

# Comprehensive study of Pb (II) speciation in soil by X-ray absorption spectroscopy (XANES and EXAFS) and sequential fractionation

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## Abstract

**Purpose** The study is aimed at the analysis of the spatial–structural organization of Pb(II) in Chernozem soils and the relationship between the metal ion and the soil components using X-ray absorption spectroscopy and chemical extractive fractionation.

**Materials and methods** In a model experiment, soil samples were artificially contaminated with elevated rates of Pb(NO<sub>3</sub>)<sub>2</sub> and PbO (2000 and 10,000 mg kg<sup>-1</sup>). The samples of mineral phases (bentonite, gibbsite, kaolinite, calcite, and hydromuscovite) were saturated with Pb<sup>2+</sup> ions. The sequential fractionation of Pb in the soil was conducted by the Tessier method. X-ray absorption near-edge fine structure (XANES) spectra at the Pb L<sub>III</sub>-edge (13.040 keV) were obtained on a Rigaku R-XAS Looper spectrometer. Extended X-ray absorption fine structure (EXAFS) L<sub>III</sub>-edge Pb was measured at the Structural Materials Science beamline of the Kurchatov Center for Synchrotron Radiation.

**Results and discussion** The results of successive extraction showed that Pb is associated with strongly bound organic substances, Fe and Mn (hydr)oxides, and carbonates. An

increase in the portion of exchangeable fraction is observed under extreme loads. At the addition of Pb in the form of oxide and nitrate to the soil, the fractional compositions were similar, which indicates the good transformation of PbO in Chernozem. The features of XANES spectra indicate different orbital transitions in the electron shells of Pb<sup>2+</sup> ions for monoxide (PbO) and soluble salt (Pb(NO<sub>3</sub>)<sub>2</sub>), which affect the ion properties and determine the individual structure of the coordination sphere. The analysis of XANES revealed that sorption of Pb in the soil samples and in the samples of mineral phases does not change its bond valence.

**Conclusions** The increased degree of soil contamination with Pb is accompanied by decreasing the stable connection between metal and soil components. Lead ions in bentonite, kaolinite, hydromuscovite, gibbsite, and calcite 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<sup>2+</sup> is also sorbed by dimer (Pb–Pb) silicate and/or aluminum groups. The structure of adsorbent surface plays the key role in the sorption of Pb<sup>2+</sup> by mineral phases.

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## 1 Introduction

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 precise 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). XANES spectroscopy is widely used for studying the electronic structure of substances: the determination of symmetry and energy of vacant molecular orbitals in molecules or electron zones in solid materials (Soldatov 2008). In particular, this method can provide information on the degree of oxidation of the absorbing atom and the symmetry of its coordination sphere. The energy of X-ray absorption edges is typical for an element with a specific atomic number; therefore, the metal and even its oxidation state in different compounds can be identified (Singh and Gräfe 2010).

Numerous current studies deal with the adsorption mechanisms of heavy metals by different soil components, including organic matter, clay minerals, Fe and Mn (hydr)oxides, etc. because some inorganic and organic phases of soil have high buffering capacity for a wide range of soil pollutants and thus ensure the protective function of the soil (Alcacio et al. 2001; Dähn et al. 2001; Elzinga et al. 2006; Furnare et al. 2005; Manceau and Matynia 2010; Minkina et al. 2013; Rouff et al. 2005; Strawn and Baker 2008; Xia et al. 1997).

Pedogenesis occurs due to numerous simultaneous or successive processes and chemical reactions based on the properties of molecules and chemical elements. The regional features of the studied soil include the accumulation of calcium-humate humus, the enrichment of soil matrix in clay minerals, and the migration of carbonates throughout the soil profile mainly consisting of calcite. The presence of carbonates in the soil determines the calcium-carbonate equilibrium, which affects the chemical composition of soil solution, the processes of dissolution and migration, the precipitation of many microelements, and the ion exchange at the phase interface (Minkina et al. 2012). The finely dispersed mineral component of Chernozem soils consists of micas and hydromicas (51 %), smectite group (27 %), and kaolinite group (22 %) (Bezuglova et al. 2010). Therefore, of special interest is the study of the sorption mechanisms of heavy metals by these mineral phases.

In soil systems, the mobility, biological availability, and hence toxicity of elements significantly depend on their forms of occurrence and the type of bonds with the sample matrix (Karpukhin and Ladonin 2008; Minkina et al. 2011, 2014; Vodyanitskii 2014). Procedures of successive fractionation

are used to extract different forms of heavy metals from soils (Minkina et al. 2008). The extracting agents may transfer different metal compounds into solution. To identify them, direct physical methods (EPR, NMR, EXAFS, XANES, and some others) can be applied. These methods make it possible to determine the type of bonds between chemical elements in different compounds. Thus, they give us direct information on the composition of the analyzed samples. However, potentials of fractionation methods are far from exhausted. The combination of modern approaches of qualitative analysis of compounds with methods of quantitative fractionation may be useful. The efficiency of such a combination is ensured by reliable qualitative data on the nature of bonds between metal compound and organic and mineral soil components and by a wealth of quantitative information on the contents of metal compounds in different soils. The obtained data cannot be identical. Though the results of these fractionation procedures characterize metal compounds “presumably bound” with particular soil components, the difference between them may carry some new information.

