Influence of Zeolites, Humic Acids, and Selenates (VI) on Lead and Cadmium Immobilization and Selected Soil Properties

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Abstract

In order to immobilize heavy metals, sorbents that meet the following three criteria can be used:

1) they are non-toxic
2) they cannot make the physicochemical properties of soil worse, and even improve them
3) they have an immobilizing and specific impact on heavy metals.

This study compares the influence of mineral and organic sorbents, as well as the presence of selenates (VI), on limiting lead toxicity in a soil. The investigations have also focused on evaluating the effects of these sorbents on select physicochemical and chemical properties of studied soil material collected during the two-year strict pot experiment. Achieved results indicate greater affinity of lead to mineral rather than organic sorbents, although it has depended on zealot and humic acid rates, as well as on physicochemical properties such as soil acidity or soil sorption capacity. Sodium selenate (VI) affected the mobilization of Pb^{2+} ions in the pot experiment and the effect was probably associated with subsoil pH changes and excessive doses of the sorbent used in the experiments.

The study also has aimed at evaluating soil conditions, under which cadmium toxicity appears, as well as at presenting the possibilities of reducing their activities through the use of unconventional immobilizing agents such as zeolites, humic acids, and selenates (VI). The immobilization of Cd^{2+} ions has been affected both by zeolites and humic acids, but only when applied at lower rates. The influences of cadmium mobilization and immobilization on changes in Cd:Zn and Fe:Mn ratios in soil also have been indicated. Clinoptilolit has appeared to be a promising binding agent for immobilizing the cadmium ions. Applying the selenium compounds has given hope as well, because the element is more often considered as required for living. However, the selenium action mechanism is complicated and not uniform, which needs to be further examined.

Keywords: lead and cadmium immoblilization, zeolites, humic acids, selenates (VI), soil properties

Introduction

Difficulties in reclaiming the soils contaminated with heavy metals result from the fact that these elements are permanently bound by a soil sorption complex, hence their interaction with biological life within the soil as well as quality and quantity of a biomass achieved is prolonged, which makes so-called chemical time bombs (CTB) [1, 2]. CTB is defined as a chain of events leading to a delayed and sudden appearance of hazardous effects due to mobilization of substances stored in a soil, as a result of long-term environmental changes [2]. In order to immobilize heavy met-

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als, sorbents that meet the following three criteria, can be used:

1) they are non-toxic
2) they cannot make the physicochemical properties of soil worse, and even improve them
3) they have an immobilizing and specific impact on heavy metals.

Accumulation of toxic elements in an environment is a serious ecological problem. The risk consists in the possibility of suddenly re-mobilizing large amounts of hazardous components, which had been inactive for a long time, under favorable circumstances [1, 2, 7, 14, 16, 21, 28]. It forces us to search for ways to reduce such environmental contamination and counteract their negative influences [8, 20, 24, 25]. Besides conventional methods for immobilizing the heavy metals, such as liming or organic fertilization, we can use unconventional binding agents, the so-called gentle remediation technique [1, 8, 10, 11, 12, 15, 18]. Applying sorbents, including zeolites, should result in immobilizing heavy metals and restoring the ionic balance and ratio of nutrients within a soil environment [9, 22, 23, 25, 26].

Experimental Procedures

Pb Experiment

The pot experiment was carried out on lessive soil developed from dusty sandy loam of the composition of particular mechanical fractions: 48% sand, 31% dust, 21% loam, and containing 1.15% organic C and showing pH 6.20 in 1 M KCl.

