



Speciation of copper and zinc compounds in artificially contaminated chernozem by X-ray absorption spectroscopy and extractive fractionation



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ABSTRACT

Extractive fractionation of metal compounds in chernozem samples, artificially contaminated with copper and zinc salts serves as evidence of absorbing the applied Cu^{2+} ions by the soil organic matter and Zn^{2+} ions – by silicates, carbonates, and Fe–Mn oxides. The study of structural organization in different soil samples and soil phases saturated with Cu^{2+} and Zn^{2+} ions by using X-ray absorption spectroscopy (XANES) allowed the determination of the mechanism of their interaction with soil phases and all the chemical bindings taken place in the course of this process. It is shown that the action of the metal bound to soil components becomes weakened in case of increasing the Cu and Zn load (from 2000 to 10000 mg/kg) especially applied in the form of soluble salts.

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1. Introduction

Ecological significance of heavy metal compounds in soil, conditioned by direct and indirect links of the soil with the other media is dependent on heavy metals firmly bound to organic and mineral components of the soil. In the course of interaction of metals with the surface of soil particles the multiphase pattern of soil plays an essential role. At present, the study of heavy metal absorption by various soil components including the organic matter, clay minerals, and Fe–Mn (hydro)oxides has become very acute. Interaction of metals with soil components determines the buffering capacity of soils for a great number of pollutants, thus ensuring the protective function of soil in ecosystem.

Since the 1960s the heavy metal compounds in soil have been determined by extraction methods. These methods are based on extracting agents of metal compounds presumably held by the solid phase of soil components due to different mechanisms and their stable binding (Minkina et al., 2010). It should be noted that the effect of extracting agents in terms of the soil is not strictly selective.

The X-ray absorption spectroscopy (XANES, EXAFS) is more informative to determine trace elements in soil. The edges of the X-ray absorption have a specific energy characteristic of the element with the given atomic number, that's why every metal and even its oxide can be identified in the composition of different compounds. The study of the fine structure in X-ray absorption spectra (EXAFS) permits to obtain the information about the soil phases as bearers of metals and the

interaction type of metal ions with soil components (Manceau et al., 2002; Manceau and Matynia, 2010; Synchrotron-Based Techniques in Soils and Sediments, 2010).

Today, in addition to EXAFS, XANES method (X-ray absorption near-edge structure) is widely applied. The XANES method proves to be the most effective for studying inorganic minerals (Berry and O'Neil, 2004; Farrel et al., 2002) and metal-organic compounds (Chan et al., 2005; Kostenko et al., 2008). Due to the heterophase pattern of soil, the metal compounds display a great variety in soil. In the XANES procedure, the length of photoelectrons is greater as compared to that in EXAFS. Thanks to the multiple dissimilation process on surrounding atoms, it is made possible to determine parameters of the atomic structure in the area surrounding the metal ion. Moreover, using the XANES method one can obtain information on the oxidation degree of absorbing atom. The most efficient is a combination of experimental investigations with theoretical “first principle” calculations (Smolentsev and Soldatov, 2006, 2009; Soldatov, 2008).

The present paper is aimed to analyze a local atomic and electronic structure of Cu^{2+} и Zn^{2+} ions in the artificially contaminated soil and its mineral and organic components using X-ray absorption spectroscopy and chemical extractive fractionation.

2. Materials and methods

2.1. Saturation method of soil samples

In a model experiment the samples taken in ordinary chernozem of Rostov region were artificially contaminated with higher portions of

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$\text{Cu}(\text{NO}_3)_2$ (2000 mg/kg) and CuO (2000 and 10 000 mg/kg). The metals were incubated in soil samples for a year. The samples of separate soil components (calcite, kaolinite, bentonite, preparations of humic acids extracted from ordinary chernozem) were saturated with Zn^{2+} and Cu^{2+} ions. In view of this, they were in a saturated solution of Cu^{2+} and Zn^{2+} nitrates, the latter being always at a constant pH level was changed twice a day during a week. The soil pH was equal to 7.0 in the presence of CuO (pH 7.0), $\text{Cu}(\text{NO}_3)_2$ (pH 3.9), ZnO (pH 7.0), ZnNO_3 (pH 5.9). One week later, the samples were extracted from the solution and dried. The incubation period of metals in soil and soil components lasted for a year.

