New Approaches to Studying Heavy Metals in Soils by X-Ray Absorption Spectroscopy (XANES) and Extractive Fractionation

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Abstract—A comprehensive approach to studying the nature of interaction between heavy-metal ions and the organic−mineral matrix of soils involves application of modern physical analytical techniques and chemical methods of extractive fractionation. XANES was used to obtain the first data on the near-edge fine structure of X-ray spectra for a number of heavy-metal species in ordinary chernozem. Data on the structure of soil samples saturated with Zn^{2+} and Cu^{2+} obtained by XANES (X-ray absorption near-edge structure) make it possible to elucidate the interaction mechanisms of the metals and the types of chemical bonds formed thereby. As contamination doze of with Cu and Zn is increased (from 2000 to 10 000 mg/kg soil), particularly if the metals are introduced in the form of readily solubility salts, bonding between the metals and soil components weakens. Data of extractive fractionation of metal compounds from samples saturated with Cu and Zn compounds testify that the Cu^{2+} ion is preferably retained in the organic matter of the soil, whereas the Zn^{2+} ion is bound mostly to silicates, carbonates, and Fe and Mn (hydro)oxides.

Keywords: soil, X-ray absorption near-edge structure (XANES), extractive fractionation, Cu and Zn compounds

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INTRODUCTION

Studying heavy metals in soils was launched more than half a century ago, and the very first data were obtained using fractionation techniques, in which various extractants were applied to dissolve metal compounds presumably bound to various components of soils (Baron, 1955; Le Rich and Weir, 1963). The spectrum of extractants utilized in these studies was eventually widened, and the sequences of their application and fractionation stages were modified. For each fraction of heavy metals, an extractant is selected based on understanding the mechanisms that bound metal compounds with soil components (Minkina et al., 2008).

The reactants must meet the following two requirements: they should as much as possible and maximally selectively extract certain metal compounds. However, these requirements are in fact practically never fully met when such complicated multiphase systems as soils are studied. Heavy-metal ions are bound with soil components by different reactions, and hence, the extractive fractionation of these components is never perfectly selective and depends on the interaction time with the soil sample and on the secondary adsorption of heavy metals by stable components of this soil.

Different in certain details, extractive techniques of chemical analysis are uniform in principle: all of them utilize extractants to transfer metal compounds into solution, with these compounds presumably bound with solid soil components via a diversity of mechanisms and via bonding of various strength (Minkina et al., 2010).

A current problem is to elucidate as to how heavy metals are adsorbed by various soil components, such as organic matter, clay minerals, Fe−Mn (hydro)oxides, and carbonates. Interaction between metals and soil components determines the buffer capacity of the soils with respect to a broad spectrum of soil contaminants and thus the protective function of soils in ecosystems.

Recently heavy-metal and metalloid speciation in soils is more and more extensively analyzed by direct techniques of X-ray spectroscopy. The application of state-of-the-art spectroscopic approaches, such as EXAFS, XANES, XAS, XPS, SFM, and others, allows the researcher to acquire information on the scatter of elements, identify mineral concentrating them in soils, and to elucidate the adsorption mechanisms of cations on the molecular scale in order to reasonably adequately understand the local atomic and electron structures (Lombi and Susini, 2009; Mon-

ceau et al., 2002; Sutton and Rivers, 1999; *Synchrotron...,* 2010; Teo, 1986). This makes it possible to succeed in selectiveness with respect of certain elements, high sensitivity to the local structure of a wide range of elements, and a high spatial resolution in combination with simple sample preparation procedures, which makes these techniques universally applicable and reasonable precise in studying the minor- and trace-element compositions and contaminants.

The edges of X-ray absorption spectra correspond to energy values for elements of certain atomic number and hence make it possible to identify not only metals themselves but also their degrees of oxidation and their states in various compounds. Studying the X-ray absorption near-edge structure (XANES) is currently widely utilized in exploring the electron structure of various materials: refining their symmetry and the energy of vacant molecular orbitals or free electron energy bands. Moreover, this technique is able to provide information on the symmetry of the coordination sphere.

