

Speciation of Cd and Pb in the soil after the biochar application

Monika Mierzwa-Hersztek, Krzysztof Gondek

Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow,
al. Mickiewicza 21, 31-120 Krakow, Poland

Abstract. The focus on speciation analytics, which allows identification of the potential risks to the environment arising from the presence or accumulation of heavy metals in soil, has been on the increase in the recent years. Total or, at least, partial detoxification of heavy metal ions, to variable extents, can be achieved by introducing biochar into the soil. The key factor and potential of biochar to reduce the content of heavy metals in soil depends on the specific properties of biochar, such as presence of functional surface groups, specific surface area, and porosity. The aim of the research was to evaluate the effect of poultry litter, as well as poultry litter-derived biochar produced at a temperature of 300 °C on Cd and Pb contents in mobile and organic matter-bound forms in soil. A micro-plot field experiment was established on Haplic Cambisol with five treatments: control soil without fertilisation; soil + NPK; soil + NPK + poultry litter at a dose of 5 t D.M. ha⁻¹; soil + NPK+ biochar at a dose of 2.25 t D.M. ha⁻¹, and soil + NPK + biochar at a dose of 5 t D.M. ha⁻¹. The soil samples were taken from each plot, from the layers: 0–10 cm, 10–20 cm and 20–30 cm. The following parameters were determined: pH – by potentiometric method, electrical conductivity – by conductometric titration, the contents of total forms of nitrogen and carbon were determined using CNS analyser. The contents of total forms of selected trace elements were determined after ashing the soil organic matter in chamber furnace (at 450 °C for 8 hours) and mineralising its residues in a mixture of concentrated nitric and perchloric acids. Selected forms of analysed trace elements (the sum of mobile, exchangeable, MnOx- and organic matter-bound fractions) were determined by the sequential extraction procedure designed by Zeien and Brümmer. The Cd and Pb contents in the resulting solutions and extracts were determined by ICP-OES using the Perkin Elmer Optima 7300 DV instrument. The sum of exchangeable alkaline cations (EAC) and hydrolytic acidity (Hh) were determined by Kappen method. It was noted that the total lead content, regardless of the soil layer (0–10 cm, 10–20 cm and 20–30 cm), ranged between 19.8 mg and 28.9 mg kg⁻¹ D.M. of soil, and the total cadmium content, between 0.61 mg and

1.16 mg kg⁻¹ D.M. of soil. The average proportion of the sum of the most mobile forms of cadmium in the total Cd content in 0–10 cm, 10–20 cm and 20–30 cm soil layers was: 82%, 76% and 63% respectively, and of lead, 22%, 20% and 24%. The proportion of lead fraction bound with organic matter in the total content was comparable in different soil layers and ranged between 37% and 41%. No Cd fraction bound to organic matter was determined in the tests.

key words: speciation of heavy metals, cadmium, lead, biochar, soil

INTRODUCTION

Soil is considered the most essential accumulation centre for heavy metals obtained from natural (bedrock and soil-forming processes) and anthropogenic (e.g. industry, mineral and organic fertilisers, waste) sources (Smith et al., 2005). In terms of potential hazard to the natural environment, it is important to define the conditions and ability of heavy metals to move in the soil profile. The mobility of heavy metals in soil is conditional upon their forms and binding mechanisms that occur between the heavy metals and organic and inorganic soil constituents. The form in which a trace element is available depends on a variety of soil properties, such as: the organic matter content, pH, cation exchange capacity, and the activity of microorganisms (Park et al., 2011; Fijałkowski et al., 2012; Ukalska-Jaruga et al., 2015). These properties of the soil are therefore crucial in the processes of sorption, complexation, and immobilisation of heavy metals, and their bioavailability for plants. The problem of trace element mobility is of particular importance for light and acidic soils which constitute more than 50% of agricultural areas in Poland. In this case, the increase of heavy metal solubility in acid medium is associated with a slow dissolution of iron, aluminium and manganese oxides and their release from primary and secondary minerals (Hołubowicz-Kliza, 2006).

