



## Studying the transformation of $\text{Cu}^{2+}$ ions in soils and mineral phases by the XRD, XANES, and sequential fractionation methods



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### ABSTRACT

Interaction of  $\text{Cu}^{2+}$  ions with the matrix of Calcic Chernozem and mineral phases of layered silicates was assessed by the Miller method of sequential fractionation and a set of synchrotron X-ray methods, including X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XANES). A model laboratory experiment was carried out to study the effect of organomineral matrix on the sorption of  $\text{Cu}^{2+}$  ions. The time of soil incubation with Cu compounds was 3 years. It was shown that the input of Cu into Calcic Chernozem in the form of monoxide (CuO) and salt ( $\text{Cu}(\text{NO}_3)_2$ ) affected the transformation of Cu compounds and their affinity for metal-bearing phases. It was found that the contamination of soil with a soluble  $\text{Cu}^{2+}$  salt increased the bioavailability of the metal and the role of organic matter and Fe oxides in the fixation and retention of Cu. During the incubation of soil with Cu monoxide, the content of the metal in the residual fractions increased, which was related to the possible entry of Cu in the form of isomorphous impurities into silicates, as well as to the incomplete dissolution of exogenic compounds at the high level of their input into the soil. A mechanism for the structural transformation of minerals was revealed, which showed that ion exchange process result in the sorption of  $\text{Cu}^{2+}$  ions from the saturated solution by active sites on the internal surface of the lattice of dioctahedral aluminosilicates. Surface hydroxyls at the octahedral aluminum atom play the main role. X-ray diagnostics revealed that excess  $\text{Cu}^{2+}$  ions are removed from the system due to the formation and precipitation of coarsely crystalline  $\text{Cu}(\text{NO}_3)(\text{OH})_3$ .

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### 1. Introduction

Metals and metalloids, their chemical equilibrium with soil solution and solid phase - play the key role in the functioning and e sustaining of ecosystems (Kalinitchenko, 2015, 2016). There is a fine line between the contents of metals essential for biological functioning and those potentially hazardous for living organisms, when their bioavailability exceeds the homeostatic control of organisms (Kabata-Pendias and Pendias, 1989; Sposito, 1989). So, copper is an essential micronutrient, but this is also one of the most common environmental pollutants.

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; Chaplygin et al., 2014). 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.,

2010). The material composition of any soil is characterized by the elementary system of chemical compounds. This is a system of compounds of a chemical element in the solid, liquid, and gaseous phases of the soil mutually related by the transformation and redistribution of matter and energy occurring at the material-phase, soil-profile, and landscape-geochemical levels (Motuzova, 1999). This system includes strongly bound mineral, organic, and organomineral compounds and mobile compounds of solid phases, soil solution substances, soil air, and biota. 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). Chemical reagents should provide the maximum completeness and selectivity of extraction for target metals. However, this is almost inaccessible for such a complex polydisperse heterogeneous system as the soil because of the internal spatial heterogeneity of soil samples. Procedures of successive fractionation are used to extract different

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forms of heavy metals (HMs) from soils (Minkina et al., 2010, 2014). 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. The determination of HMs and metalloids in soils should evolve toward direct methods ensuring selectivity and sensitivity for the local structures of numerous elements; low detection limits; high spatial resolution; and a simple procedure of sample preparation, which makes these methods universal and accurate in studying the elemental composition of pollutants (Gräfe et al., 2014; Minkina et al., 2016). 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 aim of this work was to study relationships between  $\text{Cu}^{2+}$  ions and components of soil organomineral matrix by XANES and XRD using synchrotron radiation and chemical extractive fractionation.

