APPLICATION OF METHODS BASED ON SYNCHROTRON RADIATION FOR SPECIATION OF HEAVY METAL IN SOIL

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Abstract
The study is aimed at analyze atomic and electronic structure of Cu (II) and Pb (II) ions in the artificially contaminated soil and its mineral components using X-ray absorption spectroscopy methods based on synchrotron radiation. Soil sampling was taken in the 0-20 cm topsoil of the Haplic Chernozem of the South Russia. In a model experiment the samples taken were artificially contaminated with higher portions (2000 and 10000 mg/kg) of nitrates and oxides of Cu and Pb. The experimental X-ray absorption (XANES and EXAFS) spectra at the K-edge of Cu and L_{III}-edge of Pb were performed at the Structural Materials Science beamline of the Kurchatov Center for Synchrotron Radiation (Moscow) in the fluorescence regime. The features of XANES spectra indicate different orbital transitions in the electron shells of Pb (II) and Cu (II) ions for monoxide and soluble salt, which affect the ion properties and determine the individual structure of the coordination sphere. Analysis of the EXAFS revealed that Cu (II) ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes. Lead ions in soil are incorporated in the positions of the inner-sphere complex replacing some aluminum ions in the octahedral sites. This results in changes the Pb–O distances in Pb-bearing octahedrons. We may suggest that Pb (II) is also sorbed by dimer (Pb–Pb) silicate and/or aluminum groups.

Keywords: XANES, EXAFS, Cu (II), Pb (II), contamination.

Introduction

The bioavailability of metals is closely related to their forms of occurrence. Therefore, studies of soil contamination aimed at obtaining objective information about metal speciation become of special importance (Minkina et al., 2010, 2013). The complexity of the occurrence forms of metals and metalloids is most manifested in highly dynamic, physically and chemically heterogeneous ecological systems like soils, bottom sediments, and sewage sludge (Hesterberg et al., 2011). Analytical methods used to assess metal compounds are usually suitable for the study of limited combinations of metals and metalloids in environmental objects. The mechanical transference of extraction systems developed for background soils introduces additional uncertainties and errors in the study of contaminated soils. The proportions of phosphates, sulfides, and arsenates, for which there are no adequate extractants, increase in industrially contaminated soils (Orlov et al., 2005). Heavy metals in the soils are traditionally analyzed by the indirect method of chemical fractionation; however, direct methods for the determination of heavy metals in soils based on X-ray absorption spectroscopy rapidly developed in the last decades. X-ray spectral analysis methods provide information on the dispersion of elements and contribute to the identification of carrier minerals in the soil, the determination of the mechanisms of cation sorption at the molecular level, and the specification of local atomic structure (Lombi and Susini, 2009). They ensure the selectivity and sensitivity to the local structure of a wide range of elements, low detection limits, high spatial resolution, and simple procedure of sample preparation, which makes these methods the most universal and accuracy in the study of the composition of trace elements and contaminants. X-ray

absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) are the most commonly used spectroscopic techniques. They provided essential information about the forms of heavy metals in soils (Manceau et al., 2002). The aim of this work was to analyze atomic and electronic structure of Cu (II) and Pb (II) ions in the artificially contaminated soil and its mineral components using X-ray absorption spectroscopy methods based on synchrotron radiation.

