Transformation of Heavy Metal Compounds during the Remediation of Contaminated Soils

Tatiana MINKINA [1]([✉])
Galina MOTUSOVA [2]
Saglara MANDZHIEVA [1]
Olga NAZARENKO [3]
Ivan ŠIMUNIC [4]

Summary

The effect of ameliorants, chalk, glauconite and semidecomposed cattle manure, on ordinary chernozem contaminated with Zn and Pb was studied in a long-term field experiment. The application of ameliorants significantly decreased the mobility of metals. Their effect depended on the ameliorant and was most significant at the simultaneous application of chalk and manure. This effect was presumably due to the strong binding of metals by carbonates through chemisorption and formation of low-soluble Zn and Pb compounds and to the additional fixation in the form of complexes at the addition of organic material. The share of loosely bound metal compounds in the contaminated soils decreased to the level typical for the clean soils or even below. The general evolution of the transformation of metal compounds (from less to more firmly bound compounds) accelerated by ameliorants remained for both metals.

Key words

soil, heavy metal compounds, transformation, ameliorants

[1] Southern Federal University, Faculty of Biology and Soil Science, Soil Science Department, 813, 194/1, prosp. Stachki, Rostov-on-Don, 344090, Russia
[✉] e-mail: minkina@bio.rsu.ru
[2] Moscow State University, Faculty of Soil Science, Department of Soil Chemistry, Moscow, Russia
[3] Don State Agrarian University, Department of Agriculture, Rostov region, Russia
[4] University of Zagreb, Faculty of Agriculture, Department of Soil Amelioration, Svetošimunska 25, 10000 Zagreb, Croatia

*a*CS

Introduction

The barrier function is an essential function of soil in an ecosystem. The soil protects natural waters, air, and plants from pollutants. This function is ensured by the sorption capacity of soils. It should be noted that plants also have some resistance to soil contamination. The soil under study is a highly buffering self-protecting system. However, our studies showed that the self-protection mechanisms are not always efficient. Therefore, methods should be developed for the remediation of polluted soils with the use of ameliorants.

The available data on the efficiency of specific ameliorants are insufficient to reveal the processes resulting in the redistribution of heavy metal forms in contaminated soils. In addition, the efficiency of remediation methods was better studied for slightly acid chernozems and acid soddy-podzolic and podzolic soils with different particle-size distributions. At the same time, ordinary chernozems usually escape the attention of researchers.

The soils of this genetic subtype occupy a significant area (mainly in the industrial regions of Rostov oblast and Krasnodar region (Russia) subjected to active anthropogenic pollution) and their major part is in agricultural use; therefore, analogous studies of these soils are of current interest.

The reclamation methods of arable soils contaminated with metals are mainly aimed at decreasing the content of mobile metal compounds. The selection of ameliorants should be based on the mechanisms of strong metal fixation; i.e., the action of an ameliorant should be directed to the enhancement of the barrier function of soils. Insufficient data are available on mechanisms for the strong fixation of metals by soil components, including in reclaimed soils.

The analysis of the group metal composition showed the polyfunctional nature of soil components and the capacity of each of them for both strong and weak retention of contaminant metals. The selection of ameliorants for contaminated soils was based on the presumed formation of metal compounds firmly bound to soil components corresponding to their loosely bound analogues.

The strong fixation of heavy metals in the soil is due to their chelation, precipitation, and fixation in the structure of minerals; therefore, manure (active agent in the complexation of metals with different stability), chalk (active agent in the specific sorption and precipitation of metals), and glauconite (active agent in the exchangeable sorption and fixation of metals) were used as ameliorants.

The high capacity of humus acids for binding and firmly retaining appreciable amounts of heavy metals found practical application for soil detoxification (Choi et al., 2008). Brown coal, which is also a source of natural humic acids, is used as a sorbent.

Natural zeolites having a high sorption capacity have attracted recent attention of scientists dealing with the protection of soils and plants from the contamination with heavy metals (Mineev et al., 1989; Ming and Mumpton, 1989; Knox and Adriano, 1999; Barbu et al., 2003; Kliaugiene and Baltrenas, 2003). Natural sorbents are profitable agents, because they are ecologically safe, readily available, and inexpensive. There are different opinions about the efficiency of zeolites on the soils contaminated with heavy metals. Some authors (Belousov, 2006) emphasized their high selectivity for heavy metals. Other authors (Dabakhov et al., 1998) reported the lower efficiency of zeolites compared to lime materials and a significant limitation in the mobility of heavy metals in the soil and their input into plants only at zeolites application rates of 80–100 t/ha and more. This is also true for the effect of organic fertilizers (Dabakhov et al., 1998).

