

# Copper Adsorption by Chernozem Soils and Parent Rocks in Southern Russia

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**Abstract**—Laboratory data in Cu<sup>2+</sup> adsorption by chernozems and parent rocks in Rostov region show that adsorption isotherms can be approximated by the Langmuir equation, whose parameters ( $K_1$  and  $C_\infty$ ) were calculated for all of the samples. The values of  $C_\infty$  show a strong negative correlation with the values of cationexchange capacity (CEC) ( $r = -0.88$  at  $P = 0.95$ ), and  $K_1$  is correlated with the content of physical clay (particles <0.01 mm) ( $r = 0.78$ ) and with clay (particles <0.001 mm) content in ordinary chernozem and southern chernozems of various particle size distribution ( $r = 0.80$ ). Even stronger correlations were detected between these parameters in southern chernozems ( $r = 0.89$  for the physical clay (PC) and  $r = 0.91$  for the silt). However, none of the samples displays a significant correlation of  $C_\infty$  and  $K_1$  with the contents of physical clay and silt. This led us to conclude that the composition of the samples, for example, their organic matter, can affect Cu<sup>2+</sup> adsorption by the soils and parent rocks. Acidification mechanisms of the equilibrium solutions during the Cu<sup>2+</sup> adsorption by soils are discussed, as also are the reasons for the absence of balance between Cu<sup>2+</sup> adsorbed by soils and exchangeable cations transferred into solution. Analysis of the fine structures of the XANES and EXAFS spectra suggests that Cu<sup>2+</sup> can form coordinated chelate complex compounds with humic acids (HA) of soils and can substitute Al<sup>3+</sup> at octahedral sites when interacting with clay minerals in soils.

**Keywords:** adsorption, copper, chernozem, particle size distribution in soils, parent rocks, XAFS spectroscopy

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## INTRODUCTION

A significant environmental hazard is contamination with heavy metals (HM). Anthropogenically induced fluxes of some of them are currently comparable with natural geochemical fluxes (Dobrodeev, 1978; Glazovskaya, 1997). Copper is one of the significant biospheric contaminants. It is highly technophilic and finds wide industrial applications. Copper plays a dualistic role in soils: it is one of the most important micronutrient elements at low concentrations and is involved in some enzymes and proteins necessary for the normal development of humans, but this element is highly toxic, mutagenic, and cancerogenic at its high concentrations and is prone to be accumulated in living organisms.

Copper is a pollutant of hazard class II. Coming to the environment from anthropogenic sources, this element actively affects all components of the environment, with the soil suffering thereby the greatest load (Panin and Siromlya, 2005) because soils can strongly

bond copper in low-mobility compounds and thus play a role of natural buffer and detoxicant.

The main sources of copper in soils are parent rocks and anthropogenic emissions. The enrichment coefficient of copper in anthropogenic emissions is relatively high: 10–50 (Dobrovol'skii, 1980). Heavy metals in soils are immobilized mostly by finely divided fractions of the soils by means of adsorption mechanisms, which are controlled by the mineralogical and chemical composition of these fractions, i.e., their physicochemical properties. Transformations of anthropogenic copper compounds in soils begin with the dissolution of these compounds in soil water (Pinskii, 1997). For hardly soluble copper compounds, this is the first and the slowest stage of the transformations (Ladonin and Karpukhin, 2011). According to (Tsaplina, 1994), the complete dissolution of HM oxides introduced into soil in amounts corresponding to real contamination levels takes time ranging from half a year to tens of years. Other authors (Bansal, 1982; Gorbatov, 1988; Parnunina, 1983)

point out that the rates of dissolution of Pb, Cd, and Zn oxides and the dust that contains these HM are high, and these compounds are then rapidly stabilized on the surface of soil particles.

Analyses of the fine structure of the XANES and EXAFS spectra shows that copper, which is commonly introduced into chernozem in the form of nitrate, is incorporated into organic compounds of the soil and forms humate complexes during an incubation time period of one year (Minkina et al., 2014, 2016).

Natural soils are always involved in polycationic exchange, and hence, it is important to analyze adsorption processes with regard for all cations that are present in the system and are able to exchange. It is still not fully understood how equivalent is ionic exchange in soils (Pinskii et al., 2010), and this calls for estimating the balance between the amount of  $\text{Cu}^{2+}$  cations adsorbed by soil and exchangeable cations transferred thereby into solution.

The particle size distribution of soils plays a very important role in copper adsorption. The finely divided fractions of the soils, such as physical clay (<0.01 mm), medium and fine silt (0.01–0.001 mm), and clay (<0.001 mm), according to Russian systematics (Kachinskii, 1958), being particularly important for this process. The clay and fine silt fractions, whose surface areas are high, the most dynamic and active in soils (Kryshchenko et al., 2008). These fractions have high adsorption capacity with respect to HM, including copper. For example, the adsorption capacities of Fe-bearing and clay minerals in soils are arranged in the following sequence:  $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$  (Ladonin and Plyaskina, 2004). The sequence of these metals according to the adsorption bonding strength between these HM and the clay fraction is different:  $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ . The literature provides data that hardly soluble and calcite-like compounds of HM can form surface precipitates when adsorbed by clay minerals (Borda and Sparks, 2008). In this context, it is particularly interesting to study not only the mechanisms of  $\text{Cu}^{2+}$  adsorption by soils and parent rocks but also the possibility of further transformations of the molecular–structural states of the adsorbed copper.

