

Possibilities of chemical fractionation and X-ray spectral analysis in estimating the speciation of Cu^{2+} with soil solid-phase components

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ABSTRACT

Soil phases that are likely to scavenge 'free' metals include amorphous Mn and Fe oxides, organic matter, and clays. This paper reviews free forms of Cu and the methods in current use to quantify them. The information value of sequential extraction for assessing the speciation of Cu^{2+} in artificially contaminated Haplic Chernozem (up to 2000 Cu mg/kg) was shown in the selective removal of the main solid-phase components from the soil. It was revealed that carbonates, Fe (hydr)oxides, organic matter, and layered silicates affect the uptake of Cu by the soil. The speciation of Cu in the soil was studied by the Tessier sequential extraction method. To assess the selectivity of the extractants used and to estimate the role of different soil components in Cu partitioning, carbonates, Fe-Mn sesquioxides, and organic matter were removed from soil samples prior to the application of each sequential extraction scheme. No metal was revealed in the fraction bound to the removed soil component, which indicated the selectivity of the used extractants with respect to the soil components. It was found that, in the absence of a soil component, the role of other components in the retention of metal ions increases. When organic matter was removed from the soil, nonsilicate Fe compounds become the most active components in metal sorption, and the role of organic matter in metal retention increases in the absence of Fe oxides. Upon the removal of carbonates, the accumulation of metal in the exchangeable form increases significantly. Mechanisms controlling the fixation of metal by soil solid-phase components on the molecular level were determined using synchrotron radiation X-ray absorption near edge structure (XANES) spectroscopy. It was found that the surface structure and the composition of functional groups of the adsorbent have the leading importance in metal sorption. The combined use of chemical and physical analytical techniques fully characterizes the interaction of Cu with soil solid-phase components, which reduces its availability to adjacent environments and mitigates environmental risks.

1. Introduction

The growth of anthropogenic load creates potential environmental risks of accumulation of heavy metals (HMs) in soils. HMs are very chemically reactive in the environment, which results in their mobility and bioavailability to living organisms. Therefore, works dealing with the mechanisms of HM fixation by soil solid-phase components, which prevent the migration of inorganic pollutants to ground and surface waters and plants, are increasing in importance (Kabata-Pendias, 2011; Sparks, 2003).

Full understanding and prediction of the chemical behaviour of an element in the environment is possible only through the identification

of all forms in which this element can be found under different environmental conditions. Speciation of HMs is one of the most important properties that determine the behaviour and toxicity of metals in the environment. Speciation is the process of identification and determination of different chemical and physical forms of elements present in a sample (Wang et al., 2006). Chemical speciation of an element refers to its specific forms characterized by different isotopic compositions, molecular structures, and electronic or oxidation states (Manouchehri et al., 2006). Sequential extraction is widely used to investigate the association between HMs and different mineral and organic phases in soils and sediments. HMs present in soils can be associated with several reactive components (Silveira et al., 2006). Competition between

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different soil components for the sorption of metals prevails in the soil as a multicomponent system. The mobility of HMs depends on the properties of soil, which determine whether the element will be immobilized or remain available for uptake by plants, animals, and humans (Bauer et al., 2017). Consequently, the prediction of the fate of inorganic toxicants requires knowledge of the selectivity of soil solid-phase components for HMs. The current direction in the identification of the forms of occurrence HMs in soils involves the determination of action features of standard extractants on soils that strongly differ in chemistry and mineralogy rather than a search for the best chemical extractants (Gleyzes et al., 2002). Therefore, the principle of extractant selectivity for specific soil components of HMs is replaced by the general principle of action, that is, the reducing action of hydroxylamine, the oxidative action of hydrogen peroxide, ion exchange, and acid dissolution under treatment with acetic acid (Raksasataya, 1996). The difference between soils is based on the dominance of some or other individual geochemical HM phases that differ in nature. These phases are few in number: carbonates, iron and manganese (hydr)oxides, clay minerals, and humic substances (Shen and Shen, 1993). They were used to test the selectivity of the main reagents. In a study of the selectivity of extractants in the Tessier method, Shen and Shen (1993) determined the concentrations of HMs passing into solution upon the dissolution of separate phases: haematite, calcite, pyrolusite, illite, montmorillonite, and humic acids. It was found that reagents used in the Tessier procedure showed sufficient selectivity in the extraction of HMs from these phases treated separately (Tessier et al., 1979). The procedure of removing soil components proved to be efficient for assessing their contributions to the speciation of metals (Antoniadis et al., 2018; Hinz and Selim, 1999; Michalkova et al., 2016; Oshima et al., 2015).

At present, the adsorption mechanisms of metal cations by soil solid-phase components on the molecular level can be revealed by physical methods of X-ray spectral diagnostics. The development of methods for the direct study of the local structure and fixation mechanisms of metals in active soil solid-phase components became possible due to the analysis of X-ray absorption fine structure (XAFS) using synchrotron radiation (Gräfe et al., 2014; Singh and Gräfe, 2010). Direct investigation of the speciation of HMs in soils is more challenging, because techniques that are able to resolve molecular-level information, such as XAFS and other types of X-ray absorption spectroscopy (XAS), are difficult to interpret unless it is known that a single species predominates. Therefore, to study possible molecular speciation and reactions of HMs in soils, researchers often investigate their interactions with a single soil component such as clays, oxides, soil organic matter (SOM), or carbonates (Hall, 1998).

According to data from the International Copper Study Group (ICSG), copper is the second most used nonferrous metal in the global economy. World production of copper is 22 599 000 tonne (ICSG). In Russia, the production of copper was 740 000 tons in 2017. In the Russian Federation, along with industrial sources that contaminate the soil cover with copper, the application of copper-containing pesticides is also high (State Report, 2017). Accumulation of Cu in agricultural soils is a consequence of the century-old practice of using copper sulfate (Bordeaux mixture) and other copper-containing fungicides to control downy mildew. In this context, we artificially added Cu to the model experiment as an inorganic pollutant.

