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The Use of *biochar* in the Remediation of *Pb*, *Cd*, and *Cu*-Contaminated Soils. The Impact of *biochar* Feedstock and Preparation Conditions on Its Remediation Capacity

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Abstract: Soil constitutes an important part of terrestrial ecosystems, prone to be adversely impacted by human activities. During the last decades, several methods have been developed aiming at its remediation, including the use of biochar as a soil amendment. In the present work, we have assessed the reduction of Pb, Cd, and Cu soil concentrations as a function of the mixing ratio of biochar added to soil, as well as the source of biochar employed. Furthermore, we have investigated the effects of biochar addition relating to the chemical forms of heavy metals (HMs) related to their bioavailability and mobility. The concentrations of HMs were determined by the BCR (European Community Bureau of Reference) sequential extraction procedure before and after biochar addition to the soils. Five types of biochar were used, obtained as by-products of sugarcane bagasse (B), bamboo (BB), rice straw (RSB), garden waste (GB), and paulownia (PB) treatment, respectively. Biochar derived from sugarcane (B) reduced the availability of metals, as it decreased their concentration in the acid extractable fraction, by 40.5, 66.6, and 50% for Pb, Cd, and Cu, respectively. In addition, (B) application increased the residual fraction of Cu and Pb by 9% and 24.8%, respectively. Biochar derived from garden residues (GB) and paulownia plant (PB) dramatically increased the residual fraction of Cd over 97%, minimizing its availability. Sugarcane-derived biochar appeared to significantly increase Cu and Pb residual fraction concentrations and decrease available Cd concentration. Similar changes are caused by the types of biochar in the following order: biochar from sugarcane > paulownia > garden wastes > bamboo > rice straw. The redistribution of HM concentrations causes a significant improvement of environmental quality in polluted soils, as it limits the mobility and availability of toxic metals to the soil ecosystem. The use of biochar is a low-cost and eco-friendly method for the remediation of contaminated with HMs soils in the framework of a circular economy.

Keywords: heavy metals; BCR fractionation method; bioavailability; mobility

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1. Introduction

1.1. The Soil as a Background for Human Activities

The soil represents the "living skin" of the planet, specifically, it is the upper layer of the crust. Its main components are inorganic matter consisting of various minerals and organic matter (OM), including a variety of living micro-organisms, along with air and water [1,2].

The importance of the soil should not be overlooked because its ecosystem services support life on the planet [3]. The soil is the substrate for sustaining all plant species, as they absorb the inorganic nutrients and water that are necessary for their growth [4,5]. It composes a natural filter for water and controls the surplus water rejection. It stores quantities of organic carbon as soluble organic carbon (SOC) [6]. Finally, soil contributes to

the conservation of the biodiversity, whereas different species spanning microorganisms and upper mammals interact in the numerous soil micro-habitats [2,7].

The effect of human activities on soil conditions is mainly harmful [3], exceeding the capabilities of nature to heal itself. Among the ecological changes affecting soil quality, the abrupt anthropogenic disturbances of the biogeochemical cycles of critical chemical elements, including carbon (C), nitrogen (N), phosphorus (P), and other metals is prominent [8].

The result is the creation of remarkable environmental phenomena, namely: climate change, acidification of the oceans because of the increased CO_2 emissions, depletion of stratospheric ozone, and depletion of renewable and non-renewable sources relating to food [9] and environmental pollution (air, water, soil), particularly from non-degradable pollutants that are transferred through the food chain to living organisms (bioaccumulation) [10]. Furthermore, the widespread dispersion of pollutants, such as organic pesticides [11] and fertilizers, concrete, ash, plastics, and their degradation products [8], along with invasive species population growth, have led to a massive extinction of various species and a loss of biodiversity [5,12].

1.2. The Heavy Metals (HMs) Soil Pollution

Pollution of soil by HMs is a serious environmental problem, associated with industrial activities, land use patterns, local climatic conditions, socio-economic development issues, and elevated population densities [13,14]. Heavy metals are metals and metalloids that have an atomic mass higher than 20 and an elemental density higher than 5 g cm^{-3} [1,13]. The most common HMs detected in the environment are cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), uranium (U), and zinc (Zn) [15,16]. Nowadays, the term "potentially toxic elements" (PTEs) is used instead of the older term "heavy metals". Heavy metals have adverse health effects when their concentrations exceed the permitted levels [16,17]. Potentially toxic elements pose many risks to human beings and the environment [17,18]. They have a long half-life and remain active in the environment for a long time without biodegrading. They are a cause of cancer and often leukemia in children and adults [19,20]. They are responsible for problems in biochemical systems, as they interfere with the normal functioning of enzymes (biocatalysts) [21].

The mobility and availability of HMs in the soil is determined by the nature of HMs, as well as by the physical and chemical characteristics of the soil [22]. The concentrations of HMs found in the soil may result from natural activities, mostly erosion of HM-containing rocks and volcanism [14]. In addition, the soil concentrations of HMs may have an anthropogenic component [23]. This pollution of soil by HMs is nowadays an emerging environmental problem. Soil pollution is gradually aggravated because of fast urbanization, rapid population growth, and increasing industrialization [24]. Moreover, intensive anthropogenic activities, such as mining, smelting, and usage of various metal-containing substances and materials, as well as their degradation products, have a negative effect on soil quality [25,26]. Heavy metals can reduce crop production or significantly inhibit the quality of cultivated products [27,28]. In the research of Houri et al. [29], an adverse effect of HMs on ordinary photosynthetic activities of the plants is presented. Cd stress can reduce photosynthetic rate and pigment levels, ascorbate peroxidase, guaiacol peroxidase, catalase, and superoxide dismutase enzyme activities, increasing g malondialdehyde level [30]. The antioxidants in citrus plants after exposure to high Pb and Cu concentrations were significantly increased as the metals promote lipid peroxidation, disrupt membrane integrity, reduce growth and photosynthesis, and inhibit mineral nutrition Pb and Cu treatments [31].

1.3. The Use of Biochar for Remediation of HMs Polluted Soils

Generally, there are different chemical and biological methods and strategies that aim to the effective soil remediation and removal of HMs [32,33]. Zaheer et al. [34] have studied the beneficial effect of the appropriate amount of biochar which, when incorporated into

the soil, significantly improved the quality characteristics and yield of crops. Jakubus and Bakinowska [20] found that the use of compost and fly ash influenced the content of Cu and Zn in the soil, along with the bioconcentration factor, as well as the bioavailable amount of metals and health risk index. In several studies, the use of different forms of carbon is proposed for the reduction of HM availability [35–37]. In a study by Li et al. [38], it was noted that the techniques of soil remediation can be classified in the following categories: (a) ex situ remediation, which requires the excavation of the contaminated soil and the subsequent treatment of pollutants, as well as (b) in situ remediation, which involves the on-site treatment of the pollutant-target [9]. Furthermore, the remediation can be carried out by certain species of microorganisms [39]. Comparatively, in situ remediation offers certain possible technical, financial, and environmental advantages [40,41]. Even though the choice of the most appropriate method depends on the soil characteristics, the HM concentration and the intended use of the contaminated soil must be taken into account [42,43].

Banik et al. [44] have compared the effect of biochar on nutrient availability with manure or other soil additives that are high in OM, although there is some concern about the increase in CO_2 due to the use of biochar in crops [45]. Ghorbani et al. [46] found that biochar can make a considerable contribution to raising the effectiveness of organic N-fertilizers, enhancing grain yield of wheat. Subsequent research efforts have proven that biochar can reduce the HM concentrations in contaminated soil [47,48]. Specifically, biochar is capable of effectively absorbing the HM cations from water and ties them up in its mass [49,50]. For this reason, biochar has been considered as a promising remediation material for the reduction of eco-toxicity in contaminated soils [51–53].

