

Speciation of Zinc in Soil by Synchrotron X-Ray Techniques and Chemical Fractionation Methods

¹T.M. Minkina, ¹A.V. Soldatov, ²D.G. Nevidomskaya, ¹Yu. S. Podkovyrina and ³G.V. Motuzova

¹Southern Federal University, Russia, 344006, Rostov-on-Don, Bolshaya Sadovaya str. 105

²Institute of Arid Zones of the Southern Scientific Centre RAS, Russia,
344006, Rostov-on-Don, Chekhov st. 41

³Moscow State University, Russia, 119991, Moscow, Vorob'evy goru 1

Submitted: Oct 10, 2013; **Accepted:** Nov 14, 2013; **Published:** Nov 19, 2013

Abstract: Combining XANES study and extractive fractionation is an effective approach for establishing the interaction of metallic ions with soil compounds, as well as identifying the phases-carriers of metals in soils and their bonding strength. Extracted fractionation of metal compounds in chernozem samples, artificially contaminated with zinc, indicates the priority holding of Zn²⁺ ions by silicates, carbonates and Fe-Mn oxides. Atomic structure study of soil samples saturated with Zn²⁺ ion by using (XANES) X-ray absorption spectroscopy allowed the determination of mechanism of metal ions interaction with soil.

Key words: Soil · Heavy metals · XANES spectra · Extracted fractionation methods · Compounds

INTRODUCTION

Heavy metals' compounds in soil have been mostly determined by extraction methods since the 60-ies of the last century. These methods are based on the extracting agents of metal compounds presumably fixed by the solid phase soil components with different mechanisms and strength [1]. Modern X-ray spectroscopy methods (XANES, EXAFS) reveal useful information on the trace elements in soil. The identification of the metal type and its oxidation state is possible due to the fact that an edge of the X-ray absorption has a specific energy for each chemical element. Study of the extended fine structure of the X-ray absorption spectra (EXAFS) allows to obtain the information about metal-bearing soil phases and to distinguish the interaction type between the metal ions and soil components [2].

In recent years in addition to EXAFS method XANES (X-ray absorption near-edge structure) spectroscopy became a useful tool for the research in the field of soil components local atomic and electronic structure analysis. The power of XANES method was proved in the studies related to the inorganic minerals [3] and to the metallo-organic minerals [4]. The goal of this study is to analyze 3D local atomic structure around Zn²⁺ ions after the interaction with a soil and the soil phases (both

mineral phase: carbonates, kaolinite, bentonite and organic phase: humic acid) by X-ray absorption spectroscopy and chemical extraction fractionation.

MATERIALS AND METHODS

The samples of individual soil components (calcite, kaolinite, bentonite, preparations of humic acids isolated from ordinary chernozem) were saturated by Zn²⁺ ions. The studied samples were placed in a saturated solution of Zn²⁺ nitrates. The incubation period of metals in soils and soil components lasted for one year.

The total content of Zn in the soils was determined with the X-ray fluorescence method. Sequential fractionation of heavy metals in soil was conducted by Tessier method [5]. It allows determining 5 fractions of metals in soils: exchangeable, bonded with Fe-Mn oxide, bonded with carbonate, bonded with organic matter and bonded with silicate (residual). The total content of heavy metals in soils was determined according to the total content of metals in all fractions.