The aim of this work was to study the relationships between Cu^{2+}

and soil solid-phase components by sequential extraction and XAFS.

2. Materials and methods

2.1. Model experiment

An upper (0- to 20-cm) layer of Haplic Chernozem (IUSS Working Group WRB, 2015) occurring far from potential pollution sources was used for the model experiment. Soil was sampled from a reserved virgin plot in the Persianovskaya Zapovednaya Step Specially Protected Natural Territory in the Rostov region (south of European Russia).

The studied soil was contaminated under model experimental conditions. Plastic pots with a closed drainage system were used. A 3-cm-thick layer of washed glass beads was placed onto the bottom of 2-L plastic vessels for drainage. Then, 1 kg of soil was sieved through a 2-mm sieve and thoroughly mixed with dry $\text{Cu}(\text{NO}_3)_2$ using a glass stick. Soil incubation at room temperature and normal lighting continued for one year. Previous research has shown (Minkina et al., 2010) that this amount of time is sufficient for the transformation of added metals in the Haplic Chernozem.

The experimental design included the untreated soil (original uncontaminated soil) and treatment with the addition of Cu at a rate of 2000 mg/kg. The soil was constantly wetted at 0.6 of the maximum water capacity for the best transformation of the added copper compounds. Salts of nitric acid were selected because of their good solubility and their capacity for quick and complete interaction with the soil mass. Nitrate ions are one of the main anions of the soil solution. The experiment was performed in triplicate. The application rate was selected with consideration for the existing level of metal contamination in the studied soils adjacent to industrial enterprises (Huang, 2014; Iavazzo et al., 2012; Minkina et al., 2018; Rodríguez et al., 2009). The artificial application of this metal rate makes it possible to trace the response of the soil system under high anthropogenic load and to predict the strength of metal fixation by the soil components.

Soil samples were analysed by the commonly used standard methods for the Russian Federation (Vorob'eva, 2006): the contents of exchangeable bases and cation exchange capacity (CEC) were determined by the Shaimukhametov method (Shaimukhametov, 1993); $\text{pH}_{\text{H}_2\text{O}}$ was measured by potentiometry (GOST 26423, 1985); the content of carbonates in the soil was determined by acidimetry; Fe-Mn sesquioxides were identified by the Mehra–Jackson reagent; soil organic matter (C_{org}) was determined by the Tyurin method. The soil particle size distribution was determined by the pipette method (with the pyrophosphate procedure of soil preparation). In this method, carbonates, SOM, Fe, and Al oxides were not removed before pipetting (Shein, 2009) (Table 1). There were no significant differences in the properties of untreated and contaminated soil. Soil samples were air-dried, triturated using a pestle with a rubber head, sieved through a 1-mm sieve to determine the physical and chemical properties of the soil, and sieved through a 0.25-mm sieve to determine the humus and Cu content in soil.

2.2. Sequential extraction procedures

Tessier's method (Tessier et al., 1979) was used to assess the distribution of Cu amongst the soil fractions. Tessier's method ensures the

Table 1
Physical and chemical properties of the Haplic Chernozem in the 0- to 20-cm layer.

C_{org} , %	CaCO_3 , %	$\text{pH}_{\text{H}_2\text{O}}$	CEC, cmol(+)/kg	Exchangeable bases, cmol(+)/kg			Contents of particle-size fractions, %		
				Ca^{2+}	Mg^{2+}	Na^+	Sand fractions (1.0–0.05 mm)	Silt fractions (0.01–0.001 mm)	Clay fraction (< 0.001 mm)
3.7	0.4	7.6	38.0	31.0	6.0	0.06	9.8	62.1	28.1

separation of five fractions: exchangeable [1 M MgCl₂ (pH 7.0)]; bound to carbonates [1 M NaCH₃COO (pH 5.0)]; bound to Fe–Mn oxides: [0.04 M NH₂OH·HCl in 25% (v/v) CH₃COOH]; bound to organic matter [30% H₂O₂ (pH 2)]; residual [HF + HClO₄, then HNO_{3conc}].

2.3. Procedures for the removal of soil components

The selectivity of extractants used in different fractionation methods and the effect of soil components and contamination level on the fractional distribution of Cu in the soil were studied by the selective removal of soil components and the subsequent extraction of Cu from the treated soil samples. To estimate the effect of the removal of a soil component on the fractional distribution of HM, the content of the element in the treated soil sample was compared with its content in the uncontaminated sample.

In the model experiment, the following components were removed from the uncontaminated soil and the soil contaminated with Cu nitrate at the high rate (2000 Cu mg/kg): organic matter, carbonates, and sesquioxides. These components are capable of adsorbing and retaining HMs. The removal of soil components was performed as follows (Gorbunov, 1974):

- To remove carbonates, soil was treated with 1 M HCl until effervescence ceased and then with 0.1–0.2 M HCl. After the decomposition of carbonates, hydrochloric acid and the resulting salts were washed five to six times with distilled water by decantation until the beginning of soil peptization. Carbonates were decomposed in a porcelain cup. If the reaction of acid with carbonates proceeded violently, its rate was reduced by adding water. No complete washing was done, to avoid the potential loss of fine particles.
- Fe–Mn sesquioxides were removed by treating the soil with Mehra–Jackson reagent (Mehra and Jackson, 1960). Dithionite extract was used. A 0.3 M Na citrate solution (40 mL) and 5 mL of 1.0 M NaHCO₃ solution were put into a centrifuge tube, mixed, and heated in a water bath to 80 °C; 1 g of dry Na₂S₂O₄ was then added. The mixture was stirred with a glass rod for 15 min. The treatment was performed at a solution temperature of 80–90 °C (a temperature of 90 °C was maintained for the more intensive formation of a flaky precipitate). After the end of the treatment, 10 mL of a saturated NaCl solution was added, and the mixture was heated for 5–10 min until the formation of a flaky precipitate. After this, the solution was centrifuged at 3000 rpm for 5–10 min. This treatment was repeated twice more.
- Organic matter was removed with 30% hydrogen peroxide in a porcelain cup. After the twofold treatment with 30% hydrogen peroxide, the sample was heated in a water bath for two to 3 h to complete the oxidation. When the sample became lighter in colour, it was dried, ground, and analysed further.