The use of biochar is often associated with:

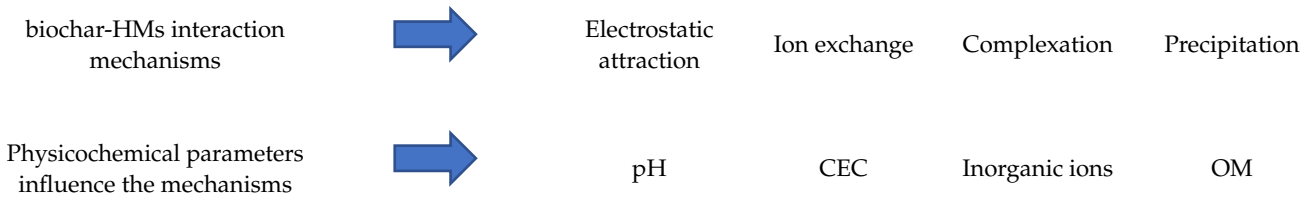
(a) charcoal, which is a material of solid nature where the carbon composition often exceeds 70%, formed by heating up under anoxic conditions, OM coming from plants, wood, or animal tissues or bones [54].
(b) decarbonized OM, which comes from the thermochemical biomass conversion under restricted oxygen conditions [55].

Pyrolysis is the most widely used thermochemical method of decomposition of biomass at temperatures over 300–700 °C in the absence of oxygen [56]. In addition, two other methods that are usually used for biochar production involve hydrothermal carbonization and gasification.

Through the procedure of pyrolysis, the products can be solid, liquid, or gaseous, and their composition depends on the characteristics of the procedure [43]. Pyrolysis is characterized by: (a) the residence time of biomass under pyrolytic conditions, (b) the maximum temperature which decisively affects the capacity to lock up carbon and the stability of biochar, and (c) by the heating rate (intensity).

Based on the above, pyrolysis is divided into three categories: (a) slow pyrolysis, (b) intermediate pyrolysis, and (c) fast pyrolysis. According to He et al. [55], the pyrolysis conditions decisively affect the physicochemical properties of biochar.

In this way, however, pyrolysis also affects the effectiveness of biochar towards the treatment of HMs [57]. More specifically, it causes variations in the pH values, the organic carbon (OC) content of the biochar, the cation exchange capacity (CEC), the porosity of the biochar, the specific contact surface, the functional groups, and the mineral content [58]. As a result, these changes in the physicochemical properties of the biochar in combination with the different composition of the soils modify the HM–biochar interactions and essentially the mobility and bioavailability of HMs after the biochar application in the soil [59]. The results so far suggest that biochar properties have a strong effect on the mobility and the bioavailability of HMs in biochar-treated soils [60]. They affect HM concentrations either directly, through specific metal–soil interactions, or indirectly, by affecting the properties of the soil where they are applied [61]. In the following graph are presented biochar–HM interaction mechanisms and physiochemical parameters that influence these mechanisms.



In detail, the biochar–HM interaction mechanisms are listed below [41]:

- **Electrostatic attraction**: recent research proves that a high degree of biochar electronegativity attracts positively charged groups. The strength of this attraction depends on the surface load of the negatively charged groups [62]. The overall negative charge of biochar grows with the increase in pH [13,63].
- **Ion exchange**: in general, biochar is characterized by high CEC and, consequently, by the presence of free cations, for example Ca^{2+} and Mg^{2+}. Between biochar and soil, an exchange of ions may be established [1,14]. The increase in biochar CEC could increase its adsorption capacity for HMs. The oxygen-containing functional groups in biochar, mostly carboxyl groups (-COOH), can also bind metal ions through ion exchange [64].
- **Complexation**: the functional groups on the surface of the biochar can immobilize HMs, forming stable complexes [58]. The functional groups provide binding points for HMs to form association complexes, increasing the rate of the specific adsorption [41,65]. This is more effective for biochar possessing a low mineral content. The complexation is enhanced by the increase in Fe, Mn, and C content. In this way, insoluble and stable metal complexes are formed. Additionally, inorganic ions containing Si, S, or Cl present in biochar, can form complexes with HMs, further reducing their mobility in the soil.
- **Precipitation**: biochar contains minerals that can bind HMs, yielding insoluble sediments. Indeed, precipitation has been observed in the case of absorption of inorganic phosphorus by biochar [41]. Nevertheless, after the modification of the soil by addition of biochar, its characteristics, including pH, SOC, sulphate concentrations, and CEC, may change [1,38], affecting the HMs–biochar interactions and, finally, the mobility and bioavailability of HMs in the soil.
- **pH**: pH has a significant influence on the chemistry of both soil and biochar [13]. More specifically, it affects the speciation and the mobility of HMs in the soil [66]. Generally, biochar is usually alkaline, and its application in the soil increases its pH, especially when the contaminated soil is acidic. In this way, however, the hydrolysis of HMs is increased, leading to an enhanced adsorption by the soil and an accelerated transformation of oxidizable and residual fractions of the pollutants. In addition, the increase in pH enhances the complexation of HMs [10], resulting in a decrease in the HM risks.
- **Cation Exchange Capacity (CEC)**: since the CEC of biochar is particularly high, it enhances the corresponding property of the soil when added to it. It has been suggested that the reduction in HM concentration and solubility in the soils is partly due to the high proportion of cations exchange points on the biochar surface [1,13].
- **The presence of inorganic elements**: biochar may contain high concentrations of elements, such as Na, K, Mg, Ca, and P [67]. These inorganic elements are free in the contaminated soil and, possibly, after adding biochar, contribute to cation-exchange processes between biochar and soil [47]. Additionally, the oxides of Ca, Si, and Mn that are contained in biochar may function as additional absorption points for metal cations present in the soil.
- **Change in the organic carbon content**: the addition of biochar to the soil results in a release of OC dissolved. In this way, a reduction of the mobility and bioavailability of HMs could be caused by the enhancement of complexation between biochar functional groups and HMs [58].

According to Manyà et al. [68], pyrolysis results in the formation of three new products: (1) the desired biochar, (2) a volatile fraction that can be compressed and give bio-oils, and (3) various gaseous products, mostly CO, CO_2, and CH_4 και H_2.

The study of the possible effects of the five types of biochar derived from various raw materials possessing different physicochemical properties constitutes the purpose of the present study, aiming at reducing the concentration of HMs in soils.

2. Materials and Methods

The basic features of the different types of soils and biochar that have been applied are listed in Table 1. The soil samples used had an acid reaction and high percentage of organic carbon.

Table 1. The contaminated soils and the basic features of biochars used.

Contaminated Soils				
Soil pollution source	Metal foundry wastewater effluent	Copper smelter gaseous emissions	Wastes disposal	Mining activities
HMs pollutants	Cd, Cu, and Pb	Cd, Cu, and Pb	Cd, Cu, Pb, and Zn	Cd, Cu, Pb, and Zn
pH	5.8	<6.0	5.5	5.5
OC (g kg^{-1})	14.5	10	23.4	23.4
Physicochemical properties of biochar types				
Feedstock	sugarcane bagasse	Bamboo rice straw	garden wastes	paulownia by-products
Treatment method/°C	pyrolysis/450 °C	pyrolysis/750 °C pyrolysis/500 °C	(1) pyrolysis/400 °C (2) pyrolysis/600 °C	pyrolysis/700–800 °C
Particle size	<2 mm	(1) < 0.25 mm (2) < 1 mm	<0.1 mm	<0.1 mm
References	[69]	[51]	[70]	[71]

Chemical fractionation of HMs was carried out to determine their bioavailability and mobility by sequential extraction [72]. The fractions of the metals, which we consider determining their availability and mobility, are usually the water-soluble and the exchangeable.

