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TRANSFORMATION OF TECHNOGENIC Cu AND Zn COMPOUNDS IN CHERNOZEM

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Abstract

The influence of exogenous form of heavy metals intake on their transformation in the soil is determined during model experiments. Distinctions in quantity of extracted mobile compounds of heavy metals in the soil depending on a form of addition various connections of Cu and Zn are established. The smallest mobility of Cu and Zn at addition of heavy metal oxides is observed. It is established that Cu accumulates mainly in the fraction connected with organic matter; Zn accumulates in residual fraction and in the fraction connected with ferric oxide and manganese oxide by consecutive fractionation technique.

Key words: attendant anion, chernozem ordinary, fractionation, heavy metals compounds, transformation

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1. Introduction

Soil contamination adversely affecting agroecosystems occurs from different sources, however, the heavy metals (HM) ranking among the first. In case of technogenic contamination, the HM input to soil leads to their accumulation in the topsoil and the quite different interaction with soil components in dependence of adsorbent properties and chemical peculiar features of the metal.

In the course of further transformation, HM are involved into different chemical and physical-chemical processes that have an influence on their behavior in soil (Kar and Berenjian, 2013; Ma et al., 2013; Minkina et al., 2008; 2013; Wiatrak, 2014). Numerous mechanisms responsible for interaction between HM and soil components depend on different HM forms, which determine their mobility, migration capacity and toxicity (Abdulla et al., 2013; Endovitsky et al., 2014; Minkina et al., 2012).

As a rule, HM are present in soil in easily and difficultly soluble forms. The easily soluble forms can effectively react with soil components, whereas due to further transformation the hardly soluble forms are subject to dissolution (Ladonin and Karpukhin, 2011).

The metal oxides and salts in soils can represent different potential threats for the environment and living organisms. In soils contaminated with metal oxides the concentration of metal mobile forms is lower than in soil contaminated with metals in the form of easily soluble salts (Minkina et al., 2014). Therefore, the metal oxides in the soil should induce a lower environmental hazard per unit of metal mass than easily soluble salts (Pinskii et al., 2014).

The present study is aimed at identifying the regularities in transformation processes of exogenic Zn and Cu compounds in ordinary chernozems.

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2. Materials and methods

2.1. Soil characteristics

Soil samples were taken in the 0-20cm topsoil of the heavy-textured ordinary chernozem on loess-like loam (Haplic Chernozem, FAO) in the virgin area.

The soil had a clay content of 286 g kg^{-1} and a physical clay content of 471 g kg^{-1}, $pH_{(water)}$ of 7.3, organic C content of 23 g kg^{-1}, $CaCO_3$ content of 1 g kg^{-1}, cation exchange capacity of 37.1 mmolc kg^{-1} and exchangeable Ca, Mg and Na contents of 29.5, 5.5 and 0.1 mmolc kg^{-1}, respectively.

The soil was air dried, homogenized and sieved to a 1 mm fraction for the experiment.

2.2. Pot experiment

In order to study transformation of Zn (II) and Cu (II) cations absorbed by soil we conducted the pot experiment. The soil (1 kg) was mixed with dry metal salts and placed into plastic pots with ceramsite drainage. We used Zn and Cu salts of oxides, acetates, sulfides, chlorides, nitrates and phosphates. These salts are the main forms in which metals entered in soil from technogenic sources. Zn and Cu salts were added in soil separately in three replicates.

The dose 300 mg kg^{-1} of Zn and Cu corresponds to the level of soil contamination by these metals in the Rostov region (Russia). The soil was irrigated to the field water capacity and this moisture level remained for the whole period of experiment (1 year).

2.3. Extraction procedures

Parallel extractions were employed to study Zn and Cu mobile forms (Minkina et al., 2008; 2013), using the following reagents: 1 N ammonium acetate buffer (NH_4OAC) at pH 4.8 for extraction of the exchangeable forms; 1% EDTA in NH_4OAC at pH 4.8 for the exchangeable and complex forms. The amount of complex compounds was calculated as differences between the HM content in extract of the mixed reagent and NH_4OAC. 1 N HCl extracted acid soluble forms.