The aim of our research was to understand relations and mechanisms of copper adsorption and stabilization in chernozem soils in Rostov oblast that have a different particle size distribution, parent rocks, and genesis.

## MATERIALS AND METHODS

We have studied the following humus horizons (0 to 20 cm) of soils and parent rocks: medium-humus calcareous heavy loamy ordinary chernozem and loess-like loam (290 to 300 cm); loamy sandy intermediate thickness calcareous southern chernozem and yellow-brown clay (190 to 200 cm); and intermediate-thickness southern chernozem on sand in Ros-

tov oblast. Table 1 summarizes the physical and chemical properties of the samples. The particle size distribution of the soils was determined according to (Kachinskii, 1958).

The qualitative composition of the finely divided mineral constituent of the chernozems is as follows: micas and hydromicas (51), smectites (27), kaolinite (22%), and very fine-grained quartz (Nevidomskaya et al., 2015). The contents of dominant clay minerals in the soils and parent rocks and fractions separated from them are presented in Table 2.

The mechanisms of copper adsorption and stabilization in the chernozems were studied using nitrate solutions (copper nitrates are highly soluble in water).

It is commonly believed that the  $\text{NO}_3^-$  anion insignificantly affects the behavior of the  $\text{Cu}^{2+}$  cation in heterogeneous systems. It was demonstrated (Zhang and Sparks, 1996) that Na-montmorillonite equally well adsorbs  $\text{Cu}^{2+}$  from 0.25 M chloride, perchlorate, nitrate, and sulfate solutions at pH of 4.32 to 4.54.

Soil samples were sieved through screens with 1 mm mesh and poured over with  $\text{Cu}(\text{NO}_3)_2$  in natural ionic form, at a ratio of soil to solution of 1 : 10. The concentrations of the initial  $\text{Cu}^{2+}$  solutions were 0.05; 0.08; 0.1; 0.3; 0.5; 0.8, and 1.0  $\text{mM L}^{-1}$ . The  $\text{Cu}^{2+}$  concentration range in the system spanned a diversity of geochemical situations and corresponded to real contamination levels with the metal.

The suspensions were stirred for 1 h, left at rest for 1 day, and then filtered. Metal concentrations in the filtrates were analyzed by atomic absorption spectrophotometry (AAS). The amounts of adsorbed  $\text{Cu}^{2+}$  ions were calculated as the difference between the metal concentration in the starting and equilibrium solutions. The raw data were statistically processed with the SigmaPlot 12.5 and Excel program packages at a 0.95 confidence level.

To study the molecular and structural organization of adsorbed  $\text{Cu}^{2+}$  ions, we used an organic phase: humic acid separated from ordinary calcareous chernozem from Rostov region and components of the mineral phase (montmorillonite, kaolinite, and hydromuscovite), which saturated with  $\text{Cu}^{2+}$  ions in  $\text{Cu}(\text{NO}_3)_2$  solution. For comparison, we used XAFS spectra of humic acid in a Cu-species ( $\text{Cu}(\text{NO}_3)_2$ ) and spectra of Cu-saturated clay minerals.

## RESULTS AND DISCUSSION

The isotherms of  $\text{Cu}^{2+}$  adsorption by ordinary chernozem and southern chernozems are presented in Fig. 1. As seen in the plots, all of the  $\text{Cu}^{2+}$  adsorption isotherms are convex curves and, hence, are described by the Langmuir equation

$$C_{\text{ad}} = C_{\infty} K_1 C_e / (1 + K_1 C_e),$$

**Table 1.** Physical and chemical properties of the soils and parent rocks

Horizon, depth, cm	Parameter						
	pH	physical clay (particles <0.01 mm)	clay (particles <0.001 mm)	humus	CaCO <sub>3</sub>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	CEC
		%				cM(+) kg <sup>-1</sup>	
Clay loamy ordinary chernozem							
A, 0–20	7.3	48.1	28.6	4.2	0.1	35.0	36.0
AB, 35–45	7.9	49.5	27.8	3.1	0.3	29.5	31.7
Parent rock: loess-like loam							
C, 290–300	8.4	50.4	30.6	0.3	4.4	22.8	19.9
Clay loamy southern chernozem							
A, 0–20	7.4	53.9	31.0	3.9	0.5	35.2	33.9
AB, 50–60	8.5	57.3	36.7	4.1	0.8	31.7	28.4
Parent rock: yellow-brown clay							
C, 190–200	9.6	57.3	33.3	0.4	9.5	23.7	17.4
Loamy sandysouthern chernozem							
A, 0–20	7.5	31.4	19.1	3.5	–	29.5	31.8
Loamy sandy southern chernozem							
A, 0–20	7.2	12.4	8.0	3.5	–	24.9	25.9