The experiment was set by means of the complete randomization method. The experimental unit consisted of a pot filled with 3 kg air-dried bulk soil. The experimental pattern included 12 variants, each replicated four times. Variants of the experiments were composed by introducing lead salts (in the form of $Pb(NO_3)_2$ in the amount of 100 mg $Pb \cdot kg^{-1}$ soil DM), immobilizing agents such as zeolites - clinoptilolite (Fluka) at the following rates: zeolite-1 – 300 mg·pot⁻¹, zeolite-2 – 600 mg·pot⁻¹, artificial humic acids as humic acid sodium salt (by Aldrich, marked as K.H.) at quantities: K.H.-1 – 300 mg·pot⁻¹, K.H.-2 – 600 mg·pot⁻¹, as well as selenium in the form of $Na_2SeO_4 \cdot 10 \ H_2O$ (in the amount of 5 mg $Se \cdot kg^{-1}$ soil DM), into the soil in pots. Variant "0" was made without adding lead ions nor immobilizing agents, although mineral nutrition was applied. Nutrition was uniform for all experimental objects and replicates: 0.15 g $N \cdot kg^{-1}$ soil DM as NH_4NO_3 (1/2 dose before sowing and 1/2 dose after emergence); 0.07 g $P \cdot kg^{-1}$ soil DM as $CaHPO_4 \cdot 2H_2O$ (all the quantity before sowing); 0.15 g $K \cdot kg^{-1}$ soil DM as KCl (all the amount before sowing). Soil humidity was maintained at 60% of field water capacity.

In the 1st experimental year, the soil material was collected from pots after common wheat (*Triticum aestivum* L., Opatka cv.) harvest at full ripeness (KD = 99, according to Zadoks) [3] and after white mustard (*Sinapis alba* L.,

Borowska cv.) harvest at the shoot elongation phase (KD = 35, according to BBA). In the 2nd year of experiment, soil was sampled after spring rapeseed (*Brassica napus* ssp. *oleifera*, Licosmos cv.) harvest at shoot elongation phase (KD = 35, according to BBA) [3] and after white mustard (*Sinapis alba* L., Borowska cv.) harvest at the shoot elongation phase (KD = 35, according to BBA). [3].

The following analyses were performed using the soil material collected after each test plant harvest:

- pH in 1 mol $KCl \cdot dm^{-3}$ and 0.01 mol $CaCl_2 \cdot dm^{-3}$ applying the potentiometric technique at soil-solution ratio 1:2.5 [4]
- hydrolytic acidity based on modified Kappen's method in 1 mol $CH_3COO \ Na \cdot dm^{-3}$ solution
- exchangeable alkaline cations content (K^+, Ca^{2+}, Mg^{2+}, Na^+) by means of Pallmann's method in 1 mol $CH_3COONH_4 \cdot dm^{-3}$ solution at pH = 7. Measurements were made by means of AAS technique [1] using a Hitachi Z-8200 with Zeeman's polarization
- content of exchangeable lead ion forms (Pb^{2+}) was determined in 1 mol $HCl \cdot dm^{-3}$ [5] at soil-solution ratio 1:10. The extraction process was improved by intensive mixing using a rotational mixer for 1 hour. Measurements were made by means of AAS technique [6] using a Hitachi Z-8200 with Zeeman's polarization.

Cd Experiment

The experiment was set by means of the complete randomization method. The experimental unit consisted of a pot filled with 3 kg air-dry bulk soil. The pot experiment was carried out on lessive soil developed from dusty sandy loam of the composition of particular mechanical fractions: 48% sand, 31% dust, 21% loam, and containing 1.15% organic C, and showing pH 6.20 in 1 M KCl. Content of cadmium ions amounted to 0.14 mg/kg of soil.

The experimental pattern included 12 variants, each replicated four times. Variants of the experiments were created by introducing soluble cadmium salts (in the form of $CdCl_2$ in the amount of 5 mg $Cd \cdot kg^{-1}$ soil DM), immobilizing agents such as zeolites-clinoptilolite (Fluka) at the following rates: zeolite-3 – 15 mg·pot⁻¹, zeolite-4 – 30 mg·pot⁻¹, artificial humic acids as sodium humates (by Aldrich, marked as K.H.) in quantities: K.H.-3 – 15 mg·pot⁻¹, K.H.-4 – 30 mg·pot⁻¹, as well as selenium in the form of $Na_2SeO_4 \cdot 10H_2O$ (in the amount of 5 mg $Se \cdot kg^{-1}$ soil DM), into the soil in pots.