The difference between the Zn and Cu content in HCl and NH_4OAC extract permitted to determine the amount of specifically sorbed compounds. The sum of the exchangeable, complex and specifically sorbed forms is weakly bound compounds. They are the most important from ecological viewpoint and capable to enter adjacent areas and the plants in particular. The data obtained by sequential extraction show a trend of transformation processes of an exogenic metal in soil and mechanisms responsible for this transformation. In order to study the interaction between HM and soil components the fractional analysis by Tessier's method (Tessier et al., 1979) was made in soil samples contaminated with metal acetate salts (Table 1). The salts of acetic acid were preferred because they are the most soluble and capable to interact quickly with the soil components. The Tessier's method is one of the most used methods of sequential fractionation (Minkina et al., 2008). The Tessier's procedure of fractionating metals is largely similar to other methods used for the analysis of soils, sediments, and bottom sediments. This procedure ensures the separation of five fractions of HM compounds:

(1) The exchangeable fraction contains metal ions mainly retained by electrostatic forces on the surface of clay and other minerals, organic substances, and amorphous compounds with the low pH values of zero charge. The fraction is affected by the ionic composition of soil solution. The exchangeable forms of HM extractable from soils by neutral salt solutions mainly correspond to adsorbed forms weakly bound to the soil matrix (Mandzhieva et al., 2014; Pinskii et al., 2014).

(2) The carbonate-bound fraction contains HM ions specifically sorbed on Ca and Mg carbonates. Partial dissolution of metal phosphates is also possible (Perelomov and Pinsky, 2003).

(3) The hydroxide-bound fraction contains HM ions occluded by amorphous Fe and Mn hydroxides or adsorbed on their surface. Metals from organic complexes and amorphous sulfides can be released during extraction.

(4) The organic matter-bound fraction contains HM ions retained by organic substances or organomineral compounds. Sulfides can undergo partial decomposition.

(5) The residual fraction contains HM ions strongly fixed in the crystal lattices of primary and secondary minerals.

This fraction can also include metals from stable sulfides and, in small amounts, stable organomineral substances. After each extraction step, the liquid and solid phases are separated by centrifugation. Metal concentration in solutions was determined by atomic-absorption spectroscopy (AAS).

3. Results and discussion

In the uncontaminated soil the distribution of Zn and Cu forms were given in the following sequence: specifically sorbed > complex > exchangeable. The content of the most mobile exchangeable forms is very low – less than 1 mg kg^{-1} (Tables 2, 3), what may be explained by the presence of carbonates in soil, their highly dispersed mycelial form and slightly alkaline pH (Minkina et al., 2013). The weakly bound Zn and Cu compounds are mainly represented by specifically sorbed forms.

Due to artificial soil contamination with Zn and Cu in the rate of 300 mg kg^{-1} their content in extracted forms reveals changes caused by chemical properties of these metals. The Zn distribution in the group of weakly bound compounds can be ranked in the following order: specifically sorbed > exchangeable > complex.

Table 1. Sequential fractionation of metals (Tessier et al., 1979)

Metal compounds	*Extractant*	*Soil : solution ratio*	*Extraction conditions*
Exchangeable	1 M $MgCl_2$, pH 7.0	1:8	shaking at room temperature for 1 h
Bound to carbonates	1 M $NaCH_3COO$, pH 5.0 (with CH_3COOH)	1:8	shaking at room temperature for 5 h
Bound to Fe, Al, and Mn (hydr)oxides	0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH	1:20	heating at 96±3°C under periodical shaking for 8 h
Bound to organic matter	0.02 M HNO_3+ 30% H_2O_2, pH 2.0 (with HNO_3), then 3.2 M NH_4CH_3COO in 20% HNO_3	1:20	heating at 85±2°C under periodical shaking for 5 h
Residual fraction	$HF+HClO_4$, then conc. HNO_3.	1:25	evaporation

Table 2. The content of weakly bound Zn compounds (mg kg^{-1}) in ordinary chernozem contaminated with this metal (300 mg kg^{-1}) in the form of different compounds

Exchangeable compounds	*Complex compounds*	*Specifically adsorbed compounds*	*Weakly bound compounds*
no metal addition			
0.3±0.01	1.4±0.1	10.9±1.2	12.6±1.4
ZnO			
83.8±7.7	19.1±2.6	111.2±10.5	214.1±18.0
$Zn(CH_3COOH)_2$			
34.5±3.9	51.8±4.7	146.5±15.2	232.8±20.0
$ZnSO_4$			
105.5±9.1	16.7±1.3	120.7±9.9	242.9±19.2
$Zn(NO_3)_2$			
96.8±8.2	27.3±2.1	163.3±14.8	287.4±23.1
$ZnCl_2$			
102.0±8.7	47.0±5.1	209.5±11.9	358.5±32.4
$Zn_3(PO_4)_2$			
101.8±9.0	63.5±7.6	192.8±18.0	358.1±22.9

An insignificant Zn concentration in complex forms is explained by its greater binding to carbonates and oxides as compared to the organic matter (Minkina et al., 2008; Pinskii et al., 2014). The Cu distribution in forms of compounds within the uncontaminated and contaminated soils is identical and can be presented according to the following order: specifically sorbed > complex > exchangeable. In the studied soil the metal mobility increases due to its complex formation with the organic matter. The data of fractional composition of Cu compounds in soil were shown that the organic matter plays a primary role in absorption of this metal (Ladonin and Karpukhin, 2011; Minkina et al., 2008; Pinskii et al., 2010).