X-ray absorption spectroscopy is currently the most widely utilized and one of the most promising techniques applied to nondestructively determine the local atomic and electron structures of various materials regardless of the long-range atomic order. Equipment required for such spectroscopic experiments is continuously modernized. In natural sciences, these techniques find widest application in physics, chemistry, and biology. Data provided by XANES techniques are proved to be highly informative in studying both inorganic minerals (Berry and O'Neil, 2004; Farrel et al., 2002) and organometallic compounds (Chan et al., 2005; Kostenko et al., 2008; Smolentsev and Soldatov, 2009). These experimental studies were proved to be particularly efficient when applied in combination with theoretical ab initio calculations (Smolentsev and Soldatov, 2006; Soldatov, 2008).

At the same time, X-ray absorption spectroscopy is still inadequately little applied in studying soils because of the complicated structuring of soils, their heterogeneity, and variable granulometric composition. However, progressively enhanced capabilities of these techniques provide sound grounds to hope that they will enable obtaining principally new information on soils and on adsorption mechanisms of various chemical compounds in them. This, in turn, should make it possible to design scientifically justified means of rehabilitation of soils after their chemical contamination and other types of degradation.

Our studies were centered on the states of the Cu^{2+} and Zn^{2+} ions in soils under various anthropogenic load. Theses studies were carried out using the technique of X-ray absorption spectroscopy and chemical extractive fractionation.

MATERIALS AND METHODS

We have studied samples of the uppermost 20-cm layers of ordinary chernozem collected in Rostov oblast. The samples were contaminated in experiments with high dozes (2000 mg/kg and 10 000 mg/kg) of Cu and Zn nitrates and oxides and contained 3.2% C_{org}, 0.4% $CaCO_3$, 53.1% physical clay, and 32.4% silt; had pH 7.7; and contained the following exchangeable cations (mmol equiv./100 g) $Ca^{2+} = 31$, $Mg^{2+} = 6$, and $Na^+ = 0.06$. The vessels were loaded with 4 kg of soil (<5 mm) mixed with dry salts. To maintain soil drainage, expanded clay aggregates were used. Each experiments was thrice replicated. The incubation time of metals in the soils was 1 year.

The composition of Cu compounds in soils was analyzed by extractive fractionation. Successive fractionation of heavy metals in soils was conducted by the method described in (Tessier et al., 1979). One of the techniques widely utilized to extract metals from soils makes use of the routine that was suggested by Tessier more than three decades ago, and this method is still widely applied worldwide. Our long-term experience in fractionating heavy-metal compounds according to the Tessier method in major soil types in southern Russia (ordinary chernozem, southern chernozem, and chestnut soils) warrants the application of this routine and suggest that the results thus obtained should be reasonably reliable (Minkina et al., 2008, 2011, 2013a; Mandzhieva et al., 2014).

The Tessier technique makes it possible to analyze five metal fractions in soils: exchangeable, bound to carbonates; bound to Fe and Mn oxides; bound to organic matter, and that bound to silicates (Table 1). The total content of heavy metals in solutions was determined as the total concentrations of the metals in all fractions (Table 2).

The experimental Zn K-edge (9659 eV) and Cu K-edge (8979 eV) X-ray-absorption near-edge structure (XANES) spectra were recorded on a Rigaki R-XAS Looper laboratory spectrometer in fluorescence mode. The use of a Ge (440) crystal monochromator allowed us to achieve a good energy resolution of 2 eV. Each of the spectrum was measured in increments of 0.5 eV. The final spectrum of each sample was obtained by statistical averaging the results on five to seven spectra (Bianconi et al., 1982; Bianconi, 1988). The CuO and $Cu(NO_3)_2$, the ZnO and $Zn(NO_3)_2$ K-edge spectra were theoretically modeled using the method of finite differences for the solution of the Schrödinger equation, with the simulations carried out using the FDMNES 2012 program package (Joly, 2001).