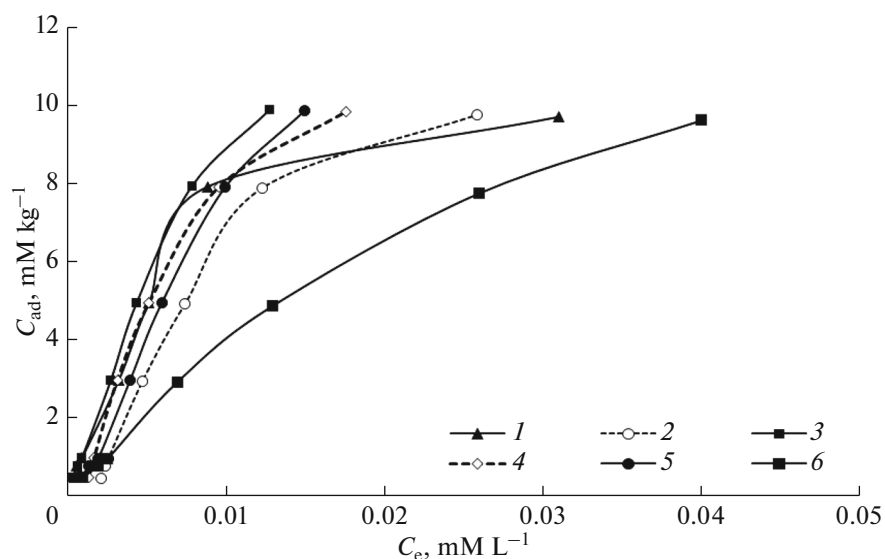
**Table 2.** Average contents of dominant clay minerals in the soils and their silt fractions (*Scientific Fundamentals...*, 1983)

Horizon, depth, cm	Content (%) of minerals							
	illite		montmorillonite		kaolinite		chlorite	quartz
	in soil as a whole	in fraction <0.001 mm	in soil as a whole	in fraction <0.001 mm	in soil as a whole	in fraction <0.001 mm		
Ordinary chernozem on loess-like loam								
A, 0–30	53.0	20.9	27.6	10.9	11.2	4.3	–	2–3
AB, 35–45	50.0	19.4	36.0	13.9	10.2	3.9	–	2–3
C, 290–300	49.0	17.5	36.0	12.6	13.6	4.7	+	2–3
Southern chernozem on yellow-brown clay								
A, 0–30	44.0	17.8	28.0	11.3	15.0	6.0	–	3–5
AB, 50–60	45.0	18.0	30.0	12.0	14.0	5.6	+	3–5
C, 190–200	45.0	16.6	41.0	15.1	14.0	5.1	+	3–5

where  $C_{ad}$  is the amount of adsorbed cations,  $C_{\infty}$  is the maximum  $Cu^{2+}$  adsorption,  $mM\ kg^{-1}$ , and  $K_1$  is the Langmuir constant. The values of parameters in the equation were calculated from experimental isotherms and are given in Table 3. The high values of the correlation coefficient ( $r = 0.94–0.99$ ) show that the experimental isotherms are in good agreement with the adsorption equation.

According to the data, the soils and rocks can be arranged in the following sequence according to their adsorption constants: clay loamy ordinary cherno-

zem  $\gg$  medium loamy southern chernozem  $>$  loamy sandy southern chernozem  $>$  clay loamy southern chernozem  $\geq$  yellow-brown clay  $\geq$  loess-like loam. The arrangement of the adsorbent in a succession according to their maximum copper adsorption can be regarded merely as a tendency in view of the significant errors in the estimates. This succession is as follows: yellow-brown clay  $>$  loess-like loam  $>$  clay loamy southern chernozem  $>$  clay loamy ordinary chernozem. The two successions are different, and the values of  $C_{\infty}$  and  $K_1$  correlate with each other, and hence, their values are controlled by different factors.



**Fig. 1.** Isotherms of  $\text{Cu}^{2+}$  adsorption by (1) clay loamy ordinary chernozem, (2) loess-like loam, (3) clay loamy southern chernozem, (4) yellow-brown clay, and (5) loamy sandy southern chernozem and (6) loamy sandy southern chernozem;  $\text{Cu}^{2+}$  was introduced in the form of nitrates.

It should be mentioned that the values of  $C_{\infty}$  show a strong negative correlation with CEC ( $r = -0.88$ ). These relations are described by an exponential equation:  $y = a \exp(-bx)$ , where  $y$  and  $x$  correspond to  $C_{\infty}$  and CEC, respectively, and  $a = 95.6$  and  $b = 0.48$  are empirical coefficients. Somewhat weaker correlations ( $r = 0.52$ ) were detected between  $C_{\infty}$  and the contents of physical clay and silt in the soil and rock samples, and the correlations between these components and  $K_1$  are weak. This means that the value of  $C_{\infty}$  depends first of all on the size of the particles, and hence, their specific surface, whereas the strength of the bonds, which is characterized by  $K_1$ , depends primarily on the chemical and mineralogical composition.

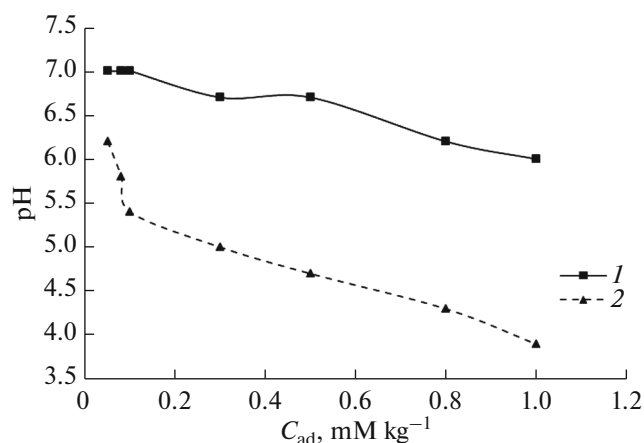
This is confirmed by the relatively strong correlations between  $K_1$  and the contents of physical clay ( $r = 0.78$ ) and silt ( $r = 0.80$ ) in chernozems of various particles size distribution. An even stronger correlation was detected between these parameters of southern chernozem:  $r = 0.89$  for physical clay and  $r = 0.91$  for silt. According to (Minkina et al., 2004) the silt frac-