## 2. Materials and methods

Objects of study included samples from the humus-accumulative  $A_1$  horizon of Calcic Chernozem (WRB, 2006) collected in the Persianovskaya Step Specially Protected Natural Territory, Rostov oblast, Russia. The soil had the following properties:  $C_{\text{org}}$  3.7%,  $\text{CaCO}_3$  0.4%,  $\text{pH}_{\text{H}_2\text{O}}$  7.6; exchangeable bases (mM(+)/100 g):  $\text{Ca}^{2+}$  31.0,  $\text{Mg}^{2+}$  6.0,  $\text{Na}^+$  0.06; physical clay 63.6%; clay 28.1%. The content of total Cu in the samples was determined by synchrotron radiation X-ray fluorescence analysis (SR XRF). Chemical compositions of the mineral component of Chernozem and the phases of layered silicates were determined using the procedure for measuring the mass fractions of element oxides in powdered samples by the X-ray fluorescence method on a MAKS-GV spectroscop.

The mineralogy of the clay and fine silt fractions from the humus-accumulative horizon of Calcic 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).

To study the effect of organomineral matrix on the sorption of  $\text{Cu}^{2+}$  ions, a 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 ( $\text{Cu}(\text{NO}_3)_2$  and CuO) were added to the soil at a rate of 2000 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  $\text{Cu}^{2+}$  ions. For this purpose, the studied samples were put into a saturated  $\text{Cu}(\text{NO}_3)_2$  solution. The solution was changed twice a day for a week. The solution pH was maintained constant at 7.0 in the presence of CuO and 3.9 in the presence of  $\text{Cu}(\text{NO}_3)_2$ . After a week, the preparation was removed from the solution, dried, and ground.

Chemical compositions of the mineral component of Calcic 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 XRF has allowed to establish quantitative differences of oxides composition for phases of layered silicates samples.

### 2.1. Sequential extraction

The composition of Cu compounds in the soil was determined by the Miller method of sequential fractionation (Miller et al., 1986) modified by Berti and Jacobs (1996). The chemical fractionation extracted the following Cu compounds (Table 2): water-soluble, exchangeable, and acid-soluble; bound to Mn oxides, organic matter, and amorphous and crystalline Fe oxides; and insoluble (bound to aluminosilicates, or residual) ones. Analysis of Cu content in soil extracts was performed by atomic absorption spectrophotometry (AAS). Statistical processing of data was performed using Statistica 2010.

Soil samples were also analyzed by X-ray powder diffraction and X-ray absorption spectroscopy at the Structural Material Science station on the 1.3b channel of a synchrotron radiation source of the National Research Center “Kurchatov Institute” (Chernyshov et al., 2009). A 1.7T bend magnet of the Siberia-2 storage ring is the source of synchrotron radiation. The electron beam energy is 2.5 GeV; the average current is 120 mA.

### 2.2. X-ray powder diffraction

Diffraction studies of monochromatic synchrotron X-ray radiation ( $\lambda = 0.68886 \text{ \AA}$ , Si monochromator) were performed in transmission geometry using a Fujifilm Imaging Plate two-coordinate detector at  $0.68886 \text{ \AA}$ . X-ray diffraction patterns were recorded in integrated mode at  $20^\circ \text{C}$ . The time of sample exposure was about 15 min. A silicon standard (NIST SRM 640C) was used for the angular calibration of the scale. The use of high-intensity monochromatic synchrotron radiation in combination with a two-coordinate detector and a Si monochromator significantly improves the intensity and resolution of diffraction patterns compared to the conventional X-ray diffractometry.

### 2.3. X-ray absorption spectroscopy

Experimental Cu K-edge X-ray absorption near edge structure (XANES) spectra ( $\sim 899\text{--}8995 \text{ eV}$ ) were measured at room temperature in fluorescence mode. A two-crystal Si(111) monochromator with the energy resolution  $\Delta E/E \sim 2 \cdot 10^{-4}$  was used to monochromate the X-ray radiation. To obtain the data for statistical method the exposition time of 60 s 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  $\text{Cu}^{2+}$  ions and reveal the differences in the analyzed samples that escaped detection during the analysis of XANES spectra. Along

**Table 1**

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

Sample	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$
Calcic 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

**Table 2**

Sequential fractionation of heavy metals by the Miller scheme (Miller et al., 1986) modified by Berti and Jacobs (1996) for 1 g sample.