The contents of organic matter, carbonates, and Fe–Mn sesquioxides, prior to the removal of the soil components, are presented in Table 2. After removal of these components, the pH values were adjusted to the pH level of the soil before treatment.

Copper contamination was conducted after removal of individual soil components (organic matter, carbonates, and sesquioxides) and compared with soil without any treatment. Fractional composition of Cu compounds was determined in the test samples by the Tessier methods. The Cu contents in the extracts were measured by flame atomic-absorption spectrophotometry (“KVANT 2-AT”).

2.4. Characterization and synthesis of reference samples

Samples of montmorillonite, kaolinite, hydromuscovite, gibbsite, goethite, calcite, and humic acids were saturated with Cu²⁺ ions using a saturated solution of Cu²⁺ nitrate (Cu(NO₃)₂·3H₂O) during a week. The Cu²⁺ nitrate (Cu(NO₃)₂·3H₂O) was High Purity Analytical quality

according to State Standard for the chemical reagents of the Russian Federation. This solution was kept at constant pH and changed twice a day. After one week, the samples were removed from the solution and air-dried. The humic acid was extracted from Haplic Chernozem; the calcite sample was taken from the carbonate horizon of the studied soil. The samples of montmorillonite (GSO 8694–2005), kaolinite (GSO 9089–2008), hydromuscovite (Enskoe deposit, Murmansk oblast), and gibbsite (BDS 1711-001-00658716-99) were used as standard reference materials. Goethite (α-FeOOH) was synthesized using the Atkinson method (Atkinson et al., 1967) by slowly adding 200 mL of 2.5 M NaOH to a solution containing 50 g Fe(NO₃)₃·9H₂O in 825 mL of deionized water under intensive stirring. The suspension was kept at 60 °C for 6 days and then purified from soluble salts by dialysis. The obtained mineral was dried at a negative temperature (–18 °C) and sieved through a 0.16-mm sieve. X-ray diffraction analysis showed the presence of peaks at 4.18, 2.69, and 2.45 Å typical for goethite.

2.5. X-ray absorption spectroscopy

The reference samples were analysed by X-ray diffraction based on synchrotron radiation. The obtained diffraction patterns confirmed the structural accordance with the mineral phases obtained at the Structural Materials Science beamline of the Kurchatov Centre for Synchrotron Radiation (Chernyshov et al., 2009). The diffraction patterns were compared with those from the crystallographic databases (Inorganic Crystal Structure Database, ICSD).

Experimental Cu K-edge X-ray absorption near edge structure (XANES) spectra (~ 899–8995 eV) were measured at room temperature in fluorescence mode. A two-crystal Si(111) monochromator with an energy resolution ΔE/E ~ 2·10^{–4} was used to monochromate the X-ray radiation. To obtain the data for the statistical methods, an exposition time of 60 s was taken for each point in the spectrum. Ten 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 analysed to specify information about the state of Cu²⁺ ions and reveal the differences in the analysed samples that escaped detection during the analysis of XANES spectra. Along with the experimental XANES spectra, experimental spectra of the original copper-containing compounds were also studied.

2.6. Statistical analysis

All laboratory tests were performed in triplicate. The experimental data (means and standard deviations) were statistically processed using statistical functions of STATISTICA 10.0 software. Results were considered statistically significant at $p \leq 0.05$.

3. Results and discussion

3.1. Interaction of Cu with the carbonate phase

In Haplic Chernozem carbonates make one of the major contributions to the adsorption of HMs. This process involves the coprecipitation, occlusion, and formation of hardly soluble surface compounds. Sorption of HM compounds on oxides (mainly Fe and Mn oxides) deposited on the surface of carbonates is also possible (Kholodov et al., 2014; Elzinga et al., 2006; Elzinga and Reeder, 2002). Therefore, the decomposition of carbonates can release a significant amount of HMs (Tessier et al., 1979).

The Haplic Chernozem is characterized by the accumulation of a significant amount of calcium-humate humus, enrichment of soil matrix with clay minerals, and migration of carbonates throughout the soil profile, which is mainly composed of calcite. The presence of carbonates in the soil determines the effect of the calcium–carbonate equilibrium, which affects the chemical composition of the soil solution,

Table 2
Changes in the fractional composition of Cu after the removal of soil components from Haplic Chernozem (mg/kg).

