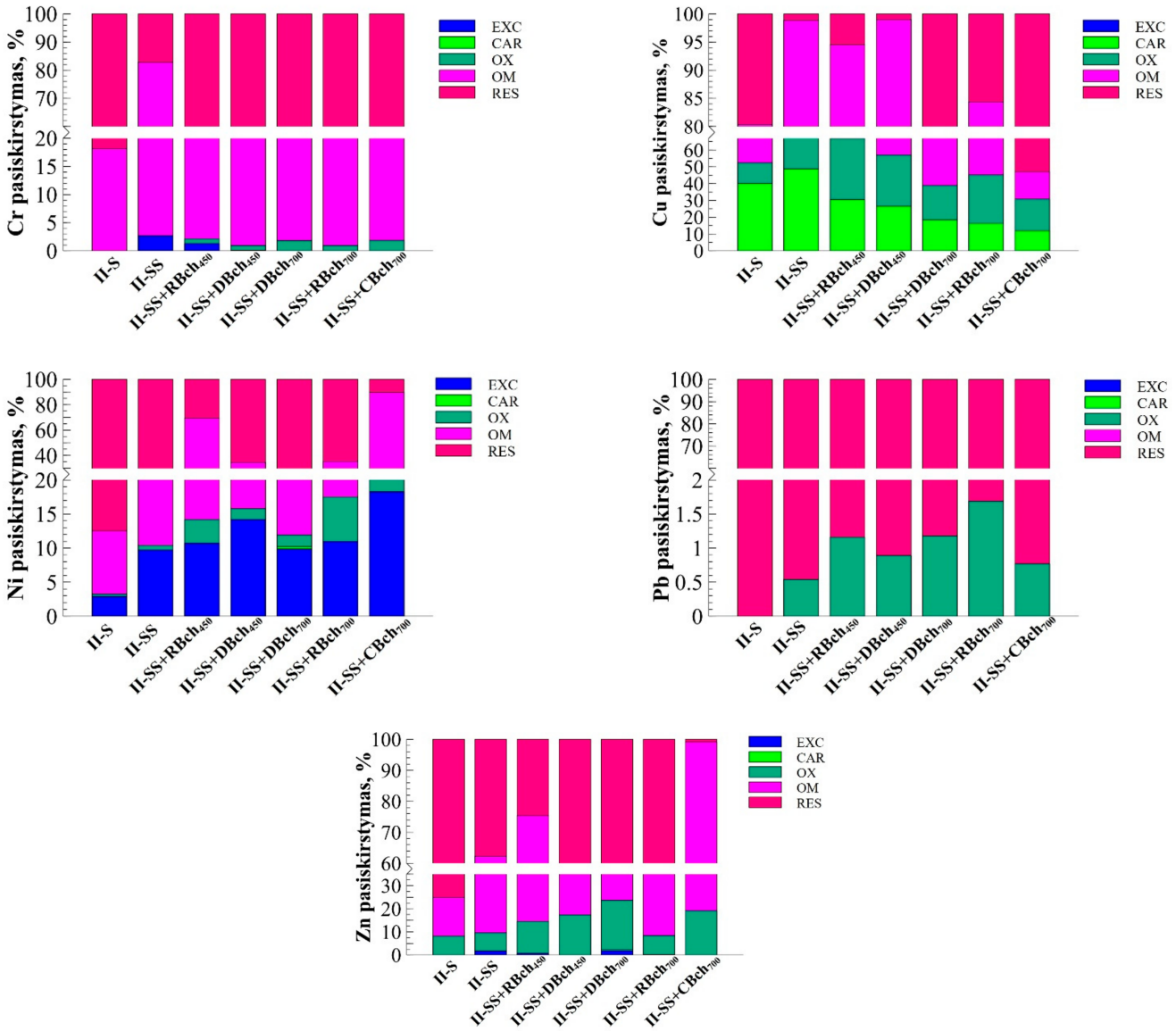

Figure 4. Distribution of heavy metals fractions in the soil after white mustard vegetation. Note: II—white mustard plant; II-S—soil; II-SS—sewage sludge; II-SS+RBch450—sewage sludge +rapeseed biochar at 450 °C; II-SS+DBch450—sewage sludge + digestate biochar at 450 °C; II-SS+RBch700—sewage sludge + rapeseed biochar at 700 °C; II-SS+CBch700—sewage sludge + corn stalk biochar at 700 °C; II-SS+DBch700—sewage sludge + digestate biochar at 700 °C.

