



## Usage of X-ray absorption spectroscopy and extractive fractionation in studies of the Cu (II) and Zn (II) ions in soils

Dina Nevidomskaya <sup>a,b,\*</sup>, Tatiana Minkina <sup>b</sup>, Alexander Soldatov <sup>b</sup>,  
Galina Motuzova <sup>c</sup>, Yuliya Podkovyrina <sup>b</sup>

<sup>a</sup> Institute of Arid Zones of the Southern Scientific Centre RAS, Rostov-on-Don, Russia

<sup>b</sup> Southern Federal University, Rostov-on-Don, Russia

<sup>c</sup> Lomonosov Moscow State University, Moscow, Russia

### Abstract

XANES spectroscopy is an effective method for the study of bonds between metals and soil components. The study of structural organization in different soil samples and soil phases saturated with Cu<sup>2+</sup> and Zn<sup>2+</sup> ions by using XANES allowed determining the mechanism of their interaction with soil phases and all the chemical bindings taken place in the course of this process. Changes in the structure of the metal ion, in particular breakdown of the symmetry of electron orbits of atoms, take place due to interaction with soil components. Application of this method demonstrated that the state of copper and zinc introduced in chernozem as oxides did not change after one year of incubation. Copper is absorbed after being introduced as soluble salts, and copper ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes. Zinc included into octahedral structures of layered minerals and hydro(oxides) can be inner- and outer-sphere adsorbed. It is shown that the action of the metal bound to soil components becomes weakened in case of increasing the Cu and Zn load (from 2000 to 10000 mg/kg) especially applied in the form of soluble salts. Extractive fractionation of metal compounds in chernozem samples, artificially contaminated with copper and zinc salts serves as evidence of absorbing the applied Cu<sup>2+</sup> ions by the soil organic matter and Zn<sup>2+</sup> ions – by silicates, carbonates, and Fe-Mn oxides.

### Article Info

Received : 12.07.2014

Accepted : 17.10.2014

**Keywords:** XANES spectroscopy, extractive fractionation, compounds, copper, zinc

© 2014 Federation of Eurasian Soil Science Societies. All rights reserved

### Introduction

The ecological importance of soil compounds of metals is determined by the composition of these compounds. Currently extraction methods are widely applied for analysis of the composition of metal compounds. However the influence of extractive agents is not selective and provides only indirect information on the relationships between metals and other soil components. The real forms of metal occurrence in soil are still unknown. During the last 20 years, development of methods of X-ray absorption spectroscopy provided information on the structural organization of soil metal compounds (Manceau et al., 2002; *Synchrotron-Based Techniques...*, 2010). Application of the EXAFS and XANES methods allows us to determine the geometric structure of these compounds, reveal real phases carrying metals in soils, and establish chemical bond types.

\* Corresponding author.

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

Tel.: +78632509832

E-mail address: [dnevidomskaya@mail.ru](mailto:dnevidomskaya@mail.ru)

ISSN: 2147-4249

Today, in addition to EXAFS XANES method (X-ray absorption near-edge structure) is widely applied. The XANES method proves to be most effective for studying inorganic minerals (Berry et al., 2004; Farrel et al., 2002) and metal-organic compounds (Chan et al., 2005; Kostenko et al., 2008). Due to the heterophase pattern of soil the metal compounds display a great variety in soil. In the XANES procedure the length of photoelectrons is greater as compared to that in EXAFS and thanks to the multiple dissimilation process on surrounding atoms it is possible to determine parameters of the atomic structure in the area surrounding the metal ion. Moreover, using the XANES method one can obtain information on the oxidation degree of absorbing atom. The most efficient is a combination of experimental investigations with theoretical «first principle» calculations (Smolentsev and Soldatov, 2006, 2009; Soldatov, 2008).

The present paper is aimed to analyze a local atomic and electronic structure of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the artificially contaminated soil using X-ray absorption spectroscopy and chemical extractive fractionation.

