Soil physical and chemical properties changes after zinc contamination

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Abstract

The aim of this work was to study the effect of a high rate of Zn on the chemical bond forms of metal in soil and on the physical properties and organic matter of Haplic Chernozem under model experiment conditions. The metal sequential extraction procedure used in this study was the classical five-step method proposed by Tessier et al. (1979). The particle size distribution was determined by the pipette method (using the pyrophosphate procedure of soil preparation) (GOST 12536-79). The microaggregate distribution was determined in the same way as the particle size distribution analysis above, except that there was no chemical dispersant (sodium pyrophosphate) applied (only mechanical agitation with water) (GOST 12536-79; Vadyunina and Korchagina, 1973). The qualitative composition of organic matter was determined using the Tyurin procedure modified by Ponomareva and Plotnikova (Vorob'eva, 2006). Contamination of Haplic Chernozem with Zn acetates at high rates of 2000 mg/kg affected the physical and chemical properties of the soil. A significant increase in the first two soil fractions least strongly bound to the soil was observed in contaminated soils. Silicates and Fe-Mn oxides made the largest contribution to the Zn adsorption and retention. The content of organo-mineral particles in colloidal size increased, which resulted in an increase of the clay fraction content up to 4.5 % compared to the control. The qualitative composition of organic matter changed: the contents of free and sesquioxide-bound humic acids and free fulvic acids increased. Studies of soil physical properties and organic matter quality changes and chemical bond forms of Zn in soil are needed to better understand metal behaviors in the environment and implement repair strategies in different polluted soils.

Keywords: zinc, soil, fractional composition, organic matter, particle size distribution, structural status, aggregate content.

Introduction

Heavy metals (HMs) pollution of soil is an increasingly urgent problem all over the industrialized world. Elevated metals concentrations in soils can pose long-term risks for soil fertility and ecosystem health. Organic matter, clay minerals, as well as Fe and Mn oxides are the most important components determining the sorption of metals in soils (Vega, Covelo, and Andrade, 2006). The organic components form stable metal-organic complexes with a variety of metals, while clay minerals and oxides concentrate heavy metal ions through surface ion exchange and metal-complex surface adsorption. Soil organic matter (SOM) that plays a key role in governing metal mobility consists mainly of humic substances: humic and fulvic acids. Organic materials have large negatively charged interfaces that compete strongly with inorganic ligands to readily immobilize metal ions through the formation of stable

complexes, thereby decreasing their phytoavailability to plants (Guo et al., 2006; Mohamed et al., 2010; Ok et al., 2011). In addition, dissolved organic matter and fulvic/humic acids can form soluble chelates with metals, which increases metal mobility, extractability and phytoavailability under certain soil conditions (Salati, Quadri, Tambone, and Adani, 2010; Hu et al., 2016). Iron and manganese oxides present in soils are frequently nanometer-sized materials, which have a large surface area to volume ratio and thus are capable of binding metals. For example, T. Phuengprasop, J. Sittiwong, and F. Unob (2011) found that one gram of iron oxide-coated sludge had a capacity to adsorb 17.3, 14.7 and 42.4 mg of Cu, Cd and Pb, respectively.

The environmental behavior of HMs in soils and potential risks to human health depend critically on the form in which they occur. The manner in which an element is bound to the components of the soil complex influences the mobility and, ultimately, the bioavailability and toxicity of the element to organisms (Bacon and Davidson, 2008). The availability depends on the nature of the chemical association between the metal and organic and/or inorganic soil constituents (Wang, Zhou, and Cang, 2009).

Determination of the chemical forms of trace elements in complex environmental matrices such as soils can be achieved by sequential extraction. Sequential extraction, although operationally defined, can give information about the association of heavy metals with the geochemical phases of soil. Thus, sequential extraction is widely used to reveal the distribution of heavy metals in soil fractions and to assess the mobility and toxicity of metals in soil (Guo et al., 2011).