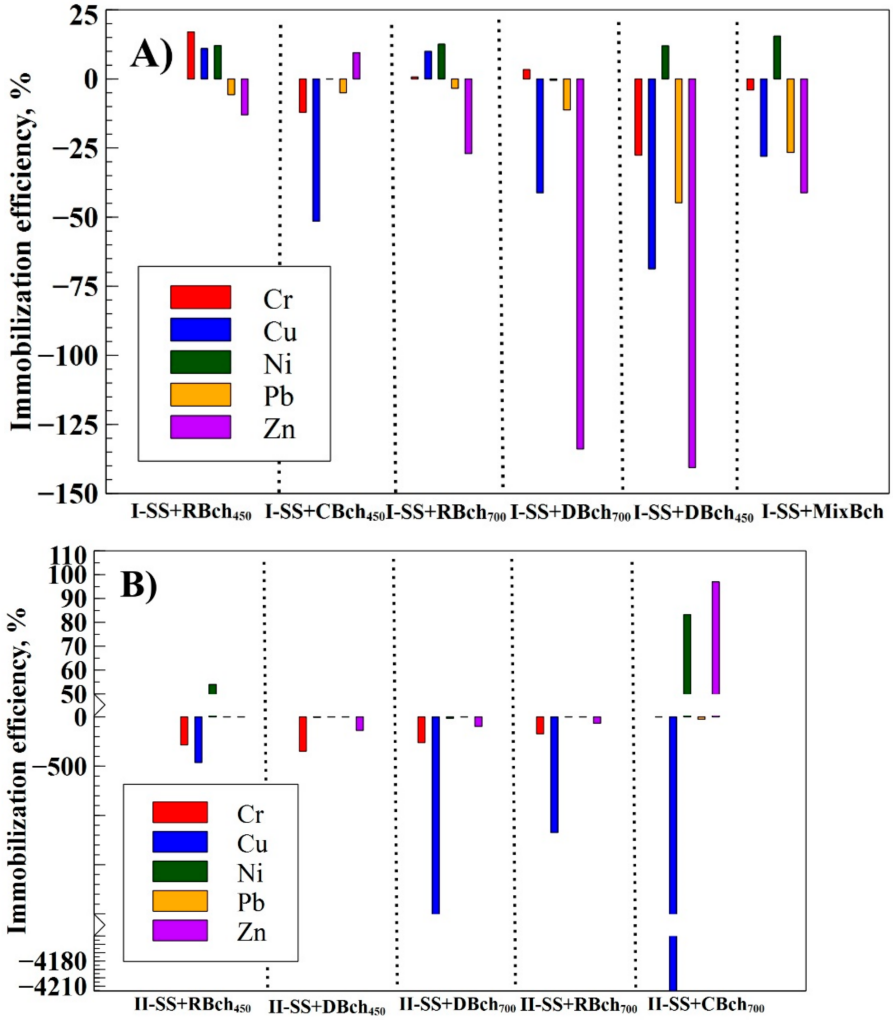

Figure 5. Heavy metals immobilization efficiency after buckwheat (**A**) and white mustard (**B**) vegetation.

Table 7. Contamination index C_f^i for individual heavy metal.

	Cr	Cu	Ni	Pb	Zn
I-S	0.06	0.8	0.11	0.01	4.86
I-SS	0.07	0.98	0.04	0.01	0.30
I-SS+RBch$_{450}$	0.32	0.98	0.2	0.01	0.37
I-SS+CBch$_{450}$	0.09	0.68	0.08	0.01	0.26
I-SS+RBch$_{700}$	0.20	1.36	0.21	0.01	0.04
I-SS+DBch$_{700}$	0.25	0.91	0.13	0.01	0.32
I-SS+DBch$_{450}$	0.07	0.89	0.22	0.01	0.13
I-SS+MixBch	0.16	0.92	0.12	0.01	0.22
II-S	0.22	4.10	0.14	0.00	0.33
II-SS	4.82	87.42	0.38	0.01	1.65
II-SS+RBch$_{450}$	0.52	17.32	2.29	0.01	3.07
II-SS+DBch$_{450}$	0.37	100.50	0.53	0.01	0.89
II-SS+DBch$_{700}$	0.32	2.41	0.38	0.01	1.34
II-SS+RBch$_{700}$	0.61	5.40	0.55	0.02	0.87
II-SS+CBch$_{700}$	1.05	0.89	8.78	0.01	121.98

Note: Different colours indicate the pollution degree: green = clean; orange = low pollution; blue = moderate pollution; violet = considerable pollution; and red = high pollution.

Soil potential ecological risk of the environment (RI) and ecological risk factor of a single metal (E_r^i) are presented in Figure 6. RI is used to assess the risk caused by heavy

metals in soils and sediments [31]. E_r^i for individual metals provides information on the amounts of heavy metals, which could cause danger to human health if it gets into the food chain [28]. In the soil after buckwheat cultivation, low RI was indicated. However, the soil after the white mustard harvest was distinguished according to the determined potential ecological risk to the environment. The soil RI after white mustard cultivation varied in a broad range from low to high risk. The treatments where sewage sludge and biochar were produced from rapeseed residues and digestate at a low temperature (450 °C) were distinguished by low Cu immobilization efficiency, and these treatments pose high RI. When T ≥ 600 °C showed a low risk to the environment, RI was determined to be caused by Cd in biochar decreasing with temperature increase [55]. Furthermore, it was investigated that sludge biochar ceramsite (SBC) does not cause contamination and could cause very low potential ecological risk from HMs when SBC is used in the environment [56]. It was demonstrated that chemical modifications could reduce the potential biocharrisk to the environment and decrease the heavy metals' bioavailability [57]. To sum up, the main factors determining the immobilization degree and metals distribution between different fractions are biochar surface area, pore size, which this study has not examined, feedstock, and producing and processing conditions.