2.2. Sequential extractive fractionation

The total content of heavy metals in soil was determined using the X-ray fluorescence method. Sequential fractionation of heavy metals in soil was conducted by Tessier method (Tessier et al., 1979). It allows determining 5 fractions of metals in soil: exchangeable, bound to Fe–Mn oxide, bound to carbonate, bound to the organic matter, and bound to silicate (residual) (Table 1). The total content of heavy metals in soils was determined by the total content of metals in all fractions.

2.3. XANES spectroscopy

The experimental XANES spectra at the K-edge of Zn (9659 eV) and K-edge of Cu (8979 eV) were obtained by spectrometer Rigaku R-XAS Looper in the fluorescence regime because the concentration of the studied metals was rather low. The Ge (440) crystal-monochromator was used, which permitted to obtain a good energy resolution (2 eV). Lead and copper foils were used as standard samples for the energy calibration. Every spectrum was measured by a step of 0.5 eV. To obtain the data for statistical method the exposition time of 60 s was taken for each point in the spectrum. 5–7 spectra were statistically averaged to determine a final spectrum for every sample. Due to the low concentration of Cu ions in the sample of humic acid, which was extracted from ordinary chernozem, the XANES spectra at the K-edge of Cu (8979 eV) and the Cu compounds $\text{Cu}(\text{NO}_3)_2$ were measured in the Kurchatov Center of Synchrotron Radiation. The copper nitrate $\text{Cu}(\text{NO}_3)_2$ was used as a reference compound. The “channel-cut” type of Si (111) monochromator was used. The copper foil was used for energy calibration.

To obtain detail information on the state of Cu^{2+} and Zn^{2+} ions in the studied soil samples the first derivatives of XANES spectra were calculated and permitted to identify differences in these spectra. The experimental spectra of initial Cu- and Zn-containing compounds helped to compare the spectra of soil and soil components. Under consideration are the following results of comparison: 1) experimental spectra of soil samples and some soil compounds treated by CuO, $\text{Cu}(\text{NO}_3)_2$, ZnO, $\text{Zn}(\text{NO}_3)_2$; 2) experimental spectra of initial CuO and $\text{Cu}(\text{NO}_3)_2$, ZnO and $\text{Zn}(\text{NO}_3)_2$ compounds; and 3) theoretical spectra of the above compounds. The calculation was performed using final differences in a complete potential FDMNES 2012 (Bunau and Joly, 2009).

3. Results and discussion

Fractionation of metal compounds showed that Cu and Zn have been dominated in the fraction associated with silicates (60 and 67%) in the unpolluted chernozem (Table 2). Such are the regional biogeochemical features of the soil microelement composition in Rostov oblast and of the mineralogical composition of the parent rocks. The yellow–brown loess – like loams and clays of the Pre-Caucasian Plain inherited the stable minerals of the initial rocks with the typical microelement composition of the minerals (Akimtsev et al., 1962). The mobility of Cu and Zn in the initial soil is low. The relative content of metals in the first two fractions doesn't exceed 3–4%, the mobile exchangeable forms make up only 1%. The differences in the fractional composition of these metal compounds are as follows: the fraction of the organic matter reveals a higher content of Cu, whereas the Zn content is rather high in the fraction bound to Fe–Mn oxides.

In soil contaminated with Cu^{2+} and Zn^{2+} ions the absolute content of all metal compounds shows an increase. In case of increasing Cu and Zn applied in the amount from 2000 to 10 000 mg/kg the metal quantity is also increased by 1.2–5 times in all the studied compounds. It was established that the fractional composition of metal compounds is highly affected by forms of metal input to soil. In case of applying Cu (2000 mg/kg) in the form of nitrate the share of mobile metal compounds made up 6% (the first 2 extracts) and in the form of oxide – only 4%.

As regards to Zn, these differences are expressed to a greater extent: the relative content of Zn applied in the form of nitrate was estimated as 22% and in the oxide form – 11%. This is conditioned by a low solubility of metal oxides. This fact speaks about the absence of direct dependence between the increase in the relative content of mobile Cu and Zn compounds and the increase in soil contamination with metal oxides (Table 2) that has been observed earlier in case of soil contamination with metals applied in the form of soluble salts (Pinskii et al., 2010).