tion of the soils contains mostly minerals, coagulated gels, iron and aluminum oxides, allophanes, mono- and polysilicic acids, and organic and organo-mineral- compounds. The mineralogical composition of the clay fraction of the soils is largely inherited from their parent rocks. The heavy parent rocks (yellow-brown clay) in the northern part of Rostov region are richer in montmorillonite component in the mixed-layer phase and finely divided quartz than the loess-like rocks in Oktyabr'skii district.

An important difference of finely divided fractions separated from the clays and soils is the presence of much organic matter in a free form and as organo-mineral compounds of various nature. It is thus reasonable to suggest that these exactly compounds are responsible for the differences in the adsorption capacity of the soils. According to (Panina and Siromin, 2005), the main factor controlling the adsorption capacity of the humus horizons of soils is their organic matter. As humus content in soils decreases,  $\text{Cu}^{2+}$  bonding with the surface of soil particles weakens. These changes are caused by the hydro-

**Table 3.** Adsorption parameters of  $\text{Cu}^{2+}$  from solutions of nitrate salts by chernozems of different texture and parent rocks

Chernozem or rock	$C_{\infty}$ , mM kg <sup>-1</sup>	$K_1$ , L mM <sup>-1</sup>	$R^2$
Clay loamy ordinary chernozem	13.30 ± 1.30	93.72 ± 20.69	0.94
Soil-forming rock: loess-like loam	34.99 ± 19.88	17.65 ± 7.90	0.94
Clay loamy southern chernozem	23.66 ± 3.54	58.25 ± 13.20	0.99
Soil-forming rock: yellow-brown clay	46.67 ± 22.97	22.77 ± 7.29	0.96
Medium loamy sandy southern chernozem	20.59 ± 9.16	54.54 ± 21.92	0.98
Loamy sandy southern chernozem	19.01 ± 1.02	25.90 ± 2.36	0.99



**Fig. 2.** Changes in the pH values of (1) equilibrium and (2) corresponding starting solutions depending on the amounts of copper adsorbed by the ordinary chernozem.

lysis of  $\text{Cu}(\text{NO}_3)_2$  and transfer of cations into solution at  $\text{Cu}^{2+}$  adsorption, association of  $\text{Cu}^{2+}$  cations with components of the equilibrium solutions (first of all,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ), and the transfer of exchangeable hydrogen, which is always present in the soil adsorption complex (SAC) (Pinskii, 1997; Davis and Leckie, 1978; Minkina et al., 2013), into solution (deprotonization). The displacement of exchangeable hydrogen at the adsorption of HM cations likely plays a leading role in acidification of the equilibrium solutions.

The occurrence of exchangeable hydrogen in soils and clays is explained primarily by the presence of weakly acidic exchange centers in the solid phases. These centers are protonated and consequently change the sign of their charge. For example, the isoelectric point (IEP) of amorphous  $\text{Al}_2\text{O}_3$  occurs at pH 7.5–8.0, that of  $\alpha\text{-AlOOH}$  (boehmite) is at pH 6.5–9.4, the point of natural magnetite ( $\text{Fe}_3\text{O}_4$ ) lies within the range of pH 6.3–6.7, and that of amorphous  $\text{Fe}_2\text{O}_3$  occurs at pH 7.0–8.6 (Pinskii, 1997).

**Table 4.** Balance of exchangeable cations at  $\text{Cu}^{2+}$  adsorption by ordinary chernozem from nitrate solutions of the metal  $\text{mM}(+) \text{kg}^{-1}$

$C_{ad}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\Sigma \text{trans.cat.}$	$\Sigma \frac{\text{trans.cat}}{C_{ad}}$
1.00	2.20	0.40	0.13	0.07	2.80	2.80
1.58	2.40	0.60	0.30	0.12	3.42	2.16
1.98	3.40	0.80	0.27	0.17	4.64	2.34
5.94	7.80	2.00	0.70	0.36	10.86	1.83
9.90	11.00	3.60	1.20	0.50	16.30	1.65
15.82	15.60	5.20	1.90	1.10	23.80	1.50
19.38	17.40	6.00	2.40	1.20	27.00	1.39