It is known that HMs contamination also changes the quality of the soil. The HMs adsorbed by soils can affect the physical and chemical properties of the soil. Many authors have studied the effects of HM cations on the specific surface area of soils, microstructure of clay minerals, sorption of water vapors, thermodynamic state of water in clay minerals, mineralogy of the clay fraction, and distribution of HMs in aggregates of soils of different genesis (Vityazev, Kaurichev, and Rabii, 1980; Vityazev, Chizhikova, and Shevchenko, 1983; Manucharov, Kharitonova, Chernomorchenko, and Zemlyanukhin, 2001; Smagin et al., 2004; Fedotov et al., 2008). It was shown that the intensities of reflections corresponding to montmorillonites and illites on the X-ray diffraction patterns of the clay fractions from heavy loamy soddy-podzolic soil and heavy loamy chernozem changed after treatment with Zn and Cu salts (Motuzova et al., 2012).

The affinity of clay minerals to HM cations is due to their high surface energy and reactivity related to the small size of particles and their morphological elements, as well as the specific properties of HM cations determined by the electron structure of their atoms. The interaction energy of HMs with clay minerals is higher than that of alkaline and alkaline-earth cations; in the general case, it changes in the following order: Pb > Cu > Ni > Co > Zn > Mn > Ba > Ca > Mg > K > Na (Pinskiy and Fiala, 1985). It also depends on the acid–base properties of the exchanger; hence, the order can vary among soils and their components (Pinskiy, 1996).

It was noted that high contamination can disturb the organic matter content and quality of soils: changes in the content of the aliphatic structures inhibit the maturation of molecules of humic acids (Grishina, Koptsik, and Makarov, 1990), increase the share of fulvic acids (Karpukhin and Bushuev, 2007), and even slightly increase the organic matter content (Bezuglova and Yudina, 2006). Hence, studies on native SOM quality changes and metal-SOM interactions are needed to better understand metal behaviors in the environment and implement repair strategies in different polluted soils.

The aim of this work was to study the effect of a high rate of Zn on the chemical bond forms of metal in soil and on the physical properties and organic matter of Haplic Chernozem under model experimental conditions.

Materials and Methods

SOIL CHARACTERISTIC

Soil for model laboratory experiments was collected from the humus-accumulative A_1 horizon of Haplic Chernozem (Clayic) (IUSS, 2015) in the Persianovskaya Steppe Specially Protected Natural Territory, Rostov Oblast, Russia. The soil has the following chemical composition: C_{org} 3.7 %; $CaCO_3$ 0.4 %; pH_{H2O} 7.6; exchangeable cations (mM(+)/100 g): Ca^{2+} 31.0; Mg^{2+} 6.0; Na^+ 0.06; cation exchange capacity (CEC) — 38.0 mM(+)/100 g. The content of the physical clay fraction (particles <0.01 mm) is 63.6 %; the content of the clay fraction (particles <0.001 mm) is 28.1 %.

The mineralogy of the clay and fine silt (0.005–0.001 mm) fractions in the humus-accumulative horizon (0–20 cm upper layer) of Haplic Chernozem is characterized by the following phase composition of layered silicates: illite, 51–54 % in the clay fraction and 51–60 % in the fine silt fraction; labile silicates, 23–27 % in the clay fraction and 12–27 % in the fine silt fraction; kaolinite, 22–23 % in the clay fraction and 22–28 % in the fine silt fraction. The fine silt fraction also contains micas, amorphous silica, and crystallized iron and aluminum oxides and hydroxides (Sokolova, 1985; Kryshchenko and Kuznetsov, 2003; Nevidomskaya et al., 2016).

EXPERIMENT DESIGN

To study the effect of adsorbed Zn on the physical and chemical properties of Haplic Chernozem, a laboratory experiment was established under controlled condi-

tions. The soil selected for the experiment (1 kg) was air-dried, triturated using a pestle with a rubber head and sieved through a 1-mm sieve. Zn acetate was then added separately as dry salt at a rate of 2000 mg HM kg^{-1}. High pollution levels are found in soils near enterprises that mine and process non-ferrous metals (Iavazzo et al., 2012; Huang, 2014; Minkina et al., 2018). It should be noted the soils such as Chernozem can retain their properties and functions even under a very high contamination level.

The soil was thoroughly mixed, wetted, and incubated for 6 months at a water content of 60 % of field capacity. Experiments were performed in triplicate. Analogous procedures, although without addition of Zn, were performed with control soil samples. After the end of incubation, an average sample was taken from each vessel for analysis. The soil was air-dried, triturated using a pest with a rubber head, and sieved through a 1-mm sieve.