Fig. 1a demonstrates experimental spectra of chernozem samples contaminated with CuO and $\text{Cu}(\text{NO}_3)_2$ as compared to those obtained for their initial forms. All the spectra display the A peak in the middle part of the spectrum edge (~8985–8990 eV). The fact that there is no chemical shift of the main absorption edge (B) in soil samples as compared to initial ones indicates that the oxidation state of Cu ions reveals no change depending on its concentration in the range from 2000 mg/kg to 10000 mg/kg and forms of applied metals. The parameters of theoretical and experimental spectra of standard samples are conformed very well.

In the near-edge area (~8975–8980 eV) a weak α maximum of the XANES spectrum derivative is observed (Fig. 1b). Most probably, it corresponds to quadrupole $1s \rightarrow 3d$ electronic transition that is characteristic for Cu bond in low-symmetry positions. The stepped pattern of the structure presented by α and β peaks in the edge area of the first derivative of experimental and theoretical spectra (Fig. 1b) is most likely caused by the Jahn–Teller effect, indicating the tetragonal distortion of octahedral type of Cu bond (Lee et al., 2005; Palladino et al., 1993; Xia et al., 1997). The distance between maxima of α and β peaks is about 10 eV. Earlier it was shown that this parameter can be used for

Table 1
Extractive fractionation of heavy metals by the Tessier scheme for 1-g sample (Tessier et al., 1979).

Step no.	Fraction	Procedure
1	Exchangeable	8 ml 1 M MgCl_2 , pH 7, shaking for 1 h (extraction of exchangeable metals)
2	Connected with carbonate	8 ml 1 M acetic acid/Na acetate, pH 5, shaking for 5 h (extraction of metals bound with carbonates)
3	Connected with Fe–Mn oxides	20 ml 0.04 M hydrochloric hydroxylamine in 25% acetic acid, pH 2, 96 °C, shaking for 6 h (reducing stage to extract metals adsorbed by Fe and Mn oxides)
4	Connected with organic matter	27% hydrogen peroxide, 3.2 M ammonium acetate in 20% nitric acid (oxidizing stage to extract metals bound with organic matter, etc.)
5	Connected with silicates (residual)	Aqua regia (residual stage)

Table 2
Fractional composition of Cu and Zn compounds in ordinary chernozem.

Addition doses of HM, mg/kg	Fraction					Sum of fraction
	Exchangeable	Connected with carbonate	Connected with Fe–Mn oxides	Connected with organic matter	Connected with silicates (Residual)	
mg/kg						
No added metal	0.4	1.2	5.0	11.1	27.3	45.0
2000 Cu(NO ₃) ₂	52.0	72.7	561.0	819.0	562.9	2067.6
2000 CuO	27.4	62.7	563.1	752.3	627.5	2033.0
10 000 CuO	67.4	78.0	4102.6	3419.4	2373.6	10041.0
% of the sum of fraction						
No added metal	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
10 000 CuO	1	1	41	34	23	100
mg/kg						
No added metal	0.6	1.8	14.2	11.5	56.9	85.0
2000 Zn(NO ₃) ₂	173.6	289.4	826.1	348.7	421.2	2059.0
2000 ZnO	49.1	56.9	777.2	346.1	844.7	2074.0
10 000 ZnO	245.0	296.0	3796.0	1624.0	4111.0	10072.0
% of the sum of fraction						
No added metal	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
10 000 ZnO	2	3	38	16	41	100

qualitative evaluation of axial and equatorial Cu–O distances in Cu-containing octahedral types. The intensity of the β peak speaks about the main $1s \rightarrow 4p_z/p_y$ transition (Furnare et al., 2005).

The form, size and peculiarities of edge and near-edge areas of XANES spectra for soil samples contaminated with CuO and Cu(NO₃)₂ have clear differences mainly associated with the difference in their local atomic structure around the central Cu ion. The spectra of soil samples contaminated with CuO demonstrate close similarity to experimental spectra of initial CuO compound. On the contrary, the spectra of soils contaminated with Cu(NO₃)₂ are significantly different from those obtained for initial Cu(NO₃)₂ providing evidence of changes in the area surrounding the copper ion introduced into the soil. Copper nitrate is soluble in water ($pK_{Cu(NO_3)_2} = 0.40$, $pK_{CuO} = -7.66$). By this reason, for a year of incubation the copper ions have been absorbed by soil components and formed various compounds, including metal-organic complexes with different functional groups (Minkina et al., 2013).