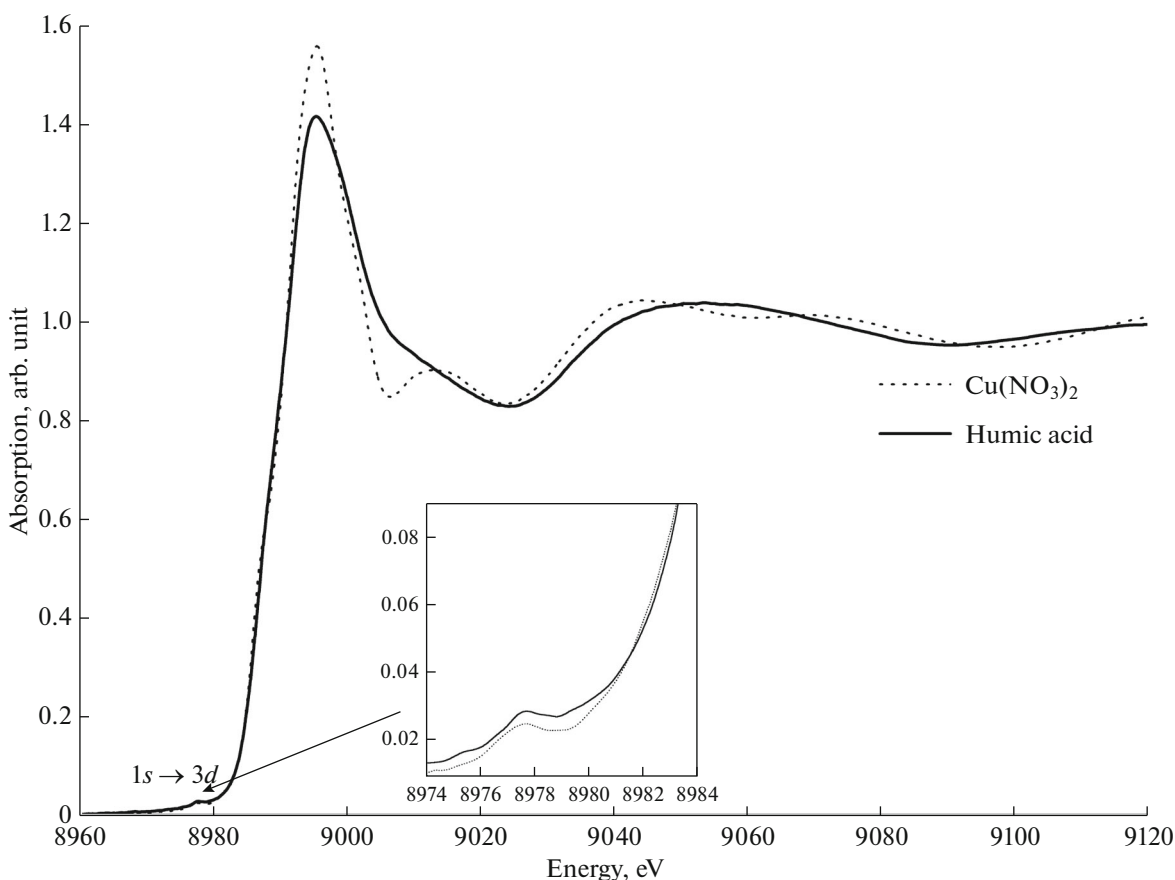
This means that at usual conditions of soil-forming processes at pH 5.5–7.2, much of the surface of these components is saturated with the  $\text{H}^+$  ion, which defines the potential in this situation. Protons are characterized by a very high affinity with exchange centers of the weakly acidic soil adsorption center (Pinskii, 1997; Plyaskina and Ladonin, 2005). The configuration of the  $\text{pH} = f(C_{ad})$  depends on all of the aforementioned factors.

Analysis of the dependences shows that pH of the starting solutions gradually decreases from 7.0 at low concentrations of the solution to 6.0 at high ones. The pH values of the equilibrium solutions at various amounts of adsorbed copper are generally more than the starting ones and vary within the range of 6.2 to 3.8, and this depends is of complicated configuration. First (up to  $\text{Cu}^{2+}$  concentrations in the adsorbed state is  $< 1 \text{ mM kg}^{-1}$ ), pH decreases slightly because of soil deprotonation. Further adsorption of  $\text{Cu}^{2+}$  is associated with a pH decrease similar to that in the starting solutions because of the hydrolysis of the dissolved salts. Such pH dependences on the amount of adsorbed HM were previously established by D.L. Pinskii (1997).

The adsorption of cations of any metal is always associated with the transfer of a number of other cations, which occur in soils and parent rocks in an exchangeable state, into solution. The most important cations of soils are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{H}^+$ . It is interesting whether the exchange between exchangeable cations transferred into solution and adsorbed  $\text{Cu}^{2+}$  cations is equivalent.

The amounts of cations transferred into solution at  $\text{Cu}^{2+}$  adsorption can be arranged in the form of the succession  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ \gg \text{H}^+$ , which corresponds to their proportions in the soil adsorption complex (Table 4). Because the concentration of  $\text{H}^+$  ions involved in exchange processes is much lower than the concentrations of other exchangeable cations and practically does not influence their totals, we did not taken them into account in our balance calculations. Analysis of data in Table 4 shows that the totals of exchangeable cations transferred into solutions are usually much greater than the amounts of adsorbed copper. The ratio of the total of exchangeable cations transferred into solution to the amount of adsorbed  $\text{Cu}^{2+}$  is always  $> 1$  and decreases with increasing amount of the adsorbed metal. By definition, ion-exchange processes in soils proceed in equivalent amounts, and hence, it is interesting to understand the reasons for the inconsistency between the amounts of soil-adsorbed copper and those of exchangeable cations transferred into solution.

Obviously, the lack of balance is explained in this particular situation by the presence of readily soluble salts, which are always formed when soils and rocks are dried to an air-dry state. These salts are rapidly dis-



**Fig. 3.** Experimental XANES spectra of *K*-Cu X-ray absorption for the original copper-bearing compound (copper nitrate) and humic acid separated from ordinary chernozem and that contaminated with copper nitrate.