## Material and Methods

In a model experiment the samples taken in ordinary chernozem of Rostov region were artificially contaminated with higher portions of  $\text{Cu}(\text{NO}_3)_2$  (2000 mg/kg) and  $\text{CuO}$  (2000 and 10 000 mg/kg). The metals were incubated in soil samples for a year.

The total content of heavy metals in soil was determined using the X-ray fluorescence method. Sequential fractionation of heavy metals in soil was conducted by Tessier method (Tessier et al., 1979). It allows determining 5 fractions of metals in soil: exchangeable, bound to Fe-Mn oxide, bound to carbonate, bound to the organic matter, and bound to silicate (residual). The total content of heavy metals in soils was determined by the total content of metals in all fractions.

The experimental XANES spectra at the K-edge of Zn (9659 eV) and K-edge of Cu (8979 eV) were obtained by spectrometer Rigaku R-XAS Looper in the fluorescence regime because the concentration of the studied metals was rather low. The Ge (440) crystal-monochromator was used, what permitted to obtain a good energy resolution (2 eV). Lead and copper foils were used as standard samples for the energy calibration. Every spectrum was measured by a step of 0.5 eV. To obtain the data for statistical method the exposition time of 60 sec was taken for each point in the spectrum. 5-7 spectra were statistically averaged to determine a final spectrum for every sample.

To obtain detail information on the state of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the studied soil samples the first derivatives of XANES spectra were calculated and permitted to identify differences in these spectra. The experimental spectra of initial Cu- and Zn-containing compounds helped to compare the spectra of soil and soil components. Under consideration are the following results of comparison: 1) experimental spectra of soil samples and some soil compounds treated by  $\text{CuO}$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{ZnO}$ ,  $\text{Zn}(\text{NO}_3)_2$ ; 2) experimental spectra of initial  $\text{CuO}$  and  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{ZnO}$  and  $\text{Zn}(\text{NO}_3)_2$  compounds; 3) theoretical spectra of the above compounds. The calculation was performed using final differences in a complete potential FDMNES 2012 (Bunau and Joly, 2009).

## Results and Discussion

Molecular-structural analysis was carried out in order to determine the type of metal bond with soil components. Figure 1a demonstrates experimental spectra of chernozem samples contaminated with  $\text{CuO}$  and  $\text{Cu}(\text{NO}_3)_2$  as compared to those obtained for their initial forms. All the spectra display the A peak in the middle part of the spectrum edge (~ 8985-8990 eV). The fact that there is no chemical shift of the main absorption edge (B) in soil samples as compared to initial ones indicates that the oxidation state of Cu ions reveals no change depending on its concentration in the range from 2000 mg/kg to 10 000 mg/kg and forms of applied metals. The parameters of theoretical and experimental spectra of standard samples are conformed very well.

In the near-edge area (~ 8975-8980 eV) a weak  $\alpha$  maximum of the XANES spectrum derivate is observed (Figure 1b). Most probably, it corresponds to quadrupole  $1s \rightarrow 3d$  electronic transition that is characteristic for Cu bond in low-symmetry positions. The stepped pattern of the structure presented by  $\alpha$  and  $\beta$  peaks in the edge area of the first derivative of experimental and theoretical spectra (Figure 1b) is most likely caused by the Jahn-Teller effect, indicating the tetragonal distortion of octahedral type of Cu bond (Lee et al., 2005; Palladino et al., 1993; Xia et al., 1997). The distance between maxima of  $\alpha$  and  $\beta$  peaks is about 10 eV. Earlier it was shown that this parameter can be used for qualitative evaluation of axial and equatorial Cu-O

distances in Cu-containing octahedral types. The intensity of the  $\beta$  peak speaks about the main  $1s \rightarrow 4p_z/p_y$  transition (Furnare et al., 2005).