Awad et al. [70] used 1 g of each soil sample or mixture of soil and biochar into a 100 mL polycarbonate tube and the following steps: the acid-soluble fraction using 0.11 M acetic acid, the Fe/Mn oxide bound fraction using 0.1 M hydroxylamine hydrochloride (pH 2), the OM bound fraction using 30% w/v H_2O_2 and 1 M CH_3COONH_4, and the residual fraction using HNO_3-HF-$HClO_4$. Lu et al. [51] followed a four-step BCR procedure as follows: 0.11 M acetic acid to extract the acid extractable fraction; 0.1 M hydroxylamine hydrochloride (pH 2) to extract the fraction bound to Fe/Mn oxides; 30% m/v H_2O_2 and 1 M CH_3COONH_4 to extract the fraction bound to OM; and HNO_3-HF-$HClO_4$ to extract the residual fraction of the metals.

The methods used by the researchers mostly included four stages, simulating the BCR method and its many modifications. The method of Tessier et al. [73] suggests five steps, giving satisfactory results for five different fractions of metals, namely: (a) acid extractable, (b) bound to carbonates, (c) bound on Fe/Mn oxides, (d) organic fraction, and (e) residual fraction. Nie et al. [69] followed the five-step sequential extraction method to assess the effect of biochar treatments on the bonding forms and redistribution of Cd, Cu, and Pb in soil. The heavy metals obtained from each step were designated as exchangeable (F1), bound to carbonates (F2), bound to Fe/Mn oxides (F3), bound to organics (F4), and bound to residual (F5), respectively. The concentrations of the metal fractions were quantified using an atomic absorption spectrometer or an ICP-OES.

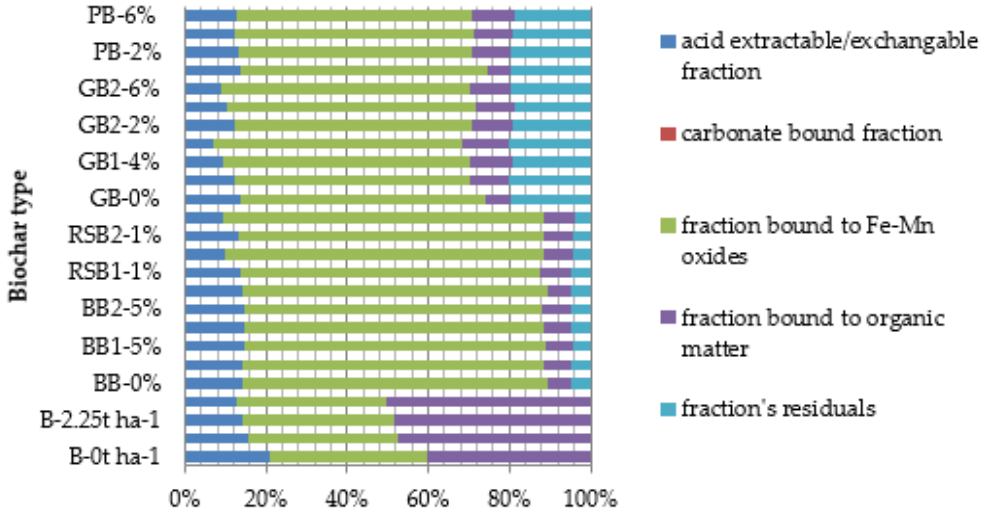
In several studies, the available and water-soluble metals concentrations were extracted using the DTPA and the $CaCl_2$ extracting solutions [36]. These concentrations of metal trace elements are compared to those extracted in the corresponding fractions of the

fractional extraction methods. Additionally, in the majority of methods used to extract the total and residual amount of metals, a mixture of strong acids is used. A strongly alkaline environment may be used to rapidly extract the total mineral concentration [74].

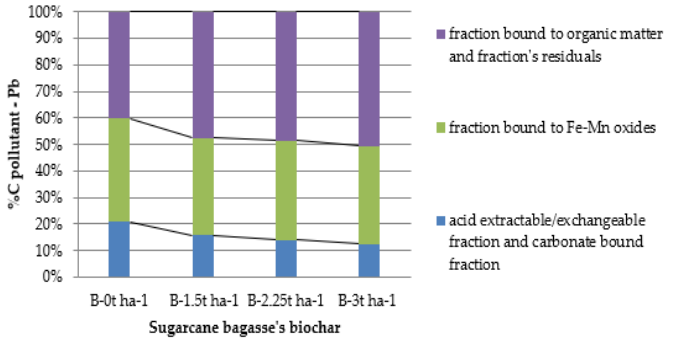
3. Results

Figures 1–3 show the fractions of Pb, Cd, and Cu, respectively. The distribution of these metals was initially examined overall for all fractions (Figures 1a, 2a and 3a) and, subsequently, for each fraction of the methods used. It must be considered that the percentage held by the acid fraction in relation to the total concentration depends both on the nature of the metal and on the nature of the added biochar. Figure 1b–f, Figures 2b–f and 3b–f show the different fractions of Pb, Cd, and Cu, respectively, labeled as b, c, d, e, and f according to the type of biochar used, derived from sugarcane, bamboo, rice straw, garden waste, and paulownia, respectively.

- **Lead (Pb)**



(**a**)



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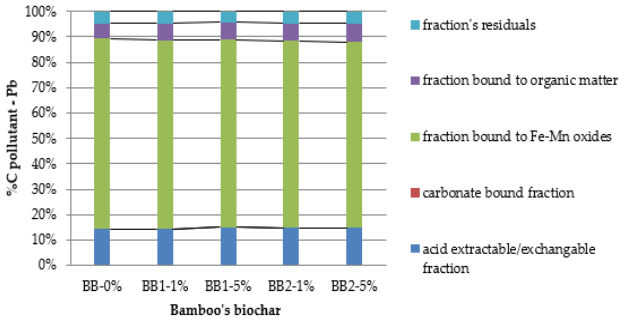


(**c**)