Variant "0" in both series was made without adding cadmium ions nor immobilizing agents, although mineral nutrition was used. Nutrition was uniform for all experimental objects and replicates: 0.15 g $N \cdot kg^{-1}$ soil DM as NH_4NO_3 (1/2 dose before sowing and 1/2 dose after emergence); 0.07 g $P \cdot kg^{-1}$ soil DM as $CaHPO_4 \cdot 2H_2O$ (all the quantity before sowing); 0.15 g $K \cdot kg^{-1}$ soil DM as KCl (all the amount before sowing). Soil humidity was maintained at 60% of field water capacity.

In the 1st experimental year, the soil material was collected from pots after common wheat (*Triticum aestivum* L., Opatka cv.) was harvested at full ripeness (KD = 99,

according to Zadoks) [3] and after white mustard (*Sinapis alba* L., Borowska cv.) was harvested at the shoot elongation phase (KD = 35, according to BBA) [3]. In the 2nd year of the experiment, soil was sampled after spring rapeseed (*Brassica napus* ssp. *oleifera*, Licosmos cv.) was harvested at shoot elongation phase (KD = 35, according to BBA) [5] and after white mustard (*Sinapis alba* L., Borowska cv.) was harvested at the shoot elongation phase (KD = 35, according to BBA) [3].

The soil material from under each test species harvest was subject to the following determinations:

- pH in 1 mol $KCl \cdot dm^{-3}$ and 0.01 mol $CaCl_2 \cdot dm^{-3}$ applying potentiometric technique at soil-solution ratio 1:2.5 [4]
- contents of exchangeable metal cations Zn^{2+} as well as Cd^{2+} ions in 1 mol $HCl \cdot dm^{-3}$ [5] at soil-solution ratio 1:10. The extraction process was improved by intensive mixing using a rotational mixer for 1 hour. Measurements were made by means of AAS technique [24] using a Hitachi Z-8200 with the Zeeman's polarization.

In both experiments, besides the above-mentioned methods, the soil also was subject to organic carbon content determination by means of Tiurin's titrimetric method consisting of oxidizing the organic matter by potassium dichromate with sulfuric (VI) acid addition and in the presence of silver sulfate (VI). The amount of oxidizer used during reaction was determined by titration of its excess using a reducing agent – Mohr's salt $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$.

Data achieved from experiments were statistically processed by means of variance analysis with Tukey confidence intervals at the significance level of 0.05. The molar ratios between selected elements were also calculated after re-calculating a given element content in the soil onto its univalent ions millimoles. All results are presented in tables.

Results

Pb Experiment

The increase of pH_{KCl} value in variants with lead addition (Table 1), as compared to those with no lead, was recorded in the first experimental year. Introducing the humic acids (K.H.) into the subsoil affected only a slight increase of pH_{KCl} value both in the control and the object with lead only, although a lower K.H. rate brought better effects. Zeolites exerted their strongest influences on the pH increase in the soil contaminated with lead compounds, namely at higher doses. The decrease of pH was recorded in variants where selenates were used as a binding agent. In object 0+Se, the pH_{KCl} value was lower by 0.9 units as compared to the control, while both values were lower by 0.7 units in object 12 (0+Pb+Se) against variant 7 (0+Pb). A general drop in soil reaction was observed after the mustard harvest in the 1st year of the experiment when compared to pH values recorded for the soil under wheat (Table 1). Humic acids contributed to higher pH values, both in

Table 1. pH_{KCl} values of the soil.

No.	Variants	1st year		2nd year	
		Soil under wheat	Soil under mustard I	Soil under rapeseed	Soil under mustard II
1	0	6.41	6.24	5.27	5.34
2	0+zeolite-1	6.37	6.32	5.08	5.32
3	0+zeolite-2	6.34	6.29	5.18	5.28
4	0+K.H.-1	6.44	6.40	5.12	5.33
5	0+K.H.-2	6.38	6.39	5.38	5.30
6	0+Se	5.55	5.26	4.94	5.14
7	0+Pb	6.37	6.36	5.25	5.25
8	0+Pb+zeolite-1	6.43	6.24	5.16	5.27
9	0+Pb+zeolite-2	6.52	6.32	5.19	5.24
10	0+Pb+ K.H.-1	6.42	6.36	5.17	5.27
11	0+Pb+ K.H.-2	6.42	6.34	5.12	5.27
12	0+Pb +Se	5.62	5.19	5.09	5.23

objects without and with lead additions. The pH_{KCl} values in both selenate-amended objects (Table 1) also decreased by about 1 unit as compared to the control and 0+Pb object.