Metal application rate	Soil fraction	Before removal	After removal of		
			carbonates	sesquioxides	organic matter
Uncontaminated soil					
Without Cu addition	exchangeable	0.5 ± 0.1	1.8 ± 0.1	1.5 ± 0.9	2.1 ± 1.2
	bound to carbonates	1.6 ± 0.1	0.01 ± 0.01	2.7 ± 0.3	2.9 ± 1.1
	bound to Fe–Mn oxides	9.7 ± 0.6	8.4 ± 1.8	1.0 ± 0.9	19.7 ± 2.6
	bound to organic matter	13.83 ± 0.7	12.3 ± 2.6	19.8 ± 2.4	0.6 ± 0.1
	residual	22.2 ± 2.0	22.5 ± 2.7	21.3 ± 2.6	24.7 ± 2.1
	total	47.3 ± 2.9	45.0 ± 3.5	46.3 ± 4.0	50.0 ± 4.5
Contaminated soil					
Cu 2000, mg/kg	exchangeable	39.1 ± 2.2	101.2 ± 15.3	74.1 ± 13.7	101.4 ± 17.9
	bound to carbonates	130.3 ± 4.0	5.0 ± 1.3	140.5 ± 12.9	141.1 ± 13.6
	bound to Fe–Mn oxides	482.3 ± 22.9	471.8 ± 15.3	27.2 ± 3.8	946.2 ± 32.3
	bound to organic matter	809.4 ± 29.6	853.6 ± 21.4	920.6 ± 32.8	44.0 ± 5.3
	residual	601.6 ± 35.0	550.5 ± 24.3	650.6 ± 26.2	750.4 ± 27.1
	total	2042.7 ± 49.0	1982.1 ± 47.7	1813.0 ± 46.1	1983.1 ± 48.1

dissolution and migration processes, precipitation of many HMs, and ion-exchange processes at the interface (Minkina et al., 2012). Therefore, study of the sorption mechanisms of metals by the calcite-containing system of Haplic Chernozem is of particular interest.

The relative content of Cu in the fraction bound to carbonates was 3% in the uncontaminated soil (Fig. 1) and 5% under contamination (Fig. 2).

After the removal of carbonates, Cu extracted with 1 M NaCH₃COO was found in trace amounts (0.3–0.4%) in untreated and contaminated soil (Figs. 1 and 2). This indicated a high selectivity of the reagent used in Tessier's method to extract HMs bound to carbonates. Analogous changes in the fractional composition of Cu were observed after the removal of carbonates from Cu-contaminated Haplic Chernozem (Fig. 2).

After the removal of carbonates, the content of exchangeable Cu compounds doubled in both uncontaminated and contaminated soil samples (Table 2). This changed the relative content of the metal in the exchangeable fraction from 1 to 6% in the original uncontaminated soil and from 2 to 9% in the soil contaminated by the studied metal (Figs. 1 and 2). The contents of Cu in the iron–manganese fraction bound to organic matter and the residual fraction remained almost unchanged after the treatment of soil.

Of special interest was the study of the Cu sorption mechanism by the carbonate phase. XANES spectra of Cu(NO₃)₂ and spectra of Cu(II)

adsorbed on calcite are given in Fig. 3a; their first derivatives are given in Fig. 3b.

In the Cu K-edge first derivative XANES spectrum, a slight pre-edge peak (8975–8981 eV) was diagnosed, which is due to a 1s → 3d transition, and two peaks, α and β, were observed in the regions of 8985 and 8995 eV, respectively, which correspond to a 1s → 4d electron transition. The presence of α and β peaks in the Cu K-edge first derivative spectra indicates tetragonal distortion of Cu²⁺ octahedrons (Lee et al., 2005). In Fig. 3b, the distance between peaks α and β was 4 eV for the pure copper compound Cu(NO₃)₂ and 6 eV for Cu²⁺ adsorbed on calcite. These qualitative differences characterize the equatorial and axial Co–O distances in the octahedrons; the intensity of α peaks depends on the covalence of equatorial ligands bound to Cu²⁺. The decrease of the α peak for the Cu–calcite-containing system is related to the active metal–ligand charge transfer (Lee et al., 2005). This fact indicates that local Cu²⁺ forms around the Cu²⁺ adsorbed on the calcite surface are presented by tetragonally disturbed inner-sphere complexes on the surface of calcite due to bonding with surface carbonate ligands. Thus, Cu has a high affinity for the calcite surface (Elzinga and Reeder, 2002; Lee et al., 2005), which limits the mobility of Cu not only in the soil but also in adjacent environments.

Untreated soil

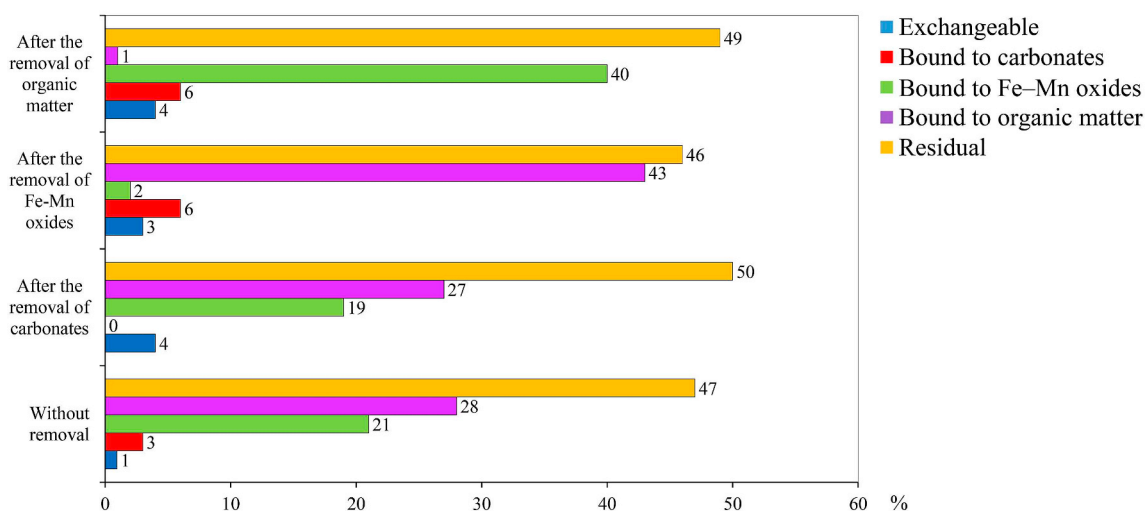


Fig. 1. Changes in the fractional composition of Cu in uncontaminated Haplic Chernozem after the removal of soil components (% of the sum of fractions).