Figure 1. *Cont.*

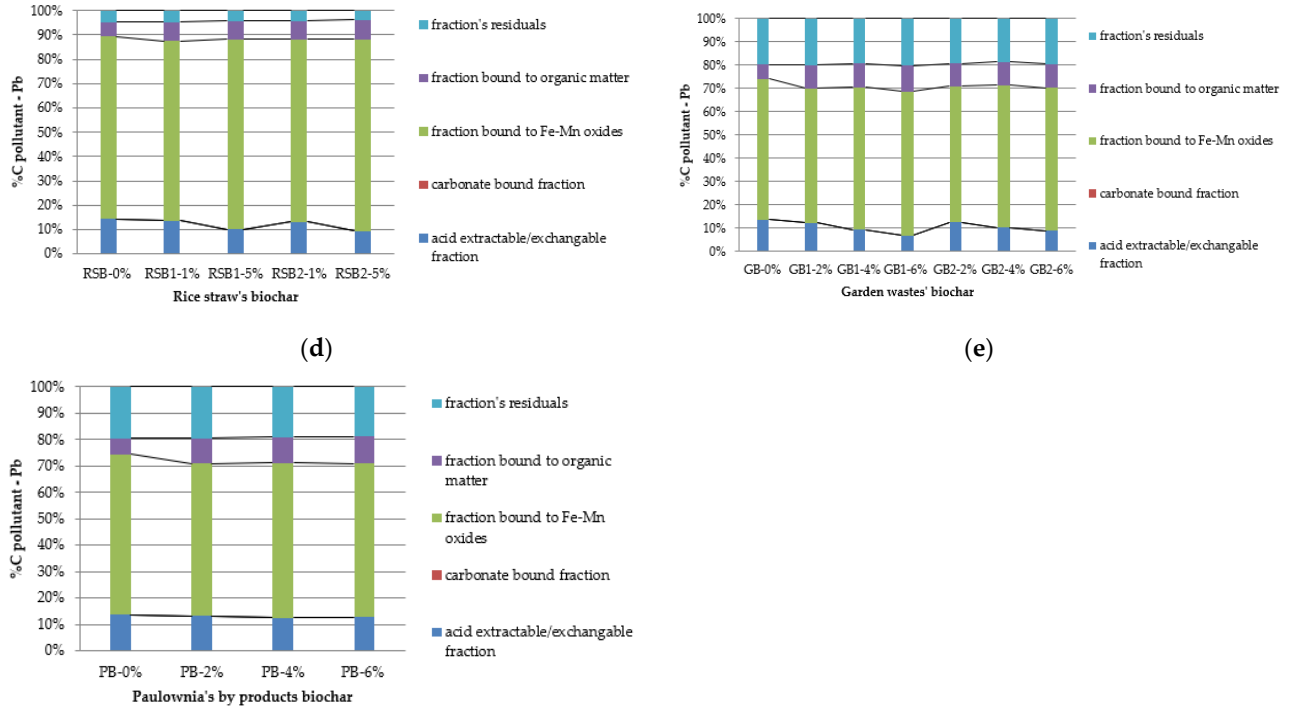
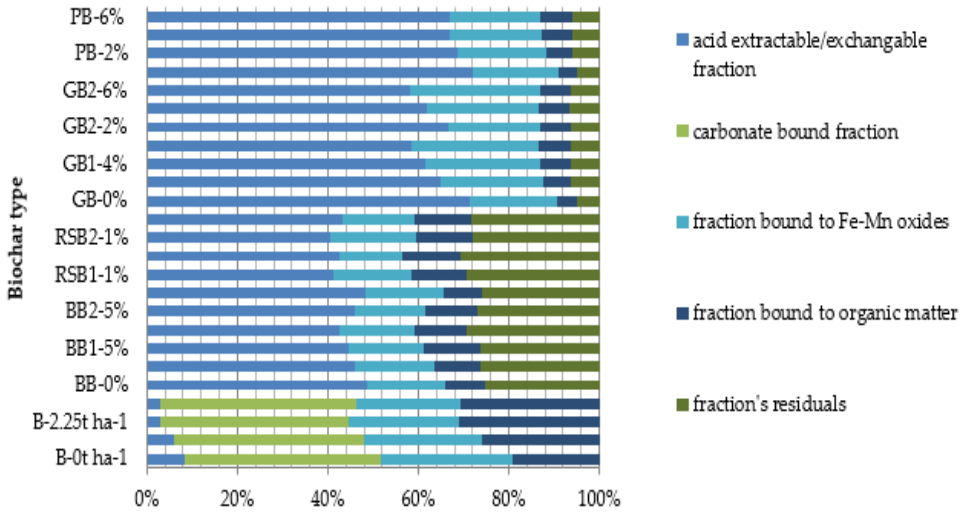


Figure 1. (**a**) Distribution of Pb fractions according to BCR method. (**b**) Impact of biochar additive (sugarcane bagasse biochar(B)) at 0, 1.5, 2.25, and 3 t ha^{-1} amounts on the immobilization of Pb (mg kg^{-1}) in contaminated soils. (**c**) Impact of biochar additives (bamboo biochar sifted at particle size <0.25 mm (BB1) and <1 mm (BB2)) at 0, 1, and 5% on the immobilization of Pb (mg kg^{-1}) in contaminated soils. (**d**) Impact of biochar additives (rice straw biochar sifted at particle size <0.25 mm (RSB1) and <1 mm (RSB2)) at 0, 1 and 5% on the immobilization of Pb (mg kg^{-1}) in contaminated soils. (**e**) Impact of biochar additives (garden wastes biochar pyrolyzed at 400 °C (GB1) and 600 °C (GB2)) at 0, 2, 4, and 6% percentages the immobilization of Pb (mg kg^{-1}) in contaminated soils. (**f**) Impact of biochar additive (paulownia by- products biochar (PB)) at 0, 2, 4, and 6% percentages the immobilization of Pb (mg kg^{-1}) in contaminated soils.

- **Cadmium (Cd)**



(**a**)