During the second experimental year, soil pH values under both test plants (rapeseed and mustard) decreased and the soil reaction became acidic instead of slightly acidic with oscillations around 4.5-5.5. Higher humic acid rates (Table 1) exerted their effects on pH_{KCl} value in the soil under rapeseed with no lead ion addition. In leaded variants, all applied sorbents had similar impacts on soil acidity, whereas none significantly affected the increase of pH level (Table 1). Humic acids at both rates applied most influenced the increase of soil reaction under mustard, although the differences were insignificant (Table 1). The pH_{KCl} values in soil under rapeseed and mustard in selenate-treated objects were lower than in the rest, though these differences were not so considerable as in the first year of the pot experiment (Table 1).

Higher levels of the total sorption capacity were recorded in variants where lead ions were introduced into the soil environment (Table 2), although the increase was affected by the presence of immobilizing agents. The significant T value increase by about 20 $mmol(+) \cdot kg^{-1}$ was recorded in variant 12 (0+Pb+Se) as compared to remaining objects. Values of the total sorption capacity between variants 0+Se and 0+Pb+Se did not significantly differ. It was found that T value increase by over 8 $mmol(+) \cdot kg^{-1}$ in the second year of experiments versus the first one. Another experimental factor – plant species – did differentiate the T values in soil, and despite this, the parameter between soil samples from under the mustard collected in the first and second year of experiment did not significantly differ. The base saturation degree (V) was within the range of optimum limits for

Table 2. Total sorption capacity (T) and bases saturation degree (V) of investigated soils.

No.	Variants	T (mmol(+)·kg⁻¹)					V (%)				
		Soil under wheat (B)	Soil under mustard I (B)	Soil under rapeseed (B)3	Soil under mustard II (B)	$\bar{x}$ (A)	Soil under wheat (B)	Soil under mustard I (B)	Soil under rapeseed (B)	Soil under mustard II (B)	$\bar{x}$ (A)
1	0	57.03	64.41	71.12	65.67	64.56	80.72	85.72	70.99	73.16	77.65
2	0+zeolite-1	59.01	67.36	73.07	68.34	66.94	81.83	86.29	68.94	73.40	77.61
3	0+zeolite-2	57.40	71.26	76.11	68.28	68.26	81.68	89.00	70.93	73.64	78.81
4	0+K.H.-1	61.90	69.00	75.79	69.79	69.12	83.36	86.25	70.31	74.74	78.66
5	0+K.H.-2	58.86	69.50	77.58	70.76	69.17	83.15	87.04	72.93	75.08	79.55
6	0+Se	77.83	85.99	87.53	82.10	83.36	74.93	80.36	71.05	75.57	75.48
7	0+Pb	63.12	57.19	77.60	71.77	67.42	85.15	86.89	72.58	74.88	79.88
8	0+Pb+zeolite-1	67.90	61.02	79.40	70.12	69.61	85.89	86.16	71.90	74.60	79.64
9	0+Pb+zeolite-2	69.53	58.15	79.45	70.89	69.50	87.22	85.81	71.69	74.08	79.70
10	0+Pb+K.H.-1	65.58	59.58	78.02	71.59	68.69	85.97	86.15	71.16	75.67	79.74
11	0+Pb+K.H.-2	67.74	58.06	76.44	73.04	68.82	86.18	86.76	70.94	78.33	80.55
12	0+Pb+Se	84.37	90.30	97.54	82.80	88.75	78.15	81.09	75.46	76.46	77.79
	$\bar{x}$ (A·B)	65.85	67.65	79.14	72.09	-	82.85	85.63	71.57	74.97	-
	$\bar{x}$ (C)	66.75		75.61		-	84.24		73.27		-
LSD₀.₀₅	A	8.45					7.55 (n.s.)				
	B	4.48					1.55				
	C	2.50					0.94				
	A·B	10.26					5.65				
	A·C	10.15					5.00				