Corresponding author:

Monika Mierzwa-Hersztek
email: monika6_mierzwa@wp.pl
phone: +48 12 662 43 41

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Various organic materials are increasingly being used for reducing the mobility of heavy metals and their immobilisation in the soil. Currently, apart from plant residues, natural and organic fertilisers, particularly great expectations are placed upon the application into the soil of a solid product obtained from thermal conversion of biomass – biochar (Lehmann, 2007; Kwapinski et al., 2010; Ahmad et al., 2014; Gondek, Mierzwa-Hersztek, 2016).

The results obtained so far have demonstrated that the specific properties of biochar, such as porous structure and substantially developed specific surface area, may favour the immobilisation of harmful organic and inorganic compounds (Al-Wabel et al., 2015; Gondek et al., 2016). The biochar potential to reduce the contents of heavy metal ions in the soil depends on the presence of functional groups (e.g. carboxyl, hydroxyl or phenol) on the biochar surface. Given the assumption that biochar varies in its surface structure, this material, as a potential sorbent, can significantly influence the binding of heavy metals to functional groups as a consequence of exchange or complexation reactions (Vithanage et al., 2015; Bożęcka et al., 2016). The results from numerous studies have shown that, depending on the amount and type of biochar introduced into the soil, not only are the chemical and biological properties of the soil modified but, above all, the nature of organic and mineral connections are altered, due to the decomposition of an organic compound in the complex. The direct consequence of changing the configuration of such connections is an alteration in heavy metal bioavailability for plants (Houben et al., 2013; Paz-Ferreiro et al., 2014; Al-Wabel et al., 2015).

Although benefits of using biochar are commonly known (Lehmann, 2007; Arthur et al., 2015; Gondek et al., 2016), the material's long-term impact on the soil environment is a phenomenon whose mechanisms have still not been fully explained. A large variety of technological factors in the production of biochar together with the variability of environmental conditions may directly affect biochar conversions in the soil, thereby affecting the mobility of heavy metals. As a consequence, the originally established equilibrium between the presence and availability of heavy metals in the soil will be subjected to various modifications, particularly when applying by-products of poultry rearing into the soil. The conversion of such materials into biochar can provide a solution for commonly disputable issues related to their management (Jindo et al., 2012; Arthur et al., 2015).

Human interference in the soil environment, which involves the introduction of various ma-

terials, significantly affects the properties and processes present therein. Given the wide range of biochar impact on the soil properties, the tests were conducted with the aim to determine the effect of its application on the mobility of selected heavy metals (Cd and Pb), including the forms bound in organic compounds.

MATERIALS AND METHODS

Biochar used in the tests was produced from poultry litter, and adequately prepared (dried at 70 °C, ground in the laboratory mill). The process of thermal conversion was carried out using test stand for biomass gasification under a limited supply of air (1–2%) (IBI, 2012). The rate of heating the combustion chamber was 10 °C min⁻¹. Temperature in the combustion chamber was 300 °C, and exposure time, 15 minutes. The pyrolysis time and temperature were established on the basis of the authors' preliminary examinations and results reported in literature (Lu et al., 2013; Mendez et al., 2013; Gondek et al., 2014). In order to identify the chemical composition of poultry litter before and after thermal conversion, the dry matter content was determined after drying the materials at 105 °C for 12 hours (Jindo et al., 2012). Subsequently, the materials were ground in the laboratory mill and subjected to chemical analysis. The contents of total forms of carbon and nitrogen were determined using CNS analyser (Vario MAX Cube manufactured by Elementar) (ElementarAnalysensysteme 2013). The total contents of macroelements and trace elements were determined after ashing the sample in chamber furnace at 450 °C for 12 hours and mineralising its residues in a mixture of concentrated nitric and perchloric acids (3:2) (v/v) by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the Perkin Elmer Optima 7300 DV instrument (Oleszczuk et al., 2007). Specific surface area (S_{BET}) of organic materials, as well as pore