At the same time, it should be noted that the use of zeolites as sorbents of heavy metals is limited by the following factors. First, the volume of zeolites applied is very large, which makes them applicable only near zeolites fields. Second, along with heavy metal cations, zeolites can sorb potassium, ammonium, and microelement ions, i.e., affect the conditions of the mineral nutrition of plants. Third, data are available that zeolites are subjected to weathering, during which they can be transformed into other minerals with different properties of cation sorption. Fourth, exchange on some zeolites minerals proceeds even more slowly than on clay minerals. The completion of this process, i.e., the penetration of exchangeable cations into channel-shaped holes, takes too much time. This property of zeolites is used in plant growing: they are mixed with organic fertilizers. Long-acting composite fertilizers are prepared by this method.

Glauconite fields are common in Rostov oblast. Glauconite enters in sands, sandstones, clay, and marls. Total predicted resources of the mineral in Rostov oblast exceed 20 million m^3 (Khardikov et al., 1999).

The adsorption properties of zeolites are determined by the unique crystal lattice characterized by a developed internal surface and a strictly determined size of input windows. Zeolites are a sort of molecular sieves capable to sorb molecules of specific size from their mixtures. Only molecules whose size is smaller than the input window can penetrate into the adsorption cavity. Zeolites can adsorb relatively large amounts of heavy metal salts. The cation exchange capacity (CEC) of natural zeolites is 100–300 mg/kg (Pinsky, 1997).

A large number of publications deal with the use of natural zeolites for the purification of water from dissolved chemical impurities, but the use of zeolites as adsorbents of heavy metals is still insufficiently understood (Panin and Bairova, 2005).

A higher efficiency of the simultaneous application of ameliorants compared to their separate application was noted repeatedly (Chen et al., 1999; Geebelen et al., 1999). In the recommendations for decreasing the toxicity of soils contaminated with heavy metals (Kryuchkov,1985), it was proposed to use lime materials and high rates of organic fertilizers (100–150 t/ha).

There are also many less common methods. The claying of coarse soils, which significantly increases their cation exchange capacity, can give good results (Sizov et al., 1990). An expensive method for decreasing the mobility of heavy metals involves the use of ion-exchange resins containing carboxyl and hydroxyl groups. Resins are used in the acid form or saturated with potassium, calcium, or magnesium ions or their mixture and applied to the soil as granules or powders.

Many authors noted the high efficiency of liming the contaminated soils (Basta, et al., 2001; Brown et al., 2001; Yang et al., 2008). The Rostov oblast has immense reserves of limestone. However, liming is widely used for acid soils but not for neutral and slightly alkaline soils.

*a*CS

Agric. conspec. sci. Vol. 76 (2011) No. 1

Therefore, the main goal of the suggested approach is to determine the group composition and mobility of heavy metals in soils for studying the possibility of using different ameliorants in chernozem contaminated with Cu, Zn, and Pb.

Material and methods

The object of research was loamy ordinary chernozem from which has following properties: Corg, 2.3%; $CaCO_3$, 0.4%, pH H_2O, 7.6; particles <0.01 mm, 53.1%; particles <0.001 mm; exchangeable Ca^{2+}, 29 meq/100 g; exchangeable Mg^{2+}, 0.4 meq/100 g; and exchangeable Na^+, 0.1 meq/100 g.

The effect of different ameliorants on ordinary chernozem contaminated with heavy metals was studied in a long-term field experiment (2000-2008) in the Rostovskii state crop testing site. Ameliorants were applied three months after the contamination of soils with Zn and Pb acetates. Chalk (2.5 and 5 mg/m²), glauconite (2 kg/m²), and semidecomposed cattle manure (5 kg/m²) were used as ameliorants, as well as their combinations according to the following experimental design:

(1) without ameliorants;
(2) metal (Me);
(3) Me + glauconite;
(4) Me + manure;
(5) Me + glauconite + manure;
(6) Me + chalk, 2.5 kg/m²;
(7) Me + chalk, 5 kg/m²;
(8) Me + chalk, 2.5 kg/m² + manure;
(9) Me + chalk, 5 kg/m² + manure.