Fraction	Soil: solution ratio	Extraction conditions	Extractant
Water-soluble	1:10	Shaking at room temperature for 16 h	Distilled water
Exchangeable	1:10	Shaking at room temperature for 8 h	0.5 M Ca(NO <sub>3</sub> ) <sub>2</sub> pH 7.0
Acid-soluble	1:10	Shaking at room temperature for 8 h	0.44 M CH <sub>3</sub> COOH pH 2.5
Bound to Mn oxides	1:14	Shaking at room temperature for 30 min	0.1 M NH <sub>2</sub> OH·HCl + 0.01 M HNO <sub>3</sub>
Bound to organic matter	1:14	Shaking at room temperature for 24 h	0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>
Bound to amorphous Fe oxides	1:14	Shaking in the dark for 4 h	0.175 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.1 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Bound to crystalline Fe oxides	1:14	Placed in a boiling water bath under periodical shaking for 5 h	0.175 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.1 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Connected with silicates (residual)	1:25	Evaporation	Extract of HF + HClO <sub>4</sub> from the residual fraction

with the experimental XANES spectra, experimental spectra of the original copper-containing compound were also studied.

### 3. Results and discussion

Fractionation of Cu compounds by the Miller method showed (Table 3) that Cu compounds in the fraction bound to silicates dominate in the uncontaminated Chernozem (60 and 67% of the sum of total fractions). This is related to the regional biogeochemical features of the microelement composition of soils in Rostov oblast and the mineralogy of parent rocks. Yellow-brown loess-like loams and clays of the Ciscaucasian plains have inherited the stable minerals enriched with microelements from the original rocks. Some microelement ions released during weathering and pedogenesis are strongly fixed in the structure of clay minerals (Akimtsev et al., 1962). Increased contents of microelements in silicates were noted earlier for different soils (Ladonin and Karpukhin, 2011; Ladonin and Plyaskina, 2003; Motuzova et al., 2006; Plekhanova and Bambusheva, 2010).

Copper compounds have low mobility in the uncontaminated soil. The relative content of Cu in the first three fractions does not exceed 1.5%, and the most mobile exchangeable forms compose only 0.4% (Table 3). It is known that Cu is an organophilic element (Vodyanitskii, 2008; Ponizovskii et al., 1999); therefore, the organic matter fraction is characterized by a high Cu content. Perelomov (2001) and Kosheleva et al. (2002) confirmed that organic matter (especially high-molecular-weight humic acids) has higher effect on the fixation of Cu than carbonates and hydroxides. Copper compounds in the original soil are distributed as follows: silicate-bound (residual) fraction > organic matter-bound fraction > crystalline Fe-bound fraction > amorphous Fe-bound fraction > Mn oxide-bound fraction > acid-soluble fraction > exchangeable fraction ~ water-soluble fraction.

The artificial contamination of soil with Cu increases the absolute contents of all its compounds (Table 3, Fig. 1) and affects their distribution among the soil fractions. The proportion of the water-soluble fraction increases to 0.3–0.5% due to free Cu<sup>2+</sup> ions and their soluble complexes with inorganic anions or organic ligands. The content of the exchangeable fraction, which includes exchangeably sorbed Cu compounds bound to different soil components (clay minerals; Fe, Al, and Mn hydroxides; and organic matter), increases to 1%. The content of Cu in the acid-soluble fraction, which characterizes its binding to carbonates, is three- to fivefold higher than that in the exchangeable

fraction (Table 3). A peculiar feature of Calcic Chernozem is the presence of micellar carbonates with a large specific surface area, which increases their activity in interaction with metals.

Thus, an increase in the mobility of the metal is observed under contamination, which is manifested in increased relative contents of water-soluble, exchangeable, and acid-soluble fractions (Fig. 1).

The content of organic matter-bound Cu increases under contamination from 11 to 29% as compared to the uncontaminated sample (Fig. 1). Similar changes in the composition of metal compounds were noted earlier for soils of technogenic landscapes (Minkina et al., 2014).

Along with organic matter and clay minerals, Al, Fe, and Mn oxides and hydroxides play a significant role in the adsorption of HMs in soils. The addition of Cu to the soil insignificantly increases the content of the metal in the Mn oxide-bound fraction compared to the uncontaminated sample (Table 3). This is related to the special importance of the separation of this fraction by the Miller method for soils with high Mn contents. The content of Mn in the studied soil is 860 mg/kg (Mn clark for soils is 850 mg/kg (Vinogradov, 1957)).