Figure 2. *Cont.*

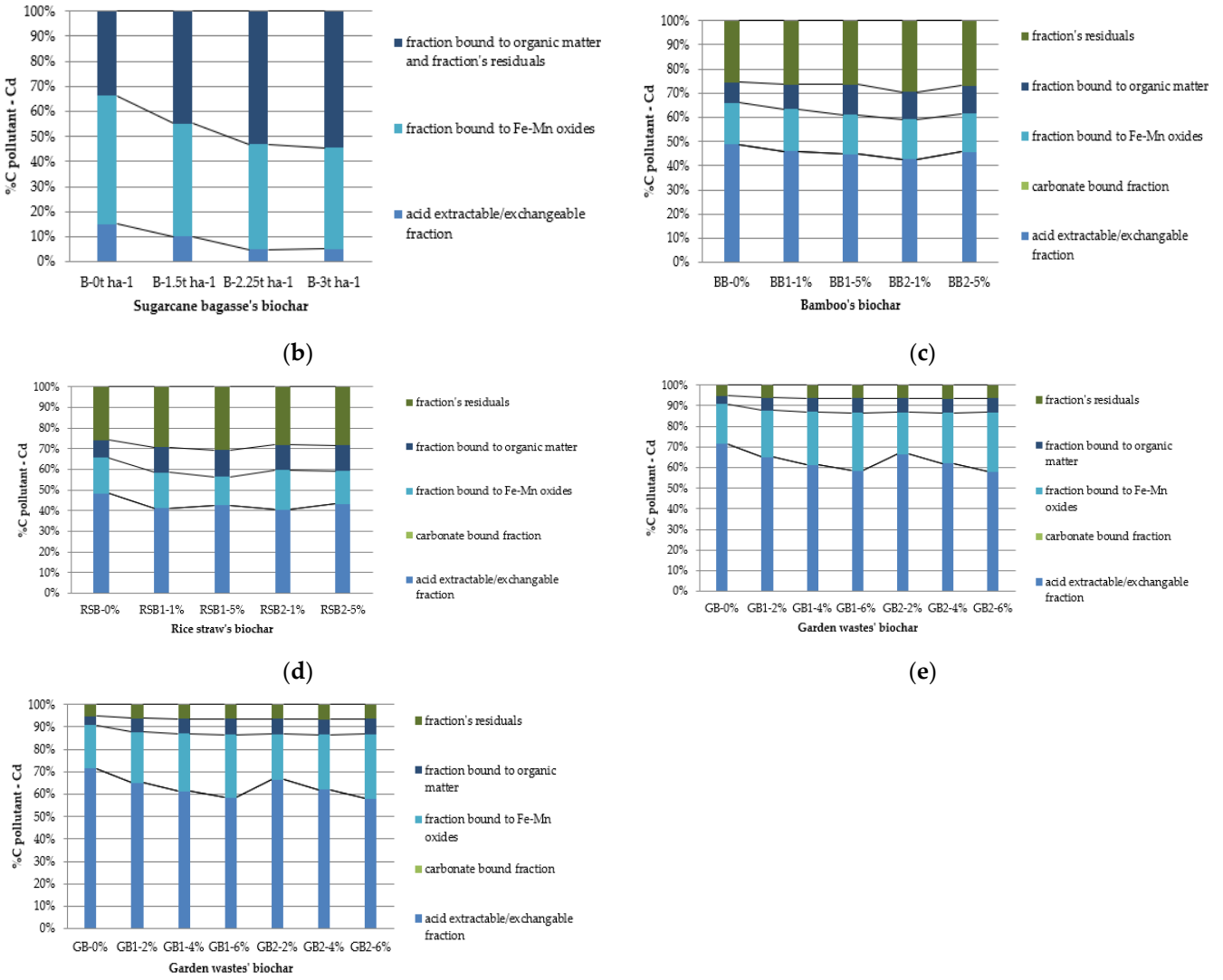


Figure 2. (**a**) Distribution of Cd fractions according to BCR method. (**b**) Impact of biochar additive (sugarcane bagasse biochar(B)) at 0, 1.5, 2.25 and 3 t ha^{-1} amounts on the immobilization of Cd (mg kg^{-1}) in contaminated soils. (**c**) Impact of biochar additives (bamboo biochar sifted at particle size <0.25 mm (BB1) and <1 mm (BB2)) at 0, 1 and 5% on the immobilization of Cd (mg kg^{-1}) in contaminated soils. (**d**) Impact of biochar additives (rice straw biochar sifted at particle size <0.25 mm (RSB1) and <1 mm (RSB2)) at 0, 1 and 5% on the immobilization of Cd (mg kg^{-1}) in contaminated soils. (**e**) Impact of biochar additives (garden wastes biochar pyrolyzed at 400 °C (GB1) and 600 °C (GB2)) at 0, 2, 4, and 6% percentages the immobilization of Cd (mg kg^{-1}) in contaminated soils. (**f**) Impact of biochar additive (paulownia by products biochar (PB)) at 0, 2, 4, and 6% percentages the immobilization of Cd (mg kg^{-1}) in contaminated soils.

- **Copper (Cu)**

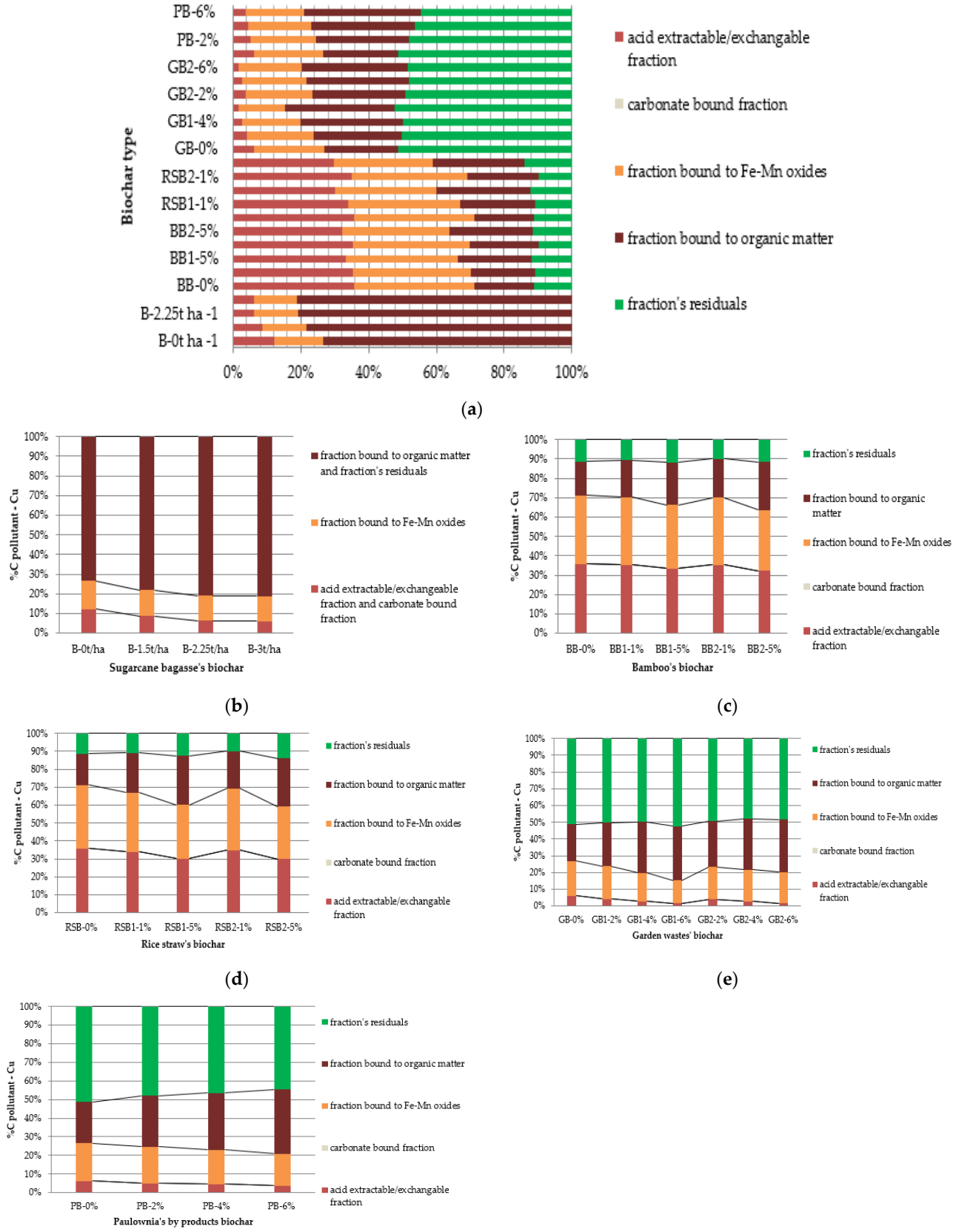


Figure 3. (**a**) Distribution of Cu fractions according to BCR method. (**b**) Impact of biochar additive (sugarcane bagasse biochar(B)) at 0, 1.5, 2.25, and 3 t ha^{-1} percentages on the immobilization of Cu (mg kg^{-1}) in contaminated soils. (**c**) Impact of biochar additives (bamboo biochar sifted at particle

size <0.25 mm (BB1) and <1 mm (BB2)) at 0, 1, and 5% on the immobilization of Cu (mg kg^{-1}) in contaminated soils. (**d**) Impact of biochar additives (rice straw biochar sifted at particle size <0.25 mm (RSB1) and <1 mm (RSB2)) at 0, 1, and 5% on the immobilization of Cu (mg kg^{-1}) in contaminated soils. (**e**) Impact of biochar additives (garden wastes biochar pyrolyzed at 400 °C (GB1) and 600 °C (GB2)) at 0, 2, 4, and 6% percentages the immobilization of Cu (mg kg^{-1}) in contaminated soils. (**f**) Impact of biochar additive (paulownia by products biochar (PB)) at 0, 2, 4, and 6% percentages the immobilization of Cu (mg kg^{-1}) in contaminated soils.

3.1. Acid Extractable/Exchangeable Fraction

In Table 2, the acid fraction of the three metals studied is presented.

Table 2. Acid extractable fraction of Pb, Cd, and Cu (mg kg^{-1}) after biochar application.