Experiments were conducted in triplicate. Samples were taken at a depth of 0–20 cm.

The chalk used in the experiment contained the following metal contents (mg/kg): Zn, 10.3; Ni, 2.56; Mn, 17.3; Cr, 17.4. As, Pb, Cu, and Fe were not found in the chalk.

Based on the results of pot experiment on soils with different contents of carbonates, the following application rates of chalk were used in the field experiment on soil remediation: 2.5 and 5 kg/m².

Glauconite was used as a natural sorbent. Glauconite (from the Greek glaucos – bluish-green) is a complex potassium-containing aluminosilicate, mineral of hydromica group, layered silicate subclass, with the formula $K[(Fe^{3+}, Al)_{1,33} (Fe^{2+}, Mg)_{0,67}]_2 Si_{3,67} Al_{0,33} O_{10}(OH)_2^-$.

Rock mineralogy: fraction >0.01 mm, 75% (including glauconite, 42%; quartz, 32%); fraction <0.01 mm, 25% (including glauconite, 24%; quartz, 1%). Montmorillonite, calcite, sponge spicules, and siliceous organism residues were not found in the samples. The total content of glauconite in the rock was 66%.

Bulk chemical composition of rocks: SiO_2, 69.5%; Al_2O_3, 4.9%; Fe_2O_3, 13.8%; FeO, 0.20%; CaO, 1.35%; MgO, 1.94%; MnO, 0.016%; K_2O, 3.60%; Na_2O, 0.18%; P_2O_5, 0.41%; TiO_2, 0.30%; SO_3(tot), 0.10%; CO_2, not det., B_2O_3, 0.06%; W_{hygr}, 2.08%; organic matter, 0.23%. The content of heavy metals in glauconite was as follows: Li, 0.0018%; Zn, 0.0034%; Cu, <0.001%; Pb, <0.01%; Ni, 0.004%; Cr, 0.0164%; V, <0.01%; F, 0.16%; Co, <0.001%; Mn, 0,010%.
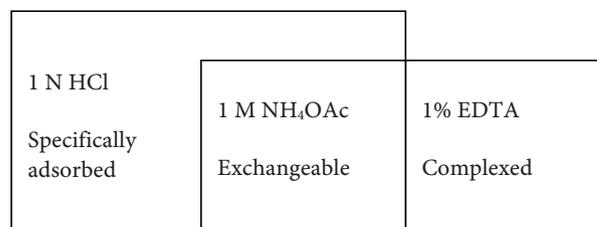
Figure 1. Sub-divisions of the loosely bound metal fraction in soils and their extractants

In the experimental glauconite samples, Pb was not found and the content of Zn was 0.1 mg/kg. With account for the application rate of 2 kg/m², 2 mg/kg Zn arrived to the soil with glauconite.

Semidecomposed cattle manure had the following parameters: water, 65.2%; ash, 26.2%; pH, 7.5; N_{tot}, 0.85%; P_2O_{5tot}, 0.87%; K_2O_{tot}, 0.90%.

Total heavy metals in manure: Zn, 60.0 mg/kg; Pb, 12 mg/kg; Cd, 4 mg/kg; Cu, 9 mg/kg. With account for the organic fertilizer rate (5 kg/m²), 3 mg/kg Zn and 0.6 mg/kg Pb were applied to the soil. The total amount of heavy metals in soils was determined by X-ray fluorescence. Metals in soil extracts were determined by atomic absorption spectroscopy.

We distinguish between two major fractions of heavy metal: (a) firmly bound (FB) and (b) loosely bound (LB) to the soil. To determine the total contents of heavy metals, the soil samples were digested with a mixture of concentrated ($HClO_4$ + HF) acids. The contents of the LB metal fractions were determined in a series of extracts. The concentrations of heavy metals in the extracts were determined using atomic absorption spectrophotometer.

The LB fraction includes exchangeable, complexed and specifically adsorbed metals (Minkina et al., 2008). It characterizes the pool of metals that can migrate from the soil into the adjacent media, including plants and natural waters.

The scheme of sub-fractioning of the LB (potentially mobile) metal compounds and the corresponding extraction procedures are shown in Figure 1.