Table 1. Selected properties of organic materials

Determination	Unit	Poultry litter (PL)	Poultry litter-derived biochar (PLB)
pH H ₂ O	-	7.53±0.02	8.10±0.02
Electrical conductivity (EC)	μS cm ⁻¹	49.1±12.4	91.5±2.6
Dry matter	g kg ⁻¹	323±2	986±0
Ash		313±1	420±0
C _{total}		323±0	377±0
N _{total}	g kg ⁻¹ D.M.	25.1±1.7	32.7±0.7
P _{total}		18.3±2.2	27.6±2.9
K _{total}		29.9±0.7	36.7±1.8
Cd _{total}	mg kg ⁻¹ D.M.	0.37±0.01	0.54±0.07
Pb _{total}		3.29±0.22	4.42±1.35
Specific surface area S_{BET}	m ² g ⁻¹	1.83±0.22	2.76±0.29
Pore volume	cm ³ g ⁻¹	0.006±0.000	0.011±0.002
Pore diameter	nm	14±2	18±3

Each value represents the mean of three replicates ± standard deviation

volume and diameter were determined using multifunction accelerated surface area and porosimetry analyser ASAP 2010 manufactured by American company – Micromeritics. Specific surface area (S_{BET}) was determined by physical nitrogen adsorption at liquid nitrogen temperature (77 K) using Brunauer-Emmet-Teller equation. Before measuring specific surface area (S_{BET}), test samples were subjected to desorption at 105 °C under vacuum conditions, and washed with pure helium. Sample degassing time was 16 hours. The status of surface degassing was controlled in an automatic manner (Barret et al., 1951). Selected chemical properties of organic materials used in the experiment are shown in Table 1.

The micro-plot tests were carried out in 2014 on arable land located in southern Poland (50° 08.404' N; 19° 85.362' E). The soil from the tested area was classified as typical Eutric Cambisols with the granulometric composition of loamy sand (Polish Soil Classification 2011). Selected soil properties (0–10 cm) before setting up the experiment presented in Table 2.

Table 2. Selected soil properties (0–10 cm) before setting up the experiment.

Determination	Unit	Value
Sand		73
Silt	%	15
Clay		12
pH H ₂ O	-	6.46±0.02
pH KCl	-	5.59±0.01
Electrical conductivity (EC)	µS cm ⁻¹	22.0±0.0
Cation exchange capacity (CEC)	mmol(+) kg ⁻¹	149±5
Total Organic Carbon (TOC)	g kg ⁻¹ D.M.	9.80±0.05
N _{total}		1.28±0.02
C:N ratio	-	7.66
Cd _{total}	mg kg ⁻¹ D.M.	0.63±0.01
Pb _{total}		25.5±0.7

Each value represents the mean of three replicates ± standard deviation

The experiment was performed on 5 treatments in 3 replicates using the method of randomised blocks. The area of one plot was 1 m². The experiment involved the application into the soil of poultry litter (5 t ha⁻¹) (NPK+PL) and poultry litter biochar in two doses: 2.25 t D.M. ha⁻¹ (NPK+BPL I) and 5 t D.M. ha⁻¹ (NPK+BPL II) against the mineral fertilisation. The scheme also included two reference treatments: control treatment without fertilisation (C) and treatment with only mineral fertilisers applied (NPK). The applied mineral fertilisation was: 100 kg N ha⁻¹, 40 kg P ha⁻¹ and 120 kg K ha⁻¹. The dose of phosphorus was applied once for the first swath, in the form of enriched triple superphosphate. Potassium was introduced in the potassium salt form, and nitrogen, in the ammonium nitrate form. Doses of potassium and nitrogen were divided into three equal parts and then, applied to each of the three swaths. The doses of poultry litter before and after the process of thermal conversion were individually mixed with the topsoil (0–10 cm), and then a pasture grass mixture (*Phleum pratense* L. – 15%, *Festuca pratensis* – 10%, *Festuca arundinacea* – 20%, *Lolium perenne* L. – 30%, *Lolium multiflorum* – 20%, red clover – 5%) was sown using 60 kg ha⁻¹ of seeds.