When comparing the first derivative of XANES spectra for Cu(NO₃)₂ with the spectrum for soil, it is possible to see that the α peak is higher as compared to that obtained for CuO (Fig. 1b). The same peculiarities of Cu(NO₃)₂ spectra have been described in Alcacio's publication (Alcacio et al., 2001).

Fig. 2a shows XANES spectra of the K-edge for Zn and their first derivative (Fig. 2b), where the pre-edge $1s \rightarrow 3d$ transition is absent, because d^{10} level is completely filled up as compared to that for Cu. The main peak in the first derivative of XANES spectra displays the $1s \rightarrow 4p$ electronic transition.

The molecular-structural state of Zn can be assessed as based upon oscillation (near ~ 9710 eV), that is characteristic of octahedral coordination of Zn ion and hence the formation of hydrated absorbed zinc and layered Zn phases (Manceau et al., 2002).

In this case the Zn ions included into the octahedral structures of layered minerals and hydroxides can be inter- and out-sphere absorbed.

Based upon a comparative analysis of experimental XANES spectra for K-edge of Zn and pure Zn(NO₃)₂ as well as the theoretical spectrum it is possible to show that all the spectra are identical in their form but they reveal differences in intensity and energy position of spectral peculiarities. The spectrum of the soil sample enriched with Zn nitrate displays a higher reflex intensity. The first derivative of the experimental XANES spectrum for the soil sample contaminated with ZnO is significantly differed from derivatives of X-ray absorption spectrum for initial compound and from theoretical spectrum, thus indicating that the

pollutant composition has been changed for a year of incubation. There is a maximum in the XANES first derivative (~ 9661 – 9665 eV) as referred to Zn-containing octahedral structures. Thus, Zn ions introduced into the soil in the form of oxides and nitrates are in low-symmetry due to octahedral distortion in their interaction.

According to the data of extractive fractionation there are a 4.5 times differences in the share of mobile Zn compounds applied in the form of nitrate and oxide. Therefore, zinc in the form of nitrate interacts more intensively with soil components and forms different compounds. The Zn content in the exchangeable fraction and specifically absorbed fraction (bound to carbonates) becomes significantly increased. The relative content of the most mobile Zn exchangeable fraction increased by 8 times and the specifically absorbed (bound to carbonates) – by 7 times in case of soil contamination with 2000 mg/kg of Zn nitrate. The significant role of carbonates in metal fixation and Zn in particular has been earlier described (Adriano, 2001; Minkina et al., 2008). The affinity of metal ions to carbonates is determined by their low solubility. Carbonates can be the major absorbents of microelements in some soils. There is some evidence that the fraction bound to carbonates is the main solid phase for many metals (Cd, Pb, Zn, Ni, and Cu) in contaminated arid and semiarid soils. Metals can be co-precipitated together with carbonates, being included into their structure or absorbed by Fe- and Mn oxides which are precipitated at the surface of carbonates (Santillan-Medrano and Jurinak, 1975).

The analysis of XANES spectra for K-edge of zinc absorbed by the carbonate phase (Fig. 3) showed that the Zn ions replace the Ca ions in the octahedral positions and display $1s \rightarrow 4p$ electronic transition. Moreover, they are coordinated with carbonate ions as ligands, forming absorbed complexes at the surface of mineral calcite in defect and broken-edge sites. In artificially contaminated soils the metals are predominantly accumulated (Table 2) in fractions bound to the organic matter and Fe–Mn oxides (up to 40% of the fractions amount). In fact, numerous studies have shown the highest affinity of Cu with the organic matter and Zn with Fe–Mn oxides (Kabata-Pendias and Pendias, 1989; Pinski and Minkina, 2013). This is also confirmed by methods of synchrotron radiation spectroscopic analysis (Minkina et al., 2013). According to Alcacio et al. (2001) the humic acids and goethite containing adsorbed copper ions have the highest intensity of β peak. As a consequence, the triple complexes with the copper ion bonded to organic and mineral component are formed.