When introducing different metal compounds into the soil, it was possible to define the difference in the amount of extracted Zn and Cu that is explained by varying solubility of their compounds (Pinskii et al., 2014). For instance, the Zn input to soil in the form of hardly soluble compounds showed that after incubation for a 1 year the content of its mobile compounds seemed to be lower by 5-7 units as compared to that applied in the form of easily soluble salts. As regards Cu, its content was decreased by 1.0-3.5 units. The Cu oxide (Ksp $4{,}79\times10^{-21}$) is soluble to a lesser extent than Zn oxide (Ksp $2{,}19\times10^{-17}$). When comparing the influence of anions on extraction of HM cations from soil, is seemed reasonable to show that the amount of weakly bound Zn compounds becomes decreased according to the following order: $PO_4^{2-} \approx Cl^- > NO_3^- > SO_4^- > CH_3COO^- > O^-$. The content of Cu compounds was presented as follows: $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{2-} > CH_3COO^- > O^-$. According to the results of experiment to study the salts solubility , it was found that zinc phosphate unlike copper dissolves in NH_4OAC at pH 4.8, 1% EDTA in NH_4OAC at pH 4.8 and 1 N HCl. The solution's pH changes in contact with the soil depending on the content of the adsorbed HM cations and the attendant anions. The values of the pH for the soil suspensions after the addition of HM salts are reduced by 0.2-0.5 units (Pinskii et al., 2014).

One of the methods to study the metal forms in soil is chemical sequential extraction permitting to distribute HM according to their binding with the main soil components as bearers of these metals. Just this method is more informative as compared to selective extracts, because it allows partitioning even conservative metal fractions containing in metal crystalline litters (Ladonin and Plyaskina, 2009). The results of the sequential extraction of initial uncontaminated soil served as evidence of the following distribution of Cu forms: residual fraction > bound to the organic matter > bound to Fe and Mn oxides > bound to carbonates > exchangeable fraction. For Zn is quite another picture: residual fraction > bound to Fe and Mn oxides > bound to the organic matter > bound to carbonates > exchangeable (Table 4). The peculiar feature of the fractional composition of Zn and Cu compounds in initial soil is that the residual fraction is found to be dominant (for Zn – 67% of the total content, for Cu – 38%). Such are the regional biogeochemical features of the soil microelement composition in Rostov oblast (south of Russia) and of the mineralogical composition of the parent rocks. The yellow brown loess like loams and clays of the PreCaucasian Plain inherited the stable minerals of the initial rocks with the typical microelement composition of the minerals (Minkina et al., 2013).

Distribution of HM fractions in non-contaminated soils is a result of soil formation processes and chemical properties of metals determining their affinity with different soil components (Ladonin and Karpukhin, 2011). The prevalence of residual fraction parallel with the low content of the other two fractions bound to soil to a lesser extent, serves as evidence that the initial soil has no HM of technogenic origin. Having analyzed the distribution of Zn and Cu fractions in the contaminated soil, it should be concluded that the fractions are differently distributed (Table 4). In case of artificial soil contamination with HM acetates (300 mg kg^{-1}) the exchangeable fraction seems to be increased by 25 for Zn and 16 for Cu. Besides, the relative content of metals in the given fraction increases insignificant: 3% and 1% respectively (Table 5).

Table 3. The content of weakly bound Cu compounds (mg kg^{-1}) in ordinary chernozem contaminated with this metal (300 mg kg^{-1}) in the form of different compounds

Exchangeable compounds	*Complex compounds*	*Specifically adsorbed compounds*	*Weakly bound compounds*
no metal addition			
0.3±0.01	0.5±0.1	2.2±0.3	3.0±0.6
CuO			
9.7±1.2	58.8±5.3	101.2±9.9	169.7±12.3
$Cu(CH_3COOH)_2$			
13.3±1.4	63.9±5.9	107.6±11.7	184.8±11.8
$Cu_3(PO_4)_2$			
31.3±2.7	76.3±8.1	141.0±11.2	248.6±12.3
$CuSO_4$			
32.5±3.4	100.5±10.2	146.5±11.3	279.5±12.9
$CuCl_2$			
61.3±4.1	109.2±10.6	145.7±10.3	316.2±11.5
$Cu(NO_3)_2$			
68.3±6.2	112.9±8.6	146.7±11.0	327.9±16.7