The experimental XANES spectra at the Zn K-edge (9659 eV) was measured by the laboratory spectrometer Rigaku R-XAS Looper. The data was obtained in the fluorescence mode because of low concentration of Zn in studied samples. The Ge (440) monochromator was used

Table 1: Fractional composition of Zn compounds in ordinary chernozem

Addition doses of HM, mg/kg	Fraction					Sum of fraction
	Exchangeable	Connected with carbonate	Connected with Fe-Mn oxides	Connected with organic matter	Connected with silicates (Residual)	
	mg/kg					
No added metal	0.6	1.8	14.2	11.5	56.9	85.0
2000 Zn(NO ₃) ₂	173.6	289.4	826.1	348.7	421.2	2059.0
2000 ZnO	49.1	56.9	777.2	346.1	844.7	2074.0
10 000 ZnO	245.0	296.0	3796.0	1624.0	4111.0	10072.0
	% of the sum of fraction					
No added metal	1	2	17	14	67	100
2000 Zn(NO ₃) ₂	8	14	40	17	20	100
2000 ZnO	2	3	37	17	41	100
10 000 ZnO	2	3	38	16	41	100

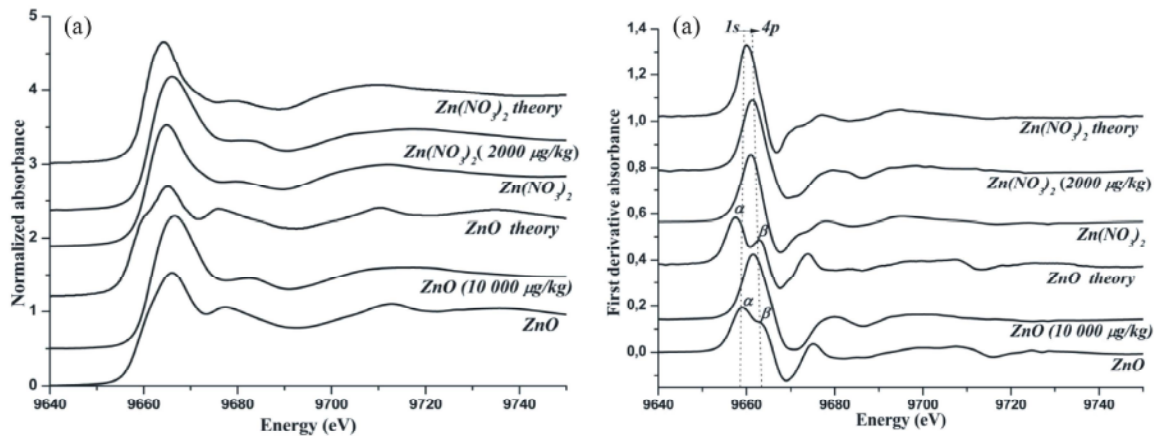


Fig. 1: The experimental and the theoretical Zn K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the soil samples: 1 - theoretical spectra of Zn(NO₃)₂, calculated by FDMNES 2012; 2 - experimental spectra of Cu(NO₃)₂-treated soil sample (2000 mg/kg); 3 - experimental spectra of Zn(NO₃)₂; 4 - theoretical spectra of ZnO, calculated by FEFF 9; 5 - experimental spectra of ZnO -treated soil sample (10000 mg/kg); 6 - experimental spectra of ZnO

to get a reasonably highenergy resolution (2 eV). Lead foils were used for energy calibration of the monochromator. XANES experimental spectra were measured in steps of 0.5 eV. To set of statistics the exposition time for one point of XANES spectrum was about 60 second. Each of the experimental spectra is an average of 5 to 7 scans. To gain the higher sensitivity the first derivatives of XANES spectra were calculated. The first derivatives highlight the differences between the experimental spectra. In order to follow the variations metal ions surroundings in soil phases and in initial compounds, the experimental spectra of the initial zinc-containing compounds is also presented. The calculations were performed using both the finite difference method in full potential FDMNES 2012 [6] and

self-consistent method of full multiple scattering in the muffin-tin approximation for the potential FEFF 9.54 [7].

Results and discussion. Fractionation of metal compounds showed that Zn has been dominate in fraction associated with silicates (67% of the total content of all fractions) in unpolluted chernozem (Table 1). The mobility of Zn in the original soil is low. The relative contents of metal in the first two fractions do not exceed 4%. Only 1% of them is the most moving exchangeable form. The absolute content of all metal compounds increases under soil contamination by Zn²⁺ ions. The metals' quantities in all compounds increase by 1.2-5 times together with the increase of Zn dose from 2000 up to 10 000 mg/kg. It was shown the influence of the way the metal is added to soil on fractional composition of their compounds.