During the experiment, the weather conditions were monitored. The highest precipitation in 2014 year was observed in June. The highest mean annual air temperature was observed in July and the smallest in April. Weather conditions (precipitation, temperature) prevailing at the time of the experiment are shown in Table 3.

Following the end of the plant vegetation, soil samples were taken from each plot, from the layers: 0–10 cm, 10–20 cm and 20–30 cm (7 months after the application of organic materials), using a stainless-steel test probe. The soil samples were dried and passed through a sieve with apertures of 1 mm, and subsequently, subjected to chemical and physicochemical analyses.

For the soil dried at room temperature and passed through a sieve with apertures of 1 mm, the following parameters were determined: pH – by potentiometric method – in the suspensions of soil and water, and soil and 1 mol dm⁻³ solution of KCl (soil : solution = 1 : 2.5), electrical conductivity – by conductometric titration – and finally, the contents of total forms of nitrogen and carbon

Table 3. Monthly and periodical sums of precipitation [mm] as well as mean daily air temperature [°C] in comparison to long-term average in 1961–1990.

Years	Months											
	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
	Precipitation [mm]											
2014	38.3	17.0	32.5	42.7	108.2	43.2	99.8	96.5	66.0	33.5	38.1	23.1
1961–1990	34.0	32.0	34.0	48.0	83.0	97.0	85.0	87.0	54.0	46.0	45.0	41.0
	Temperature [°C]											
2014	-0.9	2.0	6.4	9.8	13.8	15.7	20.1	17.6	14.6	9.8	5.9	1.3
1961–1990	-3.3	-1.6	2.4	7.9	13.1	16.2	17.5	16.9	13.1	8.3	3.2	-1.0

were determined using CNS analyser (Vario MAX Cube manufactured by Elementar) (ElementarAnalysensysteme 2013). The contents of total forms of selected trace elements were determined after ashing the soil organic matter in chamber furnace (at 450 °C for 8 hours) and mineralising its residues in a mixture of concentrated nitric and perchloric acids (3:2) (v/v) (Kopeć et al., 2013). Selected forms of analysed trace elements (the sum of mobile, exchangeable, MnOx- and organic matter-bound fractions) were determined by the sequential extraction procedure designed by Zeien and Brümmer (1989). The Cd and Pb contents in the resulting solutions and extracts were determined by ICP-OES using the Perkin Elmer Optima 7300 DV instrument, and the results were converted to the absolute dry mass of soil. The sum of exchangeable alkaline cations (EAC) and hydrolytic acidity (Hh) were determined by Kappen method (Jaremko, Kalembasa, 2014). Cation exchange capacity (CEC) was then calculated as follows (Cucarella et al., 2009):

$$\text{CEC} = \text{Hh} + \text{EAC}$$

All determinations were performed in three replicates. The value of standard deviation (SD) was calculated. The significance of differences between the arithmetic means was verified on the basis of homogenous groups determined by Duncan's test at $\alpha \leq 0.05$. All statistical calculations were performed using Statistica PL.

