

THE GROUP COMPOSITION OF METAL COMPOUNDS IN SOIL AS AN INDEX OF SOIL ECOLOGICAL STATE

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ABSTRACT

A system of indices for assessing the soil ecological state as based upon the group composition of heavy metal compounds in soils is proposed. The group composition of heavy metal were determined using combined fractionation including sequential and parallel extractions (1 N NH₄Ac, pH 8; 1% EDTA in NH₄Ac and 1 N HCl). It was shown that strongly bound compounds of Zn and Pb prevail in the original chernozem, mainly in silicates. Among mobile metal compounds, those specifically sorbed forms are predominant. At the additional input of Zn and Pb into the soil, the equilibrium in the system of metal compounds is shifted toward an increase in metal mobility. The analysis of the group composition of metal compounds was allowed to identify mechanisms of amendments effects on the metals mobility in soil and assess their efficiency. Application of chalk and glauconite leads to decreasing the Pb and Zn mobility.

Keywords: Zinc and Lead, Chernozem, Group and Fractional Composition, Contamination, Application of Sorbents, Chalk and Glauconite

1. INTRODUCTION

At present, the problem related to the elaboration of indices for assessing the soil contamination degree is becoming very acute (Kar and Berenjjan, 2013; Vinh *et al.*, 2012; Esshaimi *et al.*, 2012; Tashakor *et al.*, 2011). The study of metal compound forms, their presence in the composition of different soil components, selective account of all the metal forms in soil is very important for a better understanding the small geochemical cycles of chemical elements in technogenic landscapes (Ashraf *et al.*, 2011; Maxhuni *et al.*, 2011), for identifying a diagnostic group of metal compounds to detect the level of adverse effects on the environment (AL-Sharafat *et al.*, 2012; Babakhouya *et al.*, 2010) and to assess the soil stability to heavy metals. Based upon the study of metal compounds transformation due to their inactivation in contaminated soils it is possible to determine

the mechanism responsible for the effect of sorbents application (Minkina *et al.*, 2008b).

2. MATERIALS AND METHODS

A model experiment was carried out to study transformation of Zn and Pb compounds in soils with a higher mono-and polymetal contamination level and the effect of amendments on the fixation of these metals in soil (Motuzova and Hong Van, 1999). The Heavy Metals (HM) of interest in this study are Zn and Pb as the primary contaminants at the territory of the Rostov region (Minkina *et al.*, 2008b). Thick calcareous low-humus clay loamy ordinary chernozem on loess-like loams in the steppe zone of Rostov oblast (Oktyabr'skii region, Russia).

A model experiment was conducted with the upper (0 to 20 cm) layer of an arable calcareous clay loamy ordinary chernozem with the following properties: pH

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water 7.2; particles <0.01 mm 59%; CaCO₃ 1.1%; C org 2.3%; exchangeable cations (mmol kg⁻¹): Ca²⁺ 29; Mg²⁺ 30; Na⁺ 1.

The bottom of polyethylene vessels (1 liter in volume) was covered by a drainage 0-30 cm layer consisting of washed glass, the latter being overlain by 1 kg of soil (<5 mm) in mixture with dry metal salts. As pollutants the Pb and Zn acetates (10 000 mg kg⁻¹ of every element) were applied separately and together. The soil remained wet to 60% from the field water capacity. Two months later the amendments including chalk and glauconite were added in the amount of 50 g kg⁻¹ accounting for 5% from the soil mass. Then the soil was incubated for a year with the same level of moisture.

The scheme of this three-repeated experiment was the following: (1) without heavy metals, (2) Zn or Pb, (3) metal + CaCO₃, (4) metal + glauconite, (5) Zn + Pb. Soil samples were taken from the total volume of the soil mass for determining the total content of heavy metals and their extracted forms.

The total HM content was determined by X-ray fluorescence. The content of their mobile forms was determined by the Atomic Absorption Spectrophotometry (AAS). To detect the group and fractional composition of HM compounds, a combined scheme of their fractionation was applied (Minkina *et al.*, 2008a; 2008b). Special attention was paid to the ratio of HM amounts, firmly and loosely bound with soil components. The Loosely Bonded (LB) metal consists of mobile forms and includes exchangeable, complex and specifically absorbed compounds. The group of Firmly Bonded (FB) Pb mainly includes compounds firmly fixed in a crystal lattice of primary and secondary minerals. Also, it includes low soluble salts of Pb and stable organic-mineral complexes.