The experimental XANES spectra for K-edge of Cu in humic acid extracted from chernozem and Cu(NO₃)₂ are quite different. The intensity

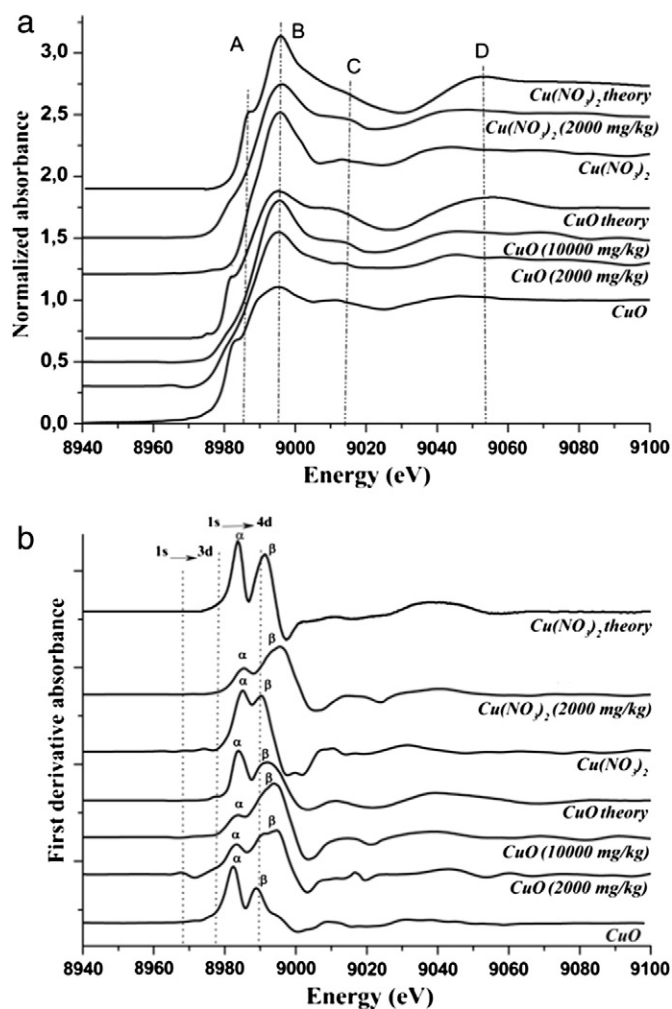


Fig. 1. The experimental and the theoretical Cu K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the soil samples: 1 – theoretical spectra of $\text{Cu}(\text{NO}_3)_2$, calculated by FDMNES 2012; 2 – experimental spectra of $\text{Cu}(\text{NO}_3)_2$ -treated soil sample (2000 mg/kg); 3 – experimental spectra of $\text{Cu}(\text{NO}_3)_2$; 4 – theoretical spectra of CuO , calculated by FDMNES 2012; 5 – experimental spectra of CuO -treated soil sample (10 000 mg/kg); 6 – experimental spectra of CuO -treated soil sample (2000 mg/kg); 7 – experimental spectra of CuO .

of main maximum in the spectrum of copper nitrate is higher than that in the spectrum of humic acid. Experimental XANES spectra of the Cu K-edge of the humic acid and copper nitrate reveal a near edge peculiarity (8975–8978 eV) that is associated with the $1s \rightarrow 3d$ electronic transition and depends on the symmetry of local medium surrounding the absorbed atom (Fig. 4a). The intensity of the near edge peculiar feature increases with increasing symmetry distortion resulting from p–d orbital mixing (Lytle, 1988). Thus, the pre-edge peculiar feature is more clearly expressed in absorption spectra in case of a higher distortion degree of octahedral configuration. Nevertheless, experimental XANES spectra of Cu K-edge reveal no energy position of the shoulder structure in edge area so typical for tetrahedral complexes of many transitional metals (Bianconi, 1988; Bianconi et al., 1982). This spectral peculiar feature is associated with dipole electronic $1s \rightarrow 4p$ transition. The absence of obvious shoulder structure in the absorption edge means that Cu forms octahedral complexes with the humic acid. It should be noted that the first derivative of the K-edge XANES spectra for Cu (Fig. 4b) reveals more detailed information and shows obvious splitting of the α and β peaks in the edge energetic diapason. Thus, it means that a weak shoulder structure nevertheless exists in XANES spectra. This fact allows the conclusion that octahedral positions of Cu ions are tetragonally distorted due to the ion exchange with functional groups of