RESULTS AND DISCUSSION

Subjecting by-products or waste materials to the process of thermal conversion alters the total trace elements contents and modifies relations between the forms in which they occur (Park et al., 2011). When applying organic materials into the soil, one should consider not only the soil properties, but also the type and amount of material introduced. In the case of biochar, the key factor to consider it as a sorbent for contaminants are its physical properties. During the thermal conversion of biomass, the specific surface area of the product (S_{BET}) increases significantly compared to the surface of material used, which is essential in view of the sorption of pollutants (Beesley, Marmiroli, 2011). In-house studies proved that thermal conversion of poultry litter at 300 °C increased the specific surface area of biochar (S_{BET}) by 51%, and pore volume and diameter, by 83% and 29% respectively (Table 1). Unfortunately, despite well-known physical and chemical properties of biochar, the material's integration with trace elements is a phenomenon whose mechanisms have still not been fully explained.

The soil collected from the tested area before the experiment was slightly acidic ($\text{pH}_{\text{KCl}} = 5.59$) and had natural cadmium and lead contents (Table 2). The soil organic carbon content was 9.80 g, while the nitrogen content was 1.28 g kg^{-1} D.M.

Compared to the control treatment (C), the biochar application into the soil (layer 0–10 cm) significantly influenced the increase of total organic carbon (TOC) in treatments

with both doses of biochar introduced against the mineral fertilisation (NPK+BPL I, NPK+BPL II), by 2.7% and 6.3% respectively. The nitrogen content increased relative to the amount of material used (2.25 t and 5.0 t D.M. ha^{-1}) decreased in subsequent layers of the soil (0–10, 10–20, 20–30). The use of a 2.25 t dose of biochar increased the content of the element in question by 2.06% – and of 5.0 t D.M. ha^{-1} dose – by 4.1%. The greatest differences in soil pH, which is considered to be one of the most important indicators of the soil quality and which exercises a decisive influence on the bioavailability of most of nutrients and heavy metals, were observed in the 0–10 cm soil layer, especially after fertilisation with a double dose of biochar. Similar findings were obtained for electrical conductivity of soil (Table 4). Liu and Zhang (2012) reported that the soil pH value was higher together with the increase in biochar dose. The lowest values of pH, electrical conductivity, soil organic carbon, and total nitrogen were noted for the soil with only mineral fertilisers applied.

Another reason for the increased soil pH followed by the application of biochar may be due to a large specific surface area of the latter and its porosity, both of which increase the cation exchange capacity (CEC) in soil. The cation exchange capacity increase is primarily attributed to the negative charge on the outer surface of the biochar, which arises from the oxidation of functional groups (Cheng et al., 2006; Anegebe et al., 2015; Gondek, Mierzwa-Hersztek, 2016). Anegebe et al. (2015) demonstrated that cation exchange capacity increased at the increased doses of biochar and according to the lapse of time from the application of material into the soil. On the other hand, Kuzyakov et al. (2009) reported that biochar introduced into the soil undergoes an aging process in the presence of air, water, and microorganism activity, which in turn leads to the formation of stable complexes of trace element and biochar.

In the available literature there are many examples of biochar described as a multi-purpose material in terms of its agricultural and environmental applications, especially in addressing contaminant-related issues (Venegas et al., 2015). This study's findings have also indicated the beneficial effects of biochar as a substance supporting the immobilisation of heavy metals in soil. The introduction of organic materials into the soil had a considerable influence on the total contents as well as mobility of cadmium and lead (Tables 5 and 6).

Regardless of the fertilisation applied, the contents of total forms of cadmium in each treatment were lower than the Cd content determined in the control soil (Table 5). The mean content of total Cd forms (for layers) was the highest in the soil taken from the control treatment (0.97 mg kg^{-1} D.M.), and the lowest in the soil taken from treatment with NPK+BPL II applied (0.72 mg kg^{-1} D.M.). It should be emphasised that the lowest contents of total cadmium forms were determined in the 0–10 cm soil layer, into which organic materials, both before and after thermal

Table 4. Selected soil properties (after 1st year of experiment).

