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## Adsorption of copper by ordinary and southern chernozems from solutions of different salts

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### ABSTRACT

The aim of this work was to study the effect of the attendant anions and particle-size distribution on the adsorption of copper by chernozems of Rostov region (Russia). The samples of soil in the natural cationic form were treated with solutions of copper nitrates, acetates, chlorides, and sulfates at a soil: solution ratio of 1:10. The concentrations of the initial copper solutions varied in the range from 0.05 to 1 mM/L. The suspensions were shaken for 1 h, left to settle for a further 24 h and then filtered. The metal concentrations in the filtrates were determined by atomic absorption spectrometry. The concentrations of the adsorbed copper cations were calculated from the difference between the metal concentrations in the initial and equilibrium solutions. The effect of the attendant anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ac}^-$ , and  $\text{NO}_3^-$  and particle size distribution on the adsorption of copper by chernozems of the Rostov region has been studied under laboratory conditions. The shape of the adsorption isotherms varies depending on the attendant anion and is described by the Henry, Freundlich, and Langmuir equations. The adsorption of copper by the soil is accompanied by the acidification of equilibrium solutions ( $pH_{\text{eq}}$ ):  $0.53 \leq \Delta pH_{\text{eq}} \leq 2.06$ , which depends on the attendant anion. The highest value of  $\Delta pH_{\text{eq}}$  corresponds to the adsorption of  $\text{Cu}^{2+}$  from the copper sulfate solution and its lowest value, from the copper chloride solution. The effect of the attendant anions decreases in the series:  $\text{Cu}(\text{Ac})_2 > \text{CuCl}_2 > \text{Cu}(\text{NO}_3)_2 >> \text{CuSO}_4$ . In the southern chernozems, a close correlation is observed between the maximum copper adsorption and the content of clay and silt ( $R = 0.99$ ). No correlation is found between the values of adsorption constants and particle size distribution, which is related to the changes in the chemistry and mineralogy of the soils studied.

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### 1. Introduction

At the present, the contamination with heavy metals (HMs) constitutes a serious environmental danger. Among the HMs, copper is one of the priority environmental pollutants. Copper is a highly technophilic element, which finds wide use in industry. This is an essential micronutrient when present in the soil in low concentrations, but its high concentrations have highly toxic, mutagenic, and carcinogenic effects on living organisms; copper is capable of bioaccumulation (Adriano, 1992; Kabata-Pendias, 2011; Silveria and Alleoni, 2003). Coming into the environment from technogenic sources, Cu actively affects all the environmental components. In this case the soil experiences the maximum load (Panin and Siromlya, 2005).

The transformation of technogenic copper compounds in the soil starts from their dissolution in soil water. For the hardly soluble copper compounds, dissolution is the initial and the slowest process (Ladonin and Karpukhin, 2011). According to Zaplina (1994), the time of the complete dissolution of HM oxides added to the soil in the amounts corresponding to the actual contamination levels can be from six

months to tens of years. Other authors (Parnunina, 1983; Gorbatov, 1988) studying the dissolution kinetics of lead, cadmium, and zinc oxides in soils, on the contrary, noted the high dissolution rate of metal oxides and the adsorption of their ions on the surface of soil particles. Our studies on the dissolution of different rates of copper oxides in ordinary chernozem using synchrotron techniques revealed the presence of metal oxides one year after their addition to the soil (Minkina et al., 2013).

It is known that a significant (usually larger) proportion of copper cations in solution is associated with the solution components (Minkina et al., 2014a, 2014b; Pinskii et al., 2010, 2014). The effect of acid precipitation on cation exchange with the participation of HMs was studied experimentally; it was shown that anions had different, frequently opposite, effects on the adsorption of HMs by soils (Chairidchai and Ritchie, 1990; Adriano, 2001).

The content of unstable complexes such as  $\text{CuNO}_3^+$  and  $\text{CuCl}^+$  in solutions equilibrated with chernozemic soils is insignificant because of their low stabilities (Minkina et al., 2009, 2014a, 2014b; Pinskii et al., 2010). It is believed that neutral complexes such as  $\text{CuSO}_4^0$  and  $\text{CuCl}_2^0$  are not involved in ion exchange because of their electrical neutrality. More stable charged metal complexes such as  $\text{CuAc}^+$  and  $\text{CuOH}^+$  – interact with the surface of the solid phase; they compensate

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**Table 1**  
Physical and chemical properties of the soils studied (0- to 20-cm Ap horizon).

Parameters	Clay loamy ordinary chernozem	Southern chernozems		
		clay loamy	loamy	loamy sandy
Clay (the particle with size <10 µm), %	48.1	53.9	31.4	12.4
Silt (the particle with size <1.0 µm), %	28.6	31.0	19.1	8.0
Humus, %	4.2	3.9	3.5	3.5
pH	7.3	7.4	7.5	7.2
CaCO <sub>3</sub> , %	0.1	0.5	-	-
P <sub>2</sub> O <sub>5</sub> , mg/100 g	1.6	1.5	1.5	1.5
K <sub>2</sub> O, mg/100 g	22.8	25.3	23.2	17.6
Ca <sup>2+</sup> + Mg <sup>2+</sup> , meq/100 g	35.0	35.2	29.5	24.9
CEC, meq/100 g	36.0	36.1	31.8	25.9

for only one charge on its surface and thus increase the maximum adsorption. The stability of the formed adsorption compounds is not directly related to the adsorption value and can vary depending on the interaction mechanism. Interaction with the surface of the soil particles through a ligand is still possible. This is especially typical for complexes of HMs with organic ligands.