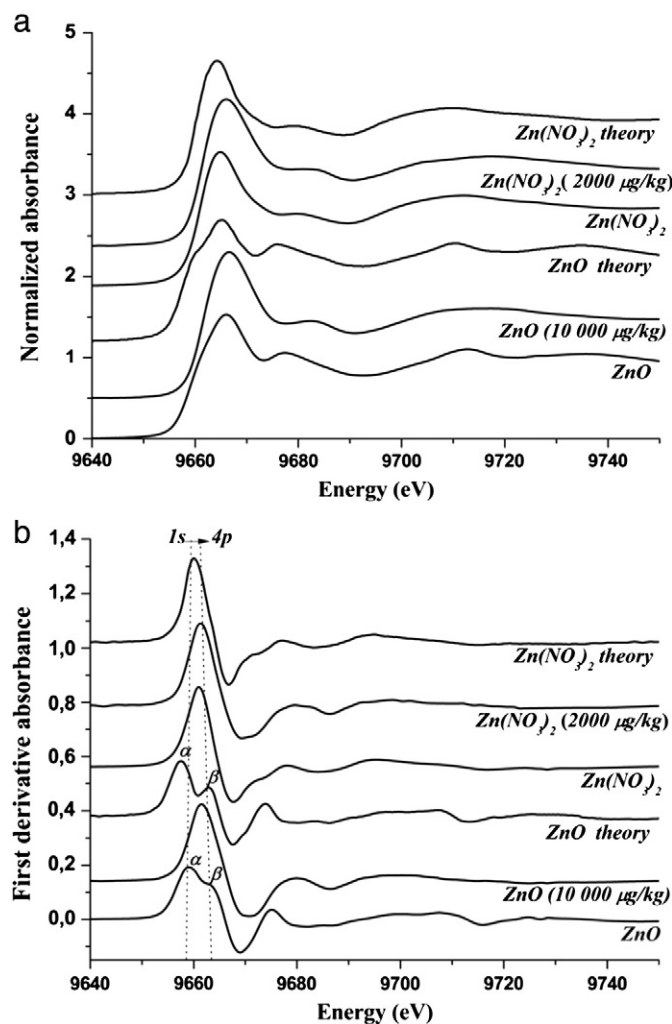


Fig. 2. The experimental and the theoretical Zn K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the soil samples: 1 – theoretical spectra of $\text{Zn}(\text{NO}_3)_2$, calculated by FDMNES 2012; 2 – experimental spectra of $\text{Zn}(\text{NO}_3)_2$ -treated soil sample (2000 µg/kg); 3 – experimental spectra of $\text{Zn}(\text{NO}_3)_2$; 4 – theoretical spectra of ZnO , calculated by FDMNES 2012; 5 – experimental spectra of ZnO -treated soil sample (10 000 µg/kg); 6 – experimental spectra of ZnO .

the humic acid and water molecules. Such distortions cannot be caused by the Jahn–Teller (Garcia et al., 1989) effect because it occurs only when all identical ligands are present. The comparison of XANES derivatives for Cu in the humic acid and in $\text{Cu}(\text{NO}_3)_2$ showed that the intensity of the β peak is higher than that of the α peak, whereas in the spectrum of the humic acid the intensity of both peaks is similar. The intensity of the α peak is decreasing with decreasing bond covalence degree.

The analysis of K-edge XANES spectra for Cu and the first derivatives as well as the results of extraction fractionation with those obtained by Xia et al. (1997) permits to assume that Cu ions can form inner-sphere complexes with the humic acid.

When comparing the intensity of the A maximum and energetic position of spectral B and C features in K-edge XANES spectra for Zn in the humic acid (Fig. 3), it is possible to observe that the metal ions have a similar interaction mechanism with the organic matter being locally surrounded in the same way. The outer-sphere instable complexes are formed by the interaction of Zn^{2+} ions with functional groups and ligands of the humic acid. It agrees well with the fractionation results obtained earlier (Minkina et al., 2009) and shows (Table 2) that the increased soil contamination leads to increasing the content of Zn compounds weakly bound to the organic matter as compared to their firmly