The study is aimed at analysis of the spatial-structural organization of Pb(II) in soil and at analysis of the relationship between metal ion and different soil components using X-ray absorption spectroscopy and chemical extractive fractionation.

## 2 Materials and methods

### 2.1 Sample description

Soil sampling was taken in the 0–20-cm topsoil of the reserve area covered by the Haplic Chernozem (WRB 2006) of the Lower Don region. The soil had a silt content of 286 g kg<sup>-1</sup> and a clay content of 471 g kg<sup>-1</sup>; pH<sub>(water)</sub> of 7.3; organic C content of 23 g kg<sup>-1</sup>; CaCO<sub>3</sub> content of 1 g kg<sup>-1</sup>; cation exchange capacity of 37.1 cmolc kg<sup>-1</sup>; and exchangeable Ca, Mg, and Na contents of 29.5, 5.5, and 0.1 cmolc kg<sup>-1</sup>, respectively (Mandzhieva et al. 2014).

The experiment was performed in four plastic vessels. To ensure drainage, a 3-cm-thick layer of haydite and 3-cm-thick layer of washed river sand were placed on the bottom of the vessels. Then, the vessels were filled with 4 kg of the ground soil sieved through a 5-mm sieve. Dry compounds of Pb (PbO and Pb(NO<sub>3</sub>)<sub>2</sub>) were added to the soil at concentrations of 2000 and 10,000 mg kg<sup>-1</sup>. The upper 20-cm thickness of the soil layer was used in the experiments. After the soil composting for 1 month, a test culture (barley of the Odesskii 100 strain) was sown. During the vegetation period, the soil moisture was at a level of 60 % from the field water capacity. Pots were used as cultivation containers in the open air for 2 years. Soil samples were collected before the experiment, 1 and 2 years later after barley harvesting in the phase of waxy

maturity. In this paper, we predominantly discuss the results obtained after 1 year of incubation. Lead associated with different soil components was extracted from the soil with the use of sequential extractants saline and acid solutions; the metal concentrations in the extracts were determined using the atomic absorption spectroscopy (AAS) method. The content of the total Pb in the soil was determined by the X-ray fluorescence method.

Samples of bentonite, kaolinite, hydromuscovite, gibbsite, and calcite were saturated with  $\text{Pb}^{2+}$  ions using a saturated solution of  $\text{Pb}^{2+}$  nitrate during a week. This solution, kept at constant pH, was changed twice a day. After 1 week the samples were removed from the solution and were air-dried. The calcite sample was collected in the illuvial horizon of the studied soil. The samples of bentonite (GSO 8694–2005), kaolinite (GSO 9089–2008), hydromuscovite (Enskoe deposit, Murmanskaya oblast'), and gibbsite (BDS 1711-001-00658716-99) are standard reference materials. The reference samples were analyzed by X-ray diffraction based on synchrotron radiation. The obtained diffraction patterns confirmed the structural accordance of mineral phases obtained at the Structural Materials Science beamline of the Kurchatov Center for Synchrotron Radiation (Chernyshov et al. 2009). The diffraction patterns were compared with the data of crystallographic databases (Inorganic Crystal Structure Database (ICSD database: [www.fiz-informationsdienste.de/en/DB/icsd/](http://www.fiz-informationsdienste.de/en/DB/icsd/))).

## 2.2 Sequential extractive fractionation

Sequential fractionation of Pb in the soil samples was conducted by the Tessier method (Tessier et al. 1979). The Tessier procedure of fractionating metals is largely similar to other methods used for the analysis of soils, sediments, and bottom sediments. The long experience in the fractionation of heavy metals from the main soils of southern Russia (Haplic Chernozems and Chestnut soils) by the Tessier method showed the validity of this scheme and the objectivity of its results (Minkina et al. 2008, 2011, 2013; Mandzhieva et al. 2014). This procedure ensures the separation of five fractions of Pb (Table 1):

1. The exchangeable fraction contains metal ions mainly retained by electrostatic forces on the surface of minerals (mainly clay minerals), organic materials, and non-crystalline compounds with the low pH values of zero charge. The fraction is affected by the ionic composition of soil solution.
2. The carbonate-bound fraction contains heavy metal ions specifically sorbed on Ca and Mg carbonates. Partial dissolution of metal phosphates is also possible.
3. The hydroxide-bound fraction contains heavy metal ions occluded by Fe and Mn (hydr)oxides or adsorbed on their surface. Metals from organic complexes and non-crystalline sulfides can be released during extraction.