To more comprehensively describe the fine structure of the XANES spectra, obtain detailed information on the state of the ions, and find possible differences between the samples that were not detected when the XANES spectra were analyzed, we analyzed

Table 1. Tessier fractionation (Tessier et al., 1979) flowchart

Extraction sequence and fractions of heavy metals	Extracting solutions
1. Exchangeable species 1	1 M $MgCl_2$ (pH 7.0) for 1 h at room temperature and soil/solution = 1 : 8
2. Carbonate-bond species	1 M $NaCH_3COO$, pH 5.0 (with CH_3COOH) for 5 h at room temperature and soil/solution = 1 : 8
3. Species bound to Fe−Mn oxides	0.04 M $NaH_2OH \cdot HCl$ in 25% CH_3COOH at heating to 96 ± 3°C, periodical stirring for 8 h and soil/solution = 1 : 20
4. Organic matter-bound species	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 then held at 85 ± 2°C for 5 h, periodically stirred, soil/solution = 1 : 20
5. Residual	HF + HNO_3, then HNO_{3conc} at soil/solution = 1 : 25, then boiling

Table 2. Composition of Cu and Zn compounds in various fractions and groups obtained from ordinary chernozem

Doze of introduced metal, mg/kg	Fraction					Total for fractions
	exchangeable	bound to carbonates	bound to Fe and Mn (hydro)oxides	bound to organic matter	bound to silicates (residue)	
mg/kg						
No metals introduced	0.4 ± 0.1	1.2 ± 0.4	5.0 ± 1.0	11.1 ± 1.0	27.3 ± 5.2	45.0 ± 5.9
2000 $Cu(NO_3)_2$	52.0 ± 5.7	72.7 ± 4.1	561.0 ± 19.1	819.0 ± 27.6	562.9 ± 24.7	2067.6 ± 48.3
2000 CuO	27.4 ± 2.6	62.7 ± 9.4	563.1 ± 23.2	752.3 ± 14.2	627.5 ± 18.8	2033.0 ± 41.9
10000 CuO	67.4 ± 5.1	78.0 ± 16.6	4102.6 ± 34.2	3419.4 ± 32.9	2373.6 ± 55.3	10041.0 ± 121.7
% of total						
No metals introduced	1	3	11	25	60	100
2000 $Cu(NO_3)_2$	2	4	27	40	27	100
2000 CuO	1	3	28	37	31	100
10000 CuO	1	1	41	34	23	100
mg/kg						
No metals introduced	0.6 ± 0.1	1.8 ± 0.1	14.2 ± 1.9	11.5 ± 1.4	56.9 ± 11.0	85.0 ± 11.5
2000 $Zn(NO_3)_2$	173.6 ± 8.6	289.4 ± 33.2	826.1 ± 27.2	348.7 ± 36.0	421.2 ± 22.6	2059.0 ± 21.9
2000 ZnO	49.1 ± 5.7	56.9 ± 7.4	777.2 ± 14.3	346.1 ± 25.8	844.7 ± 37.9	2074.0 ± 54.6
10000 ZnO	245.0 ± 11.6	296.0 ± 12.8	3796.0 ± 41.7	1624.0 ± 56.1	4111.0 ± 79.1	10072.0 ± 99.1
% of total						
No metals introduced	1	2	17	14	67	100
2000 $Zn(NO_3)_2$	8	14	40	17	20	100
2000 ZnO	2	3	37	17	41	100
10000 ZnO	2	3	38	16	41	100

the first-order derivatives of the XANES spectra. Along with the experimental XANES spectra, we also studied the experimental spectra of the original Cu- and Zn-bearing compounds.

Below we present (i) the experimental spectra of soil samples saturated with CuO and $Cu(NO_3)_2$ and with ZnO and $Zn(NO_3)_2$, (ii) the experimental spectra of original CuO and $Cu(NO_3)_2$ and of ZnO and $Zn(NO_3)_2$, and (iii) the theoretical spectra of these compounds.

RESULTS AND DISCUSSION

The fractionation of the metal compounds shows (Fig. 2) that the uncontaminated chernozem contains Cu and Zn mostly in fractions with silicates: 60 and 67%, respectively, of the total concentrations in 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. Yellowish brown loess-like loam and clay in fore-Caucasian plains inherit resistant minerals enriched in certain trace elements from the parental rocks. 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 minerals (Akimtsev et al., 1962; Motuzova and Bezuglova, 2007). Elevated concentrations of heavy metals in silicates in various soil types were documented in (Ladonin and Karpukhin, 2011; Ladonin and Plyaskina, 2003; Motuzova et al., 2006; Panin and Kalent'eva, 2009; Plekhanova and Bambusheva, 2010).

