Journal of Geochemical Exploration xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

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

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A R T I C L E   I N F O

Article history:
Received 8 August 2016
Revised 7 October 2016
Accepted 16 October 2016
Available online xxxx

Keywords:
Cu^{2+} ions
Calcic Chernozem
Mineral phases of layered silicates
Sequential fractionation
X-ray powder diffraction
XANES spectroscopy

A B S T R A C T

Interaction of 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 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 ($Cu(NO_3)_2$) affected the transformation of Cu compounds and their affinity for metal-bearing phases. It was found that the contamination of soil with a soluble 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 isomorphic 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 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 Cu^{2+} ions are removed from the system due to the formation and precipitation of coarsely crystalline $Cu(NO_3)(OH)_3$.

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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http://dx.doi.org/10.1016/j.gexplo.2016.10.007
0375-6742/

Please cite this article as: Minkina, T.M., et al., Studying the transformation of Cu^{2+} ions in soils and mineral phases by the XRD, XANES, and sequential fractionation methods, J. Geochem. Explor. (2016), http://dx.doi.org/10.1016/j.gexplo.2016.10.007

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 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_{org} 3.7%, $CaCO_3$ 0.4%, pH_{H_2O} 7.6; exchangeable bases (mM(+)/100 g): Ca^{2+} 31.0, Mg^{2+} 6.0, 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 spectroscan.

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 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 ($Cu(NO_3)_2$ 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 Cu^{2+} ions. For this purpose, the studied samples were put into a saturated $Cu(NO_3)_2$ 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 $Cu(NO_3)_2$. 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 ($\lambda = 0.68886$ Å, Si monochromator) were performed in transmission geometry using a Fujifilm Imaging Plate two-coordinate detector at 0.68886 Å. X-ray diffraction patterns were recorded in integrated mode at 20 °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 (~899–8995 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 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	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	P_2O_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

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