Material and methods

Soil for model laboratory experiments collected from the humus-accumulative A1 horizon (from the top layer, 0–20 cm) of Haplic Chernozem (IUSS, 2015) in the "Persianovskaya Step", Specially Protected Natural Territory, Rostov oblast, Russia. The A1 horizon (0-20 cm layer) has the following properties: C_{org} 3.7%, $CaCO_3$ 0.4%, pH_{H2O} 7.6; exchangeable bases (cmol+/kg): Ca^{2+} 31.0, Mg^{2+} 6.0, Na^{+}, 0.06; particle size analysis: sand fractions (particles 1.0-0.05 mm) – 42.8%, silt fractions (particles 0.01-0.001 mm) – 29.9% and clay particles (particles <0.001 mm) –28.1%. The content of total Cu and Pb in the samples was determined by synchrotron radiation X-ray fluorescence analysis (SR XRF). Chemical compositions of the mineral component of Haplic Chernozem and the phases of layered silicates samples are given in Table 1. The analyses intended to broaden information about chemical compositions of the sampling sites while improving the knowledge about the presence of possible interferences for synchrotron X-ray methods (for example Fe). The analysis of data obtained with X-ray fluorescence method XRF has allowed to establish quantitative differences of oxides composition for phases of layered silicates samples. The mineralogy of the clay and fine silt fractions from the humus-accumulative horizon of Haplic Chernozem is characterized by the following phase composition of layered silicates: the contents of illite, labile silicates, and kaolinite are 51–54 and 51–60, 23–27 and 12–27, and 22–23 and 22–28% in the clay and fine silt fractions, respectively. The fine silt fraction also contains micas, amorphous silica, and crystallized iron and aluminum oxides and hydroxides (Kryshchenko and Kuznetsov, 2003; Nevidomskaya et al., 2016; Sokolova, 1985).

Table 1. Chemical compositions of the mineral component of Calcic Chernozem and the phases of layered silicates, wt %

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	P_2O_5
Haplic Chernozem	63.95	12.08	5.26	2.35	1.35	2.16	0.16
Kaolinite	55.24	33.17	0.42	0.13	0.05	0.41	0.09
Montmorillonite	75.60	7.68	1.17	1.22	1.17	0.39	0.05
Hydromuscovite	60.69	18.97	4.66	2.22	1.45	4.54	0.17
Gibbsite	4.28	56.99	0.19	0.08	0.02	0.10	0.13

To study transformation of Cu (II) and Pb (II) ions absorbed by soil, the samples taken in uncontaminated soil (Haplic Chernozem) contaminated with compounds of Zn and Cu oxides and nitrates. The model laboratory experiment has been established under controlled conditions. The soil selected for the experiment was air-dried, triturated using a pestle with a rubber head, and sieved through a 1-mm sieve. Dry compounds of Cu ($Cu(NO_3)_2$ and CuO) and Pb ($Pb(NO_3)_2$ and PbO) were added to the soil at a rate of 2000 and 10000 Cu and Pb mg/kg. The soil was thoroughly mixed, wetted, and incubated for 3 years at 60% of the maximum water capacity. Experiments were performed in triplicates. Analogous procedures but without addition of metal were performed with the control sample. After the end of incubation (3 years layer), an average sample was taken from each pot for analysis. The soil was brought to the dry state. Samples of separate mineral phases (montmorillonite, kaolinite, hydromuscovite, and gibbsite) were saturated with Cu^{2+} and Pb^{2+} ions. For this purpose, the studied samples were put into a saturated $Cu(NO_3)_2$ and $Pb(NO_3)_2$ solution. The solution was changed twice a day for a week. After a week, the preparation was removed from the solution, dried, and grounded. The experimental Cu K-edge X-ray absorption near edge structure (XANES) spectra (~899–8995 eV) and L_{III}-edge of Pb (13040 eV) were performed at the Structural Materials Science beamline (Chernyshov et al. 2009) of the Kurchatov Center for Synchrotron Radiation (NRC “Kurchatov Institute”, Moscow) at room temperature in fluorescence

mode. A two-crystal Si(111) monochromator with the energy resolution ΔE/E ~ $2 \cdot 10^{-4}$ was used to monochromate the X-ray radiation. To obtain the data for statistical method the exposition time of 60 sec. was taken for each point in the spectrum. 10 spectra were statistically averaged to determine a final spectrum for every sample. The obtained spectra were processed using standard procedures for noise discrimination and normalization by the K-edge jump. First-derivative XANES spectra were analyzed to specify information about the state of Cu^{2+} and Pb^{2+} ions and reveal the differences in the analyzed samples that escaped detection during the analysis of XANES spectra. Along with the experimental XANES spectra (the channel-cut monochromator with routinely switchable Si(111)), experimental spectra of the original Cu-containing and Pb-containing compound were also studied. The gonimeter head of the monochromator constructed at the Institute of Crystallography of RAS (Moscow, Russia, 2004) driven by a step motor provides a rotational scanning step of 1 arcsec. Quick and reliable photon energy tuning is crucial for the X-ray absorption spectroscopy measurements. EXAFS spectra of the Cu K-edge and Pb L_{III}-edge were measured at the same synchrotron beamline in the fluorescence yield mode using a Si avalanche photodiode to count fluorescence photons and an ionization chamber to monitor the incident intensity (Chernyshov et al. 2009). The spectra were processed with the help of the Ifeffit software package (Newville, 2001).