The metal compounds extracted with 1 M NH_4OAc, pH 4.8 (soil : solution ratio of 1 : 5, extraction time 18 h) are classified as exchangeable. The 1% EDTA in 1 M NH_4OAc, pH 4.8 (soil : solution ratio of 1 : 5, extraction time 18 h) presumably extracts exchangeable heavy metals and those bound in the organometallic complexes. These extractants are recommended for determining the mobile forms of heavy metals in agricultural soils (Mineev, 1989). The difference between the metal contents in the 1% EDTA in NH_4OAc and 1M NH_4OAc extracts should characterize the content of metals bound in complexes with the soil organic matter (Minkina et al., 2006, 2009).

The 1 N HCl solution extracts (soil : solution ratio of 1 : 10, extraction time 1 h) specifically adsorbed metals together with exchangeable metals and dissolves metal oxides and carbonates. A considerable part of the specifically adsorbed heavy metals is relatively loosely fixed by iron, aluminum, and manganese oxides and hydroxides and by carbonates. The contents of specifically

*a*CS

Agric. conspec. sci. Vol. 76 (2011) No. 1

adsorbed heavy metal compounds are calculated as the differences between their amounts extracted with 1 N HCl and 1 M NH_4OAc. This group can be considered as a transitional group between loosely and firmly bound heavy metals.

The calculation of the complex-forming and specifically adsorbed compounds of heavy metals from the difference in the heavy metal contents in different extracts is based on the assumption of their additivity.

To verify this assumption, we used the procedure of sequential extraction of the metals with solutions of 1N NH_4OAc and 1% EDTA and 1N NH_4OAc and 1N HCl. The results obtained by the method of sequential extraction and those calculated from the difference of the metal contents in parallel extracts agreed with one another fairly well.

The contents of FB heavy metals with the soil organic and mineral components were calculated as the difference between the bulk contents of the metals and the contents of LB metals. The FB fractions includes the metals strongly fixed in the structures of silicate and nonsilicate minerals, in difficultly soluble compounds ((hydr)oxides and carbonates) and stable organic and organomineral compounds.

To characterize the mobility of heavy metal s in the soils, we calculated the ratio of LB fractions to FB ones:

MF = LB/FB,

where MF – mobility factor.

Results and discussion

The analysis of the group composition of heavy metal compounds in the reclaimed soils revealed the mechanism of ameliorant action on the mobility of heavy metals in soils.

The total content of metals in the soils with ameliorants remained almost similar to that in the contaminated soils (Table 1). However, the group of loosely bound compounds and, hence, the mobility of metals decreased (Tables 1, 2) because of the decrease in the absolute content of all mobile Zn and Pb forms: exchangeable, complex, and specifically sorbed ones (Table 4). The effects of chalk, manure, and glauconite on the mobilization of metal in the soil were different.

Already in the first year after the application of chalk, in distinction from other ameliorants, the content of exchangeable Zn and Pb forms in the soil decreased to the maximal admission content (MAC) and lower. The share of loosely bound compounds (Table 2) and the value of MF (Table 3) decreased to a higher extent than at the application of glauconite or manure.

The main difference between the effects of 2.5 and 5% chalk on the mobility of metals was that the share of specifically sorbed forms in the group composition of Zn and Pb increased with increasing application rate of chalk. The content of exchangeable compounds decreased respectively.

The effect of glauconite and manure applied separately on the fixation of Zn and Pb was lower, which could be related to the formation of their metal compounds with lower binding strength and insufficient interaction time.

Manure organic matter favored the relatively rapid formation of unstable zinc complexes, which were decomposed already to

Table 1. The total content (numerator) and the ratio between the loosely and firmly bound Zn and Pb compounds (denominator) during 3 years after the application of ameliorants

Experimental treatments	Zn			Pb		
	1 year	2 year	3 year	1 year	2 year	3 year
Without metal addition	68	65	67	24	24	28
	12/88	12/88	12/88	15/85	15/85	12/88
Metal (Me)	356	349	352	110	101	100
	32/68	35/65	36/64	38/62	45/55	42/58
Me + glauconite	346	358	344	106	111	108
	14/86	13/87	7/93	32/68	31/69	16/84
Me + manure	360	360	353	110	102	106
	17/83	12/88	10/90	26/74	27/73	24/76
Me + glauconite + manure	363	365	352	109	101	111
	15/85	15/85	13/87	22/78	25/75	17/83
Me + chalk, 2.5 kg/m^2	350	341	345	111	105	101
	13/87	14/86	10/90	18/82	31/69	12/88
Me + chalk, 5 kg/m^2	347	342	344	108	112	103
	16/84	16/84	9/91	17/83	23/77	17/83
Me + chalk, 2.5 kg/m^2 + manure	361	346	353	105	112	110
	11/89	12/88	5/95	19/81	18/82	16/84
Me + chalk, 5 kg/m^2 + manure	359	350	353	114	106	104
	11/89	11/89	6/94	13/87	16/84	11/89
LSD$_{0.95}$ for numerator	12,3	9,0	8,3	7,5	10,3	9,5