The addition of Cu nitrates and oxides increases the content of the metal in the fractions bound to amorphous Fe oxides to 12 and 6%, respectively, while the content of Cu in the fractions bound to crystalline Fe decreases to 5 and 3%, respectively (Fig. 1). This changes the distribution of Cu among the separated fractions compared to the original soil: silicate-bound (residual) fraction > organic matter-bound fraction > amorphous Fe-bound fraction > crystalline Fe-bound fraction > Mn oxide-bound fraction > acid-soluble fraction > exchangeable fraction ~ water-soluble fraction.

Fe oxides and hydroxides have a large active surface due to their capacity of forming polymolecular films, which interact with HMs on the surface of secondary clay minerals. The adsorption of a metal results in the displacement of H<sup>+</sup> ions, which enter into OH<sup>-</sup> or OH<sup>2-</sup> groups on the surface of oxides, or the substitution of Fe<sup>3+</sup> and Fe<sup>2+</sup> ions, which probably determines the status of many metals in the soil (Pinskii, 1997; Plekhanova et al., 2001). Almost a half of the total amount of metals in the soil is frequently bound to iron hydroxides (Dobrovolskii, 1997; Perelomov, 2001; Vodyanitskii, 2008). Pedogenic factors prevail in these soils and affect the fractional composition of microelements (Motuzova and Aptikaev, 2006).

The solubility of hydroxides depends on the form of crystallization; e.g., freshly precipitated amorphous hydroxides are more soluble than aged ones (Bushuev, 2007). The adsorption capacity of Fe hydroxides

**Table 3**

Fractional composition of Cu compounds in Calcic Chernozem of model experiment determined by the Miller method (Miller et al., 1986) modified by Berti and Jacobs (1996), mg/kg (n = 3).

Addition doses of Cu, mg/kg	Fraction									The total content
	Water-soluble	Exchangeable	Acid-soluble	Bound to Mn oxides	Bound to organic matter	Bound to amorphous Fe oxides	Bound to crystalline Fe oxides	Bound to aluminosilicates (residual)	Sum of fraction	
No added metal	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	5.1 ± 1.1	3.2 ± 0.2	4.2 ± 0.4	27.5 ± 4.5	41.0 ± 3.1	44.0 ± 3.6
2000 Cu(NO <sub>3</sub> ) <sub>2</sub>	9.4 ± 1.5	27.2 ± 3.4	69.1 ± 5.5	68.2 ± 8.9	592.7 ± 20.1	246.2 ± 19.8	106.5 ± 10.2	899.7 ± 79.2	2019.0 ± 148.0	2049.0 ± 184.1
2000 CuO	4.0 ± 0.6	12.1 ± 1.6	30.2 ± 4.0	34.2 ± 4.9	261.8 ± 31.9	120.8 ± 14.3	60.4 ± 8.5	1490.4 ± 161.7	2014.0 ± 227.5	2032.0 ± 198.6