Contaminated soil (added 2000 Cu mg/kg)

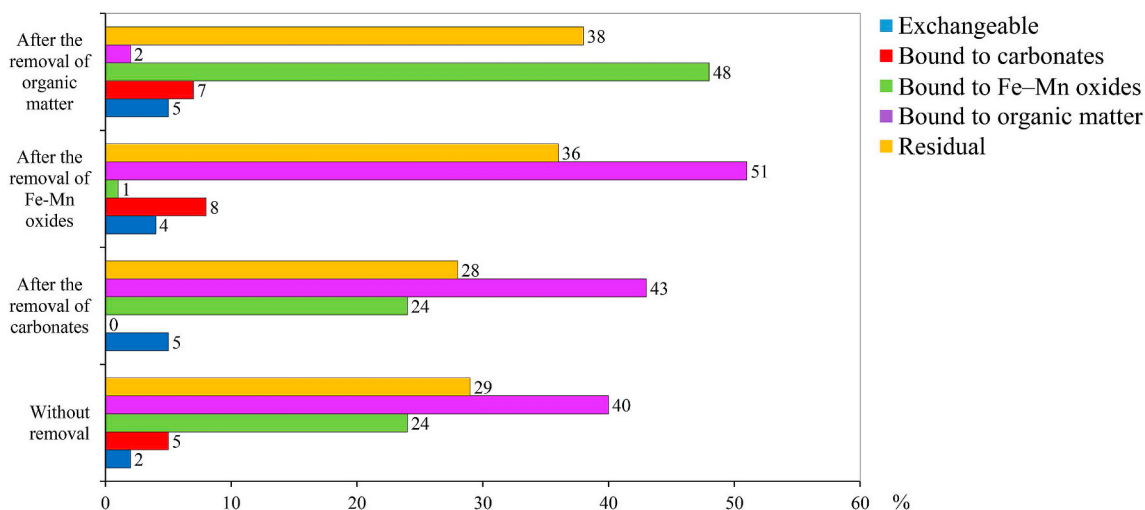


Fig. 2. Changes in the fractional composition of Cu in Haplic Chernozem contaminated with Cu at 2000 mg/kg after the removal of soil components (% of the sum of fractions).

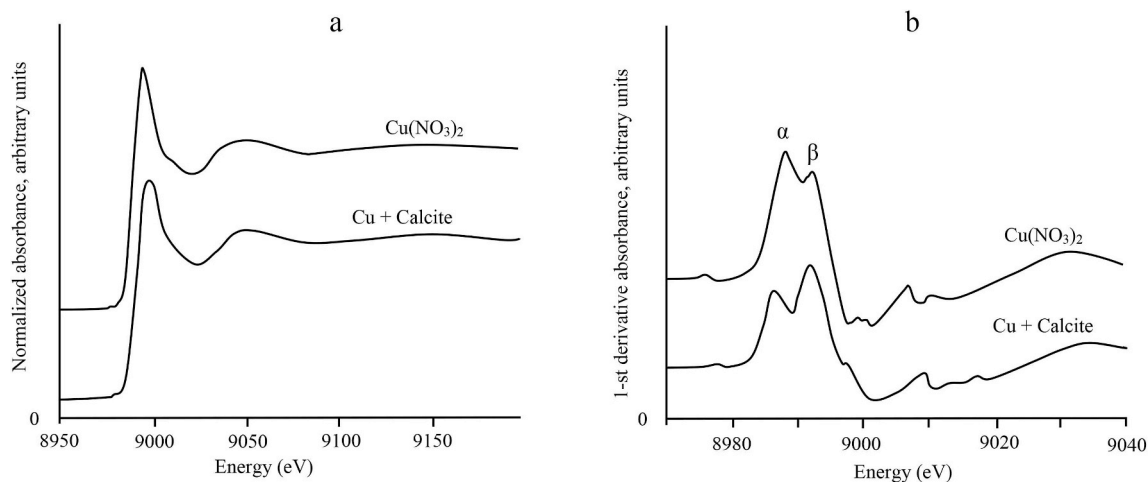


Fig. 3. Experimental (a) Cu K-edge XANES spectra and (b) the first derivative X-ray absorption spectra for the original Cu compound $\text{Cu}(\text{NO}_3)_2$ and calcite contaminated with $\text{Cu}(\text{NO}_3)_2$.

3.2. Interaction of Cu with Fe-oxide phases

The content of Cu in the fraction bound to Fe and Mn oxides was relatively high (21–24%) (Figs. 1 and 2). Fe and Mn oxides and hydroxides occur in the soil in the form of separate phases or films, which cover clay minerals. Crystallized particles of Fe oxides and hydroxides are important for the strong fixation of metals in soils of different origin. Iron oxides and hydroxides are capable of fixing significant amounts of HMs due to sorption, coprecipitation, and occlusion (Mellis et al., 2003). Sorption of metals by Fe oxides and hydroxides under CEC exceeding can occur due to positively charged surfaces.

After the removal of Fe–Mn oxide, the Cu relative content extracted with hydrochloric acid hydroxylamine solution did not exceed 1–2% in both uncontaminated and contaminated soil samples (Figs. 1 and 2).

Consequently, despite the increased capacity for extracting HMs bound to iron minerals provided by Tessier's method, reagents used for this fraction (Mehra–Jackson reagent) are sufficiently selective, which indicates the informative value of the results obtained with them.

In samples with the removed component, the content of Cu increases by 2% in the exchangeable fraction and by 3% in the fraction bound to carbonates in both uncontaminated and contamination soil

samples (Figs. 1 and 2). The highest increase in the relative content of Cu (by 11–15%) was noted in the fraction bound to organic matter (Figs. 1 and 2).