Both Cu and Zn are low mobile in the original soil. The relative concentrations of the metals in the first two fractions are no higher than 3−4%, and as little as 1% of them in contained in the most mobile exchangeable species (Table 2). The compositions of the compounds of the two metals in various fractions are different in that the Cu concentrations are higher in the organic matter fraction, while the Zn concentrations are higher in the fraction with Fe−Mn hydroxides.

If soil samples are intentionally contaminated with Cu and Zn, the absolute concentrations of all compounds of the metals in the soil samples increase (Table 2), and these metals are preferably enriched in fractions with organic matter and Fe−Mn hydroxides (up to 40% of the total for all fractions). Somewhat similar trends in the composition of the compounds of these metals were documented in soils at anthropogenically contaminated landscapes (Minkina et al., 2012). The strongest Cu affinity with organic matter and Zn affinity with Fe−Mn hydroxides also follow from data in (Kabata-Pendias and Pendias, 1989; Pinskii et al., 2013).

If the doze of introduced Cu and Zn compounds is increased from 2000 to 10000 mg/kg, the metals are preferably concentrated in the fraction with Fe−Mn hydroxides. This results in the domination of this fraction at contamination with Zn and in closely similar Cu concentrations in fractions with Fe−Mn oxides.

The increase in the concentrations of heavy metals in the residual fraction is explained by both the possibility of Cu and Zn accommodation in silicates and the incomplete dissolution of supergene compounds of the metals at their very intense introduction into the soil (Minkina et al., 2008). For example, the concentrations of the metals in the residual fraction are higher if Cu and Zn are introduced as oxides (2000 mg/kg) than if the contaminants were Cu and Zn nitrates (in same concentrations) (Table 2). Data on the molecular structure of the Cu^{2+} ion in ordinary chernozem (obtained by XANES spectroscopy and techniques of molecular dynamics) indicate that this ion can be accommodated in montmorillonite (Minkina et al., 2013b). It should also be mentioned that more intense

soil contamination with Cu and Zn leads to a decrease in their relative contents in the residual fraction.

The concentrations of the metals in various fractions also depends on the form in which these metals are introduced into the soil. If Cu was introduced (2000 mg/kg) into soil in the form of nitrate, the content of mobile compounds of the metal in the first two extracts was 6%, whereas this concentration was 4% if Cu was introduced as oxide. These differences are even more significant for Zn: the relative content of the metal was 22% if it was introduced as nitrate and 5% if it was added to soil as oxide. Similar to Cu, Zn mobility in soil was much higher (pK $Zn(NO_3)_2 = 0.30$; Lur'e, 1979) if this metal was introduced as nitrate than oxide. This fact also explains the absence of any direct correlation between an increase in the relative content of mobile Cu and Zn compounds and increasing soil contamination with oxides of these metals (Table 2), in contract to what happens if the soil is contaminated with highly soluble salts of these metals (Pinskii et al., 2010). Hence, Zn introduced in the form of nitrate should actively interact with soil components and form various compounds.

The Zn content most significantly increases in the exchangeable and specifically adsorbed (carbonate-bound) fractions. At contamination with 2000 mg/kg Zn nitrate, the relative content of the most mobile exchangeable fraction of the metal increases as much as sevenfold. A significant role of carbonates in bonding metals, first of all, Zn was mentioned in (Adriano, 2001; Minkina et al., 2008). The affinity of heavy-metal ions to carbonates is controlled by their low solubility. Heavy metals can co-precipitate with carbonates via 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).