SEQUENTIAL EXTRACTION

The metal sequential extraction procedure used in this study was the classical five-step method proposed by Tessier et al. (1979), as follows:

Step 1: *exchangeable fraction (F1)*. The solid sample (1.0 g) was extracted at room temperature (25 °C) with 8 mL of 1 mol L^{-1} MgCl$_2$ (pH 7.0) for 1 h with continuous agitation.

Step 2: *carbonate-bound fraction (F2)*. The residue from Step 1 was extracted at room temperature (25 °C) with 8 mL of 1 mol L^{-1} NaOAc adjusted to pH 5.0 with HOAc, and the mixture was shaken for 5 h.

Step 3: *Fe-Mn oxide-bound fraction (F3)*. The residue from Step 2 was extracted with 20 mL of 0.04 mol L^{-1} NH$_2$OH-HCl in 25 % (volume/volume) HOAc at 96 °C with occasional agitation for 8 h.

Step 4: *organic matter-bound fraction (F4)*. 3 mL of 0.02 mol L^{-1} HNO$_3$ and 5 mL of 30 % H$_2$O$_2$ adjusted to a pH of 2 with HNO$_3$ was added to the residue from Step 3, and the mixture was heated to 85±2 °C for 2 h with occasional agitation. A second 3-mL aliquot of 30 % H$_2$O$_2$ (pH 2 with HNO$_3$) was then added and the sample was heated for a second time to 85±2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 mol L^{-1} NH$_4$OAc in 20 % (volume/volume) HNO$_3$ was added and the sample was diluted to 20 mL and agitated continuously for 30 min.

Step 5: *residual fraction (F5)*. The residue from Step 4 was digested with an HF-HClO$_4$ mixture, and finally dissolved in 12 mol L^{-1} HCl and diluted to 25 mL.

All these extractions were conducted in centrifuge tubes; each step was performed in triplicate. Between each successive extraction, separation was completed using a centrifuge at 6000 r min^{-1} for 20 min, and the supernatant was stored at 4 °C for later analysis. Laboratory equipment used in this study was washed with 0.1 mol L^{-1} HNO$_3$, rinsed with deionized water, and placed in an air-dry oven until dry. The Zn contents in the liquid extracts were measured by atomic absorption spectrophotometry ('KVANT 2-AT'). The total content of Zn in solutions was determined as the total concentrations of the metals in all fractions.

METHODS OF PHYSICAL PROPERTIES AND ORGANIC MATTER DETERMINATION

In the studied samples, the maximum hygroscopic moisture was determined according to Russian standard (GOST 28268-89); the structural state of soils was determined by the Savvinov method of dry and wet sieving; water stability was determined by the Andrianov method (Dolgov and Bahktin, 1966). The aggregate water stability coefficient was calculated from the equation:

$$K = (a * k1) + (b * k2) + … + (n * kn) / A, \quad (1)$$

where a, b, n — number of aggregates, disintegrated in one minute; k1, k2 … kn — correction factor, which signifies aggregates water stability for each minute counting (in percentage); A — the total number of aggregates taken for analysis. The correction factor k1 is 5 for the first minute, 15 for the second minute … 100 for the eleventh minute.

The particle size distribution (PSD) was determined by the pipette method (using the pyrophosphate procedure of soil preparation) (GOST 12536-79). In this method, carbonates, SOM, Fe, and Al oxides were not removed before the pipette procedure. The particles <0.01 mm were united in the physical clay fraction, and the particles >0.01 mm were united in the physical sand fraction. The physical clay fraction, which includes the silt fraction (<0.001 mm), consists of organic, organo-mineral and mineral particles.

The microaggregate distribution was determined as in the PSD analysis above except that there was no chemical dispersant (sodium pyrophosphate) applied (only mechanical agitation with water) (GOST 12536-79; Vadyunina and Korchagina, 1973).

The saturation degree of physical clay with clay (V_α, %) was calculated by the Kryshchenko method (Kryshchenko et al., 2016):

$$V_\alpha = 100 \, \alpha/z, \quad (2)$$

the value of V_α characterizes the relationship between the varying masses of clay (α) and silt (β) present in physical clay (z).