$\bar{x}$ (A) – mean values for factor A levels (variants), $\bar{x}$ (B) – mean values of factor B levels (plants), $\bar{x}$ (C) – mean values of factor C levels (years), $\bar{x}$ (A·B) – mean values of factors A and B interaction levels, $\bar{x}$ (A·C) – mean values of factors A and C interaction levels, LSD₀.₀₅X (X = A, B, A·B, A·C) – the least significant difference for mean values of a factor or mean values of factors interaction at the significance level of α=0.05.
n.s. – no significant differences.

Polish soils not exceeding 90%. No considerable influences were recorded even after introducing all binding agents and lead ions into the soil (Table 2). The parameter was significantly differentiated by the test plant species and experimental year. It was found that the value of V indicator was higher by about 10% in the first as compared to the second year of experiments.

Table 3 presents lead contents after extracting the soil collected from under the test plants in the 1st experimental series using 1 mol HCl·dm⁻³. Lead contents in variants with added immobilizing agents were higher as compared with variant 0+Pb, both in the soil under wheat and rapeseed. The contrary effect was reported in the case of both mustards, where sorbent presence in the soil environment affected the lower concentrations of lead ions in soil; however, differences in particular variants were not statistically significant. Instead, the plant species had some influence on the factor values; it was found that lead ion content was considerably lower in the soil under both mustards than under main crops such as wheat and rapeseed.

Cd Experiment

Introducing cadmium into the soil considerably decreased its pH (Table 4). The pH_{KCl} value was recorded to be in variant 7 (0+Cd) by over 0.4, while pH_{CaCl_2} by 0.2 lower as compared to the control (pos. 1). Humic acids exerted the greatest influence on the increase of pH_{KCl} and pH_{CaCl_2} levels in objects contaminated with cadmium. Also, zeolites elevated both pH parameters, but only slightly. In soil under mustard I, all applied immobilizing agents affected the increase of pH_{KCl} and pH_{CaCl_2} values (Table 4).

In series II during the second experimental year, a decrease of soil reaction was observed. Higher zeolites and humic acid rates had effects on pH_{KCl} and pH_{CaCl_2} values in

Table 3. Lead contents in the soil (mg·kg⁻¹).

No.	Variants	Soil under wheat (B)	Soil under mustard I (B)	Soil under rapeseed (B)	Soil under mustard II (B)	$\bar{x}$ (A)
1	0+Pb	56.48	56.69	57.61	55.41	56.55
2	0+Pb+zeolite-1	55.96	56.27	59.04	56.73	57.00
3	0+Pb+zeolite-2	61.40	55.15	58.88	55.00	57.61
4	0+Pb+K.H.-1	58.59	54.37	59.75	54.88	56.90
5	0+Pb+K.H.-2	59.97	54.20	61.28	55.38	57.71
6	0+Pb+Se	60.46	55.47	59.18	58.22	58.33
$\bar{x}$ (A·B)		58.81	55.36	59.29	55.94	-
$\bar{x}$ (C)		57.08		57.61		-
LSD$_{0.05}$	A	3.43 (n.s.)				
	B	2.15				
	C	1.33 (n.s.)				
	A·B	7.50 (n.s.)				
	A·C	5.70 (n.s.)				

$\bar{x}$ (A) – mean values for factor A levels (variants), $\bar{x}$ (B) – mean values of factor B levels (plants), $\bar{x}$ (C) – mean values of factor C levels (years), $\bar{x}$ (A·B) – mean values of factors A and B interaction levels, $\bar{x}$ (A·C) – mean values of factors A and C interaction levels, LSD$_{0.05}$X (X = A, B, A·B, A·C) – least significant difference for mean values of a factor or mean values of factors interaction at significance level of α=0.05,
n.s. – no significant differences.

soils under rapeseed from objects with no cadmium added (Table 4). Increased pH$_{CaCl_2}$ value in relation to object 0+Cd was recorded in variant 9 (0+Cd+zeolite-4). In the soil under mustard II, the increase of both pH values was affected by zeolites at their lowest dose (Table 4). Variants with selenium revealed the decrease of pH in soils analyzed after each test plant species harvest (Table 4).