XANES analyses of our soil samples confirm the relations previously revealed using chemical fractionation also provide insight into the nature of the chemical transformations of metal compounds in soils. Figure 1a presents experimental XANES spectra of chernozem samples contaminated with CuO and $Cu(NO_3)_2$. These spectra are compared with the spectra of the original contaminants (CuO and $Cu(NO_3)_2$) and with the theoretical spectra, which demonstrate the sensitivity of the method to changes in the nearest neighborhood of the metal ion in this structure. All of the spectra show peak A in their middle parts (~8985−8990 eV) due to the presence of Cu^{2+}. The absence of chemical shift of the main absorption edge characterized by the absence of the shift of the main peak B in the experimental spectra of the soils relative to the spectra of the original contaminants testifies that the charge of the Cu ion in soil does not change regardless of the contaminant species and its doze. It should also be mentioned that the theoretical
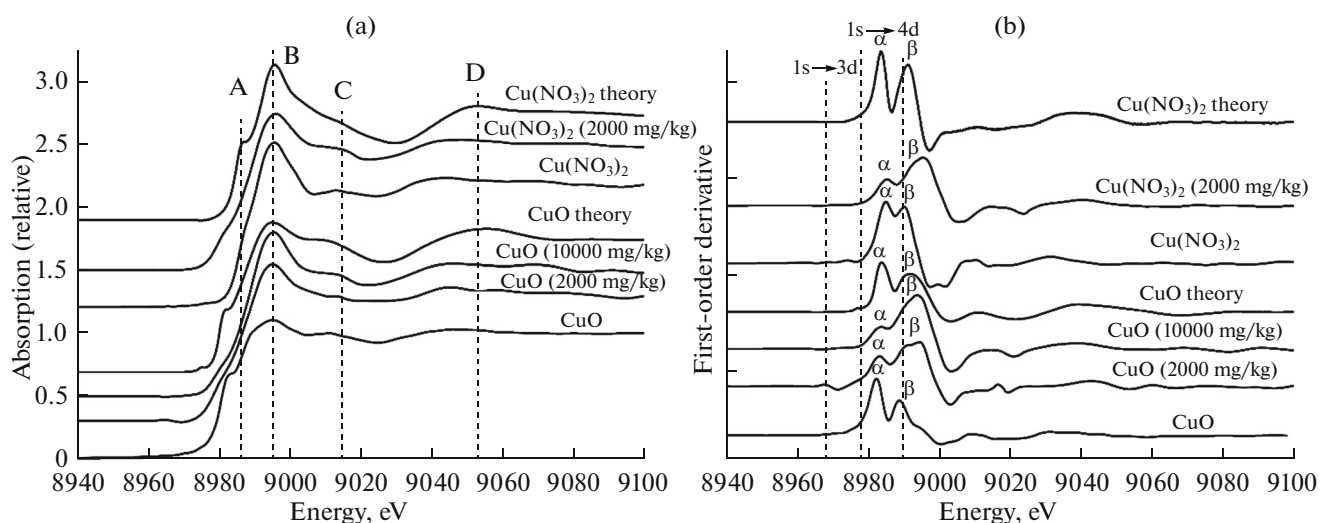
Fig. 1. (a) Experimental and theoretical XANES spectra and (b) first-order derivative of the XANES spectra for the original Cu-bearing contaminants and soil samples contaminated with them.

and experimental spectra of the standard reference samples are consistent.

The near-edge region of the spectrum (~8975–8980 eV) shows a weak maximum of the α derivative of the CuK-edge XANES spectrum (Fig. 1b), which is likely related to the $1s \rightarrow 3d$ quadrupole electron transition that is characterizes low-symmetry Cu bonding. The step structures represented by α and β peaks in the edge region of the first-order derivatives of the experimental and theoretical XANES spectra (1b) are explained by the Jahn–Teller effect, which reflect tetragonal distortions of Cu bonding centers in octahedra (Lee et al., 2005; Palladino et al., 1993; Xia et al., 1997).