The methods of sequential and parallel fractionation of metal compounds are widely used separately, but they can form basis for their combined use (Minkina *et al.*, 2008b). It is advisable to use the Tessier scheme of sequential fractionation (Tessier *et al.*, 1979) in combination with the parallel extraction using individual reagents.

According to this scheme the loosely bound forms were represented by HM compounds extracted by 1 n Ammonium-Acetate Buffer solution (AAB) with pH 4.8; 1% EDTA in 1 n AAB, 1 n HCl. The used extracting agents were not selective. 1 n AAB with pH 4.8 proposed by Krupskiy and Aleksandrova (1957) extracted presumably the HM exchangeable compounds. 1% EDTA was able to extract the metals that are present in soil as organic complexes. The HM content in composition of organic-mineral complexes was calculated through the difference between the metal content in 1% EDTA 1 n

AAB and 1 n AAB (Minkina *et al.*, 2008a). The HM content in the extract 1 n HCl was characteristic of potential amount of labile metal compounds in soil. HM acid-soluble compounds were presumably represented by exchangeable and specifically absorbed HM compounds, the latter being determined by means of the difference between their amounts extracted by 1 n HCl and 1 n AAB. Firmly bound HM compounds were identified by their constituents represented by the compounds connected with the organic matter, Fe and Mn (hydr) oxides and silicates.

3. RESULTS

In the soils under study the total content of Zn averages 67 mg kg⁻¹, Pb-25 mg kg⁻¹ (**Table 1**), what corresponds to their initial level in ordinary chernozems (Minkina *et al.*, 2008b; Nikityuk, 1998; Samokhin, 2003). According to Vinogradov (1964) the Clarke of these elements is equal to 50 mg kg⁻¹ for Zn and 10 mg kg⁻¹ for Pb, what means that the concentration of these metals in the studied soils is exceeding their Clarke by 1.3 and 2.5 times respectively.

The major part of Zn and Pb was firmly bound in soils, the share of loosely bound forms made up 13 and 18% of their total content (**Table 2**). The loosely bound compounds of the studied heavy metals were predominantly represented by specifically absorbed forms (69 and 85% from the amount of loosely bound compounds). Their share was especially high in the composition of loosely bound compounds of zinc. The content of exchangeable and complex compounds of these metals was insignificant (**Table 2**).

The ordinary chernozem artificially contaminated with Zn and Pb revealed an increase in their total content reaching almost 10 000 mg kg⁻¹ (**Table 1**). Besides, an absolute content of three fractions of mobile metal compounds increased as well. The amount of exchangeable forms became higher by 3500 times for Zn and 3000 times for Pb, the content of complex compounds by 3000 and 5000 times and specifically absorbed compounds by 600 and 800 times respectively (**Table 1**).

4. DISCUSSION

In the course of soil contamination the content of dominant firmly bound compounds was changed to be prevailed by loosely bound ones (to 86-81% from the total content). This change was oriented towards increasing the share of mobile compounds among the loosely bound forms. This process seemed accelerated for Zn in case of its application together with Pb (**Table 2**). The ratio of loosely bound compounds in the group was also changed.

Table 1. The total content and the content of loosely bound Zn and Pb compounds in ordinary chernozem contaminated by these metals and after application of sorbents, mg kg⁻¹

Experimental treatments	Exchangeable		Complex		Specifically sorbed		Total content	
	Zn	Pb	Zn	Pb	Zn	Pb	Zn	Pb
Without metal addition	0,7	0,9	0,6	0,5	7,1	3,0	67	25
Metal (Me)*	2478	2962	1628	2443	4386	2568	9890	9851
Me + CaCO ₃	782	1062	660	1267	2578	1986	9791	9826
Me + glauconite	1034	1462	916	1385	2537	2047	9633	9776
Zn + Pb	2844	2658	1545	2434	4183	2334	9776	9940
LSD _{0,95} for numerator	235	244	158	232	323	205	317	459

* - separate application of metals (Zn and Pb) in the rate of 10 000 mg kg⁻¹**Table 2.** Indices for the group composition of Zn and Pb compounds in mono- and polymetal contaminated ordinary chernozem

Experimental treatments	Loosely bound compounds/ Firmly bound compounds **		Exchangeable /Complex/ Specifically sorbed ***	
	Zn	Pb	Zn	Pb
Without metal addition	13/87	18/82	8/7/85	20/11/69
Metal (Me)*	86/14	81/19	29/19/52	37/31/32
Zn+ Pb	88/12	75/25	33/18/49	36/33/31