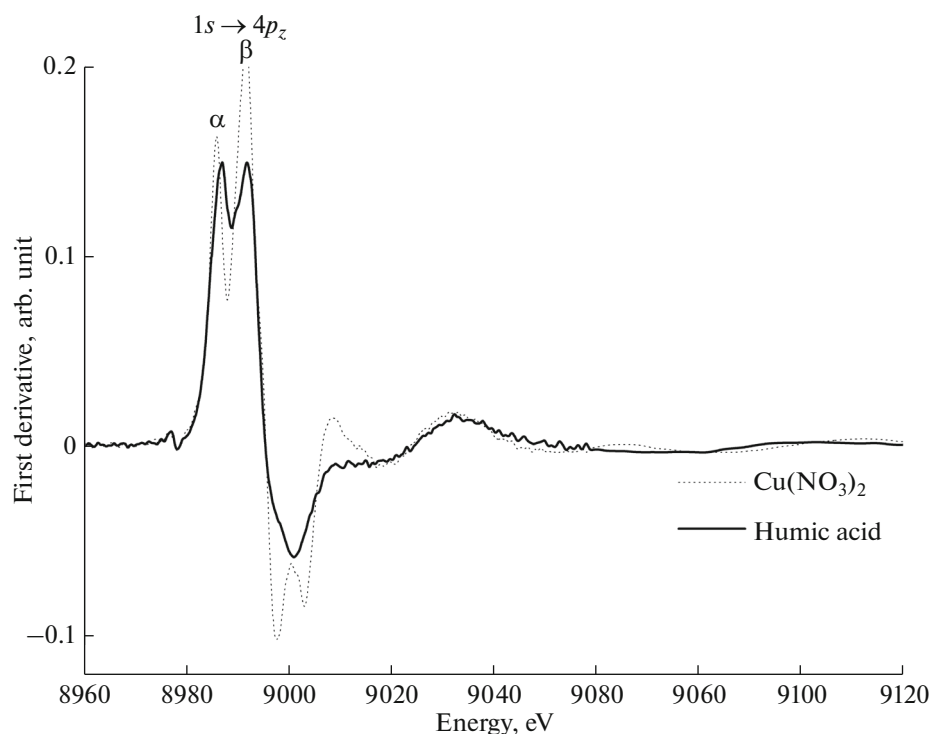
solved when water is added. Their amounts and composition are roughly the same at each point of the isotherm because they are not directly related to the exchange process. Because of this, as the amount of adsorbed  $\text{Cu}^{2+}$  is increased, equivalent amounts of exchangeable cations are transferred into solution at a constant amount of high-solubility salts. The greater the amount of the exchangeable cations, the smaller the contribution of the high-solubility salts to the overall balance between adsorbed copper and the total of the exchangeable cations.

It is interesting as to what happens next to the adsorbed  $\text{Cu}^{2+}$  cations. Nowadays researchers start to more and more widely apply techniques that enable them to directly study the local structure and the character of bonds of an element in solid phases by analyzing the fine structure of X-ray absorption spectra (XAFS) (Fetisov, 2007; Gräfe et al., 2014; *Synchrotron-Based Techniques...*, 2010). Figure 3 presents XANES spectra of the *K*-edge of the initial salt  $\text{Cu}(\text{NO}_3)_2$  and of Cu–humic acid, which was obtained from chernozem contaminated with this salt.

The intensity of the peak in the middle region of the spectrum (at  $\sim 8985$ – $8990$  eV), which is caused by

the occurrence of  $\text{Cu}^{2+}$  in the experimental spectrum of the humic acid, is lower than the intensity of the peak in the spectrum of  $\text{Cu}(\text{NO}_3)_2$ , and this indicates that  $\text{Cu}^{2+}$  interacts with humic acid. In the near-edge region (Fig. 3, inset for  $\sim 8975$ – $8980$  eV), the XANES spectrum of the *K*-edge of  $\text{Cu}^{2+}$  shows a weak maximum, which is explained by the  $1s \rightarrow 3d$  quadrupole electron transition that characterizes  $\text{Cu}^{2+}$  binding in low-symmetry octahedral and tetrahedral sites. It should be mentioned that the origin of tetrahedral complexes of many transition metals is reflected in XANES spectra as pronounced shoulders near the absorption edges, which is caused by  $1s \rightarrow 4p$  dipole electron transitions (Bianconi et al., 1982). The absence of a shoulder in this absorption region means that  $\text{Cu}^{2+}$  forms octahedral inner-sphere chelate complexes.

The first-derivative  $\text{Cu}(\text{NO}_3)_2$  spectrum shows two peaks:  $\alpha$  and  $\beta$ . The intensity of peak  $\beta$  is much greater than that of peak  $\alpha$  (Fig. 4) because of an increase in the  $\text{Cu}-\text{O}_{\text{ax}}$  bond length, and the length of the  $\text{Cu}-\text{O}_{\text{eq}}$  bond thereby does not change. In the Cu–HA spectrum, the intensities of peaks  $\alpha$  and  $\beta$  are roughly equal. The stepped structure of peaks  $\alpha$  and  $\beta$  in the



**Fig. 4.** First derivative of experimental XANES  $K$ -Cu spectrum of the original copper-bearing compound (copper nitrate) and humic acid separated from ordinary chernozem and that contaminated with copper nitrate.

edge region of the first derivative of the  $\text{Cu}(\text{NO}_3)_2$  XANES spectrum is caused by the Jahn–Teller effect, which reflects tetragonal distortions of Cu bonding in the octahedrons (Lee et al., 2005; Palladino et al., 1993; Xia et al., 1997) and indicates a symmetry

decrease with the transformation of the octahedral region into tetrahedral one (Hyun and Hayes, 2015). The octahedral symmetry is characterized by a single peak in the first-derivative spectrum, whereas the tetrahedral distortions yield two peaks:  $\alpha$  and  $\beta$ .