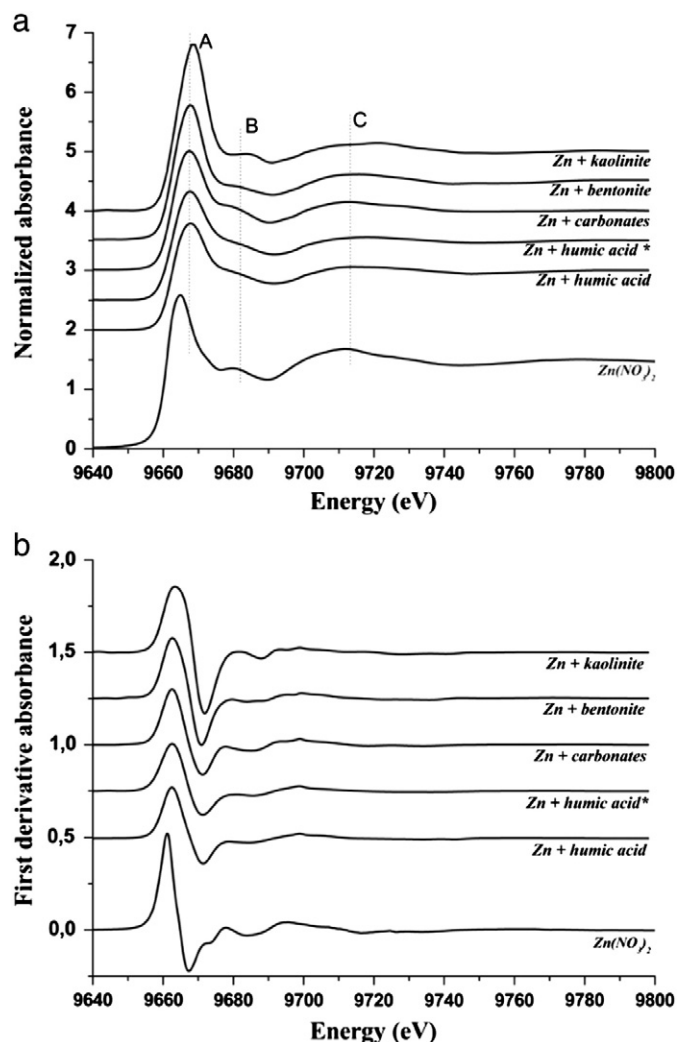


Fig. 3. The experimental Zn K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compound (zinc nitrate) and the soil phase samples.

bound forms. The absolute content of Cu and Zn increased by 21 and 7 times, respectively in the residual fraction (metal compounds bound to silicates) in soils contaminated with metal nitrates. However, the relative content of Cu and Zn decreased as a consequence of intensive accumulation of metals of the other fractions. Similar changes in Cu and Zn composition was observed earlier in the study of technogenic soil (Minkina et al., 2012). This fact can speak about the possible metal inclusion into the mineral structure and explain the increase in the amount of Zn compounds bound to the silicate phase in soils contaminated with this metal.

The comparison of XANES spectra for the initial compound of zinc nitrate and such minerals as bentonite, kaolinite saturated with Zn ions (Fig. 3) showed an insignificant shift (~ 1 eV) indicating that the charge state is changed as resulted from transferring the electron from the metal to ligand.

The inter-layer sorption of heavy metal ions in bentonite occurs due to a low charge value, a slightly expressed interaction between pockets and inter-layer cations. Therefore, in the inter-pocket layer the continuous replacement of Na ions by Zn ions takes place. Zinc in bentonite can be octahedral and tetrahedral surrounded by oxygen atoms. The formation of mono- and bidentate complexes associated with TOT (tetrahedron–octahedron–tetrahedron) pocket occurs through Al–O and Si–O in places of fracture and defect as a result of low ionic strength. It means that Zn ions are adsorbed by silicate and/or aluminum groups which have insufficient coordination. The process can occur due to changes in the length of