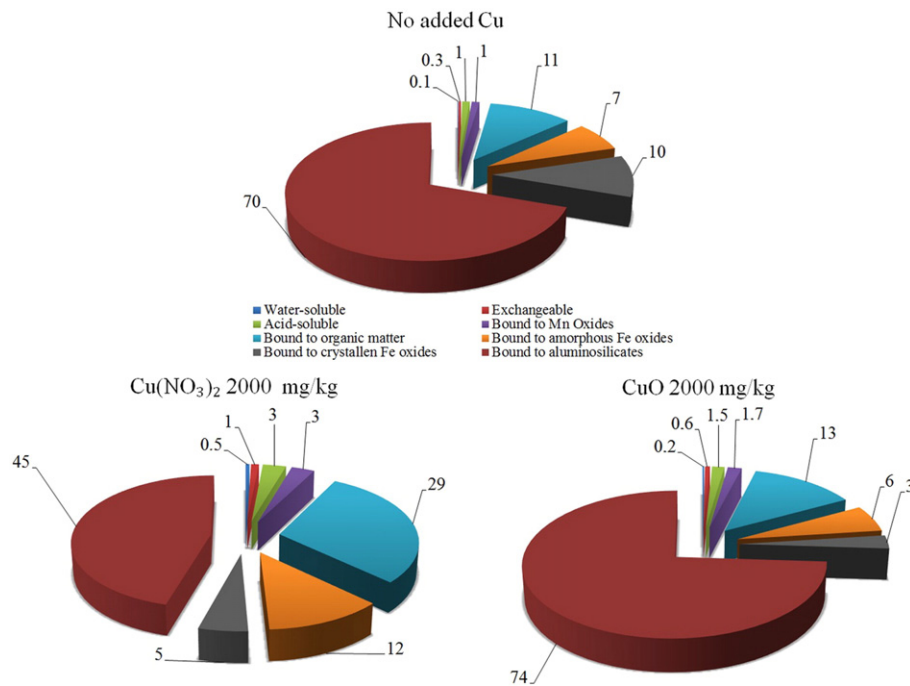


Fig. 1. Distribution of Cu among fractions in the original Calcic Chernozem and that contaminated with  $\text{Cu}(\text{NO}_3)_2$  and CuO from the Miller method, % of the sum of fractions.

is higher than that of aluminum oxides. Oxides are capable of binding metal ions during their precipitation via sorption (Gorbatov, 1988).

The age of soil contamination can be estimated from the presence of the fraction bound to amorphous Fe oxides (Vodyanitskii, 2010). The crystallization of Fe oxides proceeds for a sufficiently long time, and an abrupt increase in the content of metals in the amorphous Fe oxide indicates a recent contamination. The relative content of the fraction bound to amorphous Fe almost doubles at the addition of soluble copper nitrate, while the difference from the contaminated soil is insignificant, if any, at the addition of copper oxide (Fig. 1).

During the incubation of soil with CuO, the increase in the share of Cu in the residual fraction to 74% (Fig. 1) is related to the potential entry of Cu in the form of isomorphous impurities into silicates, as well as to the incomplete dissolution of exogenic metal compounds at the high level of their input into the soil (Minkina et al., 2008). So, the content of metal in the residual fraction at the addition of Cu oxide at 2000 mg/kg is higher than at the addition of the equivalent rate of Cu nitrate (Table 3).

The molecular structural analysis of  $\text{Cu}^{2+}$  ions in Calcic Chernozem by XANES and molecular dynamic methods showed that the metal could enter into montmorillonite (Minkina et al., 2013).

Experimental X-ray powder diffraction patterns for the original soil samples and the mineral phases of layered silicates, as well as calculated models from the ICSD database (ICSD database: [www.fiz-informationsdienste.de/en/DB/icsd/](http://www.fiz-informationsdienste.de/en/DB/icsd/)), are shown in Fig. 2. This approach allows estimating the actual crystalline structure of individual layered silicate phases in experimental samples and identifying their chemistry and mineralogy.

The diffraction patterns of the original uncontaminated soil were compared to the diffraction patterns of soil separate phases (Fig. 2). The main revealed crystalline components of the soil are: quartz, hydromuscovite, kaolinite, gibbsite, and smectites (the mineral phase of montmorillonite as an example). All diffraction maximums of the soil sample correspond to those of the phase diffraction patterns (Fig. 2).

The comparison of diffraction patterns for the soil samples and layered silicate phases before and after modification with a saturated  $\text{Cu}(\text{NO}_3)_2$  solution (Fig. 3) showed no appreciable changes in the diffraction pattern of the contaminated soil compared to the original samples. However, additional diffraction peaks corresponding to a new

