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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$Cu(NO_3)_2$ (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), $Cu(NO_3)_2$ (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 $Cu(NO_3)_2$ were measured in the Kurchatov Center of Synchrotron Radiation. The copper nitrate $Cu(NO_3)_2$ 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, $Cu(NO_3)_2$, ZnO, $Zn(NO_3)_2$; 2) experimental spectra of initial CuO and $Cu(NO_3)_2$, ZnO and $Zn(NO_3)_2$ 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 $Cu(NO_3)_2$ 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 10 000 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 derivate 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)