the second year after application, and the released metal passed into more stable organomineral forms.

For lead, the formation rates of metal complexes with manure organic substances were lower; however, their amount significantly increased for three years (Tables 2, 4). The content of specifically sorbed lead compounds increased because of the reinforcement of their bond with soil components and transition into firmly bound compounds.

It should be noted that the change in mobility of heavy metals in the soil at the application of manure was related not only to the formation of metal-organic compounds, but also to the degree of organic matter decomposition. The mineralization of semidecomposed manure in the soil could be accompanied by the formation of water-soluble low-molecular-weight organic complexes, which increased the migratory capacity of metals. As organic matter was decomposed, the immobilizing effect became more manifested due to the formation of more firmly bound compounds of heavy metals with organic matter. A similar phenomenon was observed at the application of fresh manure and undecomposed and semidecomposed straw to the soil (Sizov et al., 1990).

According to the efficiency of the separate application of ameliorants in the fixation of Zn and Pb in the soil, they form the series: chalk > glauconite ≈ manure. Thus, chalk is the best sorbent for Pb, as well as for Zn.

The following possible mechanisms of its effect on metals in contaminated soils are supposed:

1) chemisorption of metals on the surface of $CaCO_3$ particles;
2) formation of separate solid phases (precipitates of heavy metal carbonates and hydroxocarbonates);
3) increase in the sorption activity of Fe, Al, and Mn oxides in the presence of carbonates; and

*a*CS

Agric. conspec. sci. Vol. 76 (2011) No. 1

Table 2. Loosely bound Zn and Pb compounds in ordinary chernozem during three years after the application of ameliorants, mg/kg

Experimental treatments	Exchangeable			Complex			Specifically sorbed		
	1 year	2 year	3 year	1 year	2 year	3 year	1 year	2 year	3 year
			Zn						
Without metal addition	0.6	0.6	0.6	0.4	0.5	0.4	6.5	6.8	6.9
Metal (Me)	33.0	27.6	26.1	27.9	23.7	24.4	52.3	69.8	76.6
Me + glauconite	27.8	16.2	6.9	8.1	6.4	1.36	14.4	24.1	16.4
Me + manure	25.1	18.1	8.4	14.5	5.7	7.6	20.3	17.7	19.1
Me + glauconite + manure	25.4	12.6	3.6	10.6	5.6	13.2	19.9	36.2	29.5
Me + chalk, 2.5 kg/m²	21.6	9.3	3.9	7.8	7.2	3.0	17.2	30.9	29.3
Me + chalk, 5 kg/m²	18.0	4.5	1.0	8.8	14.0	4.88	29.9	37.8	25.0
Me + chalk, 2.5 kg/m² + manure	15.4	6.8	4.7	8.2	6.15	0.5	15.3	27.4	12.1
Me + chalk, 5 kg/m² + manure	10.2	4.0	1.0	9.8	6.0	4.05	20.0	26.5	13.2
LSD$_{0.95}$	6.4	8.0	2.3	1.4	2.01	2.2	10.3	9.9	5.1
			Pb						
Without metal addition	0.8	0.9	1.0	0.3	0.3	0.1	2.4	2.5	2.2
Metal (Me)	12.8	10.8	8.7	6.0	12.8	14.7	22.9	21.7	18.3
Me + glauconite	8.4	6.1	3.0	4.9	8.7	4.8	20.9	19.4	9.5
Me + manure	8.0	6.6	5.3	3.6	4.0	7.5	17.1	16.9	12.4
Me + glauconite + manure	7.2	5.3	1.5	1.8	6.8	6.6	14.9	13.1	10.5
Me + chalk, 2.5 kg/m²	6.7	3.2	2.7	4.5	9.5	2.6	9.3	20.0	6.8
Me + chalk, 5 kg/m²	4.6	3.0	0.9	4.2	5.4	1.8	9.5	17.7	14.5
Me + chalk, 2.5 kg/m² + manure	5.7	2.2	1.5	1.5	7.3	5.1	12.9	11.1	10.5
Me + chalk, 5 kg/m² + manure	4.5	2.0	1.0	0.2	4.9	3.4	9.8	10.0	7.1
LSD$_{0.95}$	1.4	4.0	1.1	1.3	2.3	1.6	9.9	10.5	4.0