Treatment [#]	Soil layer [cm]	pH H ₂ O	pH KCl	EC [μ S cm ⁻¹]	CEC [mmol kg ⁻¹]	TOC [g kg ⁻¹ D.M.]	N _{total} [g kg ⁻¹ D.M.]
C	0–10	6.40 ab \pm 0.2	5.62 ab \pm 0.2	17.0 a \pm 0.0	135 ab \pm 1.7	9.18 abcd \pm 0.9	0.97 def \pm 0.0
	10–20	6.40 ab \pm 0.1	5.55 ab \pm 0.3	16.7 a \pm 0.0	105 ab \pm 5.2	10.7 d \pm 1.1	0.97 def \pm 0.0
	20–30	6.58 bcd \pm 0.1	5.88 abcd \pm 0.3	16.0 a \pm 0.0	141 ab \pm 2.4	10.4 cd \pm 0.9	0.87 bcd \pm 0.1
NPK	0–10	6.21 a \pm 0.1	5.34 a \pm 0.0	15.3 a \pm 0.0	132 ab \pm 7.8	8.30 ab \pm 1.1	0.89 bcde \pm 0.1
	10–20	6.49 bc \pm 0.1	5.59 ab \pm 0.4	15.0 a \pm 0.0	139 ab \pm 5.6	8.41 ab \pm 1.5	0.82 ab \pm 0.1
	20–30	6.55 bcd \pm 0.2	5.70 abc \pm 0.5	27.7 ab \pm 0.0	134 ab \pm 7.4	7.80 a \pm 1.7	0.73 a \pm 0.1
NPK + PL	0–10	6.44 abc \pm 0.1	5.73 abcd \pm 0.0	22.0 ab \pm 0.0	128 ab \pm 8.9	9.28 abcd \pm 0.7	1.03 g \pm 0.0
	10–20	6.71 cde \pm 0.1	6.00 bcd \pm 0.4	19.0 ab \pm 0.0	110 ab \pm 2.6	10.1 bcd \pm 0.8	0.95 defg \pm 0.0
	20–30	6.78 de \pm 0.2	6.23 cd \pm 0.4	30.0 b \pm 0.0	121 ab \pm 1.1	8.85 abcd \pm 1.3	0.91 cdef \pm 0.0
NPK+BPL I	0–10	6.47 abc \pm 0.1	5.60 ab \pm 0.0	22.7 ab \pm 0.0	137 ab \pm 1.3	9.43 abcd \pm 0.4	0.99 efg \pm 0.1
	10–20	6.51 bc \pm 0.1	5.56 ab \pm 0.2	19.0 ab \pm 0.0	154 ab \pm 7.0	9.98 bcd \pm 0.5	0.94 defg \pm 0.0
	20–30	6.41 ab \pm 0.1	5.58 ab \pm 0.2	20.0 ab \pm 0.0	126 ab \pm 4.8	8.74 abc \pm 0.7	0.85 bc \pm 0.0
NPK+BPL II	0–10	6.87 e \pm 0.2	6.30 d \pm 0.0	51.3 c \pm 0.0	136 ab \pm 1.7	9.76 bcd \pm 0.2	1.01 fg \pm 0.0
	10–20	6.53 bcd \pm 0.1	5.54 ab \pm 0.3	25.7 ab \pm 0.0	117 ab \pm 1.5	8.72 abc \pm 0.6	0.89 bcde \pm 0.0
	20–30	6.41 ab \pm 0.2	5.54 ab \pm 0.3	25.7 ab \pm 0.0	88.4 a \pm 3.8	8.36 ab \pm 0.6	0.87 bcd \pm 0.0

C – without fertilization, PL – poultry litter, BPL I – biochar (2.25 t D.M. ha⁻¹), BPL II – biochar (5.0 t D.M. ha⁻¹)

Each value represents the mean of three replicates \pm standard deviation

Mean values marked with the same letters in column do not differ significantly according to the Duncan's-test at $\alpha \leq 0.05$; factor: fertilization x soil layer

Table 5. Selected cadmium forms in the soil material after 1st year of experiment.