Cadmium content in cadmium-contaminated soils increased, resulting from zeolite and humic acid additions (Table 5), while a higher increase was recorded for variants 0+Cd+zeolite-4 and 0+Cd+K.H.-4, in which double sorbent doses were used. A significant increase of active cadmium forms was found in variant 6 (0+Cd+Se), where content of the element was higher by 0.34 mg·kg⁻¹ in relation to the object with cadmium only (Table 5). Variety – as another experimental factor in series II – had a significant influence on the contents of mobile cadmium forms in the soil environment. Only in the soil under rapeseed, were considerably higher cadmium levels (by over 0.3 mg·kg⁻¹ in relation to soil under mustard II) recorded. No significant differences in reference to soils collected in the first year of experiment were found. Cadmium concentrations in soils varied within years. A significant drop of cadmium content by about 0.2 mg·kg⁻¹ was observed in the second experimental year.

Table 6 presents Cd:Zn ratios. Introducing selenium compounds resulted in the decrease of Cd:Zn ratio in the soil under all test plant species by 2 units, on average. The presence of zeolites (Table 6) affected the enhancement of the ratio. In the soil under wheat, humic acids (namely their

Table 4. The pH$_{KCl}$ values of the soil.

No.	Variants	1st year Soil under wheat	1st year Soil under mustard I	2nd year Soil under rapeseed	2nd year Soil under mustard II
1	0	6.41	6.24	5.27	5.34
2	0+zeolite-3	6.36	6.25	5.13	5.31
3	0+zeolite-4	6.40	6.37	5.28	5.25
4	0+K.H.-3	6.29	6.28	5.22	5.28
5	0+K.H.-4	6.41	6.36	5.27	5.18
6	0+Se	5.55	5.26	4.94	5.14
7	0+Cd	6.06	6.04	5.11	5.15
8	0+Cd+zeolite-3	6.07	6.08	4.97	5.18
9	0+Cd+zeolite-4	6.08	6.06	5.06	5.13
10	0+Cd+K.H.-3	6.13	6.07	5.06	5.13
11	0+Cd+K.H.-4	6.15	6.08	5.00	5.12
12	0+Cd+Se	5.66	5.18	4.85	5.14

Table 5. Contents of cadmium in soil (mg·kg⁻¹).

No.	Variants	Soil under wheat (B)	Soil under mustard I (B)	Soil under rapeseed (B)	Soil under mustard II (B)	$\bar{x}$ (A)
1	0+Cd	4.73	4.82	4.78	4.41	4.68
2	0+Cd+zeolite-3	4.77	4.91	4.84	4.64	4.79
3	0+Cd+zeolite-4	4.78	4.96	4.98	4.50	4.81
4	0+Cd+K. H.-3	4.72	4.93	4.81	4.42	4.72
5	0+Cd+K. H.-4	5.00	4.92	4.86	4.47	4.81
6	0+Cd+Se	4.74	5.41	5.07	4.85	5.02
$\bar{x}$ (A·B)		4.79	4.99	4.89	4.55	-
$\bar{x}$ (C)		4.89		4.72		-
LSD₀.₀₅	A	0.23				
	B	0.13				
	C	0.09				
	A·B	0.30				
	A·C	0.35				

$\bar{x}$ (A) – mean values for factor A levels (variants), $\bar{x}$ (B) – mean values of factor B levels (plants), $\bar{x}$ (C) – mean values of factor C levels (years), $\bar{x}$ (A·B) – mean values of factors A and B interaction levels, $\bar{x}$ (A·C) – mean values of factors A and C interaction levels, LSD₀.₀₅X (X = A, B, A·B, A·C) – least significant difference for mean values of a factor or mean values of factor interaction at the significance level of α=0.05.

Table 6. Cd:Zn ratios in the soil of series II of pot experiments.