The form, size and peculiarities of edge and near-edge areas of XANES spectra for soil samples contaminated with CuO and Cu(NO<sub>3</sub>)<sub>2</sub> have clear differences mainly associated with the difference in their local atomic structure around the central Cu ion. The spectra of soil samples contaminated with CuO demonstrate close similarity to experimental spectra of initial CuO compound. On the contrary, the spectra of soils contaminated with Cu(NO<sub>3</sub>)<sub>2</sub> are significantly different from those obtained for initial Cu(NO<sub>3</sub>)<sub>2</sub> providing evidence of changes in the area surrounding the copper ion introduced into the soil. Copper nitrate is soluble in water (pK Cu(NO<sub>3</sub>)<sub>2</sub> = 0.40, pK CuO = - 7.66). By this reason, for a year of incubation the copper ions have been absorbed by soil components and formed various compounds, including metal-organic complexes with different functional groups (Minkina et al., 2013).

When comparing the first derivative of XANES spectra for Cu(NO<sub>3</sub>)<sub>2</sub> with the spectrum for soil, it is possible to see that the  $\alpha$  peak is higher as compared to that obtained for CuO (Figure 1b). The same peculiarities of Cu(NO<sub>3</sub>)<sub>2</sub> spectra have been described in Alcacio's publication (Alcacio et al., 2001).

Figure 2a shows XANES spectra of the K-edge for Zn and their first derivative (Figure 2b), where the pre-edge  $1s \rightarrow 3d$  transition is absent, because  $d^{10}$  level is completely filled up as compared to that for Cu. The main peak in the first derivative of XANES spectra displays the  $1s \rightarrow 4p$  electronic transition.

The molecular-structural state of Zn can be assessed as based upon oscillation (near  $\sim 9710$  eV), that is characteristic of octahedral coordination of Zn ion and hence the formation of hydrated absorbed zinc and layered Zn phases (Manceau et al., 2002).

In this case the Zn ions included into the octahedral structures of layered minerals and hydroxides can be inter- and out-sphere absorbed. Based upon a comparative analysis of experimental XANES spectra for K-edge of Zn and pure Zn(NO<sub>3</sub>)<sub>2</sub> as well as the theoretical spectrum it is possible to show that all the spectra are identical in their form but they reveal differences in intensity and energy position of spectral peculiarities. The spectrum of the soil sample enriched with Zn nitrate displays a higher reflex intensity. The first derivative of the experimental XANES spectrum for the soil sample contaminated with ZnO is significantly differed from derivatives of X-ray absorption spectrum for initial compound and from theoretical spectrum, thus indicating that the pollutant composition has been changed for a year of incubation. There is a maximum in the XANES first derivative ( $\sim 9661$ - $9665$  eV) as referred to Zn-containing octahedral structures. Thus, Zn ions introduced into the soil in the form of oxides and nitrates are in low-symmetry due to octahedral distortion in their interaction.

Fractionation of metal compounds showed that Cu and Zn have been dominated in the fraction associated with silicates (60 and 67%) in the unpolluted chernozem (Table 1). Such are the regional biogeochemical features of the soil microelement composition in Rostov oblast and of the mineralogical composition of the parent rocks. The yellow-brown loess – like loams and clays of the Pre-Caucasian Plain inherited the stable minerals of the initial rocks with the typical microelement composition of the minerals (Akimtsev et al., 1962). The mobility of Cu and Zn in the initial soil is low. The relative content of metals in the first two fractions doesn't exceed 3-4%, the mobile exchangeable forms make up only 1%. The differences in the fractional composition of these metal compounds are as follows: the fraction of the organic matter reveals a higher content of Cu, whereas the Zn content is rather high in the fraction bound to Fe-Mn oxides.

In soil contaminated with Cu<sup>2+</sup> and Zn<sup>2+</sup> ions the absolute content of all metal compounds shows an increase. In case of increasing Cu and Zn applied in the amount from 2000 to 10 000 mg/kg the metal quantity is also increased by 1.2-5 times in all the studied compounds. It was established that the fractional composition of metal compounds is highly affected by forms of metal input to soil. In case of applying Cu (2000 mg/kg) in the form of nitrate the share of mobile metal compounds made up 6% (the first 2 extracts) and in the form of oxide – only 4%.