Table 3. Mobility factor (MF) of Zn and Pb in the soil during three yeas after the application of ameliorants

Experimental treatments	MF Zn			MF Pb		
	1 year	2 year	3 year	1 year	2 year	3 year
Without metal addition	0.1	0.1	0.1	0.2	0.2	0.1
Metal (Me)	0.5	0.5	0.6	0.6	0.8	0.7
Me + glauconite	0.2	0.2	0.1	0.5	0.4	0.2
Me + manure	0.2	0.1	0.1	0.4	0.4	0.3
Me + glauconite + manure	0.2	0.2	0.2	0.3	0.3	0.2
Me + chalk, 2.5 kg/m²	0.2	0.2	0.1	0.2	0.5	0.1
Me + chalk, 5 kg/m²	0.2	0.2	0.1	0.2	0.3	0.2
Me + chalk, 2.5 kg/m² + manure	0.1	0.1	0.1	0.2	0.2	0.2
Me + chalk, 5 kg/m² + manure	0.1	0.1	0.1	0.1	0.2	0.1

4) formation of heavy metal hydroxocomplexes at increasing pH, which can increase their sorption by the soil.

The dissolution of chalk in the field and model experiments mainly occurred in the first year after application; insignificant changes were observed in the following years (Minkina et al., 2007), which pointed to the possible formation of chemically sorbed metal carbonates and the further stabilization of the calcium–carbonate system.

The formation of separate solid phases of heavy metal carbonates can play a significant role in the immobilization of pollutants, because the addition of carbonates to the contaminated soil under field experimental conditions creates conditions for the precipitation of low-soluble metal compounds.

Thus, it can be supposed that chemisorption and precipitation can be the main mechanisms of Zn and Pb sorption by carbonates in ordinary chernozem. The increase in the sorption activity of Fe–Mn (hydr)oxides in calcareous soils plays an important role in the fixation of pollutants.

The simultaneous application of manure and chalk enhanced the sorption effect and resulted in the maximum decrease in the content of loosely bound Zn and Pb compounds. Already in the first year of their simultaneous use, the group ratio and, hence, the mobility of metals was similar to the analogous parameters of the initial soil (Tables 1, 3).

This could be related to the fact that the stabilization of organic manure compounds with the formation of stable organomineral complexes occurred in the presence of chalk. These complexes strongly fixed heavy metals and made them unavailable for extraction by the reagents used. The addition of 10% of humic acids to calcite under model experimental conditions increased the adsorption of Zn compared to the pure $CaCO_3$ (Brummer et al., 1983).

The results of studies showed differences in the behavior of Zn and Pb under the application of manure. When the soil was composted with manure, the share of complex Zn forms and specifically sorbed Pb forms increased and the content of loosely

*a*CS

Agric. conspec. sci. Vol. 76 (2011) No. 1

Table 4. Loosely bound Zn and Pb compounds (numerator) and the ratio of their exchangeable, complex, and specifically sorbed forms (denominator) during three years after the application of ameliorants

Experimental treatments	Zn			Pb		
	1 year	2 year	3 year	1 year	2 year	3 year
Without metal addition	8 8/5/87	8 8/6/86	8 8/5/87	4 23/9/68	4 24/8/68	3 30/3/67
Metal (Me)	113 29/25/46	121 23/19/58	127 21/19/60	42 31/14/55	45 24/28/48	42 21/35/44
Me + glauconite	50 55/16/29	47 35/14/51	25 28/6/67	34 25/14/61	34 18/25/57	17 17/28/55
Me + manure	60 42/24/34	42 43/14/43	35 24/22/54	29 28/12/60	28 24/15/61	25 21/30/49
Me + glauconite + manure	56 45/20/35	55 23/11/66	46 8/28/64	24 30/8/62	25 21/27/52	19 8/36/56
Me + chalk, 2.5 kg/m²	47 46/17/37	47 20/15/65	36 11/8/81	21 33/22/45	33 10/29/61	12 22/22/56
Me + chalk, 5 kg/m²	57 32/16/52	56 8/25/67	31 3/16/81	18 25/23/52	26 11/21/68	17 5/11/84
Me + chalk, 2.5 kg/m² + manure	39 40/20/40	40 17/15/68	18 26/6/68	20 28/8/64	21 11/35/54	17 9/30/61
Me + chalk, 5 kg/m² + manure	40 25/25/50	37 11/16/73	18 5/22/73	15 31/1/68	17 12/29/59	12 9/29/62
LSD$_{0,95}$ for numerator	10.3	9.9	5.1	9.9	10.5	4.0