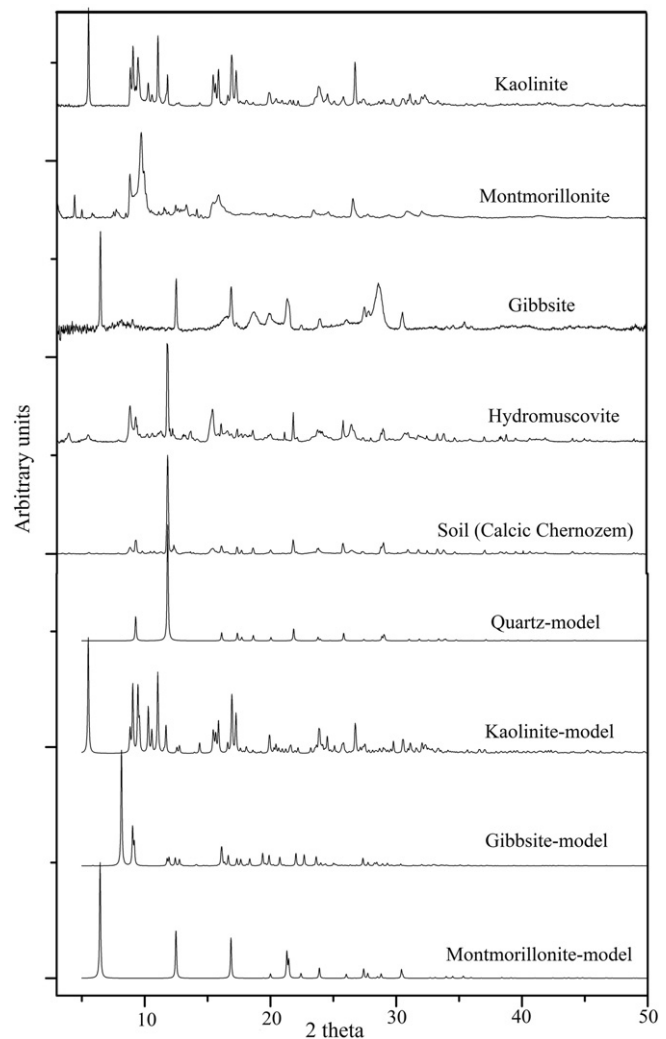


Fig. 2. X-ray powder diffraction patterns for the original soil samples and the mineral phases of layered silicates, and calculated models from the ICSD database.