As regards Zn, these differences are expressed to a greater extent: the relative content of Zn applied in the form of nitrate was estimated as 22% and in the oxide form – 11%. This is conditioned by a low solubility of metal oxides. This fact speaks about the absence of direct dependence between the increase in the relative content of mobile Cu and Zn compounds and the increase in soil contamination with metal oxides (Table 1) that has been observed earlier in case of soil contamination with metals applied in the form of soluble salts (Pinskii et al., 2010).

According to the data of extractive fractionation there are a 4.5 times differences in the share of mobile Zn compounds applied in the form of nitrate and oxide. Therefore, zinc in the form of nitrate interacts more intensive with soil components and forms different compounds. The Zn content in the exchangeable fraction and specifically absorbed fraction (bound to carbonates) becomes significantly increased. The relative content of the most mobile Zn exchangeable fraction increased by 8 times and the specifically absorbed (bound to carbonates) – by 7 times in case of soil contamination with 2000 mg/kg of Zn nitrate. The significant role of carbonates in metal fixation and Zn in particular has been earlier described (Adriano, 2001; Minkina et al., 2008). The affinity of metal ions to carbonates is determined by their low solubility.

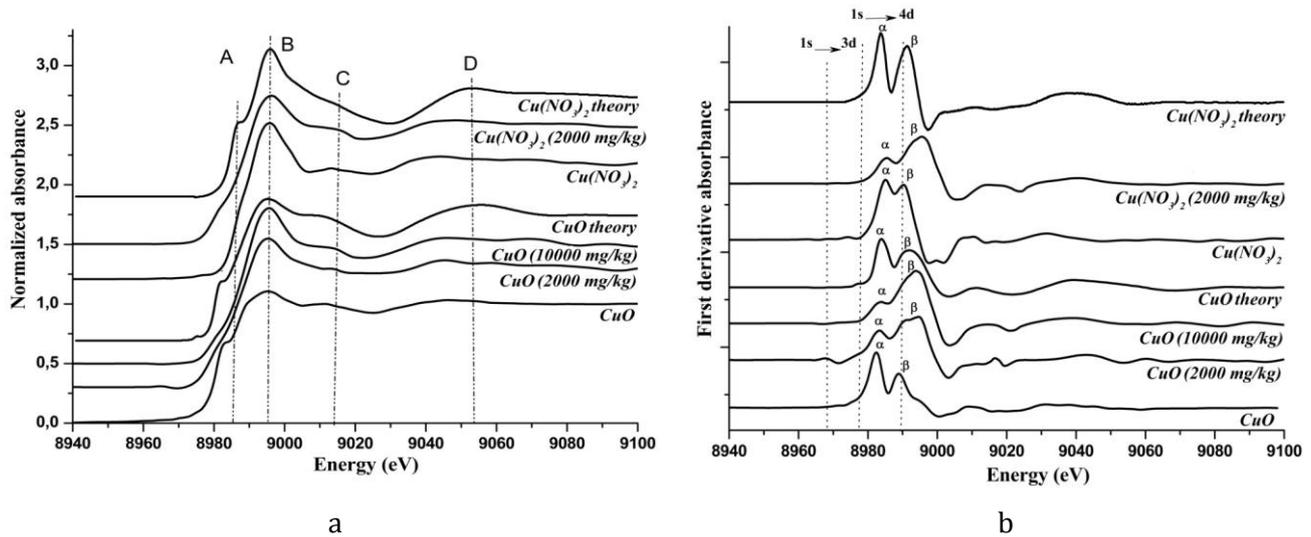


Figure 1. The experimental and the theoretical Cu K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the soil samples: 1 - theoretical spectra of  $\text{Cu}(\text{NO}_3)_2$ , calculated by FDMNES 2012; 2 - experimental spectra of  $\text{Cu}(\text{NO}_3)_2$ -treated soil sample (2000 mg/kg); 3 - experimental spectra of  $\text{Cu}(\text{NO}_3)_2$ ; 4 - theoretical spectra of  $\text{CuO}$ , calculated by FDMNES 2012; 5 - experimental spectra of  $\text{CuO}$ -treated soil sample (10 000 mg/kg); 6 - experimental spectra of  $\text{CuO}$ -treated soil sample (2000 mg/kg); 7 - experimental spectra of  $\text{CuO}$