The qualitative composition of organic matter was determined using the Tyurin procedure modified by Ponomareva and Plotnikova (Vorob'eva, 2006), which involved the separation of organic matter into humic acids (HAs), fulvic acids (FAs), and nonhydrolyzable

residue (humin) followed by the fractionation of HAs and FAs depending on their bonds with the mineral soil component.

STATISTICAL DATA ANALYSES

All laboratory tests were performed in triplicate. The experimental data (means and standard deviations) were statistically treated using STATISTICA 10.0. Results were considered statistically significant at $p \leq 0.05$.

Results and Discussion

As previously indicated, a sequential chemical extraction was carried out in order to identify the distribution of the metal in the different geochemical soil fractions. Table 1 shows the contents of Zn associated with the fractions of each soil. The relative amounts of Zn expressed as a percent of the cumulative total extracted are given in Fig. 1. In the uncontaminated soil most of the Zn is in the residual fraction (48 % of the sum of all fractions). These values reflect the regional trace-element specifics of the composition of soils in Rostov Oblast and the mineralogy of the soil-forming rocks. Yellow brown loess-like loams and clays in Pre-Caucasian plains inherited stable minerals from the parental rocks enriched in trace elements. Ions released from the rocks in the course of their weathering and the origin of soils are partly strongly bound in the structures of clay min-

erals (Minkina et al., 2016; Motuzova and Bezuglova, 2007). Organic matter also significantly contributes to the strong fixation of Zn: it constitutes 32 % of the total metal content (Fig. 1). The relative content of Zn in the first two fractions, which are least strongly bound to the soil, is 3 %, including 1 % of the most mobile exchangeable forms. The low mobility and dominance of Zn in the residual fraction confirm the absence of significant amounts of anthropogenic metal in the original soil. In the uncontaminated Haplic Chernozem, the following distribution of Zn among the compounds forms is revealed: residual fraction > organic matter–bound fraction > Fe-Mn oxide-bound fraction > carbonate-bound fraction > exchangeable fraction.

Addition of metal to the soil at a rate of 2000 mg kg^{-1}, the absolute concentrations of all compounds of the metals in the soil samples increase (Table 1). The relative content of metal in the exchangeable and specifically adsorbed (carbonate-bound) fractions increases: 2 % and 4 % respectively (Fig. 1). A significant role of carbonates in bonding Zn was previously mentioned (Adriano, 2001; Minkina et al., 2016). The affinity of metal ions to carbonates is controlled by their low solubility. Heavy metals can co-precipitate with carbonates by being incorporated into their structures or can be adsorbed in Fe-Mn hydroxides that are precipitated on the surface of carbonates (Santillan-Medrano and Jurinak, 1975).

Fe-Mn oxides play a dominant role in Zn accumulation. The Zn amount in the fraction bound to Fe-Mn

Table 1. Fractional composition of Zn in Haplic Chernozem under model experimental conditions, mg kg^{-1} (n=3)

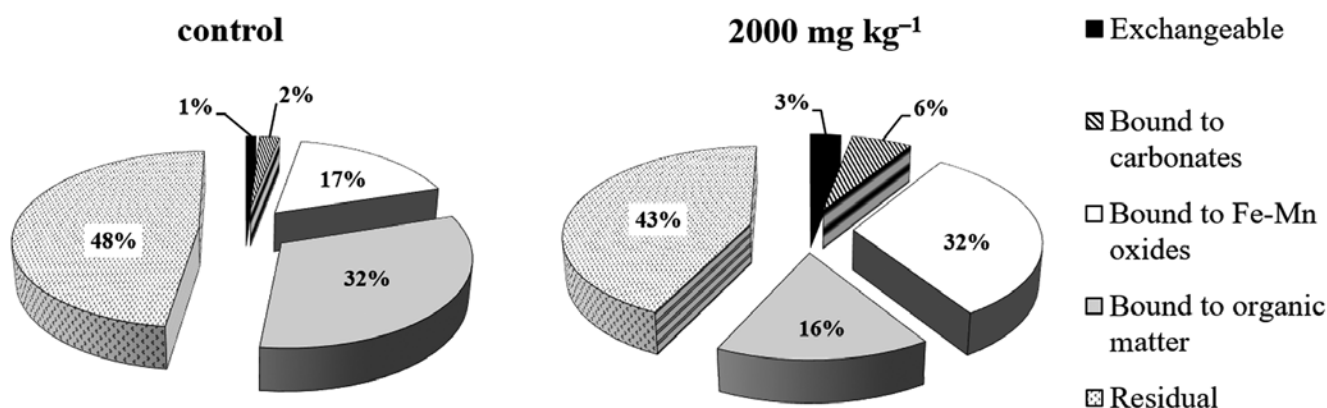| Soil	Fraction					Sum of fractions
	Exchangeable	Bound to carbonates	Bound to Fe-Mn oxides	Bound to organic matter	Residual	
Uncontaminated soil (control)	0.6±0.1	1.8±0.3	14.2±2.3	27.5±3.4	41.0±6.5	85.1±12.3
Artificially contaminated soil	64.8±8.7	119±13	670±17	321±15	899±22	2074±64