**Table 1** Extractive fractionation of heavy metals by the Tessier scheme for 1-g sample

Fraction	Soil/solution ratio	Extraction conditions	Extractant
Exchangeable	1:8	Shaking at room temperature for 1 h	1 M $\text{MgCl}_2$ , pH 7.0
Connected with carbonate	1:8	Shaking at room temperature for 5 h	1 M $\text{NaCH}_3\text{COO}$ , pH 5.0 (with $\text{CH}_3\text{COOH}$ )
Connected with Fe–Mn oxides	1:20	Heating at $96 \pm 3$ °C under periodical shaking for 8 h	0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25 % $\text{CH}_3\text{COOH}$
Connected with organic matter	1:20	Heating at $85 \pm 2$ °C under periodical shaking for 5 h	0.02 M $\text{HNO}_3$ + 30 % $\text{H}_2\text{O}_2$ , pH 2.0 (with $\text{HNO}_3$ ), then 3.2 M $\text{NH}_4\text{CH}_3\text{COO}$ in 20 % $\text{HNO}_3$
Connected with silicates (residual)	1:25	Evaporation	Extract of $\text{HF} + \text{HClO}_4$ from the residual fraction

Source: Tessier et al. (1979)

4. The organic-matter-bound fraction contains heavy metal ions retained by organic substances or organomineral compounds. Sulfides can undergo partial dissolution.
5. The residual fraction contains heavy metal ions strongly fixed in the crystal lattices of primary and secondary minerals. This fraction can also include metals from stable sulfides and, in small amounts, stable organomineral substances.

After each extraction step, the liquid and solid phases were separated by centrifugation. To decrease the effect of the multicomponent composition of extracts on the determination of their metal content by AAS, the standard addition method was used. The corresponding extracts from background soil samples were used for the reference scale.

## 2.3 XANES and EXAFS spectroscopy

The experimental XANES spectra at the  $L_{\text{III}}$ -edge of Pb (13.040 keV) were obtained by spectrometer Rigaku R-XAS Looper in the fluorescence regime because the concentration of the studied metals was rather low. The Si (620) crystal monochromator was used, what permitted to obtain a good energy resolution (1.1 keV). Lead foils were used as standard samples for the energy calibration. Every spectrum was measured by a step of 0.5 keV. To obtain the data for the statistical method, the exposition time of 60 s was taken for each point in the spectrum. Five to seven spectra were statistically averaged to determine a final spectrum for every sample.

The measurements of X-ray absorption spectroscopy EXAFS were performed at the Structural Materials Science beamline (Chernyshov et al. 2009) of the Kurchatov Center for Synchrotron Radiation (NRC “Kurchatov Institute,” Moscow). EXAFS spectra at the Pb L<sub>III</sub>-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. A Si (111) channel-cut monochromator was providing an energy resolution of  $E/E \sim 2 \cdot 10^{-4}$ .

The measured EXAFS data were analyzed using the Viper and UWXAFS packages (Klementiev, available on-line at: [www.desy.de/~klmn/viper.html](http://www.desy.de/~klmn/viper.html); Klementiev 2001; Newville et al. 1993; Stern et al. 1995). All the spectra were normalized and the EXAFS signal was obtained by subtraction of the atomic background from the raw data.  $k^2$ -weighted EXAFS was then Fourier-transformed to  $R$  space. The Fourier transformation was made over the  $k$  range 25–95 nm<sup>-1</sup>. Data processing and analysis were performed using the IFEFFIT suite (Ravel and Newville 2005). FEFF ab initio photoelectron phase and amplitude functions (Newville 2001) were used in the non-linear curve-fitting procedure. A fit to the experimental XAFS was performed in the  $R$  distance range 0.12–0.25 nm.

To obtain detailed information on the state of Pb<sup>2+</sup> 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 Pb-containing compounds helped to compare the spectra of soil and mineral phases. Under consideration are the following results of comparison: experimental spectra of soil samples and some mineral phases treated by PbO and Pb(NO<sub>3</sub>)<sub>2</sub>.

## 2.4 Statistical analysis

The results of chemical analysis correspond to the mean of three replicates. Descriptive data analysis, comprising minimum value, mean value, maximum value, and confidence limits for mean, was carried out with STATISTICA 10.0. Differences were considered not significant at values of  $P > 0.05$ .

## 3 Results and discussion

The total Pb content in the original uncontaminated soil (0- to 20-cm layer) was  $26.0 \pm 3.8$  mg kg<sup>-1</sup>, which agreed with the literature data (Minkina et al. 2009; Sobornikova and Kizilshstein 1990). No significant variation of Pb occurs in the original soil because the regional geochemical features are characterized by the relative homogeneity of the parent rocks. A relative non-uniformity of the metal distribution

was observed in the upper humus horizons of the Chernozem profile in the same area (Minkina et al. 2013).

The mobility of Pb in the original uncontaminated Chernozem soil is low. The fractionation of compounds showed that the relative content of Pb in the first two fractions does not exceed 3–4 %; the mobile exchangeable forms make up only 1 % (Table 2). The organic fraction reveals a higher content of Pb (26 %). In the uncontaminated Chernozem, soil dominated the fraction associated with silicates (55 %).

In the soil contaminated with Pb<sup>2+</sup> ions, the absolute content of metal compounds shows an increase (Table 2). When the Pb application rate increased from 2000 to 10,000 mg kg<sup>-1</sup>, the metal content also increased by 1.2–5 times in all the studied compounds. It was established that the fractional composition of Pb associated with different soil components is highly affected by the forms of metal input to soil. The share of mobile soil compounds to which Pb is associated made up 1.7–1.8 % (the first two extracts) at the application of Pb (2000 mg kg<sup>-1</sup>) in the form of nitrate and its application in the form of oxide. The sum of the two first fractions for the soil contaminated with Pb (10,000 mg kg<sup>-1</sup>) in the forms of nitrate and oxide attains 25.9–28.0 %.