No.	Variants	Cd : Zn ratio			
		Soil under wheat	Soil under mustard I	Soil under rapeseed	Soil under mustard II
1	0	0.01	0.01	0.01	0.01
2	0+zeolite-3	0.01	0.01	0.01	0.01
3	0+zeolite-4	0.01	0.01	0.01	0.01
4	0+K. H.-3	0.01	0.01	0.01	0.01
5	0+K. H.-4	0.01	0.01	0.01	0.01
6	0+Se	0.01	0.01	0.01	0.01
7	0+Cd	0.24	0.26	0.15	0.23
8	0+Cd+zeolite-3	0.27	0.27	0.17	0.24
9	0+Cd+zeolite-4	0.28	0.25	0.16	0.25
10	0+Cd+K.H.-3	0.19	0.28	0.15	0.23
11	0+Cd+K.H.-4	0.17	0.27	0.16	0.23
12	0+Cd+Se	0.21	0.24	0.14	0.21

lower rates), reduced Cd:Zn ratio, while higher ratio values were recorded after applying humic acids under mustard I. Such an increase was observed in the soil under rapeseed only for variant 11 (0+Cd+K.H.-4). A lower dose of sodium selenate added to soil under rapeseed, as well as both rates under mustard II, did not differentiate the Cd:Zn ratio in reference to variant 0+Cd (Table 6).

Discussion of Results

Pb Experiment

These are commonly assumed to be the most important factors determining the mobility of heavy metals in the soil: pH, organic matter, and minerals, as well as ionic antago-

nism and synergism [7-12]. A significant increase of Pb mobility can be observed at pH below 5, while at pH above 7 (and in the presence of organic substances), a major part of soluble lead can occur in soluble complexes with organic matter [6, 7, 10, 13, 14]. Here, presented results of the pot experiments revealed that soil pH considerably determined the changes of toxic element contents in soil.

Characteristics of the soil sorption complex indicated that applied immobilizing agents had an impact on its properties improvement through the increase of total sorption capacity (T) and bases saturation degree (V), both invariants with no heavy metals and lead contaminated ones, which may be contributed to soil pH increase and, in consequence, a lower share of acidic cations. Mainly zeolites at their double doses and sodium humates applied at both levels affected the increase of total soil sorption capacity, which was probably the consequence of pH changes. It could even be confirmed by other authors [15-18, 28], who found that organic matter composes the prevailing part of a buffering sorption capacity, and it is responsible for pH-dependent negative charges, i.e. variable ones. Numerous authors have reported [1, 7, 9, 10, 19] that minerals in the soil contain permanent charges, while sorption capacity increases along with soil pH value, mainly due to dissociation of H^+ and Al^{3+} ions originating from these permanent charges on mineral fragments of the sorption complex. The number of instable charges also increases along with the pH increase, mainly on organic parts of the sorption complex [6-8, 10]. To improve the physicochemical properties of a soil is one of the basic conditions that sorbents used for detoxicating the soils contaminated with heavy metals should meet [12, 16, 19]. Here, performed experiments revealed that all applied binding agents met the above conditions.

The influence of immobilizing agents on lead mobility in a soil was evaluated on a base of its separation using 1 M HCl solution. Achieved results revealed that applied sorbents contributed to the decrease of mobile lead ion concentrations in soil. In the soil under wheat, lead ion detoxication was observed after introducing a lower clinoptilolite dose, whereas higher rates of the zeolite appeared to be the most efficient Pb^{2+} immobilizing agent in the soil under rapeseed. In the soil under mustard I and mustard II, the lead detoxicating effects were recorded after zeolites and sodium humates application, though humic acids at both levels were more efficient under mustard I, while a lower rate of clinoptilolite and higher dose of sodium humates immobilized Pb^{2+} ions most efficiently under mustard II. Sodium selenate (VI) has affected Pb^{2+} ion immobilization in the pot experiments. That influence has probably been associated with the subsoil pH changes and excessively high dose of the sorbent applied in the experiments [9, 12, 16, 20-23].

Cd Experiment

A considerable increase in Cd and Zn mobility can be recorded at pH < 6.0-6.5, while cadmium mobility, in general, decreases at 5.5-6.0 through 7.4 [7, 24, 26-28]. On the other hand, some authors [8, 18, 21, 22] often considered the influence of root leachates: organic substances in a form of low-molecular organic acids and phenolic compounds, that may cause interference during the heavy metal immobilization process.