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Sugarcane bagasse (B)	450	<2	0 t ha^{-1}-control	74a	0.12a	34a
			1.5 t ha^{-1}	55ba	0.08ab	24ab
			2.25 t ha^{-1}	49ba	0.04b	17b
			3 t ha^{-1}	44b	0.04b	17b
Bamboo (BB)	700	<0.25	0%-control	71a	0.4a	190a
			1%	71a	0.4a	175ab
			5%	69a	0.4a	158ab
		<1	1%	71a	0.4a	175ab
			5%	65a	0.4a	144b
Rice straw (RSB)	500	<0.25	0%-control	71a	0.4a	190a
			1%	68a	0.3a	173b
			5%	51b	0.3a	127c
		<1	1%	67a	0.3a	180b
			5%	49b	0.4a	123c
Garden wastes (GB)	400	<0.1	0%-control	138a	1.8a	2a
			2%	120a	1.5a	1.3b
			4%	95ba	1.4a	0.9c
			6%	67b	1.4a	0.5c
	600		2%	125a	1.6a	1.3b
			4%	104a	1.4a	0.9c
			6%	86ba	1.4a	0.5c
Paulownia (PG)	700–800	<0.1	0%-control	137a	1.9a	2a
			2%	126a	1.7a	1.7ab
			4%	125a	1.6a	1.5ab
			6%	123a	1.6a	1.3b

Note: In the case of the applied sugarcane biochar to the contaminated soil samples, the metal concentrations in acid extractable and carbonate bound fractions (unstable metal fractions) have been calculated together, as is also the case for the organic and residual metal fractions (stable metal fractions).

3.2. Carbonate Bound Fraction

In Table 3, the carbonated bound fractions of Pb, Cd, and Cu (mg kg^{-1}) after biochar application are presented.

Table 3. Carbonate bound fraction of Pb, Cd, and Cu (mg kg^{-1}) after biochar application.

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Sugarcane bagasse (B)	450	<2	0 t ha^{-1}-control	74a	0.12a	34a
			1.5 t ha^{-1}	55ba	0.08b	24b
			2.25 t ha^{-1}	49b	0.04c	17c
			3 t ha^{-1}	44b	0.04c	17c
Bamboo (BB)	700	<0.25	0%-control	0	0	0
			1%	0	0	0
			5%	0	0	0
		<1	1%	0	0	0
			5%	0	0	0
Rice straw (RSB)	500	<0.25	0%-control	0	0	0
			1%	0	0	0
			5%	0	0	0
		<1	1%	0	0	0
			5%	0	0	0
Garden wastes (GB)	400	<0.1	0%-control	0	0	0
			2%	0	0	0
			4 %	0	0	0
			6%	0	0	0
	600		2%	0	0	0
			4%	0	0	0
			6%	0	0	0
Paulownia (PG)	700–800	<0.1	0%-control	0	0	0
			2%	0	0	0
			4%	0	0	0
			6%	0	0	0

Note: In the case of the applied *bamboo*, *rice straw*, *garden wastes*, and *paulownia biochar* the concentration of the metals carbonate bound metal fraction is considered negligible.

3.3. Fe/Mn Oxides Fraction

In Table 4, the fraction of Pb, Cd, and Cu (mg kg^{-1}) bounded in Fe/Mn oxides after biochar application is presented.

Table 4. Fe/Mn oxides fraction of Pb, Cd, and Cu (mg kg^{-1}) after biochar application.

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Sugarcane bagasse (B)	450	<2	0 t ha^{-1}-control	136a	0.4a	40a
			1.5 t ha^{-1}	128a	0.4a	36a
			2.25 t ha^{-1}	130a	0.3b	35a
			3 t ha^{-1}	128a	0.3b	35a
Bamboo (BB)	700	<0.25	0%-control	377a	0.2a	187a
			1%	369a	0.1b	172ab
			5%	343a	0.1b	155ab
		<1	1%	356a	0.1b	172a
			5%	321a	0.1b	141b
Rice straw (RSB)	500	<0.25	0 %-control	377a	0.2a	187a
			1%	369a	0.1b	170ab
			5%	400a	0.1b	125b
		<1	1%	386a	0.2a	177ab
			5%	412a	0.1b	121b

Table 4. *Cont.*

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Garden wastes (GB)	400	<0.1	0 %-control	620a	0.5a	6.9a
			2%	561b	0.5a	6.3a
			4%	614a	0.6ba	5.5b
			6%	593ab	0.7b	4.3b
	600		2%	583ab	0.5a	6.6a
			4%	616a	0.6ba	6.4a
			6%	593ab	0.7b	6.4a
Paulownia (PG)	700–800	< 0.1	0 %-control	609a	0.5a	6.7a
			2%	549b	0.5a	6.5a
			4%	593ab	0.5a	6.3a
			6%	558b	0.5a	5.9a

3.4. Organic Bound Fraction

In Table 5, the organic bound fractions of Pb, Cd, and Cu (mg kg^{-1}) after biochar application are presented.

Table 5. Organic bound fraction of Pb, Cd, and Cu (mg kg^{-1}) after biochar application.

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Sugarcane bagasse (B)	450	<2	0 t ha^{-1}-control	141a	0.3b	205a
			1.5 t ha^{-1}	165ba	0.4a	218ab
			2.25 t ha^{-1}	168ba	0.4a	224ab
			3 t ha^{-1}	176b	0.4a	225b
Bamboo (BB)	700	<0.25	0%-control	30a	0.1a	60a
			1%	34a	0.1a	53a
			5%	31a	0.1a	56a
		<1	1%	34a	0.1a	49b
			5%	33a	0.1a	52a
Rice straw (RSB)	500	<0.25	0%-control	30a	0.1a	60a
			1%	38b	0.1a	56b
			5%	38b	0.1a	52b
		<1	1%	38b	0.1a	51b
			5%	41b	0.1a	58a
Garden wastes (GB)	400	<0.1	0%-control	62a	0.1b	17a
			2%	96ba	0.1b	16a
			4%	105b	0.2a	16a
			6%	109b	0.2a	17a
	600		2%	97ba	0.2a	17a
			4 %	100b	0.2a	16a
			6 %	100b	0.2a	17a
Paulownia (PG)	700–800	<0.1	0%-control	62a	0.1b	17a
			2%	91ba	0.1b	16a
			4%	99ba	0.2a	16a
			6%	100b	0.2a	15a

Regarding Cu, the maximum concentration of the organic fraction was observed when sugar bagasse biochar was added to the soils (Figure 3b), followed by the concentrations derived from the addition of garden waste (Figure 3e). The three metals studied have a common chemical behavior, as they seem to have apparent complexation dynamics along with the organic compounds included in the soil organic fraction.

3.5. Residual Fraction

In Table 6, the residual concentrations of Pb, Cd, and Cu (mg kg^{-1}) after biochar application are presented.

Table 6. Residuals' concentration of Pb, Cd, and Cu (mg kg^{-1}) after biochar application.

Biochar Type	Temperature (°C)	Particle Size (mm)	Biochar Soil Application Amount	Pb	Cd	Cu
Sugarcane bagasse (B)	450	<2	0 t ha^{-1}-control	141a	0	205a
			1.5 t ha^{-1}	165ba	0	218a
			2.25 t ha^{-1}	168ba	0	224a
			3 t ha^{-1}	176b	0	225a
Bamboo (BB)	700	<0.25	0%-control	23a	0.2a	60
			1%	23a	0.2a	53
			5%	20a	0.2a	56
		<1	1%	22a	0.2a	49
			5%	20a	0.2a	52
Rice straw (RSB)	500	<0.25	0%-control	23a	0.2a	60
			1%	24a	0.2a	56
			5%	22a	0.3a	52
		<1	1%	22a	0.2a	51
			5%	20a	0.2a	58
Garden wastes (GB)	400	<0.1	0%-control	197	0.1a	17a
			2%	194	0.1a	16a
			4%	194	0.2b	16a
			6%	194	0.1a	17a
	600		2%	193	0.2b	17a
			4%	187	0.2b	16a
			6%	188	0.2b	17a
Paulownia (PG)	700–800	<0.1	0%-control	196a	0.1a	17a
			2%	187ba	0.1a	16a
			4%	194ba	0.1a	16a
			6%	181b	0.1a	15a

Note: In the case of the applied *sugarcane bagasse biochar*, the concentration of the organic bound metal fraction for Cd is considered negligible.