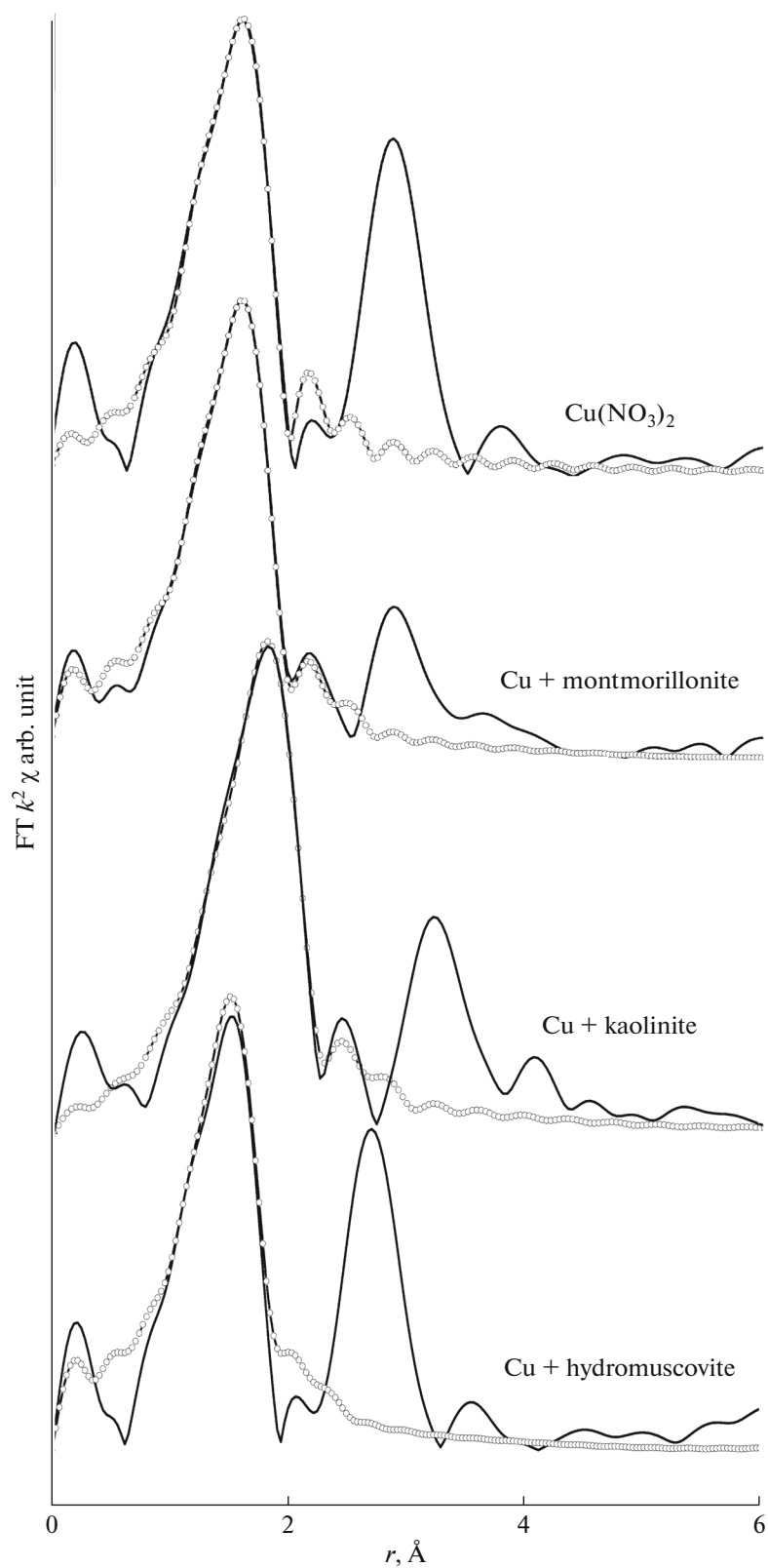
**Table 5.** Structural data on pure copper nitrate, contaminated soil, and individual soil phases obtained by fitting EXAFS data ( $R$ , Å is the interatomic spacing,  $N$  is the coordination number,  $\sigma^2$  is the Debye–Waller factor, and  $Q$ , % is a fitting quality function)