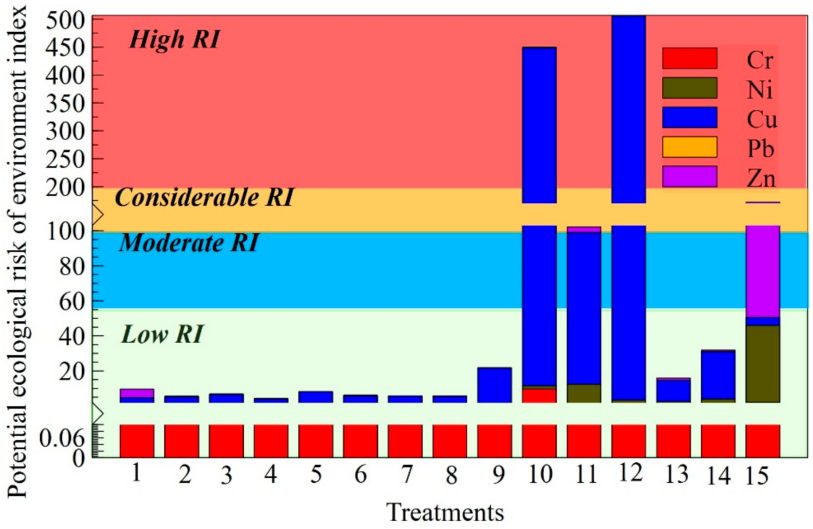

Figure 6. Potential ecological risk of the environment (RI) and ecological risk factor of a single metal (E_r^i). 1—I-S; 2—I-SS; 3—I-SS+RBch$_{450}$; 4—I-SS+CBch$_{450}$; 5—I-SS+RBch$_{700}$; 6—I-SS+DBch$_{700}$; 7—I-SS+DBch$_{450}$; 8—I-SS+MixBch; 9—II-S; 10—II-SS; 11—II-SS+RBch$_{450}$; 12—II-SS+DBch$_{450}$; 13—II-SS+DBch$_{700}$; 14—II-SS+RBch$_{700}$; 15—II-SS+CBch$_{700}$.

4. Future Directions

Biochar application is a promising strategy for the remediation of contaminated soil while ensuring sustainable waste management and biomass conversion to resources with higher added value. Biochar remediation of heavy metal-contaminated soil primarily depends on the properties of the soil, nature and production of biochar, kind of HMs, and cultivated plants. The main problem with the HMs immobilization is that at the same time, as they become less bioavailable, the total concentration remains the same or higher due to the metal's existence in the immobilization agents such as biochar. The process should be controlled and monitored because once the metals are transferred from non-bioavailable to bioavailable form, they could be leached to the groundwater, uptaken by plants or other living organisms, and cause damage to the environment. The current findings could be used for future research on HMs behavior in acidic soil after biochar treatment over time. Based on this study's results, it will be useful to carry out a long-term experiment with a focus on the HMs' bioavailability changing. It would be reasonable to continue research on the effectiveness of HMs immobilization after soil treatment with biochar and in the presence of plants. The search and analysis of the properties of alternative

feedstock for biochar production have direct practical value as well. Studying functional groups, porosity, and surface area of biochar can also expand its selective capabilities for efficient soil remediation caused by the pollution of particular metals. This study's findings could be applied to revise the existing requirements for the phytoremediation technology's application when the analysis shows that after specific treatment or amendments to the soil, there is no chemical activity of the heavy metals for a particular period.

5. Conclusions

Three different origin-derived biochar effects on heavy metals immobilization and two (buckwheat and white mustard) plants have been examined. It was determined that the low potential ecological risk (RI) of the environment after buckwheat cultivation while RI varied from low to high risk after the white mustard harvest. Organic amendments incorporated into the soil increase its pH, which is one of the most important factors determining the HMs' bioavailability. After biochar application, the predominant HMs fraction in the soil was residual (RES), indicating that HMs are unavailable for plant uptake. Biochar incorporation increased the amount of Cr, Ni, Cu, and Zn bonded to organic matter. HMs immobilization efficiency differs due to cultivated plant properties, uptake mechanism, and HMs accumulation features. Soil treatment and remediation conditions should be chosen according to future plants and soil use. The HMs immobilization efficiency in this study can be summarized as follows Ni > Pb > Cr > Zn > Cu in terms of the predominant RES fraction.

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