4. Discussion

The addition of the different types of biochar to the contaminated soil samples that have been selected for this study caused a redistribution among HMs fractions, which resulted in changes in their final availability to plants. The chemical fractions that bioavailability and mobility can be relatively determined are usually the acid extractable and the exchangeable fraction, as well [36]. On the other hand, the reducible metallic fraction of every soil pollutant-HM, linked with the Fe/Mn oxides, is thermodynamically variable and potentially available in the absence of oxygen [43]. These metal fractions are characterized as highly variable due to the particularly loose bonds between metals and solid surface of oxides. For this reason, they can be easily affected by environmental conditions, such as pH variation [61]. Additionally, it should be noted that the fraction of HMs that is found bound to the OM (organic fraction) [58] can be oxidized, potentially affecting the bioavailability of the HMs under oxidizing conditions [75].

4.1. Acid Extractable/Exchangeable Fraction

The acid extractable/exchangeable fraction of metals is presented in Table 2. The addition of sugarcane bagasse biochar to the contaminated soil caused a reduction in the concentration of the unstable metal fractions (acid extractable/carbonate bound). More specifically, their concentration was reduced after the addition of 3 t ha^{-1} of the biochar

as follows: Pb (from 74 to 44 mg kg^{-1}), Cd (from 0.12 to 0.04 mg kg^{-1}), and Cu (from 34 to 17 mg kg^{-1}). The use of biochar caused a significant reduction in metal availability, as Abbas et al. [9] have also observed. The application of biochars obtained by bamboo and rice straw led to a reduction of the concentration of unstable acid extractable fraction Pb and Cu in the soil. The greatest change was noted after adding 5% of the rice straw biochar and especially with a particle size of 1 mm. Additionally, the reduction of their concentrations was: Pb (from 71 to 49 mg kg^{-1}) and Cu (from 190 to 123 mg kg^{-1}). No significant change was observed for Cd fraction concentration after bamboo biochar application. However, a decrease was observed after the addition of rice straw biochar at 1% and 5% and with particle size of 0.25 and 1 mm.

The addition of biochar produced by the garden wastes biochar caused a significant reduction of metal concentration in both acid extractable and exchangeable fractions. The Pb concentration remarkably changed after the biochar application obtained from pyrolysis with a temperature of 400 °C. Its greatest reduction was observed after the application of 6% of garden wastes biochar under this pyrolysis temperature (from 138 to 67 mg kg^{-1}). The acid extractable fraction concentrations of Cd and Cu were also reduced after the application of the biochar, but it seems that the pyrolysis temperature had no effect upon the experimental outcome. The application of 6% of paulownia biochar mostly reduced the acid extractable fraction concentration of the three pollutants: Pb (from 137 to 123 mg kg^{-1}), Cd (from 1.9 to 1.6 mg kg^{-1}), and Cu (from 2.0 to 1.3 mg kg^{-1}). Alam et al. [67] discussed the presence of inorganic ions, either in the plant or in the soil solution. The coexistence of ions in an aqueous environment in contact with the solid surface of the soil often alters the available fractions of both toxic and trace (nutrient) elements [13].

The acidic and exchangeable fraction of Pb was almost constant for all types of biochar added to the soil as depicted in Figure 1b–f. However, in the case of Cd, the fluctuations in the concentration of the acidic fraction are quite high. We noticed the lower values were obtained when sugar bagasse biochar was added (Figure 2b), while higher values, up to 70%, were noticed when biochar derived from garden waste and paulownia gas was incorporated (Figure 2e,f).

Regarding Cu, the maximum concentration of the acidic fraction was observed when biochar from bamboo (Figure 3c) and rice waste (Figure 3d) was added to the soils. When biochar derived from garden waste was added, the availability of Cu was significantly reduced. This is probably due to the large percentage of organic matter contained in the specific type of biochar and the fact that Cu easily forms complexes with the groups contained in the organic molecules [13,70]. As is obvious from Table 1, the contaminated soil has high values of both salinity and alkalinity. The presence of salts with elevated ionic strength can change the values of soil electrical conductivity and in some cases may cause changes in soil reaction (pH). These changes in soil physicochemical parameters can significantly affect metal mobility [1,17].

4.2. Carbonate Bound Fraction

Table 3 shows the variations in metal concentrations after the addition of biochar derived from sugarcane bagasse. When the maximum amount of biochar was added (i.e., 3 t ha^{-1}), the maximum reduction in the concentration of Pb, Cd, and Cu was achieved. Pb and Cu in the fraction of carbonates are lower compared to the other fractions. Cd, however, shows a greater affinity for this fraction, as it appears to be bound in a larger amount compared to the organic and residual fractions. Devi and Bhattacharyya [10] found that the carbonated soil fraction may contribute to metal availability, as the metals are loosely captured by the solid soil phase.

4.3. Fe/Mn Oxides Fraction

The fraction of metals bound to Mn/Fe oxides (Table 4) can contribute to the availability of metals to plants, depending on environmental conditions. Lu et al. [49] have studied the adsorption of metallic toxic elements on iron and manganese oxides. In Figures 1–3,

the concentration of Pb, Cd, and Cu bounded to the Fe/Mn oxides was reduced after the application of sugarcane bagasse biochar. The biochar application amount of 3 t ha^{-1} had the greatest effect, as the reduction was as follows: Pb (from 136 to 128 mg kg^{-1}), Cd (from 0.4 to 0.3 mg kg^{-1}), and Cu (from 40 to 35 mg kg^{-1}).

The bamboo biochar and the rice straw biochar reduced the fraction concentration of the soil pollutants [51]. The greatest reduction of Cd and Cu concentrations was accomplished when 5% of rice straw biochar with the particle size of 1 mm was incorporated in the soil, as follows: Cd (from 0.2 to 0.1 mg kg^{-1}) and Cu (from 187 to 121 mg kg^{-1}). On the other hand, the Pb concentration reduced after the application of 5% of bamboo biochar with the particle size of 1 mm (from 377 to 321 mg kg^{-1}) and increased after the incorporation of 5% of rice straw biochar with the particle size of 1 mm (from 412 to 377 mg kg^{-1}).

The researchers Khan et al. [14], Taraqqi-A-Kamal et al. [61], and Amin et al. [37] discussed intensively about the impact of different types of biochar on the retention of metals in different soil fractions. The biochar obtained by garden wastes leads to a reduction of Pb concentration (from 593 to 602 mg kg^{-1}), an increase in Cd concentration (from 0.5 to 0.7 mg kg^{-1}), and a reduction of Cu concentration when it was applied in soils. The metals seem to have a different chemical affinity with the Fe–Mn oxides. This has been extensively discussed in the review paper of Amoah-Antwi et al. [6]. Pb and Cu show higher affinity with the Fe-Mn oxides than Cd. The addition of 6% of paulownia biochar mainly reduced the Fe/Mn oxides Pb and Cu concentration, although it had no effect on Cd concentrations.