Fig. 1. Fractional distribution of Zn in Haplic Chernozem, % of the sum of fractions.

oxides and hydroxides is the greatest as compared to the residual fraction increased by 25 % (Fig. 1). In agreement with these results, other authors have also reported the high affinity of Zn for Fe oxides (Mahanta and Bhattacharyya, 2011; Yin et al., 2016; Ghayoraneh and Qishlaqi, 2017). This may be due to the stability constants of Zn oxides being high enough to be concentrated in this fraction (Ramos, Hernandez, and Gonzalez, 1994). Kabala and Singh (2001) concluded that Zn sorption by Fe oxides is probably the most important mechanism that controls the behavior of this element in the soils. The similarity in the effective ionic radii of Zn^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, and Al^{3+} allows its incorporation in a large number of soil minerals (Manceau et al., 2004).

In the case of soil contamination with Zn in the dose of 2000 mg kg^{-1}, a share of the organic fraction is decreased by 16 %. Zn is capable of forming stabile complexes to a lesser extent. The organic matter plays a significant role in Zn immobilization in view of forming the unstable outer sphere and intrasphere complex compounds capable of transfering into the other forms of compounds (Kabata-Pendias, 2010; Rodríguez-Oroz et al., 2012).

Metal input to soil in the dose of 2000 mg kg^{-1} reveals a decrease in the share of the firmly bound residual fraction in the total content of the metal extracted from soil (Fig. 1). This serves as evidence that this metal is weakly involved in the structure of the most stable soil components. Such a peculiarity in distribution of Zn fractions can be used as a diagnostic criterion for natural or anthropogenic contamination of soils and the level of their contamination (Minkina et al., 2015).

The significant increase of Zn content in the first two fractions, which are least strongly bound to the soil, reflected the changes of soil properties.

According to the Kachinskii classification, PSD in Haplic Chernozem corresponds to the variety of light silty loess-like clays (Table 2). The content of physical clay in the control samples is 63.6 %. The silt fractions are predominant: the content of medium and fine silt is 35.5 %. The content of the clay fraction is 28.1 %. The saturation degree of physical clay with clay ($V_α$, %) is 44.2 %.

The contamination of the studied soil with Zn is accompanied by changes in PSD due to the reliable increase in the content of the clay fraction compared to the control to 4.5 %. The content of physical clay increases respectively. The clay fraction, along with the silt fraction, becomes predominant, which allows classifying the contaminated soil samples as light clayey-silty clays. Soil samples under Zn contamination are characterized by an increase of the saturation of physical clay (soil particle <0.01 mm) with clay (soil particle <0.001 mm) up to 48.4 % (Table 2).

Analysis of the microaggregate size composition of the studied soil (Table 3) shows that the content of coarser aggregates (1–0.25 mm) increases and the content of finer (0.05–0.001 mm) aggregates decreases after the addition of Zn.

The transformations of microaggregate composition are interrelated to the structural parameters of soil. High concentrations of Zn affect the structure of Haplic Chernozem. We observed a significant decrease in the coefficient of water stability in the control from 3 to 1.4 in the contaminated treatments (Table 4).

The aggregate status (estimated from total agronomically valuable aggregates) changes from excellent to good. Kachinskii (1958) studied the structure of soil and noted that the aggregate water stability coefficient is related to the coagulating effect of organic colloids coagulated by Ca^{2+} and Fe^{2+} ions. Some authors (Dobrovol'skii, 2004; Gülser, Minkina, Sushkova, and Kızılkaya, 2017) noted the important role of HAs in the binding of mineral particles with the formation of microaggregates. The interaction of HMs with HAs fixes them in organic films formed on the surface of aggregates.