The shape, size, and characteristics of the edge and near-edge regions of the experimental XANES spectra of our soil samples contaminated with CuO and $Cu(NO_3)_2$ are clearly different, first and foremost, because of the local atomic structure around the Cu ion. These differences suggest that the local atomic structures of Cu in the soils depend on whether the metal is introduced as CuO or $Cu(NO_3)_2$. The experimental spectra of the soil samples contaminated with Cu in the form of CuO are closely similar to the experimental spectra of pure CuO (Fig. 1b). Conversely, the spectra of the soil samples treated with $Cu(NO_3)_2$ are remarkably different from the spectra of pure $Cu(NO_3)_2$. The reason for this is the much higher solubility of $Cu(NO_3)_2$ than CuO (pK $Cu(NO_3)_2$ = 0.40, pKCuO = 20.32; Lur'e, 1979), which causes the more rapid and complete release of Cu ions from nitrate during the one-year incubation period of the soil samples and their chemical transformation with the origin of humate coordination complexes (Minkina et al., 2013). In the experimental spectra of pure Cu compounds (Fig. 1b), the intensities of the α and β peaks

are practically equilibrated, and correspondingly, Cu retains its ordered settings in both compounds. The decrease in the intensity of the α peak in the experimental first-order derivatives of the CuO and $Cu(NO_3)_2$ XANES spectra of the soils (Fig. 1b) is explained by the $1s \rightarrow 4p_z$ transition, at which a charge is transferred from the metal to ligand in an excited state. This suggests that Cu octahedral sites are tetragonally distorted because of ion exchange with functional groups of humic acid and water molecules, because these distortions can be caused by the Jahn–Teller effect. As a consequence of this interaction of Cu ions with humic acid, a $Cu[H_2O]_2\big[RCO_2^-\big]_4$ humate-complex six-coordinated multisided 3D structure of is formed, as was previously demonstrated for pure phases of humic acids (Minkina et al., 2014). The intensity of the α peak is controlled by the degree of covalent bonding and distortion of sites with Cu atoms, which makes it possible to obtain information on the coordination geometry and bonding of the uptaken metal atom and its neighborhood. A decrease in the energy of the α peak of the experimental spectra suggests that bonding between Cu and soil complexes is dominantly covalent.

The intensity of the β peak of the XANES spectra characterizes the main $1s \rightarrow 4p_z/p_y$ transition (Furnare et al., 2005). It has been proved (Alcacio et al., 2001) that the β peak is the most intense in humic acid and goethite samples containing adsorbed Cu ions. Thereby triple complexes are formed with a central Cu ion bound to organic components.

Figure 2a displays K-edge XANES spectra of Zn, and Fig. 2b presents the first-order derivatives of these spectra, from which the near-edge $1s \rightarrow 3d$ transition is absent (in contrast to the K-edge XANES spectra of
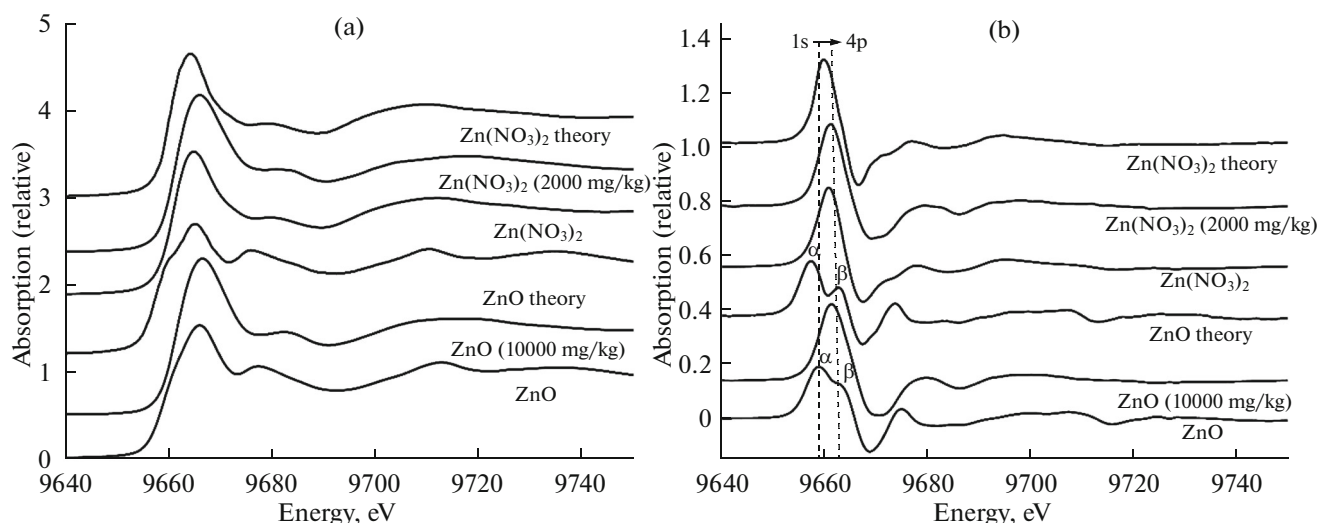
Fig. 2. (a) Experimental and theoretical XANES spectra and (b) first-order derivative XANES spectra for the original Zn-bearing contaminants and soil samples contaminated with them.