At the same time, Zhang and Sparks (1996) found that Na-montmorillonite adsorbed similar amounts of Cu<sup>2+</sup> from 0.25 M chloride, perchlorate, nitrate, and sulfate solutions in the pH range from 4.31 to 4.54. Bingham et al. (1964) obtained the following series for the effect of anions on the adsorption of copper and zinc by montmorillonite from salt solutions: Ac<sup>-</sup> > Cl<sup>-</sup> ≥ NO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup>.

Highly dispersive soil particles play an essential role in all the inter-phase interactions in the soil: the ion exchange, adsorption, water retention capacity, structuring, plant nutrition, immobilization of HMs. Numerous works (McBride, 1989; Perelomov and Pinskii, 2003) are devoted to the study of this problem. However, the interaction features of different particle-size soil fractions and their role in the immobilization of HMs studied insufficiently. Therefore, the assessment of the effect of the particle size distribution on the adsorption properties of soils is a vital task. The clay (the particle with size <10 µm) and silt (the particle with size <1.0 µm) fractions are the most dynamic and active soil components. The clay fraction mainly contains secondary mineral components: clay minerals, coagels, iron and aluminum oxides, allophanes, mono- and polysilicic acids, and organic and organomineral compounds. It is characterized by a high adsorption capacity for HMs, including copper. According to the sorption capacities of the iron and clay minerals in the clay fractions, the HM cations form the following sequence: Cd<sup>2+</sup> > Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> (Ladonin and Plyaskina, 2004). According to the strength of ion retention by the surface of particles in the clay fraction, these elements form a different sequence: Pb<sup>2+</sup> > Zn<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup>.

The aim of this work was to study the effect of the attendant anions and particle-size distribution on the adsorption of copper by chernozems of Rostov region (Russia).

## 2. Materials and methods

### 2.1. Soil

In Russia soils of the Rostov region attract special attention, as a region which is one of the major agricultural producers and, at the same time, a huge industrial center exerting strong anthropogenic pressure on the environment and soils. The Rostov region belongs to the steppe and dry steppe zones with diverse environmental conditions; the high population density; and the high concentration of industry, including metallurgical plants and coal-mining and ore-mining factories. The steppe soils are represented by chernozems, the most fertile and valuable soils of Russia with highly buffering self-protecting system. The transformation of heavy metal compounds in these soils has its own specificity conditioned.

The objects of study included the upper humus horizons of a medium-deep clay loamy calcareous southern chernozem on yellow-brown structural clays, a medium-deep loamy southern chernozem on yellow-brown loess-like loams, a medium-deep loamy sandy southern chernozem on sands (Haplic Chernozems, ID 14-1, FAO, 1990), and a medium-humus clay loamy calcareous ordinary chernozem on loess-like loams (Calcic Chernozems, ID 14-2, FAO, 1990) from Rostov region (Russia). The soil samples for studying the soil properties were taken from the depth of 0–20 cm. Basic physical and chemical properties of the studied soils were determined (Methodological guidelines for the integrated monitoring of soil fertility of agricultural lands, 2003). The properties are given in Table 1. The content of humus was determined by the Tyurin method modified by Simakov, the cation exchange capacity (CEC) was determined by the Bobko–Askinazi method, the available phosphorus and exchangeable potassium were determined by the Machigin method, the pH was determined by potentiometry, and the carbonates were determined by the Kudrin method (Agrochemical Methods of Soil Studies, 1990). The exchangeable cations were determined by the Shaimukhametov Method (1993). Soil particle size distribution was determined by the pipette method after the pyrophosphate treatment (Vadyunina and Korchagina, 1986).

In the study of the soil particle-size distribution, attention is focused on the content of clay (the particle with size <10 µm) and sand (the particle with size >10 µm), because these data are used for the classification of soils according to their particle-size distribution (Kachinskii, 1958). It mainly consists of quartz and small amounts of amphiboles and feldspars with small adsorption capacity. These components act as a mechanical diluter for the substances mainly concentrated in the fractions <0.01 mm (Kryshchenko et al., 2008).

Analytical quality of the measurements was controlled by analyzing reference standard soil sample “Chernozem” № 29,107. Duplicates and reagent blanks were also used as a part of the quality control.

### 2.2. Adsorption experiment

Solutions of Cu<sup>2+</sup> nitrates, acetates, chlorides, and sulfates were used to study the effect of the chemical composition of added salts on the Cu adsorption by soil. Samples of the soil sieved through a 1-mm sieve in the natural ionic form were treated with solutions of the corresponding Cu salts at a soil: solution ratio of 1:10. The concentrations of the initial Cu solutions were 0.02, 0.05, 0.08, 0.1, 0.3, 0.5, and 1.0 mM L<sup>-1</sup>. The range of Cu<sup>2+</sup> concentrations in the studied system covers different geochemical situations corresponding to the actual levels of soil contamination with the metal under study.

The suspensions were shaken for 1 h, left to settle for a further 24 h and then filtered through paper (pore size 2–3 µm). The ion exchange equilibrium in soil is determined by the inner and outside diffusion of ions. Per se the process of ion exchange is very quick - a few seconds. At intensive shake the ion exchange equilibrium stables relatively quickly - during one hour. This method was verified in special kinetic experiments (Minkina et al., 2009). The HM concentrations in the

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