Table 4. Fractional Zn and Cu distribution in ordinary chernozem, mg kg^{-1}

Dose of metal, mg kg^{-1}	*The exchangeable fraction*	*The carbonate-bound fraction*	*The hydroxide-bound fraction*	*The organic matter-bound fraction*	*The residual fraction*	*Sum of fraction*
$Zn(CH_3COOH)_2$						
no metal addition	0.6±0.2	1.8±0.3	14.2±2.1	11.5±3.5	56.9±6.0	85.0
300	15.2±1.9	24.6±2.2	144.5±10.2	30.7±2.6	153.0±12.8	368.0
$Cu(CH_3COOH)_2$						
no metal addition	0.4±0.1	1.2±0.3	10.0±2.2	16.1±4.3	17.3±2.4	45.0
300	6.5±1.1	27.8±3.2	116.4±10.4	110.1±9.9	80.2±8.6	341.0

Table 5. Relative content of Zn and Cu forms in ordinary chernozem, % of the sum of fractions

Dose of metal, mg kg^{-1}	*The exchangeable fraction*	*The carbonate-bound fraction*	*The hydroxide-bound fraction*	*The organic matter-bound fraction*	*The residual fraction*
$Zn(CH_3COOH)_2$					
no metal addition	1	2	17	13	67
300	4	7	39	8	42
$Cu(CH_3COOH)_2$					
no metal addition	1	3	22	36	38
300	2	8	34	32	24

The fraction bound to carbonates becomes enhanced by 14 for Zn and by 23 for Cu with the metal introducing into the soil. Fe-Mn oxides play a dominating role in accumulation of this HM. In this case the relative content of Cu shows an increase by 12%. The Zn amount in the fraction bound to Fe-Mn oxides and hydroxides is the greatest as compared to the residual fraction increased by 22% (Table 4). Zn is characteristic of rather great affinity to reactionary center of mineral soil components (Guisti, 2011; Minkina et al., 2008; Nimirciag, 2012; Pinskii et al., 2014).

In case of contaminating the soil with Cu in the dose of 300 mg kg^{-1}a share of the organic fraction gets decreased by 4%. The Zn amount in the given fraction increases by 2.7 units. In view of this, the percentage content of Zn decreases by 5%. Zn is capable to form stabile complexes to a lesser extent. The organic matter plays a significant role in Zn immobilization in view of forming the unstable out- or intrasphere complex compounds capable to transfer into the other forms of compounds (Mandzhieva et al., 2014; Perelomov and Pinsky, 2003; Pinskii et al., 2010; Rodríguez-Oroz et al., 2012).

The HM input to soil in the doze of 300 mg kg^{-1} reveals decreasing a share of the firmly bound residual fraction in the total content of the metal extracted from soil (14% for Cu and 25% for Zn). This serves as evidence that this metal is weakly involved into the structure of the most stable soil components. Such a peculiarity in distribution of HM fractions can be used as a diagnostic criterion for natural or anthropogenic contamination of soils and the level of their contamination (AL-Sharafat et al., 2012; Minkina et al., 2013).

4. Conclusions

1. The form of applied metal exerts an impact on its mobility in soil. Cu and Zn become mobile to a lesser extent when the soil is supplemented with HM oxides. The influence of attendant anions upon the content of weakly bound HM forms shows a decrease in the following order: $PO_4^{2-} \approx Cl^- > NO_3^- > SO_4^- > CH_3COO^- > O^-$ for Zn and $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{2-} > CH_3COO^- > O^-$ for Cu.

2. The main role in the interaction with soil components and hence in the distribution according to the HM compounds plays the specific characteristics of the metal, not the attendant anion. Based upon a model experiment it has been established that in non-contaminated soils the main HM share is predominantly concentrated in crystalline litters of the primary and secondary minerals. In contaminated soils the HM are found to be in the following fractions: Cu – in the fraction bound to the organic matter; Fe and Mn oxides take an active part in accumulation of this metal. Zn – in the residual fraction as well as in the fraction bound to Fe-Mn oxides. The regularity in Zn and Cu distribution according to mobile forms in control and contaminated soils with Cu is in the sequence: specifically sorbed > complex > exchangeable. In soils contaminated with Zn the initial position of mobile forms reveals a change: specifically sorbed > exchangeable > complex.

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