Results and discussion

The morphology, size, and peculiarities of edge and near-edge areas on XANES spectra of soil samples contaminated by CuO and $Cu(NO_3)_2$ have clear differences mainly controlled by the differences in their local atomic structure around the central Cu ion (Fig. 1). The intensity of the α peak is controlled by the degree of bond covalence and characterizes the coordination environment and chemical bonds of the absorbed metal ion with its closest surroundings. With a decrease in the α peak energy, Cu complexes with soil components have predominantly the covalent character of the bond. The intensities of the α and β peaks in the experimental spectra of the initial copper-bearing compounds are close (Fig. 1b). Analysis of the EXAFS revealed that lead to ion exchange in the tetragonal plain of water molecules with ligands. The interaction between copper ions and humic acid may result in the formation of multilateral 6-coordinated spatial structure of humate complex (Minkina et al., 2017). Application of this method demonstrated that the state of copper introduced in Haplic Chernozem as CuO did not change after three year of incubation (Fig. 1). Copper is absorbed after being introduced as $Cu(NO_3)_2$, and Cu ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes.

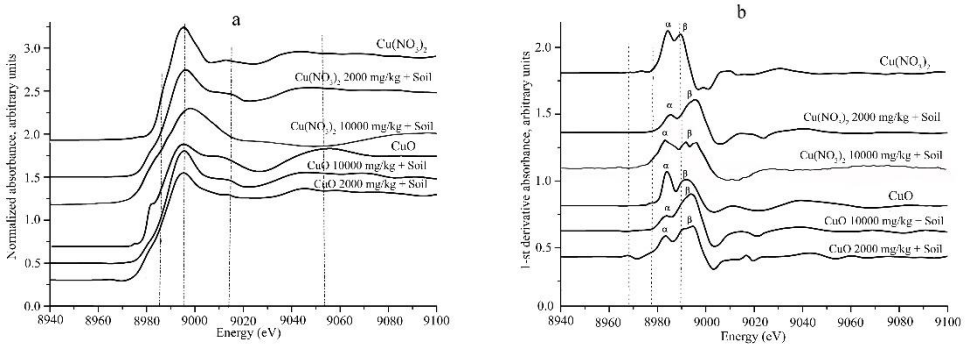


Figure 1. The experimental Cu K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the Cu-treated soil samples

Parameters of the experimental XANES spectra obtained for the studied soil samples saturated with high rates of Pb compounds, as well as the spectra of the initial PbO and $Pb(NO_3)_2$ are given in Fig. 2. The spectra are characterized by an energy region of ~13030–13058 eV related to the presence of lead ions, from which the molecular-structural state of the metal is assessed. The highest absorption intensity is recorded in the energy region of ~13038–13040 eV for the samples saturated with PbO

and at ~13042 eV for the samples saturated with $Pb(NO_3)_2$, which characterizes the $2p_{3/2}\rightarrow 6d$ electron transition (Fig. 2b). The modulations of $2p_{3/2}$ electrons in the first derivative spectra of PbO and PbO-saturated soil samples are appreciably different (Fig. 2b), which is due to the different shoulder amplitudes in the energy region of ~13032 eV, especially for the initial PbO. This X-ray absorption peak is manifested only for the spectra of PbO and PbO-saturated soil samples and is related to the $2p_{3/2}\rightarrow 6s$ electron transition, indicating the 6s and 6p hybridization for Pb and $2p_{x,y}$ for oxygen; therefore, Pb^{2+} participates in the formation of numerous distorted complexes, because the adsorbed Pb ions can have different O–Pb–O valent angles.