In to the case of Zn these differences are expressed by a larger degree: Zn relative content under metal added in nitrate form was 22% and when added in the oxide form was 11%. The fact is due to the low solubility of metals oxides.

Figure 1a shows the Zn K-edge XANES spectra and their first derivatives represent in Fig. 1b. The main peak in the first derivatives of Zn XANES spectra describes the $1s \rightarrow 4d$ electronic transition. On the basis of the oscillation near ~ 9710 eV, it is possible to estimate the molecular and structural state of zinc. This oscillation determines mainly octahedral coordination of zinc ions, that indicating the formation of a hydrated adsorbed zinc and possibly as well as a layer zinc phases. Thus, the zinc ions, which enter in octahedral structures in various clay minerals and hydroxides, can be adsorbed as inner- and outer-sphere.

The experimental Zn K-edge XANES spectra for pure $Zn(NO_3)_2$ and nitrate-treated soil sample and the theoretical spectrum are similar, but they differs from each other in relative peak intensity and in an energy position of the spectral features.

The experimental spectrum of the nitrate-treated soil sample differs from other by its high intensity spectral feature in after edge region. The first derivative of the experimental XANES spectrum for the ZnO-treated soil sample is significantly different from the derivatives of X-ray absorption spectrum for pure ZnO and from. According to the fractionation extraction data, there is a 4.5 times difference in the rates of Zn mobile compounds in the soil treated with nitrate and oxide forms of Zn. Therefore, zinc, added in the form of nitrate, will interact intensively with soil components, forming different local structure around Zn ion. The Zn content in the exchangeable fraction and specifically sorbed fraction (bonded with carbonates) increased most significantly. The relative content of the most mobile Zn exchangeable fraction increased by 8 times and of the specifically absorbed (bonded with carbonates) – by 7 times under 2000 mg/kg Zn nitrate contamination. The significant role of carbonates in metal atoms adsorption, especially of zinc, was indicated previously [8, 9].

The affinity of metal ions to carbonates is determined by their low solubility. Carbonates can be the major absorbents of microelements in some soils. There is some evidence that the fraction bound to carbonates is the main solid phase for many metals (Cd, Pb, Zn, Ni and Cu) in arid and semiarid soils especially contaminated ones. Metals could be co-precipitated by carbonate, entering their structure or absorbed by Fe- and Mn oxides which are deposited on the surface of carbonates [10].

Metals are predominantly accumulated (Table 1) in the Fe-Mn oxides (40% of the amount of fractions) in artificially polluted soil. In fact, numerous research studies have shown the highest affinity of Zn with Fe-Mn oxides [11]. This is also confirmed by the methods of synchrotron radiation spectroscopic analysis [12]. The humic acids and goethites containing adsorbed copper ions have the highest intensity of β peak [13]. As a consequence, the triple complexes with the copper ion bonded to organic and mineral component are formed.

Conclusion. A large portion of Zn compounds (67% of the total of fraction) is composed of primary and secondary silicates that is a characteristic of the regional feature of soil in PreCaucasian Plain. Decrease of Zn bonding with soil compounds occurs with increasing of soil pollution rate. Fe-Mn nonsilicate compounds and carbonates play pivotal roles in bonding of Zn ions. The result of the extraction fractionation of metals in the investigated soils is consistent with the results of XANES spectroscopic study. This allows one to complete the knowledge of qualitative changes in metal compounds (determined by the XANES method) by means of quantitative data analysis on the metal ions bonded with different strengths to soil components.

ACKNOWLEDGMENTS

This work was supported by projects of Southern federal university 213.01-24/2013-92.

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