At the application of Pb at a rate of 2000 mg kg<sup>-1</sup>, the residual fraction contributes less to its sorption: 43.7 % for nitrate and 48.7 % for oxide (Table 2). Under the high concentration of Pb application (10,000 mg kg<sup>-1</sup>) to the soil, the percentage of Pb in the residual fraction decreased dramatically.

The study of soil compounds connected with Pb by the Tessier method showed the following distribution of Pb in the original uncontaminated soil: residual fraction > fraction bound to organic matter > fraction bound to Fe and Mn (hydr)oxides > fraction bound to carbonates > exchangeable fraction (Table 2). Many authors noted the tendency of Pb to accumulate in soil organic matter, as well as its affinity for iron and manganese oxides (Adriano 2001; Kabata-Pendias and Pendias 1989; Plekhanova and Bambusheva 2010). This regularity is manifested in the Tessier scheme for the uncontaminated soil. At the addition of 2000 mg kg<sup>-1</sup> Pb, the absolute and relative concentrations of the fractions bound to organic matter and to Fe and Mn (hydr)oxides increase. When the contamination increases, the contribution of iron minerals to the adsorption of Pb decreases. This can be due to the leading role of organic substances in the strong retention of the high concentration of added Pb<sup>2+</sup> ions because of the high metal capacity of forming inner-sphere complexes (chelates) with organic matter (Karpukhin and Ladonin 2008). Lead is predominantly chelated by the functional groups of aromatic rings with the formation of bidentate complexes (Manceau et al. 2002). It was noted earlier (Ladonin and Karpukhin 2011; Vodyanitskii 2014) that Pb is the least mobile heavy metal because it is associated with all the major soil components (organic matter, clay minerals, carbonates, and Fe and

**Table 2** Fractional composition of Pb in Haplic Chernozem

Addition doses of Pb, mg kg <sup>-1</sup>	Fraction					Sum of fraction
	Exchangeable	Connected with carbonate	Connected with Fe–Mn oxides	Connected with organic matter	Connected with silicates (residual)	
mg kg <sup>-1</sup>						
No added metal	0.4±0.1	1.6±0.5	2.8±0.3	6.9±1.2	14.7±2.1	26±4.2
2000 Pb(NO <sub>3</sub> ) <sub>2</sub>	15.6±2.2	19.7±2.9	408.5±28.8	705.6±29.7	890.6±39.9	2040±103.5
10,000 Pb(NO <sub>3</sub> ) <sub>2</sub>	1443.0±41.6	1476.0±45.1	1615.0±29.4	4498.0±35.9	1250.0±32.3	10282±184.3
2000 PbO	14.3±1.9	18.7±3.0	424.0±30.6	587.0±31.2	991.0±38.4	2035±105.1
10,000 PbO	1284.0±25.9	1345.0±40.6	1362.0±38.7	4613.0±44.7	1520.0±46.2	10124±196.1
% of the sum of fraction						
No added metal	2.0	6.0	11.0	26.0	55.0	100
2000 Pb(NO <sub>3</sub> ) <sub>2</sub>	0.8	1.0	20.0	34.6	43.7	100
10,000 Pb(NO <sub>3</sub> ) <sub>2</sub>	14.0	14.0	16.0	44.0	12.0	100
2000 PbO	0.7	1.0	20.8	28.8	48.7	100
10,000 PbO	12.6	13.3	13.5	45.6	15.0	100

Mn (hydr)oxides) and is strongly fixed by them. This is confirmed by the minimum concentration of exchangeable and specifically sorbed fraction at the application of 2000 mg kg<sup>-1</sup>. At the high (10,000 mg kg<sup>-1</sup>) absolute and relative contamination rate, the exchangeable fraction is most affected, which is the most hazardous consequence of soil pollution with high rates of heavy metals. This is most manifested at the addition of Pb(NO<sub>3</sub>)<sub>2</sub> to the soil. A high activity of Pb in its interaction with carbonates is observed under the maximum contamination. In this case, the following distribution of Pb is as follows: fraction bound to organic matter > fraction bound to Fe and Mn (hydr)oxides > exchangeable fraction > fraction bound to carbonates > residual fraction (Table 2).

It was shown (Ladonin and Karpukhin 2011) that the fractional composition of heavy metals after the addition of nitrates reflects the metal reactions occurring in the soil well, while the fractional composition after the addition of oxides is primarily sensitive to the solubility of the oxide added. In the Chernozem contaminated with PbO and Pb(NO<sub>3</sub>)<sub>2</sub>, it revealed no significant differences in their fractional composition (Table 2). The similarity of fractional compositions after the addition of PbO and Pb(NO<sub>3</sub>)<sub>2</sub> indicates a high interconnection of Pb for the soil and its strong retention.