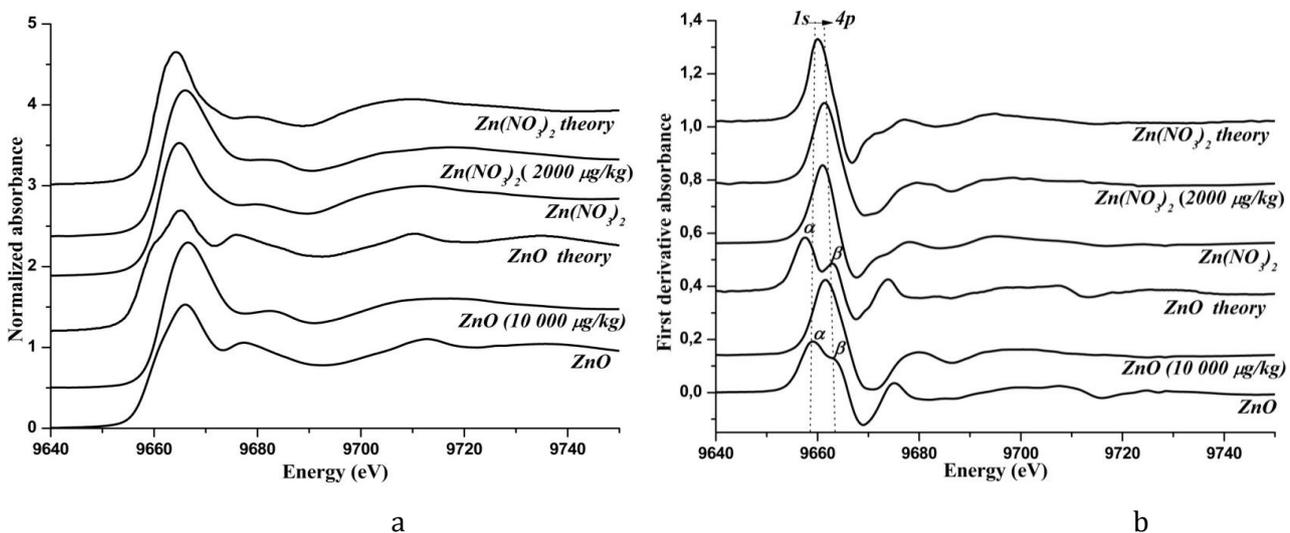


Figure 2. The experimental and the theoretical Zn K-edge X-ray absorption spectra (a) and their first derivatives (b) for the reference compounds and the soil samples: 1 - theoretical spectra of  $\text{Zn}(\text{NO}_3)_2$ , calculated by FDMNES 2012; 2 - experimental spectra of  $\text{Zn}(\text{NO}_3)_2$ -treated soil sample (2000 mg/kg); 3 - experimental spectra of  $\text{Zn}(\text{NO}_3)_2$ ; 4 - theoretical spectra of  $\text{ZnO}$ , calculated by FDMNES 2012; 5 - experimental spectra of  $\text{ZnO}$ -treated soil sample (10 000 mg/kg); 6 - experimental spectra of  $\text{ZnO}$