Note: Data in numerator and denominator are given in mg/kg and % of the group of loosely bound compounds, respectively.

sorbed metal compounds decreased in the first year (Table 4). In the following two years, the share of complex forms decreased for Zn and increased for Pb. This could be due to the formation of mobile Zn complexes with organic ligands and more stable Pb complexes.

The efficiency of remediation was significantly higher in the second and third years after the application of ameliorants, which was related to the transformation rates of metal compounds and their more complete interaction with the sorbents.

It is suggested that the effect of metal nature on the transformation of its compounds becomes the most important with time, regardless of the ameliorant.

General and specific features were revealed in the transformation of compounds of two metals under the effect of ameliorants. The general tendencies were as follows:

– the application of all ameliorants decreased the mobility of metals;

– the addition of manure to chalk or glauconite increased the binding strength by soils and decreased the content of their exchangeable compounds;

– the highest ameliorating effect was observed at the simultaneous application of chalk and manure to the contaminated soils;

– in the contaminated soils and those treated with ameliorants, most of the loosely bound metal compounds were specifically sorbed forms representing the nearest reserve of firmly bound metal compounds;

– the transformation of metal compounds occurred in the contaminated soil during three years after the application of ameliorants, which resulted in a decrease in their mobility and in the share of the most migration-capable exchangeable forms and the corresponding increase in the content of firmly bound forms.

The difference in the state of soils polluted with lead and zinc salts contained in ameliorants was that the rates of zinc fixation in soils were higher. Therefore, the share of firmly bound zinc compounds reached and even exceeded the values typical for clear soils (Table 1). As for lead, only the simultaneous application of chalk and manure increased the relative content of its firmly bound forms to the level of the initial soil.

Conclusion

The application of ameliorants significantly decreased the mobility of metals. Their effect depended on the ameliorant and was most significant at the simultaneous application of chalk and manure. This effect was presumably due to the strong binding of metals by carbonates through chemisorption and formation of low-soluble Zn and Pb compounds and to the additional fixation in the form of complexes at the addition of organic material. Therefore, the share of loosely bound metal compounds in the contaminated soils decreased to the level typical for the clean soils or even below (in the case of zinc). The general evolution of the transformation of metal compounds (from less to more firmly bound compounds) accelerated by ameliorants remained for both metals, but the rates of these processes for Zn compounds were higher than for Pb compounds.

References

Barbu C., Sand C., Oprean L. (2003). Use of natural zeolites to remediate soils polluted with heavy metals. In: Proc 7th International Conference on the Biogeochemistry of Trace Elements, vol. 1. Uppsala, Sweden, pp 250-251.

Basta N.T., Armstrong F.P., Hanke E.M. (2001). Effect of chemical remediation of contaminated soil on arsenic mobility and gastrointestinal availability. In: Proc 6th International Conference on the Biogeochemistry of Trace Elements. Canada, pp 40.

Belousov V.S. (2006). Zeolite-containing rocks of Krasnodar krai. Agrokhimiya 4: 78-84.

Brown S., Christiansen B., McGrath S.P., Lombi E., McLaughlin M., Vangronsveld J. (2001). Use of soil amendments to restore a vegetative cover on zinc and lead mine tailings. In: Proc 6th International Conference on the Biogeochemistry of Trace Elements. Canada, pp 43.

Brummer G., Tiller K. G., Herms U., Clayton P. (1983). Adsorption–Desorption and/or Precipitation–Dissolution Processes of Zinc in Soils. Geoderma 31 (4): 337–354

Chen Z., Looi K., Liu J. (1999). Chemical remediation methods influence on the uptake of cadmium and lead by vegetables in contaminated soils. In: Proc 5th International Conference of Biogeochemistry of Trace Elements. Vienna, Austria, pp 1012-1013.