The adsorption of Zn^{2+} ions by the soil exchange complex largely follows the mechanism of ion exchange (Ponizovskii, Studenikina, and Mironenko, 1999; Ponizovskii and Mironenko, 2001; Strawn and Baker, 2008; Minkina et al., 2014). The substitution of HM cations for Ca^{2+} and Fe^{2+} ions can significantly affect the water stability of the corresponding aggregates.

An increase in the specific surface area of soil and fine fractions under the treatment of soils with Cu and Zn salts was shown by Motuzova et al. (2012). The author explained this fact by the formation of Me-organic complexes with HM cations and the partial decomposition of mineral-organic compounds, which play an important role in structure formation. The highest effect was observed for the clay fraction of chernozem at the interaction with Cu^{2+} and Zn^{2+} ions: the specific surface area determined by nitrogen adsorption increased by 69 % compared to the initial value.

The changes in the amphiphilic properties of HM-contaminated soils are of a different nature. They can be related to changes in the relative content, composition, and properties of organic and organomineral soil components (Motuzova et al., 2012). It is shown that the formation of organomineral complexes significantly affects the hydrophilic-hydrophobic properties of soils (Perelomov, Pinskiy, and Violante, 2011). The most probable mechanisms of the HM effect on the physical properties of soil can be the changes in the occurrence forms of HMs and organic matter in soils, including the formation of relatively stable complexes with organic components (Grishina, Makarov, and Baranova, 1988; Minkina, Motusova, and Nazarenko, 2006). Therefore, some organic substances acting as structuring agents are removed from the solid phase, and aggregates are disintegrated into finer units. The formation of hardly soluble HM precipitates, e.g., lead humates, gives the same effect (Manceau, Marcus, and Tamura,

Table 2. Effect of high concentration of Zn on the particle-size fraction of Haplic Chernozem under model experimental conditions, %

Soil	The particle-size fraction content							The saturation degree of physical clay with clay, (V_α)
	Fine sand 0.25–0.05 mm	Coarse silt 0.05–0.01 mm	Medium silt 0.01–0.005 mm	Fine silt 0.005–0.001 mm	Clay < 0.001 mm	Physical sand > 0.01 mm	Physical clay < 0.01 mm	
Uncontaminated soil	3.7±0.1	32.7±2.2	11.0±0.8	24.5±1.1	28.1±1.6	36.4±2.3	63.6±3.5	44.2±0.2
Artificially contaminated soil	1.3±0.2	31.3±1.8	10.4±0.7	24.4±1.3	32.6±2.2	32.6±2.0	67.4±4.2	48.4±0.2

Table 3. Effect of high concentration of Zn on the microaggregate composition of Haplic Chernozem under model experimental conditions, %

Soil	1–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	< 0.001	> 0.01	< 0.01
Uncontaminated soil	41.3±2.8	20.4±1.4	26.2±1.8	5.6±0.3	6.4±0.9	1.2±0.1	86.8±6.0	13.2±1.3
Artificially contaminated soil	43.9±3.7	20.8±1.2	24.6±1.2	4.6±0.2	4.4±0.6	1.6±0.2	89.3±6.1	10.7±0.9

Table 4. Effect of high concentration of Zn on the structural status of Haplic Chernozem under model experimental conditions

Soil	The structural state coefficient		The aggregate content (0.25–10.0 mm), %		The agroecological estimation of the structural state (Dolgov, Bahktin 1966)		The water stability coefficient, %
	dry sieving method	wet sieving method	dry sieving method	wet sieving method	dry sieving method	wet sieving method	
Uncontaminated soil	2.0	3.0	66.5	75.5	good	excellent	100.0
Artificially contaminated soil	1.9	1.4	64.9	60.5	good	good	77.4

Table 5. Effect of high concentration of Zn on the fractional and group composition of organic matter in Haplic Chernozem, % of C_{tot} in the soil

Soil	C_{tot}, %	The humic acids content (HAs)			∑ HAs	The fulvic acids content (FAs)				∑ FAs	HAs + FAs	HAs / FAs	The humin content
		1	2	3		1a	1	2	3				
Uncontaminated soil	3.7	1.4	21.3	5.9	28.6	1.6	1.3	7.8	4.6	15.3	43.9	1.9	56.1
Artificially contaminated soil	3.8	2.5	22.0	6.7	31.2	3.1	1.7	8.5	5.9	19.2	50.4	1.6	49.6

2002; Scheinost, Kretzchmar, and Pfister, 2002). Another mechanism can include the experimentally proved fragmentation of HAs during interaction with HM cations (Motuzova and Makarychev, 2014).