During the present experiment, the strongest effect of pH increase was recorded after introducing organic sorbents in the form of sodium humates. Sodium selenate (VI) affected the lower pH values, hence the increase of soil acidification. Selenium added into the soil environment as sodium selenate (VI) – in the majority of cases – mobilized heavy metals, which could be affected by its high dose (5 mg Se·kg^{-1} soil DM). Some authors [20-22] reported that content below 0.15 mg Se·kg^{-1} soil is assumed as limiting value considered as deficient, whereas upper limits for selenium in soils are within the range 1.6-10 Se·kg^{-1} soil. The immobilizing effects of selenium toward cadmium were recorded only in the soil under wheat.

Reducing the content of mobile cadmium ion forms within the soil was observed after applying sodium humates at a lower dose. Worse, cadmium mobility also was affected by a lower clinoptilolite rate. Despite numerous reports about the lower affinity of cadmium rather than lead ions towards zeolites, here presented results did not reveal that cadmium can be equally sufficiently bound by those minerals. Cadmium shows a great affinity to organic matter and its binding strength depends on soil pH [1, 9, 14, 15, 26]. Some authors [8, 10, 23, 24] have claimed that high-molecular humic acid complexes are more durable in acidic environment (although pH should not be lower than 4) than in alkaline, in which functional groups of humic acids become dissociated and deprotoned, and H^+ ions originating from organic matter make pH lower, which favors the release of metal ions. Cadmium is strongly bound at pH values above 5.5 [1, 7, 10, 28]. Considerable detoxication abilities of organic matter in relation to Cd^{2+} are confirmed here by presented study results – namely narrow values of Cd:Zn ratios in variants with humic acids in the soil of pot experiment, particularly at higher rates of the sorbent. Changes in the Cd:Zn ratio in the presence of humic acids may also result from mobilization of zinc that is strongly bound by organic matter only in alkaline environments. Some authors [1, 10, 24], moreover, found that the presence of Zn^{2+} ions inhibited Cd^{2+} adsorption.

Conclusions

Soil pH values have been changing due to applied sorbents, which in the majority determined the forms of toxic metals in soils. Lead immobilizing effects have been observed after introducing the binding agents and along with pH increase. Detoxication of mobile lead forms contained in the soil has been affected the most by clinoptilolite, although its higher rate has appeared to be the most efficient. Both doses of sodium humates immobilized lead ions as well. Cadmium immobilization effect has been invoked by binding agents and increased pH value. Both zeolites and humic acids have affected the Cd^{2+} immobilization, but only at their lower doses. The investigations have indicated greater affinity of cadmium to organic sor-

bents, although it has depended on a rate of both zeolite and humic acids, test plant species, and pH value.

Binding agents applied in the experiments have improved properties of the soil sorption complex through the increase of total sorption capacity as well as base saturation degree, which met the necessary condition of the lack of toxicity to detoxify the heavy-metal-contaminated soils. The experiments have indicated higher affinity of lead to mineral rather than organic sorbents; however, it has depended both on zeolite and humic acid rates, as well as such physicochemical properties as pH or soil sorption capacity.

Clinoptilolite has appeared to be a promising binding agent that immobilizes cadmium ions. Selenium compounds also bring much hope, because the element is more often assumed as necessary for living. However, the selenium action mechanism is very complicated and not uniform, thus it needs to be recognized in the future. Evaluating the selenium amounts in compounds to reduce the mobility of heavy metals that would not be toxic for plants, animals, and humans, seems to be a priority.

Sodium selenate (VI) has affected Pb^{2+} ion immobilization in the pot experiments. That influence has probably been associated with the subsoil pH changes and excessively high dose of the sorbent applied in the experiments.

Changes in Cd:Zn ratio in the presence of humic acids may also result from mobilization of zinc that is strongly bound by organic matter only in alkaline environments. The presence of Zn^{2+} ions inhibited probably Cd^{2+} adsorption, which has been found also by some other authors.

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