Treatment	Soil layer [cm]	Cd _{total}	Cd – Σ of fractions mobile exchangeable and bound with MnOx	Cd – bound with organic matter
			mg kg ⁻¹ D.M.	
C	0–10	0.74 abcd \pm 0.03	0.63 efg \pm 0.02	n.d.
	10–20	1.16 f \pm 0.14	1.02 h \pm 0.14	n.d.
	20–30	1.02 e \pm 0.14	0.72 g \pm 0.06	n.d.
NPK	0–10	0.64 ab \pm 0.08	0.44 ab \pm 0.05	n.d.
	10–20	0.85 d \pm 0.04	0.66 a \pm 0.04	n.d.
	20–30	0.69 abc \pm 0.12	0.50 abcd \pm 0.05	n.d.
NPK + PL	0–10	0.70 abc \pm 0.01	0.59 def \pm 0.03	n.d.
	10–20	0.78 cd \pm 0.00	0.60 def \pm 0.05	n.d.
	20–30	0.76 bcd \pm 0.02	0.46 abc \pm 0.07	n.d.
NPK+BPL I	0–10	0.62 a \pm 0.03	0.55 bcde \pm 0.07	n.d.
	10–20	0.81 cd \pm 0.03	0.52 abcd \pm 0.02	n.d.
	20–30	0.80 cd \pm 0.02	0.46 abc \pm 0.04	n.d.
NPK+BPL II	0–10	0.61 a \pm 0.05	0.49 abcd \pm 0.01	n.d.
	10–20	0.77 cd \pm 0.05	0.55 cdef \pm 0.06	n.d.
	20–30	0.78 cd \pm 0.05	0.43 a \pm 0.04	n.d.

C – without fertilization, PL – poultry litter, BPL I – biochar (2.25 t D.M. ha⁻¹), BPL II – biochar (5.0 t D.M. ha⁻¹)

Each value represents the mean of three replicates \pm standard deviation

Mean values marked with the same letters in column do not differ significantly according to the Duncan's-test at $\alpha \leq 0.05$; factor: fertilization x soil layer

n.d. – not determined

conversion, were introduced. Probably, the reduce of the total content of Cd in the soil was the result of diluting the Cd content after application of organic materials. Organic materials contained less Cd than soil (Table 1). Moreover, the Cd could be bound to the functional groups of organic materials before and after thermal conversion. In addition, functional groups present on the biochar surface “control” the content of mobile forms of heavy metals in soil, by

forming specific complexes. But mechanisms of forming chelate compounds with heavy metals as well as their stability in soil depend on numerous factors (Al-Wabel et al., 2015).

The cadmium immobilisation after applying organic materials was observed for cadmium mobile forms. Analogically to the case of total forms, the lowest, statistically significant average content of cadmium, which was

Table 6. Selected lead forms in the soil material after 1st year of experiment.

Treatment	Soil layer [cm]	Pb _{total}	Pb – Σ of fractions mobile, exchangeable and bound with MnOx	Pb – bound with organic matter
			mg kg ⁻¹ D.M.	
C	0–10	26.9 cd ±2.24	7.12 e ±0.31	10.9 def ±0.58
	10–20	28.9 d ±0.83	6.97 e ±0.77	12.0 f ±0.78
	20–30	24.0 abcd ±2.46	6.13 d ±0.46	8.96 abcd ±0.63
NPK	0–10	24.4 abcd ±3.43	6.05 cd ±0.45	9.06 abcd ±0.59
	10–20	26.4 cd ±3.31	5.04 ab ±0.66	10.6 cdef ±2.17
	20–30	19.8 a ±4.38	4.76 ab ±0.29	8.67 abc ±1.75
NPK + PL	0–10	27.5 d ±2.41	5.51 bcd ±0.35	10.3 bcdef ±0.36
	10–20	28.4 d ±2.65	5.04 ab ±0.28	11.4 ef ±0.37
	20–30	21.8 abc ±1.60	4.90 ab ±0.79	8.70 abc ±0.91
NPK+BPL I	0–10	25.1 bcd ±0.90	5.56 bcd ±0.52	9.09 abcd ±0.89
	10–20	27.7 d ±1.38	5.31 abcd ±0.47	9.48 abcde ±0.24
	20–30	21.7 abc ±0.29	5.21 abc ±0.09	9.49 abcd ±1.56
NPK+BPL II	0–10	24.7 abcd ±5.87	4.55 a ±0.56	8.52 ab ±0.54
	10–20	25.2 bcd ±1.08	4.74 ab ±0.23	9.68 abcde ±1.27
	20–30	20.8 ab ±1.61	4.48 a ±0.35	8.02 a ±0.60