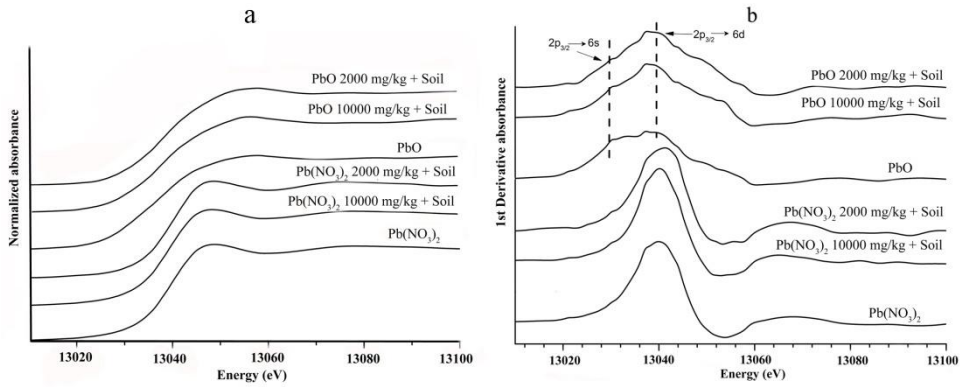


Figure 2. The experimental Pb L_{III}-edge XANES spectra (a) and their first derivatives (b) for the reference compounds (PbO and $Pb(NO_3)_2$) and the Pb-treated soil samples

Using results of EXAFS method was determined that lead ions incorporated in the phyllosilicate minerals structure favoring a decrease in the bond distances between Pb^{2+} ions and O atoms in equatorial and axial coordination positions in Pb-bearing octahedrons. Divalent Pb has the $6s^2$ electronic configuration of the outer shell. This lone electron pair is frequently stereochemically active and causes a strong deformation of divalent Pb in polyhedrons. Thus, it can be concluded that Pb is sorbed as a bidentate inner-sphere complex at the edges of the octahedrally coordinated aluminum ions. XANES data for the studied soil samples and mineral phases of layered minerals artificially contaminated with $Cu(NO_3)_2$ are shown in Fig. 3. Comparison of the first-derivative Cu K-edge XANES spectra for all samples with the spectrum of the $Cu(NO_3)_2$ standard showed sensitivity of the method for changes in the immediate surrounding of Cu (II) ions in these structures. The samples are characterized by the existence of peak A in the middle part of the spectrum (~899–8995 eV) due to the presence of Cu^{2+} ions. The absence of chemical shift of the main absorption edge in contrast to the initial spectrum of the compound indicates that the charge of Cu^{2+} ion in the soil does not change. The spectral features of the central peak and low-amplitude lateral maximums of layered silicates, their shapes, and shifts against the original copper-containing compound indicate a shortening of interatomic distances between the adsorbed Cu^{2+} ions and the oxygen surrounding in accordance with the Natoli rule (Natoli, 1984). This agrees with data of X-ray diffraction analysis and earlier molecular dynamic simulation (Minkina et al., 2013).

Parameters of the experimental XANES spectra obtained for the studied soil phases are given in Fig. 4a; their first derivatives are given in Fig 4b. The spectra of these phases include the energy region of ~13035–13055 eV. Absorption spectra of soil phases saturated with Pb nitrate together with those of $Pb(NO_3)_2$ are shown at the Fig. 4a and their first derivatives are shown at the Fig. 4b. Comparison the first derivative of the Pb L_{III}-edge XANES of all the soil samples to the reference spectrum of $Pb(NO_3)_2$ show similarity of the main features: a central peak and low amplitude left- and right-hand shoulder features.