Consequently, after the removal of Fe oxides, changes were observed in the fractional composition of metal in Haplic Chernozem, which were mainly related to their accumulation in the fraction of organic matter and, to a lesser extent, in the exchangeable fraction and fraction bound to carbonates. The relative content of Cu in the fraction bound to Fe–Mn oxides does not exceed 2%.

The high organophilicity of Cu was repeatedly noted in the presence of organic soil compounds; however, in the presence of separate phases of Fe and Mn oxides and hydroxides, copper acts as a manganophile element (Ponizovskii et al., 1999; Liu et al., 2002).

Experimental XANES Cu K-edge spectra for Cu^{2+} adsorbed on goethite and the reference copper-containing compound $\text{Cu}(\text{NO}_3)_2$ are shown in Fig. 4a. The spectra have a common reflection in the region of 8995 eV, which indicates the presence of Cu^{2+} . The first-derivative spectra (Fig. 4b) for the pure Cu compounds and Cu^{2+} adsorbed on goethite are different. Cu adsorbed on goethite has two inflections corresponding to derivative peaks at 8986 and 8991 eV. The remote peak β represents the main absorption transition and characterizes the

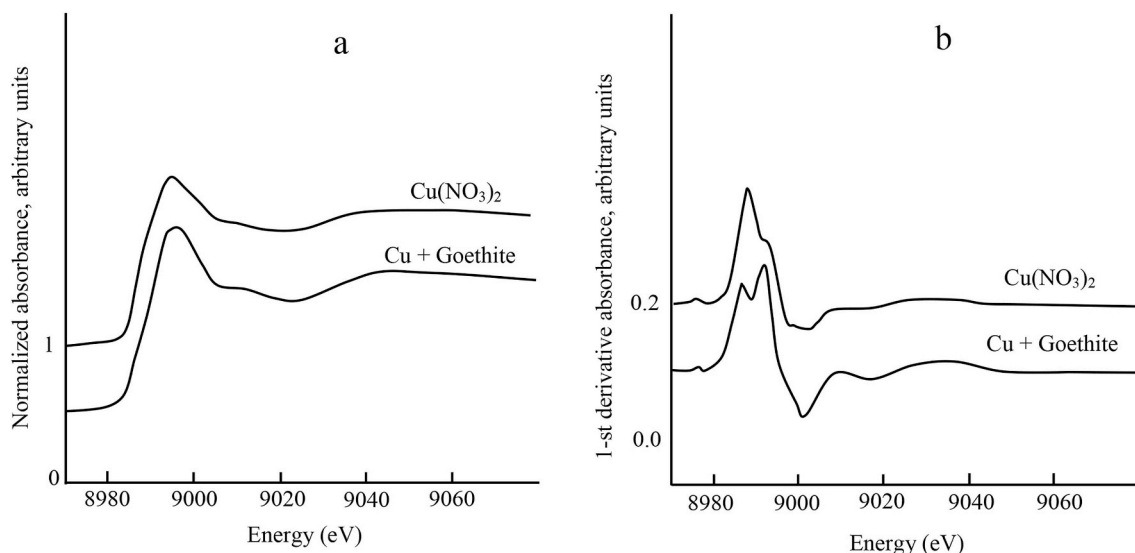


Fig. 4. Experimental (a) Cu K-edge XANES spectra and (b) the first derivative X-ray absorption spectra for the original copper-containing compound $\text{Cu}(\text{NO}_3)_2$ and goethite ($\alpha\text{-FeOOH}$) contaminated with $\text{Cu}(\text{NO}_3)_2$.

degrees of bond covalence and structural disorder (Alcacio et al., 2001; Palladino et al., 1992).

It was shown that the peak intensity of Cu for the reference material $\text{Cu}(\text{NO}_3)_2$ was higher than for Cu adsorbed on goethite. This is related to the decrease in the Cu–O bond length and the formation of Cu–Fe bonds, which indicates that Cu^{2+} is bound to the functional groups of inorganic goethite. The interaction mechanism of Cu with the surface of iron hydroxide is specific sorption (Pinskii and Minkina, 2013), which is accompanied by the displacement of protons from the surface functional groups with the formation of Cu–hydroxyl clusters and an abrupt increase of the sorbed metal in a narrow pH range. Specific sorption is considered as the main mechanism of metal interaction with the surface of hydroxides. Adsorption occurs on the surface sites with uncompensated valence forces, whose existence is frequently related to crystal lattice defects (Minkina et al., 2009).

3.3. Interaction of Cu with the organic matter phase

Soil organic matter plays an important role in metal fixation. A direct correlation between the content of metal in the soil and organic matter is frequently noted. The bond of metals with organic matter is determined by ion exchange, formation of complex compounds, and adsorption. Humic substances have the highest capacity; the dependence of CEC on pH is most pronounced for them (Karpukhin, 1998).

The low content of Cu (1–2%), extracted with 30% H_2O_2 (pH 2), was determined after the removal of organic matter from the original and contaminated soil (Figs. 1 and 2). Thus, the use of hydrogen peroxide under acid conditions by Tessier's method for characterization of Cu bound to organic matter of Haplic Chernozem is reasonable.

In soils with removed organic matter, the mobility of Cu increased by 3% (Figs. 1 and 2). The content of Cu increased in the fractions bound to carbonates (by 2%) and Fe–Mn oxides (by 24%). Experimental Cu K-edge XANES spectra for Cu-humic acids isolated from Chernozem and saturated with $\text{Cu}(\text{NO}_3)_2$, as well as the pure copper-containing compound $\text{Cu}(\text{NO}_3)_2$, are given in Fig. 3a.