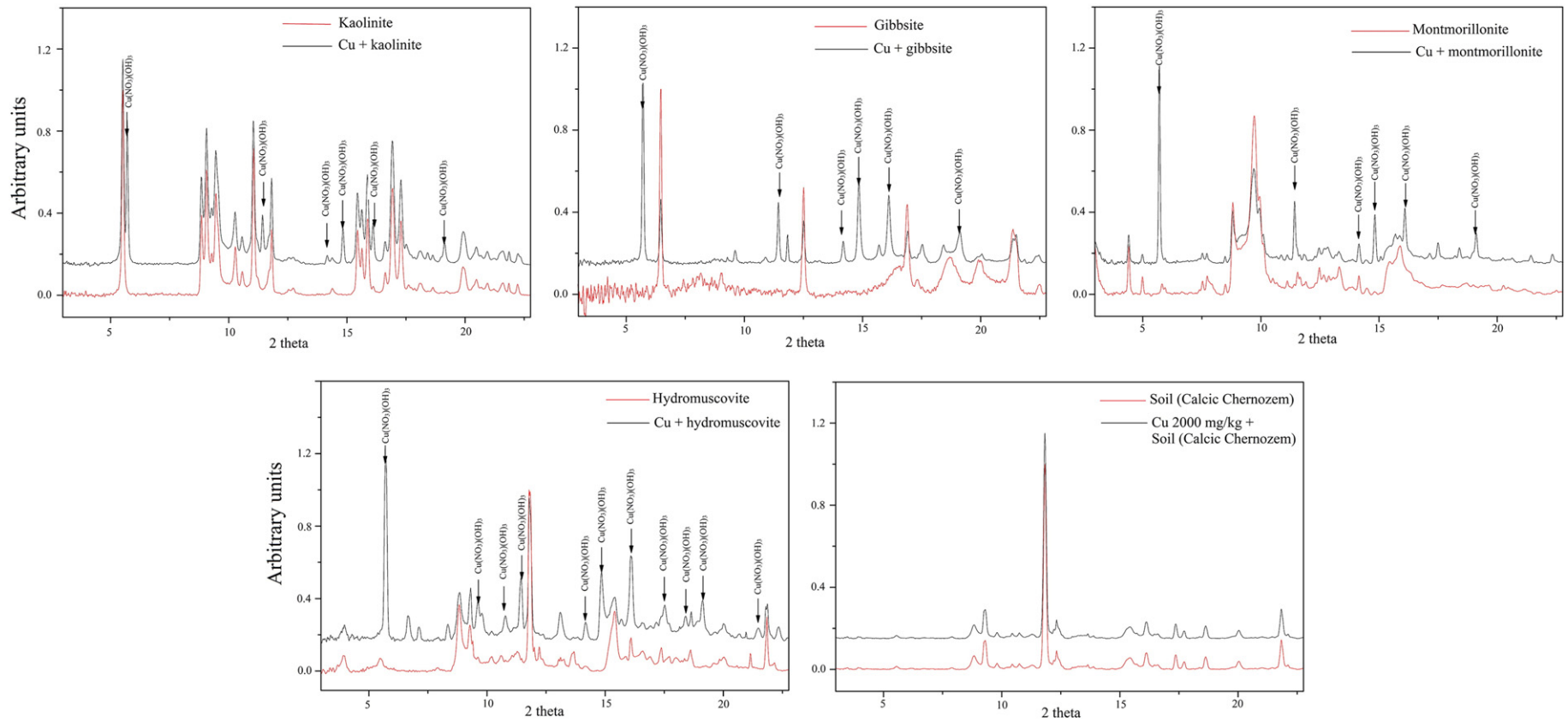


Fig. 3. Comparative analysis of X-ray powder diffraction patterns for soil samples and layered silicate phases before and after modification with a saturated  $\text{Cu}(\text{NO}_3)_2$  solution.

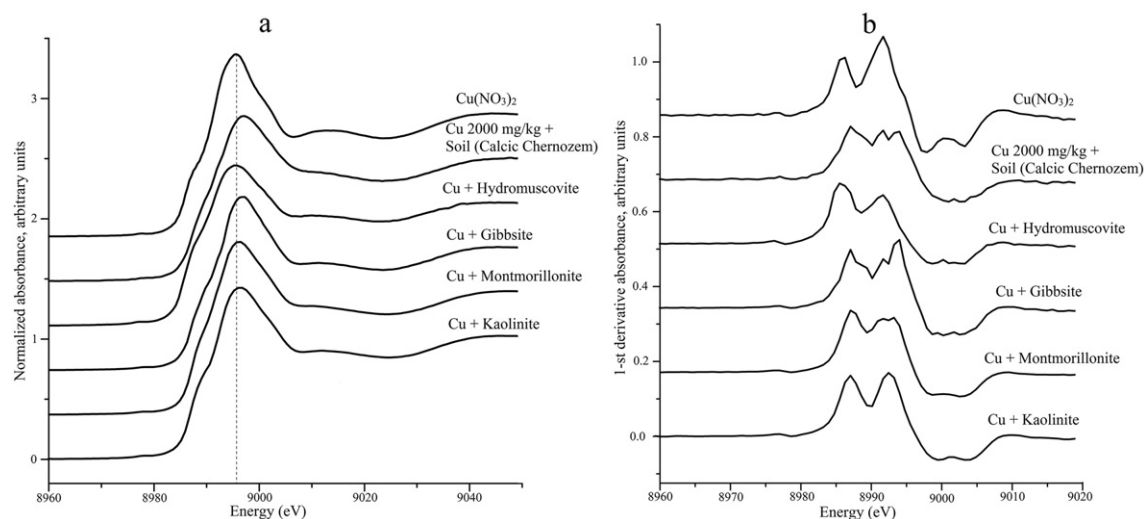


Fig. 4. (a) Experimental Cu K-edge XANES spectra and (b) 1st-derivative X-ray absorption spectra for soil, layered silicate phases, and  $\text{Cu}(\text{NO}_3)_2$  standard.

crystalline phase appeared in the diffraction patterns of layered phases saturated with  $\text{Cu}^{2+}$  ions.