*- separate application of Zn and Pb in the rate of 10 000 mg kg⁻¹

**- % from the total content,

*** - % from the content of loosely bound compounds

Table 3. The fractional and group composition of Zn and Pb compounds in contaminated chernozem after the application of amendments, mg kg⁻¹

Experimental treatments	Loosely bound compounds				Firmly bound compounds			
	Exchangeable		Specifically sorbed		With organic matter		With Fe and Mn (hydr)oxides	
	Complex	On carbonates	On Fe and Mn (hydr)oxides	With silicates	Sum of fractions			
Zn								
Without metal addition	0.3	0.6	6.3	0.8	1.1	6.1	55.5	71
Metal (Me)*	2226.0	1628.0	2714.0	1672.0	127.0	867.0	278.0	9512
Me + CaCO ₃	656.0	660.0	1988.0	590.0	809.0	1797.0	3113.0	9613
Me+ glauconite	923.0	916.0	1826.0	711.0	635.0	1521.0	3241.0	9773
Pb								
Without metal addition	0.4	0.5	1.6	1.4	6.4	1.4	14.7	26
Metal (Me)*	2443.0	2443.0	1476.0	1092.0	2055.0	523.0	250.0	10282
Me + CaCO ₃	948.0	1267.0	1758.0	228.0	2781.0	1204.0	2229.0	10415
Me + glauconite	1379.0	1385.0	1666.0	381.0	1992.0	732.0	2461.0	9996

* - separate application of metals (Zn and Pb) in the rate of 10 000 mg kg⁻¹

The metal mobility increased predominantly due to such mobile compounds as exchangeable Zn and Pb complex forms. The share of exchangeable compounds proved to be higher by 3.6 and 4.1 for Zn and 1.8 times for Pb. The complex forms showed an increase by 2.7 for Zn and 2.8-3.0 for Pb, but the specifically absorbed forms of these metals decreased almost by 2 times (**Table 2**).

The soil contamination with these heavy metals is especially dangerous because not only the content but also the mobility of pollutants show a great increase (Glazovskaya, 1994; Abdu *et al.*, 2011). Zn mobility increases as compared to Pb, what speaks about a

relative high mobility of technogenic zinc. The increased Zn mobility is connected with increasing a mobile exchangeable fraction of this element. In view of this, qualitative changes take place in the mobility of metals. This is confirmed by changes in the content of different fractions in the composition of loosely bound compounds.

Regularities in the metal absorption by soil can be considerably changed, if cations of the other elements are present in soil. It happens due to competition between ions to be interacted with soil reaction centers. The intensity of such an interaction between heavy metals is determined by an amount of reaction centers in

soil components. In the model experiment with higher pollutant doses (10000 mg kg^{-1}) practically all the reaction centers seemed to be completely filled up; the ions of the metal are predominantly absorbed when they are close to the sorbent surface. According to the authors (Ladonin and Plyaskina, 2009) Zn is highly affected by the other elements, what is testified by its lower absorption when Zn is present in the solution together with Cu and Pb (Minkina *et al.*, 2010; Pinskiy *et al.*, 2010).

When applying the studied amendments in contaminated soils, it is possible to observe that the total content of heavy metals is not changed in soils. However, the amount of loosely bound Zn and Pb compounds and their mobility become decreased (**Table 1 and 2**).

The chalk application contributes to metal fixation to a greater extent in comparison with glauconite. Thanks to chalk the content of loosely bound compounds of Zn and Pb decreased by 45 and 37% but due to glauconite-only by 39 and 31% respectively (**Table 2**).

One should notice that the ratio of loosely bound compounds was changed as well. Both amendments (chalk and glauconite) stimulated declining the share of exchangeable compounds and increasing their specifically absorbed compounds (**Table 2**). The share of complex compounds remained almost unchanged.

The application of the above amendments in the rate of 25 and 50 t/ha respectively displayed an identical situation in chernozems artificially contaminated with Zn and Pb in the field experiment (Minkina *et al.*, 2008b). In contrast to glauconite the content of Zn and Pb exchangeable forms became lower in the first year after the chalk application. The share of loosely bound compounds in contaminated soils reached a level inherent to uncontaminated soils. Due to decreasing the metal mobility the barley productivity and the quality of its grain were improved for 3 years after the application of these amendments.

A comprehensive analysis of changes in the fractional and group composition of HM compounds in contaminated soils helped to understand the mechanism of amendment effects on the metal immobilization, to study the redistribution of compounds and orientation of their transformation processes. The obtained results showed that the amendments have a significant influence on transformation of Zn and Pb compounds in soil. The decreased content of loosely bound compounds is accompanied by the formation of their firmly bound compounds (**Table 3**).