The peak intensity in the middle part of the spectral edge (~8985–8990 eV) due to the presence of Cu_{2+} in the experimental spectrum of humic acids (Fig. 5a) was lower than in the spectrum of $\text{Cu}(\text{NO}_3)_2$, which indicates the interaction of Cu_{2+} with humic acids. In the pre-edge region (Fig. 5a, inset ~8975–8980 eV), a slight maximum in the Cu K-edge XANES spectrum for Cu_{2+} was observed, which is associated with the quadrupole $1s \rightarrow 3d$ electron transition

characterizing the binding of Cu_{2+} in low-symmetry octahedral and tetrahedral positions. It should be noted that a pronounced shoulder in the region of the absorption edge of the XANES spectra related to the $1s \rightarrow 4p$ transitions corresponds to the formation of tetrahedral complexes of many transition metals (Bianconi, 1988). The absence of a shoulder in this absorption region signifies that Cu_{2+} forms octahedral inner-sphere chelate complexes.

Two peaks, α and β , were observed in the first-derivative spectrum of $\text{Cu}(\text{NO}_3)_2$. The intensity of peak β was significantly higher than that of α (Fig. 5b). This is related to the increase in the length of the Cu–Oax bond, the Cu–Oeq bond length remaining unchanged. In the Cu–HAA spectrum, the intensities of peaks α and β were almost similar. The stepwise structure of peaks α and β in the edge region of the first-derivative XANES spectrum for $\text{Cu}(\text{NO}_3)_2$ is due to the Jahn–Teller effect, which reflects the tetragonal distortions of Cu binding centres in octahedrons (Lee et al., 2005; Palladino et al., 1992; Xia et al., 1997) and indicates a reduction in symmetry, when the octahedral structure changes to tetrahedral (Hyun and Hayes, 2015). A single peak in the first-derivative spectrum is typical for octahedral symmetry, and two peaks α and β are typical for tetrahedral distortions.

The change in the intensity of the α peak in the first-derivative XANES spectrum of Cu–humic acids is related to the $1s \rightarrow 4p_z$ electron transition and indicates a metal–ligand electron transition due to ion exchange in the tetragonal plane of water molecules with ligands (Xia et al., 1997). The intensity of the β peak in the XANES spectra is determined by the probability of the $1s \rightarrow 4p_z/p_y$ electron transition (Furnare et al., 2005).

3.4. Interaction of Cu with layered silicate phases

A peculiar feature of layered silicate phases is the chemical and energetic heterogeneity of their surfaces, which are characterized by the presence of structural defects and functional groups of different composition, which can act as active centres during metal adsorption. Active surface centres, for example, in montmorillonite, can include exchangeable cations, surface hydroxyl groups, and oxygen in the tetrahedral lattice. Some active centres are located on the cleavage faces of minerals (Strawn and Baker, 2008).

During the saturation of separate phases of layered silicates with a $\text{Cu}(\text{NO}_3)_2$ solution at a constant pH of 3.9, the amount of acid active centres increases, which finally affects the proportions of the acid-base active centres on the surface of mineral phases (Ponizovskii and

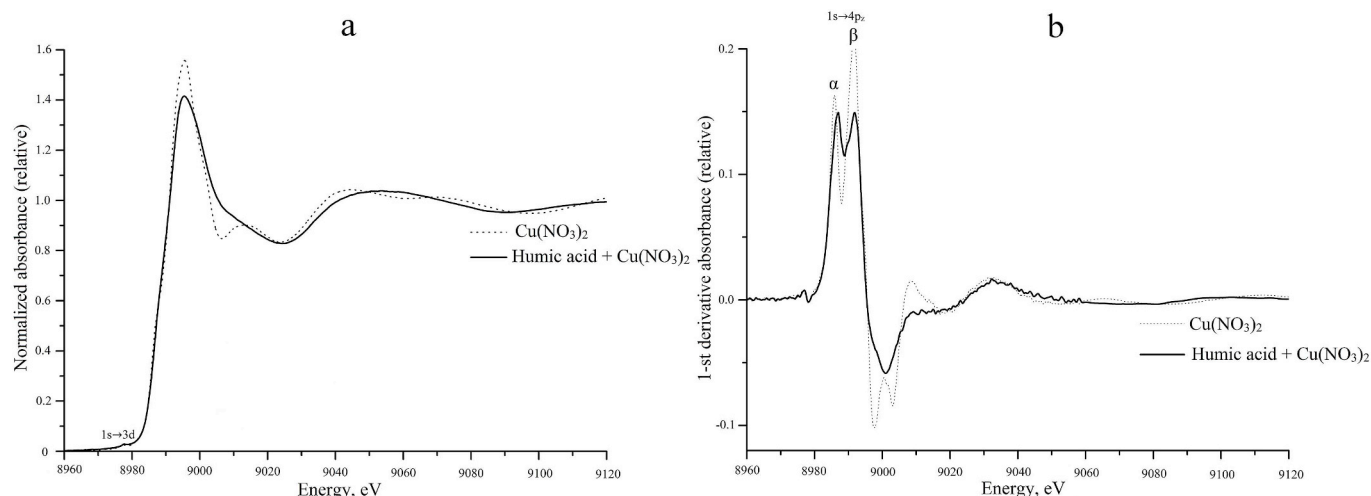


Fig. 5. Experimental (a) Cu K-edge XANES spectra and (b) the first derivative X-ray absorption spectra for the original copper-containing compound $\text{Cu}(\text{NO}_3)_2$ and humic acids isolated from Haplic Chernozem and contaminated with $\text{Cu}(\text{NO}_3)_2$.

Mironenko, 2001). This is also favoured by hydrolysis processes, which shift the acid-base equilibrium of the system. In the early period of saturation, desorption of Ca^{2+} cations occurs from the interlayer positions of layered silicates, especially smectites, into the contacting solution.