The XANES spectra are very sensitive to the electronic state of the absorbing atom and its local surrounding; therefore, any changes in the symmetry of the surrounding affect the X-ray absorption spectra.

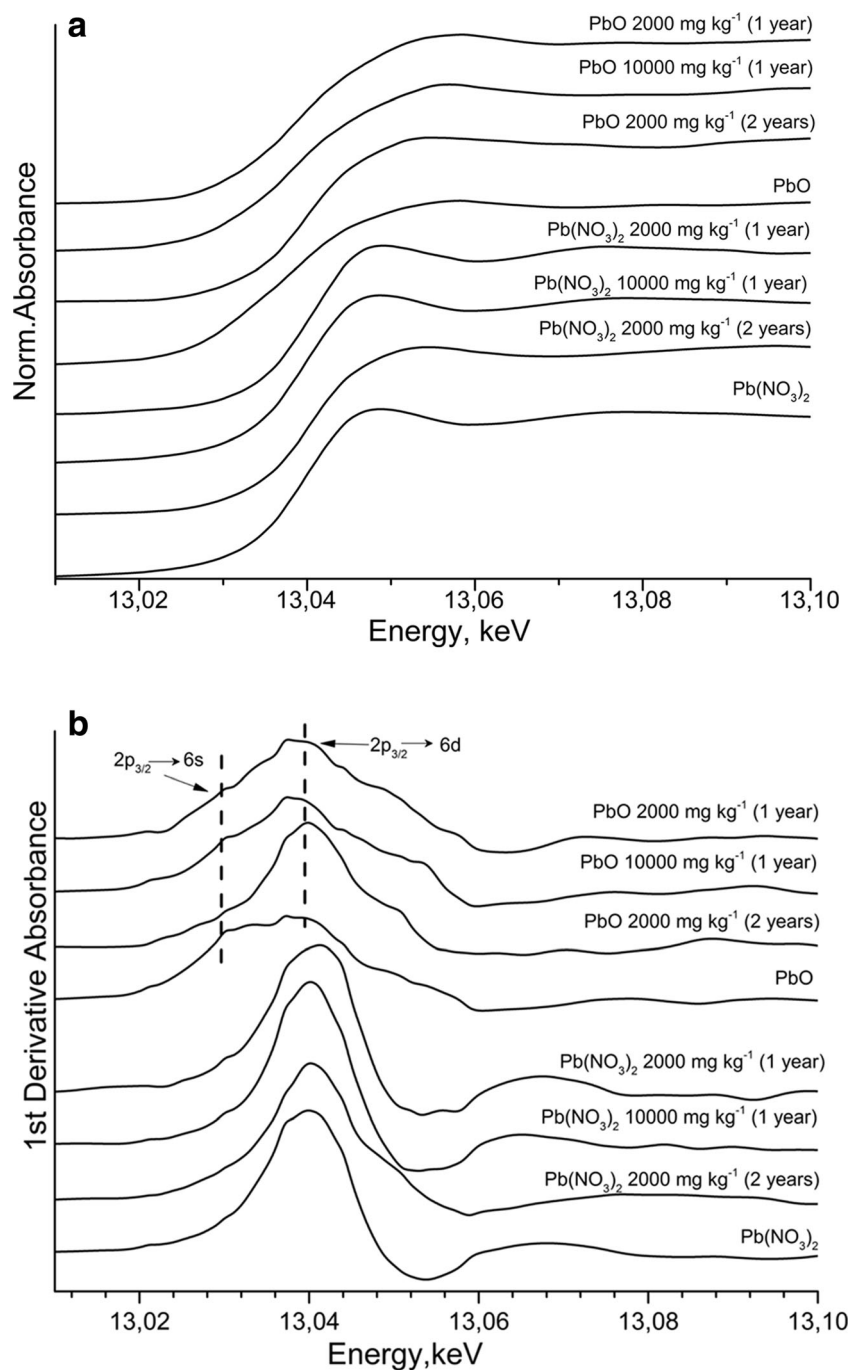
The Pb L<sub>III</sub>-edge XANES spectra are very sensitive to the local atomic surrounding in the first coordination sphere. Parameters of the experimental XANES spectra obtained for the studied soil samples saturated with high rates of Pb compounds, as well as the spectra of the initial PbO and Pb(NO<sub>3</sub>)<sub>2</sub>,

are given in Figs. 1 and 2. The spectra are characterized by an energy region of ~13.030–13.058 keV related to the presence of Pb ions, from which the molecular-structural state of the metal is assessed. The highest absorption intensity is recorded in the energy region of ~13.038–13.040 keV for the samples saturated with PbO and at ~130.42 keV for the samples saturated with Pb(NO<sub>3</sub>)<sub>2</sub>, which characterizes the 2p<sub>3/2</sub>→6d electron transition (Figs. 1 and 2). The modulations of 2p<sub>3/2</sub> electrons in the first derivative spectra of PbO and PbO-saturated soil samples are appreciably different (Fig. 1b), which is due to the different shoulder amplitudes in the energy region of ~130.32 keV, 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<sub>3/2</sub>→6s electron transition, indicating the 6s and 6p hybridization for Pb and 2p<sub>x,y</sub> for oxygen; therefore, Pb<sup>2+</sup> participates in the formation of numerous distorted complexes because the adsorbed Pb ions can have different O–Pb–O valent angles.