Sample	Atom	$N$	$R$ , Å	$\sigma^2$	$Q$ , %
$\text{Cu}(\text{NO}_3)_2$	Cu–O1	2	1.87	0.0036	3.58
	Cu–O2	2	1.99	0.00048	
Hydromuscovite + $\text{Cu}(\text{NO}_3)_2$	Cu–O1	2	1.91	0.0082	1.98
	Cu–O2	2	1.98	0.0043	
	Cu–Cu	1	2.65	0.0090	
	Cu–Al	4	3.35	0.0080	
Kaolinite + $\text{Cu}(\text{NO}_3)_2$	Cu–O1	2	1.88	0.0048	1.97
	Cu–O2	2	1.99	0.0019	
	Cu–Cu	1	2.64	0.0096	
	Cu–Al	4	3.31	0.0085	
Montmorillonite + $\text{Cu}(\text{NO}_3)_2$	Cu–O1	2	1.86	0.0066	1.83
	Cu–O2	2	1.98	0.0024	
	Cu–Cu	1	2.62	0.0073	
	Cu–Al	4	3.36	0.0084	

A change in the intensity of peak  $\alpha$  in the first-derivative XANES spectrum of Cu–humic acid is explained by a  $1s \rightarrow 4p_z$  electron transition and indicates that an electron is transferred from the metal to ligand because of ion exchange in the tetragonal plane of molecules with ligands (Xia et al., 1997). The intensity of XANES peak  $\beta$  is defined by the probability of a  $1s \rightarrow 4p_z/p_y$  electron transition (Furnare et al., 2005). It has been established (Alcacio et al., 2001) that the intensity of peak  $\beta$  is at a maximum in the spectra of samples of humic acids and goethite that contain adsorbed copper ions. Thereby triple complexes are formed with a copper ion bounded to organic and mineral components at the center.

Figure 5 shows Fourier transforms of EXAFS spectra. The data indicate that the adsorbed  $\text{Cu}^{2+}$  ions complicatedly interact with the surface of mineral particles: the local surroundings of adsorbed Cu ions of the first coordination sphere consist of four oxygen atoms with Cu–O1 and Cu–O2– pairs in between (Table 5). One of the Cu–O pairs, with a greater spacing, characterizes an apical setting of the O atoms. According to fitting calculations of the EXAF spectra obtained by Fourier filtering, some  $\text{Cu}^{2+}$  ions adsorbed





**Fig. 5.** Experimental EXAFS spectra of layer minerals and a reference compound ( $\text{Cu}(\text{NO}_3)_2$ ) and Fourier transform models derived from experimental EXAFS spectra: experimental (solid line) and models (circles).



on layer aluminosilicates are accommodated in octahedral structures, in which they substitute  $\text{Al}^{3+}$  ions and form something like an inner-sphere complex. It is also reasonable to suggest that  $\text{Cu}^{2+}$  ions are sorbed, as Cu–Cu dimers, by incompletely coordinated silicate and/or aluminosilicate groups. This is confirmed by structural data on our samples obtained by fitting EXAFS data (Table 5). This process can occur at structural defects of minerals: defects of bond lengths and the origin of double bonds.

## CONCLUSIONS

(1) The isotherms of  $\text{Cu}^{2+}$  adsorption in the upper horizons of chernozems and their parent rocks are reasonably well approximated by the Langmuir equation. The maximum Cu adsorption  $C_{\infty}$  is determined to be negatively correlated with the cation-exchange capacity. Analysis of correlations of  $C_{\infty}$  and  $K_1$  with the contents of physical clay and silt in samples of soils and parent rocks shows that  $\text{Cu}^{2+}$  adsorption depends mostly on the size of the particles, and the strength of adsorption is largely controlled by the chemical and mineralogical composition of the soils and rocks. The correlations are stronger for soil varieties (southern chernozem,  $r = 0.89\text{--}0.91$ ) than for soil subtypes (chernozems,  $r = 0.78\text{--}0.80$ ). An important factor controlling the bonding strength of adsorbed  $\text{Cu}^{2+}$  with the examined adsorbents is the presence of organic matter ( $r = 0.76\text{--}0.88$ ).

(2) It was determined, with reference to ordinary chernozem, that  $\text{Cu}^{2+}$  adsorption is associated with significant acidification of the starting ( $\Delta\text{pH}_s \leq 2.4$ ) and equilibrium ( $\Delta\text{pH}_e \leq 0.9$ ) solutions, and thereby  $\text{pH}_s < \text{pH}_e$ . The overall pH increase is caused by the acid–base buffer properties of the soils and rocks. The changes in  $\text{pH}_0$  is related to the hydrolysis of copper nitrate, and the change in  $\text{pH}_e$  are induced by the hydrolysis of metal ions in the solution and the transfer of exchangeable hydrogen (which is always present in the adsorption composition of soils and rocks) into solution.

(3) Data on the amounts of adsorbed  $\text{Cu}^{2+}$  and exchangeable cations transferred into solution seem to indicate the absence of their balance. This is explained by that soils contain easily soluble salts, certain changes in  $\text{pH}_e$  in the course of adsorption, adsorption of certain  $\text{Cu}^{2+}$  species from the solution, and the possible origin of precipitates of low-solubility salts on the surface of the adsorbent and near it because of local pH heterogeneities as a result of surface protonation.

(4) Analysis of the fine structure of XANES spectra shows that interaction between  $\text{Cu}^{2+}$  ions and humic acids of soils may lead to the origin of octahedral inner-sphere chelate complexes. Soil-adsorbed  $\text{Cu}^{2+}$  cations can partly substitute octahedrally coordinated  $\text{Al}^{3+}$  ions in clay minerals. Copper can also be adsorbed in the

form of a Cu–Cu dimer by silicate and/or aluminosilicate groups that are incompletely coordinated or possess structural defects (bond lengths and double bonds).

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