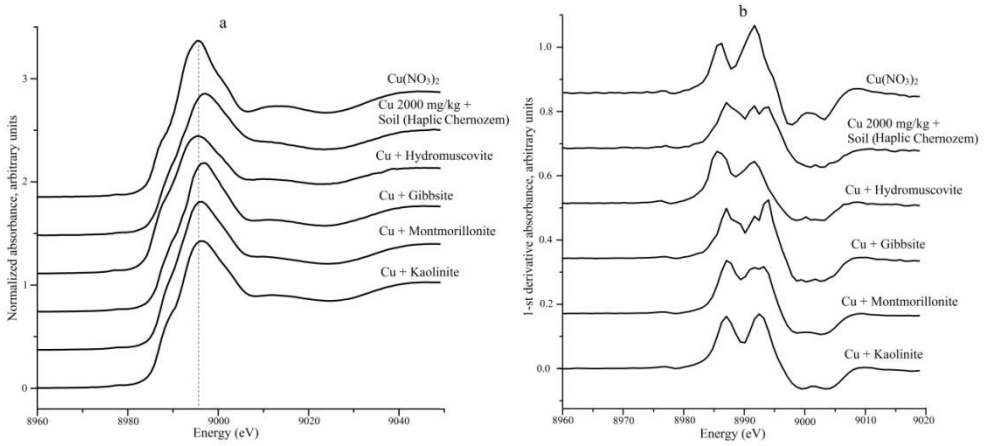


Figure 3. (a) Experimental Cu K-edge XANES spectra and (b) 1-st-derivative X-ray absorption spectra for soil, layered silicate phases, and $Cu(NO_3)_2$ standard

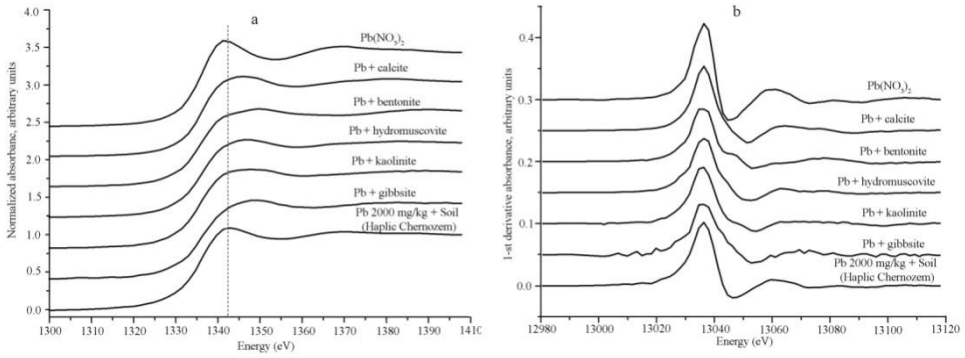


Figure 4. (a) Experimental Pb L_{III}-edge XANES spectra and (b) 1-st-derivative X-ray absorption spectra for soil, layered silicate phases, and $Pb(NO_3)_2$ standard

Analysis of the EXAFS revealed that Pb^{2+} ions in soil are incorporated in the positions of the inner-sphere complex replacing some aluminum ions in the octahedral sites. Lead oxides show a particularly wide variety of nearest Pb-O distances. According to the structural database (ICSD database) the shortest Pb-O distance ranges from 0.216 nm in PbO up to 0.275 nm in $Pb(NO_3)_2$. Thus the distribution of the oxygen atoms around Pb can serve as a sensitive probe for structural changes in the samples. This results in changes the Pb–O distances in Pb-bearing octahedrons. We may suggest that Pb (II) is also sorbed by dimer (Pb–Pb) silicate and/or aluminum groups.

Conclusions

Synchrotron radiation's methods are an effective approach for the study of bonds between metals and soil components. Application of these methods demonstrated different orbital transitions in the electron shells of Cu^{2+} and Pb^{2+} ions for monoxide and soluble salt, which affect the ion properties and determine the individual structure of the coordination sphere. Copper is absorbed after being introduced as Cu $(NO_3)_2$, and Cu^{2+} ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes. Lead ions are sorbed as a bidentate inner-sphere complex at the edges of the octahedrally coordinated aluminum ions. This results in changes the Pb–O distances in Pb-bearing octahedrons. We may suggest that Pb (II) is also sorbed by dimer (Pb–Pb) silicate and/or aluminum groups.