The chalk application decreased the share of exchangeable Zn and Pb compounds in the group of loosely bound compounds being accompanied by increasing the share of their compounds bound with

carbonates. Differences in the action of amendments were well seen in the group composition of firmly bound compounds. Absolute and relative amounts of these metals bound with silicates became higher in the group composition of these compounds. An increase in this fraction was marked in case of glauconite application. The role of Fe hydroxides became more significant in Zn fixation: The share of these compounds increased by 2 times thanks to chalk application and by 1.7 times due to glauconite (**Table 3**). This is conditioned by differences between the mechanisms responsible for fixing these metals by the given amendments.

Glauconite can bind any metal taking part in the ion exchange, in its interstructural fixation. The input of molecules to an adsorbing cave is observed in that case when their size is lower than the entrance window. It is known that zeolites enable to adsorb a higher amount of HM salts due to their cation exchange capacity accounting for $100\text{-}300 \text{ mg kg}^{-1}$ (Pinskiy, 1997).

The glauconite-induced increase in the absolute content of heavy metals in the fractions enriched with Fe and Mg non-silicate forms and organic substances is probably conditioned by different fixation of chemical elements by sorbents. The results of the long-term field experiment showed that the glauconite efficiency in the metal fixation becomes higher in the second year after its application (Minkina *et al.*, 2008b) because in the crystal lattice the metal is fixing for a long period of time. Probably it serves as evidence of a slightly expressed influence of glauconite on the fixation of Zn and Pb as compared to chalk.

The changes in the group composition of HM compounds in contaminated soils caused by carbonate application and chalk in particular occur thanks to some possible mechanisms responsible for increasing the soil absorbing capacity (Minkina *et al.*, 2010). Thus, the analysis of fractional and group composition of HM compounds in contaminated and uncontaminated soils allowed identifying mechanisms of amendment effects on the HM mobility in soils.

6. CONCLUSION

The application of higher Zn and Pb rates (10000 mg kg^{-1}) changes significantly the group composition of their compounds. The content of exchangeable forms becomes increased what is most dangerous for soils. Because the content of heavy metals bound with silicates is more stable even at the significant level of soil contamination, the relative HM content in soil can serve as an indicator of technogenic effects on the environment.

A comprehensive analysis of the group composition of HM compounds allowed identifying mechanisms of

amendments effects on the HM mobility in soil and assessing their efficiency. Application of chalk and glauconite leads to decreasing the Pb and Zn mobility. The inhibited action of amendments is manifested in declining the content of loosely bound compounds what is accompanied by increasing the content of firmly bound compounds. The effect is dependent on the proper amendment: Chalk proved to be the best sorbent.

The testing of combined fractionation method for determining the group composition of metal compounds in soils under different conditions (original soil, polluted soil and the soil after amendments) confirm the validity of the developed combined scheme of HM fractionation and the information value of parameters determined using this method as an index of soil ecological state. The method of parallel extractions can be used for the rapid assessment of heavy metal mobility in the monitoring observations of soils. The combined fractionation system is efficient in studying the transformation of metals in contaminated soils, because it can not only separate the metal compounds with different mobility's under specific conditions, but also predict the behavior of pollutants.