Choi H. J., Ro H. M., Yun S.I. and Lee M. J. (2008). Chemical speciation of Cu and Zn in mine soil as affected by organic chelating agents with different C/N ratio. In: Proc 14th International Conference on Heavy Metals in the Environment. Taipei, Taiwan, pp 515-517.

Dabakhov M.V. Solov'ev G.A., Egorova V.S. (1998). Effect of agrochemicals on the mobility of Pb and Cd in light gray forest soil and their input into plants. Agrokhimiya 3: 54-59.

*a*CS

Agric. conspec. sci. Vol. 76 (2011) No. 1

Kryuchkov V.V. (1985). Determination of the Toxicity of Metal-Contaminated Soils and Some Problems of Its Assessment. Apatity

Geebelen W., Nangronsveld J., Clijsters H. (1999). Lead immobilization in lead contaminated soils. In: Proc 5th International Conference of Biogeochemistry of Trace Elements. Vienna, Austria, pp 1016-1017.

Katsnel'son Yu.Ya. (1981). Geochemical features of glauconite-containing micronodules in the Rostov oblast and methods of their practical use. Extended Abstract of Candidate's Dissertation in Geology. Rostov-on-Don

Khardikov A.E., Boiko N.I., Agarkov Yu.V. (1999). Zeolites in the Southern Russia. Lithology and Mineral Resources 4: 389-399.

Kliaugiene E., Baltrenas P. (2003). Research on heavy metals immobilization in roadside soil by natural zeolites. In: Proc 7th International Conference on the Biogeochemistry of Trace Elements. vol. 1. Uppsala, Sweden, pp 76-78.

Knox A.S., Adriano D.C. (1999). Effect of zeolite and apatite on mobility and speciation of metals. In: Proc 5th International Conference of Biogeochemistry of Trace Elements". Vienna, Austria, pp 990-991.

Mineev V.G. (1989). Laboratory Manual of Agricultural Chemistry. Mosk. Gos. Univ., Moscow

Mineev V.G., Kochetavkin A.V., Nguen Van Bo. (1989). Use of natural zeolites for preventing the contamination of soils and plants with heavy metals. Agrokhimiya 8: 89-95.

Ming D.W., Mumpton F.A. (1989). Zeolities in soils. In: Mineral in soil environments (J.B. Dixon and S.B. Weed, eds), Madison WI, 873-911.

Minkina T.M., Motuzova G.V, Nazarenko O.G., Mandzhieva S.S. (2009). Group Composition of Heavy Metal Compounds in the Soils Contaminated by Emissions from the Novocherkassk Power Station. Eurasian Soil Science 42 (13): 1–10.

Minkina T.M., Motuzova G.V, Nazarenko O.G. (2006). Interaction of heavy metals with the organic matter of an ordinary chernozem. Eurasian Soil Sciences 7: 804-811.

Minkina T.M., Motuzova G.V, Nazarenko O.G., Kryshchenko V.S., Mandzhieva S.S. (2008). Forms of heavy metal compounds in soils of the steppe zone. Eurasian Soil Science 41: 708–716.

Minkina T.M., Motuzova G.V, Nazarenko O.G., Samokhin A.P., Kryshchenko V.S., Mandzhieva R.S. (2007). Effect of different ameliorants on the mobility of zinc and lead in contaminated chernozem. Agrokhimiya 10: 67-75.

Panin M.S., Bairova A.M. (2005). Sorption of lead by chestnut soils of the Semipalatinsk Irtysh region depending on the particle-size distribution of the zeolites added. Agrokhimiya 10: 92-96.

Pinsky D.L. (1997). Ion Exchange in Soils. Ross. Akad. Nauk, Pushchino

Sizov A.P., Khomyakov D.M. (1990). Problems in the Control of Soil and Crop Contamination. MGU, Moscow

Yang J.E, Ok Y.S., Kim W.S., Lee J.S. (2008). Remediation of heavy metal-contaminated soil amendments and management method solutions. In: Proc 14th International Conference on Heavy Metals in the Environment. Taipei, Taiwan, pp 166-169.

acs76_04

aCS

Agric. conspec. sci. Vol. 76 (2011) No. 1