The differences in the morphology, size, and features of edge and near-edge areas in the XANES spectra of soil samples contaminated (2000 mg kg<sup>-1</sup>) with PbO and Pb(NO<sub>3</sub>)<sub>2</sub> after 1 and 2 years of incubation are mainly due to the differences in their local atomic structure around the central Pb ion (Fig. 1b). The spectra of soil samples contaminated with PbO after 2 years of incubation significantly differ from the spectra of the initial lead-bearing compound and those after 1 year of incubation, which provides evidence for the transformation of the environment of the Pb ion introduced into the soil with time.

Parameters of the experimental XANES spectra obtained for the studied soil phases are given in Fig. 2a; their first derivatives are given in Fig. 2b. The spectra of these phases include the energy region of ~13.035–13.055 keV.

**Fig. 1** The experimental Pb L<sub>III</sub>-edge XANES spectra (a) and their first derivatives (b) for the compounds (PbO and Pb(NO<sub>3</sub>)<sub>2</sub>) used in the dry preparation and added to the soil samples before incubation (1 and 2 years) with different concentrations of Pb



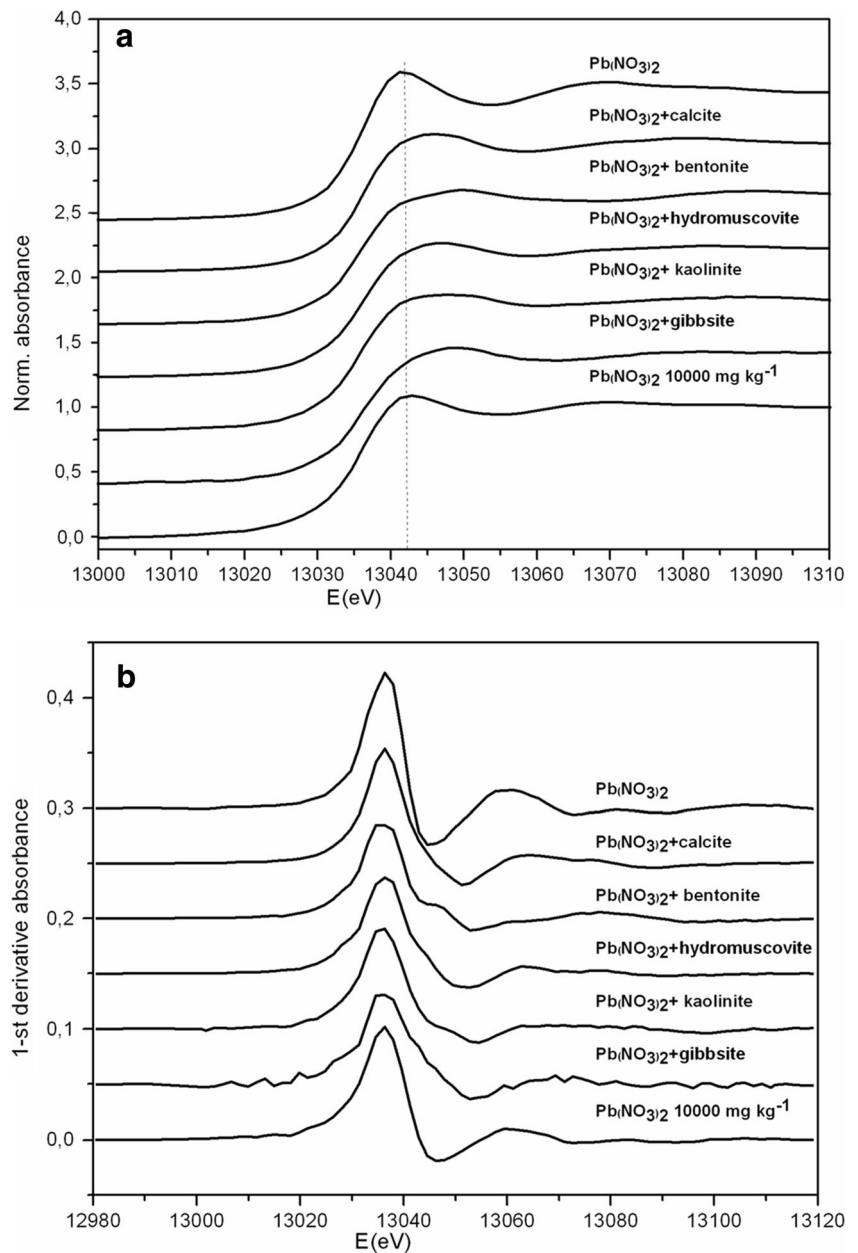
Absorption spectra of the soil phases saturated with Pb nitrate together with those of Pb(NO<sub>3</sub>)<sub>2</sub> are shown in Fig. 2a and their first derivatives are shown in Fig. 2b. Comparison of the first derivative of the Pb L<sub>III</sub>-edge XANES of all the soil samples to the reference spectrum of Pb(NO<sub>3</sub>)<sub>2</sub> shows similarity of the main features: a central peak and low-amplitude left- and right-hand shoulder features.