Cu) because the d^{10} level is completely filled. The main peak of the first-order derivatives of the XANES spectra characterizes the $1s \rightarrow 4p$ transition.

The molecular-structural state of Zn can be estimated by analyzing oscillation at ~9710 eV, which characterizes first of all the octahedral coordination of the Zn ion and suggests the origin of hydrated adsorbed Zn and, perhaps, also Zn-bearing layer phases (Vodyanitskii, 2010). The Zn ion is thereby accommodated in octahedral structures in layer minerals and (hydro)oxides and forms both inner- and outer-sphere complexes on the adsorbent surface (Pinskii et al., 2014). Interacting with humic acids in chernozem, the Zn^{2+} ion is coordinated by functional groups and ligands and forms unstable outer-sphere complexes (Minkina et al., 2014).

It follows from the comparative analysis of the experimental and theoretical K-edge absorption spectra of Zn for $Zn(NO_3)_2$ and ZnO that, being generally similar, these spectra still show certain differences in the intensity and energy of some spectral features. The experimental XANES spectra of soil samples contaminated with $Zn(NO_3)_2$ and ZnO and the first-order derivatives of these spectra are similar, in contrast to the spectra of the pure original compounds. This suggests that the pollutant structure was not modified during soil incubation for the one-year period of time. A new maximum appeared at 9661−9665 eV, which is typical of Zn-bearing octahedral structures. Thereby Zn ions introduced into the soil samples in the form of Zn oxides and nitrates occur in a low-symmetrical neighborhood because of distortion of the tetrahedrons via changes in the bond lengths and angles and their preferable origin at local defects of the crystal structure. Comparative analysis of our results on Zn and Cu shows that ZnO is more rapidly than CuO

transformed in soils. This may be explained by the higher ZnO solubility (pK ZnO = 11.6; Lur'e, 1979) compared to that of CuO.

CONCLUSIONS

The application of XANES techniques in combination with extractive fractionation enables the researcher to obtain comprehensive information on the state of metals in contaminated soils, interaction between the metals and soil components, phases containing the metals in the soils, and the strength of bonds between these phases and metals. Increasing soil contamination with Cu and Zn is associated with the relative weakening of bonds between these metals and soil components, an increase in the percentage of the most mobile heavy-metal fractions, and a decrease in the percentage of heavy metals bound to silicates. These changes are more significant if the contaminants are nitrates of the metals, first of all Zn.

The agents most actively retaining the metal ions are organic components of soils for Cu and nonsilicate Fe and Mn compounds and carbonates for Zn. Copper ions introduced into soils are bound on tetrahedral and octahedral sites and can form coordinate humate complexes. Interaction with soil components modifies the electron structure of the metal ions themselves.

Much Cu and Zn compounds are contained in uncontaminated soils in stable primary and secondary silicates inherited from the parental rocks, which is a regional trait of soils in the fore-Caucasian plain.

The results obtained by means of extractive fractionation of metal compounds from the soils are consistent with the data derived from analysis of XANES spectra. The extractive fractionation data append the XANES results on the qualitative changes in the states of metals

in contaminated soils and provide quantitative information on metal compounds variably strongly bound to soil components, which is important for protecting ecosystems from metal contamination.

Further coupled application of conventional chemical techniques and modern physical instrumental methods shall significantly widen understanding the mechanisms of chemical transformations of heavy metals in soils.

ACKNOWLEDGMENTS

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