The results of studying the fractional and group composition of organic matter from the uncontaminated Haplic Chernozem (Table 5) agree with the data of earlier studies of regional Chernozems (Bezuglova, Zvyagintzeva, and Goryainova, 1996). In the upper horizon of virgin Haplic Chernozem, the coefficient of humification is 1.9, which characterizes the fulvate-humate type of organic matter. In the organic matter composition, HAs presumably bound to Ca (HA-2) prevail over FAs. Their content in the upper horizons of Haplic Chernozem is 21.3 %. The contents of free and sesquioxide-bound HAs (HA-1) and free FAs (FA-1a) in the control soil are low:

1.4 and 1.6 %, respectively (Table 5), which agrees with literature data (Bezuglova and Yudina, 2006).

The content of free HAs (HA-1) and FAs (FA-1a) increased after Zn application to the soil (Table 5). The contamination of Haplic Chernozem with Zn also increases the content of mobile HAs bound to sesquioxides (HA-3). These fractions are more mobile and responsive to changes in ecological conditions. The C_{HA}/C_{FA} ratio in soils contaminated with Zn decreased from 1.9 to 1.6.

The qualitative composition of organic matter in contaminated soil is largely determined by adsorbed Zn added in the form of soluble salt. Adsorbed HM cations partially interact with SOM (Kabata-Pendias and Kabata, 1985; Onyatta and Huang, 1999; Gray, McLaren, Robert, and Condron, 2000), including in the studied soil (Minkina et al., 2016).

SOIL BIOLOGY

Metals coming into the soil are mainly concentrated in fine silt (0.005–0.001 mm) and clay (<0.001 mm) fractions (Trofimenko and Kizyakov, 1976; Titova et al., 1996a; Titova, Travnikova, and Shaymukhametov, 1996b; Pinsky and Minkina, 2013). It is known that particle-size fractions significantly vary in properties of bound organic matter and, hence, affinity for HMs. The clay fraction includes stable adsorption complexes of the youngest humic substances (predominantly of fulvate nature) with clay minerals and iron and aluminum oxides. In the fine silt fraction, SOM consists of humic substances in the form of HAs unbound by strong chemical bonds to clay minerals. It is found (Motuzova et al., 2012) that Zn is mainly concentrated in the clay fraction of Haplic Chernozem. So, the content of Zn is 82 mg kg^{-1} in the silt fraction and 162 mg kg^{-1} in the clay fraction. Thus, the adsorbing capacity of fine particle-size fractions for HM cations is variable. The capacity of HMs to accumulate in different particle size fractions is related to their density (Titova, Travnikova, and Shaymukhametov, 1996b) and properties of their organomineral matrix (Motuzova et al., 2012).

Conclusions

Based upon a model experiment it has been established that the main Zn share was predominantly concentrated in the crystalline primary and secondary minerals in uncontaminated soil. In contaminated soil the metal was found in the residual fraction as well as in the fraction bounded to Fe-Mn oxides.

Under model experiment conditions the contamination of Haplic Chernozem with Zn was followed by changes in particle size distribution due to the increase of the organo-mineral particles content in colloidal size in the clay fraction compared to the control by 4.5 %. Consequently, the degree of physical clay saturation with clay increased from 44.2 to 48.4 under contamination.

The high concentrations of metal salt affected the structural state of Haplic Chernozem: the coefficient of water stability decreased and the aggregate status (estimated from total agronomically valuable aggregates) changed from excellent to good.

The addition of Zn to the soil affected the quantitative composition of organic matter. The contents of mobile fractions (free and sesquioxide-bound HAs (HA-1) and free FAs (FA-1a)) increased. Contamination with Zn caused the aliphatization of organic matter, which decreased the CHA/CFA ratio from 1.9 to 1.6.

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