Table 1. Fractional composition of Cu and Zn compounds in ordinary chernozem

Addition doses of HM, mg/kg	Exchangeable	Fraction				Sum of fraction
		Connected with carbonate	Connected with Fe-Mn oxides	Connected with organic matter	Connected with silicates (Residual)	
No added metal	0.4±0.1	1.2±0.4	5.0±1.0	11.1±1.0	27.3±5.2	45.0±5.9
2000 Cu(NO <sub>3</sub> ) <sub>2</sub>	52.0±5.7	72.7±4.1	561.0±19.1	819.0±27.6	562.9±24.7	2067.6±48.3
2000 CuO	27.4±2.6	62.7±9.4	563.1±23.2	752.3±14.2	627.5±18.8	2033.0±41.9
10 000 CuO	67.4±5.1	78.0±16.6	4102.6±34.2	3419.4±32.9	2373.6±55.3	10041.0±121.7
% of the sum of fraction						
No added metal	1	3	11	25	60	100
2000 Cu(NO <sub>3</sub> ) <sub>2</sub>	2	4	27	40	27	100
2000 CuO	1	3	28	37	31	100
10 000 CuO	1	1	41	34	23	100
mg/kg						
No added metal	0.6±0.1	1.8±0.1	14.2±1.9	11.5±1.4	56.9±11.0	85.0±11.5
2000 Zn(NO <sub>3</sub> ) <sub>2</sub>	173.6±8.6	289.4±33.2	826.1±27.2	348.7±36.0	421.2±22.6	2059.0±21.9
2000 ZnO	49.1±5.7	56.9±7.4	777.2±14.3	346.1±25.8	844.7±37.9	2074.0±54.6
10 000 ZnO	245.0±11.6	296.0±12.8	3796.0±41.7	1624.0±56.1	4111.0±79.1	10072.0±99.1
% of the sum of fraction						
No added metal	1	2	17	14	67	100
2000 Zn(NO <sub>3</sub> ) <sub>2</sub>	8	14	40	17	20	100
2000 ZnO	2	3	37	17	41	100
10 000 ZnO	2	3	38	16	41	100

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 contaminated arid and semiarid soils. Metals can be co-precipitated together with carbonates, being included into their structure or absorbed by Fe- and Mn oxides which are precipitated at the surface of carbonates (Santillan-Medrano and Jurinak, 1975).

## Conclusion

Changes in the structure of the metal ion, in particular breakdown of the symmetry of electron orbits of atoms, take place due to interaction with soil components.

The increased degree of soil contamination with Zn and Cu is accompanied by relative decreasing the stable connection between these metals and soil components. The most active is the organic matter to fix the copper ions in soil but non-silicate compounds of Fe and Mn and carbonates retain Zn ions to a lesser extent.

Copper is absorbed after being introduced as soluble salts, and copper ions are incorporated in the octahedral and tetrahedral sites of minerals and bonded with humic materials at the expense of covalent bond and the formation of coordination humate copper complexes. Zinc included into octahedric structures of layered minerals and hydro(oxides) can be inner- and outer-sphere adsorbed.

The results of extractive fractionation of metal compounds in the studied soil are coincided with those obtained by XANES method. These results permit to add and extend the knowledge about qualitative changes in the state of metals in contaminated soils determined by XANES method and to obtain the quantitative data about the metal compounds fixed by soil components with different stability.

## Acknowledgements

This research was supported by projects of the Ministry of Education and Science of Russia, no. 5.885.2014/K, the Russian Foundation for Basic Research, no. 14-05-31469 mol\_a, no. 14-05-00586-a.