C – without fertilization, PL – poultry litter, BPL I – biochar (2.25 t D.M. ha⁻¹), BPL II – biochar (5.0 t D.M. ha⁻¹)

Each value represents the mean of three replicates ± standard deviation

* Mean values marked with the same letters in column do not differ significantly according to the Duncan's-test at $\alpha \leq 0.05$; factor: fertilization x soil layer

accumulated in fractions potentially available to plants, was determined with 5 t D.M. ha⁻¹ biochar dose introduced (NPK+BPL II, and the highest, in the soil of control treatment (C). Reduced mobility of available forms of heavy metals, followed by the introduction of organic substances into the soil, was discovered also by Park et al. (2011) and Anegebe et al. (2015). The above authors indicated that the immobilising effect of biochar regarded as binder is connected with the increase in the soil organic carbon content and in the soil pH value, resulting from the dissolution of alkaline compounds. No Cd fraction bound with organic matter was determined in the tests.

For lead, the lowest total Pb content was determined in soil taken from treatment with mineral fertilization (NPK), and the highest, in the soil of control treatment (C) (Table 6). The mean (across the layers) proportions of lead accumulated in mobile, exchangeable and manganese oxide-bound fractions in the total element content were 22.4%, 19.8% and 23.6% for the 0–10 cm, 10–20 cm and 20–30 cm soil layers, respectively (Table 6). It should be noted that the application of organic materials before and after thermal conversion substantially reduced the Pb mobility compared to the control treatment. Undoubtedly, this may be due to the significant increase in the soil pH, resulting from the application of materials, biochar in particular. The results are confirmed by the findings published by Park et al. (2011) and Lucchini et al. (2014).

An inverse relationship was observed for lead bound to the soil organic matter. In this particular case, organic materials caused the reduction of Pb in organic compounds. The share of lead fraction bound to organic matter in the

total content was comparable in different soil layers and ranged between 34% and 44%. According to Anegebe et al. (2015), the lead immobilisation in soil after the biochar application is caused by the sorption capacity of the material, although, not as much as by a large content of biochar-derived phosphorous compounds with which lead precipitates in the form of phosphates, thus enhancing the element's immobilisation effect in the soil. Also, Ahmad et al. (2014) showed that the application of biochar may result in conversions of available forms of heavy metals into more chemically stable forms, with the consequent reduction of their mobility and bioavailability.

CONCLUSIONS

Lead and cadmium are considered as elements showing high toxicity in the natural environment, also to humans. High mobility in soil and the ability to penetrate to water make these elements potentially dangerous at any stage of the food chain. The introduction into the soil of organic materials such as poultry litter, before and after the process of thermal conversion, substantially affects the factors determining the extent to which Cd and Pb will undergo the sorption, complexation, and immobilisation processes in soil, or accumulation in the plant biomass. The experiment clearly shows that the use of biochar with the purpose to immobilise cadmium and lead in the soil proved to be an effective method to reduce the mobility of their ions. The material may be successfully used not only as a reservoir of nutrients, but also serve as a binder for contaminants.

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