Lead oxides show a particularly wide variety of nearest Pb–O distances. According to the structural database (ICSD), the shortest Pb–O distance ranges from 0.216 nm in PbO up to

0.275 nm in Pb(NO<sub>3</sub>)<sub>2</sub>. Thus, the distribution of the oxygen atoms around Pb can serve as a sensitive probe for structural changes in the samples.

The *k*<sup>2</sup>-weighted EXAFS spectra and their Fourier transforms are shown in Fig. 3a and b, respectively. In the lower *k* region, the EXAFS oscillations are dominated by backscattering from the light atoms of the first coordination sphere, while intensive signal at high *k* is indicative of the presence of heavy atoms in the vicinity of the absorbing atom. It can be seen that the spectra of Pb(NO<sub>3</sub>)<sub>2</sub>-saturated gibbsite and Pb(NO<sub>3</sub>)<sub>2</sub>-

**Fig. 2** The experimental Pb L<sub>III</sub>-edge XANES spectra (a) and their first derivatives (b) for the Pb(NO<sub>3</sub>)<sub>2</sub> (used in the aqueous solutions preparation added to the mineral phases samples), soil sample (10,000 mg Pb kg<sup>-1</sup>), and the reference minerals saturated with Pb(NO<sub>3</sub>)<sub>2</sub>



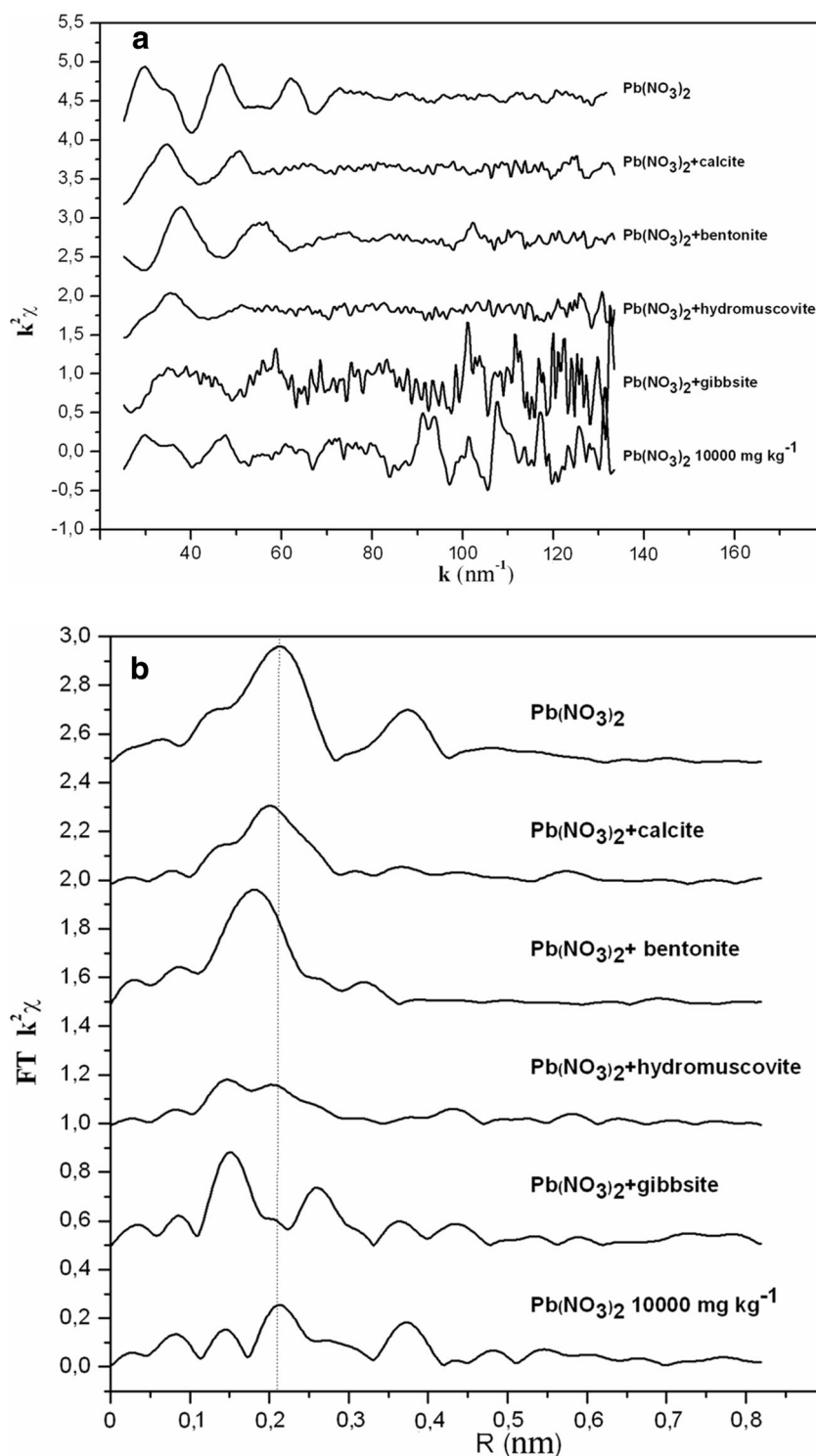
saturated soil in contrast to other spectra show quite intensive high- $k$  oscillations suggesting coordination of Pb with heavy atoms.