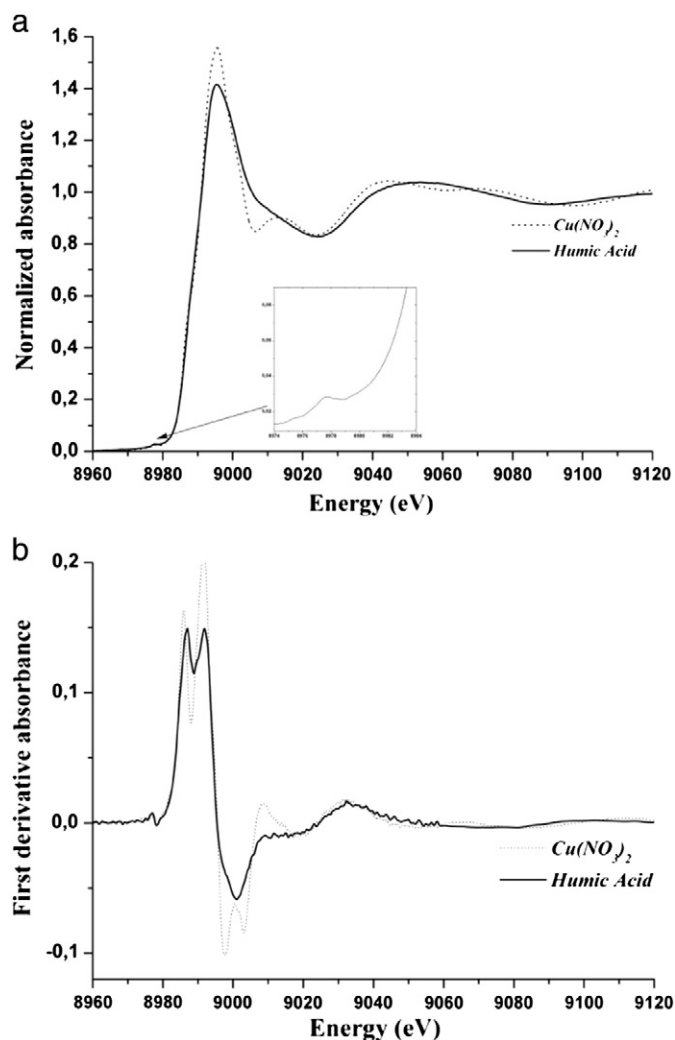


Fig. 4. The experimental Cu K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compound (copper nitrate) and the humic acid sample treated with copper nitrate.

the connection and their appearance in the place of local defects in the crystal lattice due to coulombic forces.

The adsorption of zinc ions by kaolinite differs from that of the other soil phases in form, degree and intensity of absorption in the energetic diapason ~ 9670 eV. First of all, it is connected with differences in their local atomic structure around the central metal atom and the formation of inner-sphere bidentate complexes on crystal faces.

Thus, the analysis of XANES spectra for Zn and Cu in soil phases showed that in dependence on the value of the ionic force the metal ions can form different complexes replacing a part of existing ions. The metals form mainly outer-sphere complexes at the basal mineral surface or in the inter-pocket layer, when the ionic force is rather low. On the contrary, the metals form inner-sphere complexes in mineral edges in case of a higher ionic force.

4. Conclusion

The combined use of X-ray absorption spectrometry and extractive fractionation is an effective approach for studying the interaction of metal ions with soil compounds and identifying the phase-carriers of metals in soil and their stable fixation. The increased degree of soil contamination with Zn and Cu is accompanied by relative decrease in the stable connection between these metals and soil components. The most active is the organic matter to fix the copper ions in soil but non-

silicate compounds of Fe and Mn and carbonates retain Zn ions to a lesser extent.

A large share of Cu and Zn compounds in unpolluted chernozem is found to be in the composition of primary and secondary silicates which is regarded as a regional peculiar feature of soils in Pre-Caucasian Plain. Zinc included into octahedral structures of layered minerals and hydro(oxides) can be inner- and outer-sphere adsorbed. The Zn^{2+} ions enable to replace Ca^{2+} ions in octahedral positions being coordinated with carbonate ions as ligands, thus forming absorbed complexes at the surface of mineral calcite. In case of interaction with the humic acid the Zn^{2+} ions are coordinated with functional groups and ligands, thus forming outer-sphere complexes, while Cu ions – inner-sphere metal–organic complexes.

The results of extractive fractionation of metal compounds in the studied soil are coincided with those obtained by XANES method. These results permit to add and extend the knowledge about qualitative changes in the state of metals in contaminated soils determined by XANES method and to obtain the quantitative data about the metal compounds fixed by soil components with different stability which is especially important for evaluating the soil ability to protect the ecosystem from contamination with heavy metals.

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