4.4. Organic Bound Fraction

In Table 5 the Pb, Cd, and Cu concentrations related to organic soil fraction are presented. The maximum concentrations of the organic fraction of Pb and Cd were observed when sugar bagasse biochar was added to the soils (Figures 1b and 2b). Cd's organic fraction increased over 97% after application of biochars derived from garden residues (GB) and paulownia plant (PB). When an amount of 2.25 t ha^{-1} biochar, derived from sugarcane bagasse, was used, Cu's organic fraction increased over 10%. Chen et al. [75] discussed the metal immobilization by OM of soils. The chemical affinity of Cu and Pb with the OM of the soil is significant, as chelate complexes between metal ions and ligand molecules with various molecular weight [56,57,74]. In the organic fraction, the metals are bound, forming complex compounds with low molecular weight organic compounds. The percentage of metals bound to the fraction may vary with environmental conditions. The value of the soil reaction (pH) and the normal redox potential affect the oxidation number of the metals and the type of ligands of the complex compounds [70,75].

4.5. Residual Fraction

In Table 6, the residual fractions of the metals studied are presented. The highest concentrations of the residual fraction of Pb and Cu were observed when biochar from garden residues (Figures 1e and 3e) and from paulownia (Figures 1f and 3f) was added to the soils, probably due to organic molecules in the plant residues present in both cases. On the other hand, Cd appears in low concentrations in the residual fraction of Cd were observed when biochar from garden residues (Figure 2e), as well as from paulownia (Figure 2f), which was added to the soils. The residual fraction of metals corresponds to the fraction that is not available to plants and, therefore, not available to humans. Therefore, it is important to find the ideal conditions for biochar preparation and the appropriate mixing ratios with the contaminated soils in order to increase the percentage of metals in the residual fraction, minimizing their availability [70,71].

The effect of biochar from the paulownia plant on metal-contaminated soil was significant, causing changes in its physicochemical properties, such as pH, OM content, and EC [71]. After the application of paulownia biochar, pH and OM content increased, while EC decreased. This behavior was probably due to the absorption of salts in paulownia and their retention, which decreased the EC value of the soil solution and the soil surface

area. Through the formation of stable complexes of HMs with biochar functional groups, the application of this biochar type reduced the toxicity of the studied HMs as soil pollutants by stabilizing their soluble forms [6,58]. Generally, the application of paulownia proved to be effective in immobilizing the pollutants. This result must be attributed to the increased pH and the EC values that are associated with the increased content of paulownia functional groups. As it has been proved in previous cases of acidic and contaminated soils amendment by application of biochar, the increasing addition of paulownia biochar resulted in an increase in the pH, inversely correlated to the available concentration of the studied HMs [17,22].

4.6. Effects of Pyrolysis Temperatures and Application Percentages of Biochar Used

Both biochar types (GB400, GB600) contributed to the toxicity reduction of the soil HMs by stabilizing the soluble forms of HMs. The GB400 was found to be more effective in immobilizing the metal forms of the pollutants than that the GB600. The immobilization of HMs was affected by functional groups containing O, K, Ca, Mg, and P elements, leading to insoluble forms of HMs [24]. Complexes were also formed after an exchange between HMs cations and Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}, which are located on groups containing O, S, and P elements in biochar. As expected, the addition of biochar at a 6% percentage had a greater effect on the studied HMs than the other two applications at 4% and 2%, respectively.

Pyrolysis at low temperatures (slow pyrolysis) induces the formation of outer sphere complexes, resulting in a ''short term" immobilization of HMs, but also resulting in a ''strong absorption" of their concentrations from the biochar [33]. On the other hand, pyrolysis in high temperatures (fast or intensive pyrolysis) leads to the formation of negative surface charges, i.e., internal sphere complexes, resulting into a ''long term" immobilization of HMs, but resulting in a ''weak absorption" of their concentrations [68]. Functional groups, which essentially represent the sites at which the metals can bind, are found in the bioindicators obtained at low temperatures (300 °C–500 °C). This was also discussed further in the research of Manyà et al. [68] and Meng et al. [56].

The contaminated soil pH, in which the action of GB400 and GB600 has been studied, was acidic. In this case, the increase in the pH observed was also associated with an increased amount of added biochar. This is also confirmed by the results obtained regarding the effect of the two garden waste biochar types on the concentrations of the soil pollutants. More specifically, a decrease in their acid extractable/exchangeable fraction was found to be proportional to the increase in the biochar added amount. The reaction effect (pH) of the soil environment is crucial for the sequestration and reduction of metal mobility [1,13]. On the other hand, it was observed that the soil pollutants fraction bound to OM (organic fraction) increased after the application of the two biochar types and this is shown by comparing their concentrations with those in the control sample. The decreases in the acid extractable/exchangeable fraction concentration of the soil pollutants were accompanied by the increases in their fraction bound to OM concentration. Those changes proceed in parallel dependent on the added amount and pyrolysis temperature of GB400 and GB600. This occurs because HMs can form stable, organic complexes, which are precipitated in biochar, further enhancing their immobilization and reducing their concentration in the soil solution. It should also be noted that the pH increase, proportional to the increase in the biochar amount, enhanced the adsorption of HMs and, consequently, their immobilization [14].

The increased adsorption on the biochar surface and the formation of insoluble forms contributes significantly to the solubility reduction of the pollutants. In the case of the paulownia biochar, most Pb concentration as a soil pollutant was bound to Fe–Mn oxides, possibly because of the high chemical affinity of Pb with the Fe–Mn oxides. Amoah-Antwi et al. [6] and Liang et al. [47] have discussed the availability of metals in soils.

The biochar addition on the contaminated soil is characterized by its ability of immobilizing HMs, but this mechanism has not been fully determined. It is likely that

HM stabilization in a modified soil after biochar addition is due the action of various mechanisms [41], such as:

- the physical adsorption on the biochar surface
- the chemical bonds with the ions on the biochar surface
- the formation of complexes with the active functional groups
- the precipitation on the biochar surface by the phosphate ions
- the precipitation due to the pH increase in the contaminated soil, especially when the soil is acidic

Every mechanism responds to one or more specific soil pollutants. Its activation depends on the characteristics of the soil pollutant. Usually, Cd is mostly absorbed on the biochar surface area, and Cu is chemically bound on the biochar surface area, whereas Pb is precipitated via complexation with the biochar functional groups [41].

5. Conclusions

The study of the effectiveness of five different types of biochar on the distribution fractions of Pb, Cd, and Cu was the main purpose of the present study.

The nature of the materials used to prepare the different types of biochar, the pyrolysis temperature, the final dimensions of their grains, along with their physicochemical properties, contributed to their capacity in reducing the mobility and availability of metals in soil. The amounts of OM, salinity, and alkalinity in the soils were also discussed. On the other hand, the nature of metals effectively determined their interactions with the added types of biochar, along with the redistribution of their concentration in the fractions, determined by the BCR fractionation method.

The decrease in their acid extractable/exchangeable fraction was found to be proportional to the increase in the biochar added amount. On the other hand, it was observed that the soil pollutants fraction bound to OM (organic fraction) was increased after the application of the garden waste types of biochar. In the present study, Pb was found captured, and consequently less was available in the residual fraction. Cd is commonly absorbed on the biochar surface area, reducing its presence in the exchangeable (available) fraction. Cu is chemically bound on the biochar surface area, making chelate complexes with organic groups.

The pyrolysis temperature and the amount of biochar added into the contaminated soils are decisive factors in enhancing the effectiveness of the approach. Furthermore, the remediation of the contaminated soil effected by biochar addition (organic amendment) may also significantly affect the HM mobility and bioavailability, which depend on the metal type, the nature of soil, and its physicochemical parameters. The use of biochars is an easily applicable, inexpensive, and eco-friendly method for the remediation of HM-polluted soils in the context of circular economy, as it has immediate effects and leads to a reduction of the available amounts of Pb, Cd, and Cu in moderately contaminated soils.

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