Oscillations in the EXAFS spectrum of Pb(NO<sub>3</sub>)<sub>2</sub>-saturated hydromuscovite are damped, which is possibly due to broad distribution of bond lengths between Pb and near-neighboring atoms. A remarkable variation of peak positions at the EXAFS Fourier transforms can be observed in Fig. 3b. The Fourier transformation was made over the shortened  $k$  range 25–95 nm<sup>-1</sup> in order to suppress the contribution from the heavy atoms. The first peak, which is seen at  $R$  values ranging from 0.15 to 0.22 nm in different samples, can be attributed to Pb–O distance. In all the soil and mineral phase samples, the peak appeared to be shifted to lower  $R$  region comparative to

Pb(NO<sub>3</sub>)<sub>2</sub> indicating the contraction of Pb–O bonds. The strongest contraction of the radius of the first coordination shell is observed in Pb(NO<sub>3</sub>)<sub>2</sub>-saturated gibbsite, while in Pb(NO<sub>3</sub>)<sub>2</sub>-saturated calcite, the changes are weak. Substantial differences in the spectra of the studied samples show that Pb local atomic environment may vary strongly depending on the structure of mineral phase's samples. According to Elzinga and Reeder (2002) and Elzinga et al. (2006), Pb ions form inner-sphere adsorption complexes with trigonal–pyramidal oxygen coordination geometry and hydroxyl ions as ligands on calcite. The metal remains available for exchange even after the long time of sorption.

Lead ions are incorporated in the positions of the inner-sphere complex replacing some aluminum ions in the

**Fig. 3**  $k^2$ -weighted Pb L<sub>III</sub> EXAFS spectra of soil and the mineral phase samples saturated by Pb(NO<sub>3</sub>)<sub>2</sub> (a) and Fourier-transformed  $k^2$ -weighted Pb L<sub>III</sub> EXAFS spectra for soil sample and the mineral phase samples (b)



octahedral sites. We may suggest that Pb<sup>2+</sup> is also sorbed by dimer (Pb–Pb) silicate and/or aluminum groups with incomplete coordination. The process may take place due to variations in the bond distances and the appearance of double bonds in the places of local defects of the crystal cell. Lead ions incorporated in the phyllosilicate mineral structure favoring a decrease in the bond distances between Pb<sup>2+</sup> ions and O

atoms in equatorial and axial coordination positions in Pb-bearing octahedrons. Divalent Pb has the 6 s<sup>2</sup> 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. Lead ions can



form different complexes depending on the ionic strength. Lead mainly forms outer-sphere complexes on the basal plane of the phyllosilicate minerals or in the intersheet layer under low ionic strength and inner-sphere complexes at the edges of the mineral under high ionic strength (Xia et al. 1997).

Thus, the structure of adsorbent surface plays the key role in the sorption of  $\text{Pb}^{2+}$  ions by soil solid phases.

#### 4 Conclusions

The study of soil compounds connected with Pb in Chernozem by successive fractionation showed the following distribution of metal in the initial uncontaminated soil: residual fraction > fraction bound to organic matter > fraction bound to Fe and Mn (hydr)oxides > fraction bound to carbonates > exchangeable fraction. This distribution remained under contamination at  $2000 \text{ mg kg}^{-1}$ . The increased degree of Chernozem contamination with Pb is accompanied by relative decreasing of the stable connection between this metal and soil components. Under the contamination with Pb added as nitrate at a rate of  $10,000 \text{ mg kg}^{-1}$ , the following distribution of Pb is observed: fraction bound to organic matter > fraction bound to Fe and Mn (hydr)oxides > exchangeable fraction > fraction bound to carbonates > residual fraction.

At the addition of PbO and  $\text{Pb}(\text{NO}_3)_2$  to the soil, similar fractional compositions are observed, which indicates the dissolution of PbO in Chernozem and high interconnection of Pb ions for the soil.

The features of XANES spectra indicate different orbital transitions in the electron shells of  $\text{Pb}^{2+}$  ions for Pb monoxide (PbO) and soluble salt ( $\text{Pb}(\text{NO}_3)_2$ ), which affect the ion properties and determine the individual structure of the coordination sphere. The analysis of X-ray absorption spectroscopy near-edge fine structure revealed that sorption of Pb on the soil solid phases and on the samples of mineral phases does not change its bond valence.

Lead ions are incorporated in the positions of the inner-sphere complex replacing some aluminum ions in the octahedral sites. This results in changes in the structure of octahedrons, namely, the Pb–O distances in lead-bearing octahedrons. Oscillations in the EXAFS spectrum are indicative of the presence of heavy atoms in the vicinity of the absorbing atom.

Thus, the structure of adsorbent surface plays the key role in the sorption of  $\text{Pb}^{2+}$  ions by soil solid phases.

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