A peculiar feature of layered silicate phases is the chemical and energetic heterogeneity of their surface characterized by the presence of structural defects and different functional groups, which can act as active centers during metal adsorption. These active centers on the surface of, e.g., montmorillonite can include exchangeable cations, surface hydroxyl groups, and oxygen atoms of the tetrahedral lattice. Some active centers occur on the lateral faces of minerals formed during the splitting of minerals.

The saturation of separate phases of layered silicates with a  $\text{Cu}(\text{NO}_3)_2$  solution at a constant pH of 3.9 increases the share of acidic active centers, which affects the proportions of acid–base active centers on the surface of mineral phases (Ponizovskii and Mironenko, 2001). Hydrolysis processes, which shift the system equilibrium, also contribute. During the initial saturation period,  $\text{Ca}^{2+}$  cations are desorbed from the interlayer positions of layered silicates, especially smectites, into the contacting solution.

X-ray diffraction data showed that  $\text{Cu}^{2+}$  ions are sorbed from the saturated solution by active centers on the internal surface of the lattice of dioctahedral aluminosilicates, and surface hydroxyls at the octahedrally coordinated aluminum atom play the main role (Furnare et al., 2005; Strawn et al., 2004; Strawn and Baker, 2009).

Molecular dynamic simulation (Minkina et al., 2013) revealed interactions between  $\text{Cu}^{2+}$  ions and montmorillonite, when  $\text{Cu}^{2+}$  ions are embedded into the inner-sphere complex and displace some of structural  $\text{Al}^{3+}$  ions in octahedral positions. This favors the shortening of bonds between  $\text{Cu}^{2+}$  ions and O atoms in equatorial and axial coordination positions and the decrease in the  $\text{O}_{\text{eq}}-\text{Al}(\text{Cu})-\text{O}_{\text{ax}}$  bond angle in copper-containing octahedrons.

X-ray diagnostics revealed that excess  $\text{Cu}^{2+}$  ions are removed from the system due to the formation and precipitation of coarsely crystalline  $\text{Cu}(\text{NO}_3)(\text{OH})_3$  (Fig. 3). This fact agrees with the chemical fractionation data (Table 3, Fig. 1), which indicate an increase in the content of Cu in the silicate-bound residual fraction.

XANES data for the studied soil samples and mineral phases of layered minerals artificially contaminated with  $\text{Cu}(\text{NO}_3)_2$  are shown in Fig. 4. Comparison of the first-derivative Cu K-edge XANES spectra for all samples with the spectrum of the  $\text{Cu}(\text{NO}_3)_2$  standard showed sensitivity of the method for changes in the immediate surrounding of  $\text{Cu}^{2+}$  ions in these structures. The samples are characterized by the existence of peak in the middle part of the spectrum (~899–8995 eV) due to the presence of  $\text{Cu}^{2+}$  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  $\text{Cu}^{2+}$  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  $\text{Cu}^{2+}$  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).

#### 4. Conclusions

Thus, contributions of different Cu forms to the distribution of the metal among soil components are shown. It is found that the contamination of soils with a soluble  $\text{Cu}^{2+}$  salt increases the bioavailability of the metal; the role of organic matter and Fe oxides in the fixation and retention of Cu also increases.

During the incubation of soil with Cu monoxide, the content of the metal in the residual fraction increases, which is related to the potential entry of Cu in the form of isomorphic impurities into silicates, as well as to the incomplete dissolution of exogenic metal compounds at the high level of their input into the soil.

XANES data revealed the mechanism for the structural transformations of  $\text{Cu}^{2+}$  ions: they are sorbed from the saturated solution by active centers on the internal surface of the lattice of dioctahedral aluminosilicates, and surface hydroxyls at the octahedrally coordinated aluminum atom play the main role. X-ray diagnostics revealed a shortening of interatomic distances between the adsorbed  $\text{Cu}^{2+}$  ions and O atoms due to the displacement of some  $\text{Al}^{3+}$  ions in octahedral positions.

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