## References

- Adriano, D.C., 2001. Trace elements in terrestrial environments, Springer-Verlag, New York, Berlin, Heidelberg.
- Akimtsev, V.V., Boldyreva, A.V., Golubev, S.N., Kudryavtsev, M.I., Rudenskaya, K.V., Sadimenko, P.A., Sobornikova, I.G., 1962. "The Contents of Trace Elements in Soils of Rostov Oblast". In: Trace Elements and Natural Radioactivity of Soils (Workshop Materials), Izd. Rostovsk. Univ., Rostov-on-Don, pp. 38–41 [in Russian].
- Alcacio, T.E., Hesterberg, D., Chou, J.W., Martin, J.D., Beauchemin, S., Sayers, D.E., 2001. Molecular scale characteristics of Cu (II) bonding in goethite-humate complexes. *Geochimica et Cosmochimica Acta* 65 (9): 1355–1366.
- Berry, A.J., O'Neil, H.S.C., 2004. A XANES determination of the oxidation state of chromium in silicate glasses. *American Mineralogist* 89: 1597–1609.
- Bunau, O., Joly, Y., 2009. Self-consistent aspects of x-ray absorption calculations. *Journal of Physics: Condensed Matter* 21, 345501 (11 pp.).
- Chan, J., Merrifield, M.E., Soldatov, A.V., Stillman M.J., 2005. XAFS spectral analysis of the cadmium coordination geometry in cadmium thiolate clusters in metallothionein. *Inorganic Chemistry* 44: 4923–4933.
- Farrel, S.P., Fleet, M.E., Stekhin, I.E., Kravtsova, A.N., Soldatov, A.V., 2002. Evolution of Local Electronic Structure in Alabandite and Ninningerite Solid Solutions [(Mn,Fe)S, (Mg,Mn)S, (Mg,Fe)S] using Sulfur K- and L-edge XANES Spectroscopy. *American Mineralogist* 87: 1321–1332.
- Furnare, L.J., Strawn, D.G., Vailionis, A., 2005. Polarized XANES and EXAFS spectroscopic investigation into copper (II) complexes on vermiculite. *Geochimica et Cosmochimica Acta* 69 (22): 5219–5231.
- Kostenko, A.V., Kravtsova, A.N., Soldatov, A.V., Feiters, M., 2008. Determination of the local atomic structure of the active center of bromoperoxidase protein via the analysis of X-ray absorption spectra. *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques* 2 (6): 900–903.
- Lee, Y.J., Elzinga, E.J., Reeder, R.J., 2005. Cu (II) adsorption at the calcite–water interface in the presence of natural organic matter: kinetic studies and molecular-scale characterization. *Geochimica et Cosmochimica Acta* 69 (1): 49–61.
- Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. Applications of Synchrotron Radiating in Low-Temperature Geochemistry and Environmental Science. Reviews in Mineralogy and Geochemistry 49, DC., Washington, pp. 341–428.
- Minkina, T.M., Motuzova, G.V., Nazarenko, O.G., Kryshchenko, V.S., Mandzhieva, S.S., 2008. Forms of Heavy Metal Compounds in Soils of the Steppe Zone. *Eurasian Soil Science* 41 (7): 708–716.
- Minkina, T.M., Soldatov, A.V., Motuzova, G.V., Podkovyrina, Yu.S., Nevidomskaya, D.G., 2013. Molecular–structural analysis of the Cu (II) ion in ordinary chernozem: evidence from XANES spectroscopy and methods of molecular dynamics. *Doklady Earth Science*. 449, part 2, 418–421.

- Palladino, L., Della Longa, S., Reale, A., Belli, M., Scafati, A., Onori, G., and Santucci, A., 1993. X-ray absorption near edge structure (XANES) of Cu(II)-ATP and related compounds in solution: Quantitative determination of the distortion of the Cu site. *Journal of Chemical Physics* 98: 2720–2726.
- Pinskii, D.L., Minkina, T.M., Gaponova, Yu.I., 2010. Comparative analysis of mono- and polyelement adsorption of copper, lead, and zinc by an ordinary chernozem from nitrate and acetate solutions. *Eurasian Soil Science* 43 (7): 748–756.
- Santillan-Medrano, J., Jurinak, J.J., 1975. The chemistry of lead and cadmium in soil solid phase formation. *Soil Science Society of America Proceedings* 39 (5): 851–856.
- Smolentsev, G.Y., Soldatov A.V., 2009. Analysis of time-resolved XANES spectra for determining the organometallic compound structure in solution. *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques* 3 (3): 398–401.
- Smolentsev, G.Y., Soldatov, A.V., 2006. Quantitative local structure refinement from XANES: multy-dimensional interpolation approach. *Journal of Synchrotron Radiation* 13 (1): 19–29.
- Soldatov, A.V., 2008. X-ray absorption near edge structure as a source of structural information. *Journal of Structural Chemistry* 49 (Supp): 102–106.
- Synchrotron-Based Techniques in Soils and Sediments, 2010. Balwant Singh and Markus Gräfe (Eds). Elsevier B.V. The Netherlands. 34, pp. 1-480.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844–851.
- Xia, K., Blear, W., Helmke, P., 1997. Studies of nature of binding sites of first row transition elements bound to aquatic and soil humic substances using X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* 61 (11): 2223–2235.