XANES spectra of the studied soil samples and the mineral phases of layered silicates artificially contaminated with $\text{Cu}(\text{NO}_3)_2$ are shown in Fig. 6. Comparison of the first-derivative Cu K-edge XANES with the spectrum of the reference compound $\text{Cu}(\text{NO}_3)_2$ shows the sensitivity of the method to changes in the nearest surroundings of the Cu^{2+} ion for these structures. The samples have a peak in the middle part of the pre-edge spectral region (~899–8995 eV) due to the presence of Cu^{2+} ions. The absence of a chemical shift of the main absorption edge compared to the initial spectrum of the compound indicates that the Cu^{2+} ion charge does not change in the soil.

Characterization of the spectral features of the central peak and low-amplitude side maximums of layered silicates and their shape and shift with respect to the original copper-containing compound indicates a

reduction of interatomic distances between the adsorbed Cu^{2+} ion and its surrounding oxygen, according to the Natoli rule (Natoli, 1984). This agrees with the X-ray structural analysis data and earlier molecular-dynamic simulation (Minkina et al., 2013).

4. Conclusions

Joint use of the methods of chemical and physical analysis increases the information value of Cu^{2+} speciation and immobilization by soil components in diagnostics.

It was found that the removal of some or other soil component significantly decreases the content of Cu in the fraction bound to this component. This fact points to the selectivity of the extractants applied for the characterization of Cu bound to soil components in Haplic Chernozem. The mobility of Cu characterized by the first two fractions using the Tessier method increased by 3–5% after the removal of active soil components (carbonates, sesquioxides, and organic matter).

The XANES analysis revealed the mechanisms of Cu^{2+} sorption by

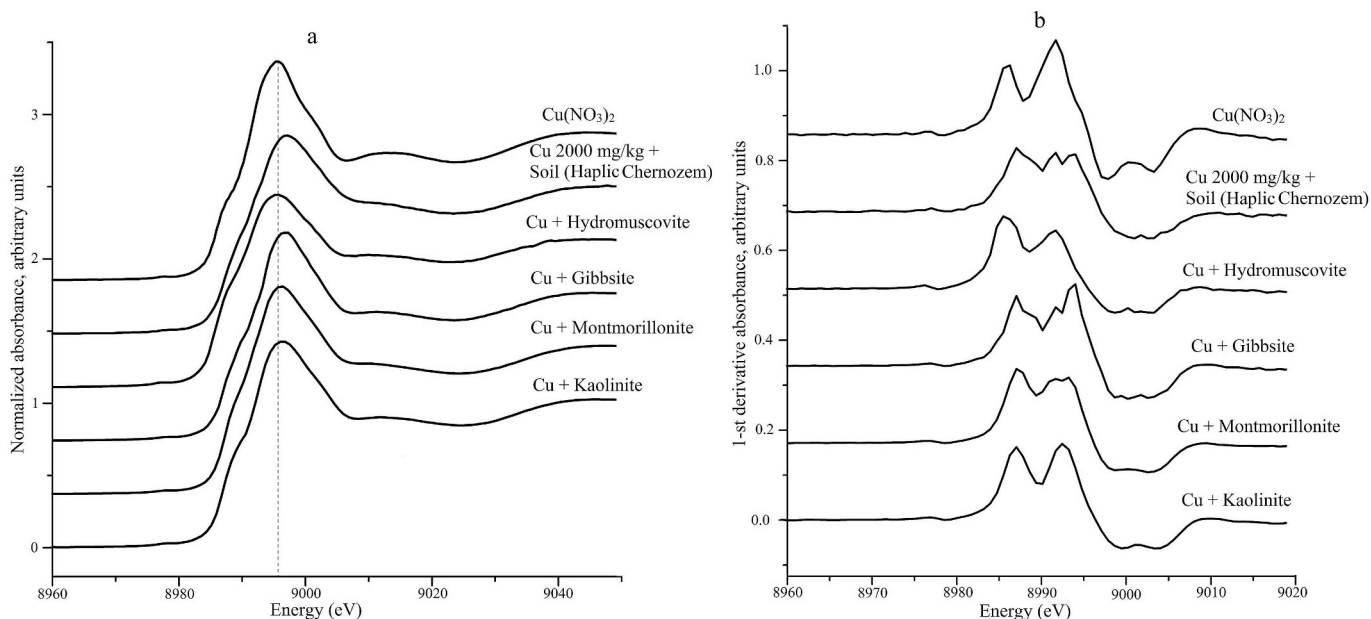


Fig. 6. Experimental (Aa) Cu K-edge XANES spectra and (b) the first derivative X-ray absorption spectra for soil, layered silicate phases, and the original copper-containing compound $\text{Cu}(\text{NO}_3)_2$ (as a reference sample).

soil solid-phase components. The leading role of the surface structure and the composition of functional groups of the adsorbent in metal sorption were revealed. In the interaction between Cu^{2+} ions and humic acids of soils, octahedral inner-sphere chelate complexes can be formed. In the interaction of Cu^{2+} with the calcite phase, local Cu^{2+} forms are presented by tetragonally distorted inner-sphere complexes on the calcite surface due to bonding with surface carbonate ligands. In the interaction of Cu with the surface of iron hydroxide, specific sorption with the formation of Cu–hydroxyl clusters is the essential mechanism.

The interaction mechanism of Cu^{2+} with aluminosilicates involves the active centres on the inner surface of the crystal lattice of dioctahedral aluminosilicates. Surface hydroxyls of aluminium atoms in octahedral coordination play the leading role.

The revealed qualitative and quantitative relationships between Cu^{2+} and soil solid-phase components can form the basis for the investigation of other heterogeneous systems (bottom sediments, silts, sewage sludge, industrial sludge) and can be used to predict the mobility and potential bioavailability of metals and to develop methods for the remediation of metal-contaminated soils.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.01.005>.

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