7. ACKNOWLEDGMENT

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8. REFERENCES

- Abdu, A., N. Aderis, H. Abdul-Hamid, N.M. Majid and S. Jusop *et al.*, 2011. Using Orthosiphon stamineus B. for phytoremediation of heavy metals in soils amended with sewage sludge. *Am. J. Applied Sci.*, 8: 323-331. DOI: 10.3844/ajassp.2011.323.331
- AL-Sharafat, A., M. Altarawneh and E. Altahat, 2012. Effectiveness of agricultural extension activities. *Am. J. Agric. Biol. Sci.*, 7: 194-200. DOI: 10.3844/ajabssp.2012.194.200.
- Ashraf, M.A., M.J. Maah and I. Yusoff, 2011. Developmental design of anaerobic wetland system for mining waste water treatment. *Am. J. Environ. Sci.*, 7: 383-396. DOI: 10.3844/ajessp.2011.383.396
- Babakhouya, N., S. Boughrara and F. Abad, 2010. Kinetics and thermodynamics of Cd(II) ions sorption on mixed sorbents prepared from olive stone and date pit from aqueous solution. *Am. J. Environ. Sci.*, 6: 470-476. DOI: 10.3844/ajessp.2010.470.476.
- Esshaimi, M., N. Ouazzani, M. Avila, G. Perez and M. Valiente *et al.*, 2012. Heavy metal contamination of soils and water resources kettara abandoned mine. *Am. J. Environ. Sci.*, 8: 253-261. DOI: 10.3844/ajessp.2012.253.261
- Glazovskaya, M.A., 1994. Criteria for classification of soils according to lead-pollution risk. *Eurasian Soil Sci.*, 26: 58-74.
- Kar, S.Z. and A. Berenjjan, 2013. Soil formation by ecological factors: Critical review. *Am. J. Agric. Biol. Sci.*, 8: 114-116. DOI: 10.3844/ajabssp.2013.114.116.
- Krupskiy, N.K. and A.M. Aleksandrova, 1957. To a Question of Definition of Mobile Forms of Microcells. In: *Microcells in Life of Animals, Plants and the Person*, Ukraine, Kiev, Naukova Dumka, pp: 24-31.
- Ladonin, D.V. and O.V. Plyaskina, 2009. Heavy metal pollution of urban soils. *Eurasian Soil Sci.*, 42: 816-823. DOI: 10.1134/S1064229309070138.
- Maxhuni, A., F. Faiku, M. Pacarizi, M. Zeka and V. Mehmeti, 2011. Determination of lead in soil along the highways of kosova. *Am. J. Environ. Sci.*, 7: 531-533. DOI: 10.3844/ajessp.2011.531.533
- Minkina, T.M., D.L. Pinskii and Yu.I. Gaponova, 2010. Comparative analysis of mono- and polyelement adsorption of copper, lead and zinc by an ordinary chernozem from nitrate and acetate solutions. *Eurasian Soil Sci.*, 43: 748-756. DOI: 10.1134/S1064229310070045.
- Minkina, T.M., G.V. Motuzova, O.G. Nazarenko, V.S. Kryshchenko and S.S. Mandzhieva, 2008a. Combined approach for fractioning metal compounds in soils. *Eurasian Soil Sci.*, 41: 1171-1179. DOI: 10.1134/S1064229308110057
- Minkina, T.M., G.V. Motuzova, O.G. Nazarenko, V.S. Kryshchenko and S.S. Mandzhieva, 2008b. Forms of heavy metal compounds in soils of the steppe zone. *Eurasian Soil Sci.*, 41: 708-716. DOI: 10.1134/S1064229308070053
- Motuzova, G.V. and N.T. Hong Van, 1999. The geochemistry of major and trace elements in the agricultural terrain of South Viet Nam. *J. Geochem. Explorat.*, 66: 407-411. DOI: 10.1016/S0375-6742(99)80002-8
- Nikityuk, N.V., 1998. Mobility of heavy metals in chernozem carbonate soils and ways of its assessment. PhD Thesis, KGAU, Russia, Krasnodar.
- Pinskii, D.L., 1997. *Ion-Exchange Processes in Soils*. 1st Edn., Publishing house of ONTI PNTs Russian Academy of Sciences, Russia, Pushchino, pp: 166.

- Pinskii, D.L., T.M. Minkina and Y.I. Gaponova, 2010. Comparative analysis of mono-and polyelement adsorption of copper, lead and zinc by an ordinary chernozem from nitrate and acetate solutions. *Eurasian Soil Sci.*, 43: 748-756. DOI: 10.1134/S1064229310070045
- Samokhin, A.P., 2003. Transformation of compounds of heavy metals in soils of Nizhny of Don. PhD Thesis, Rostov-on-don, Russia.
- Tashakor, M., W.Z.W. Yaacob and H. Mohamad, 2011. Speciation and availability of Cr, Ni and Co in serpentine soils of ranau, Sabah. *Am. J. Geosci.*, 2: 4-9. DOI: 10.3844/ajgsp.2011.4.9
- Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chem.*, 51: 844-850. DOI: 10.1021/ac50043a017
- Vinh, N.C., I. Oborn, P.Q. Ha, N.D. Minh and R.L. Hough *et al.*, 2012. Potential environment and public health risk due to contamination of heavy metals from industrial waste water in lam thao, phu tho, vietnam. *Am. J. Environ. Sci.*, 8: 71-78. DOI: 10.3844/ajessp.2012.71.78
- Vinogradov, A.P., 1964. *Geochemistry of Rare and Scattered Chemical Elements in Soils*. 1st Edn., Russia, Moscow, pp: 68.