

Combining Sequential Extractions and X-ray Absorption Spectroscopy for Quantitative and Qualitative Zinc Speciation in Soil

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The combined use of X-ray absorption spectrometry and extractive fractionation is an effective approach for studying the interaction of metal ions with soil compounds and identifying the phases-carriers of metals in soil and their stable fixation. These studies were carried out using the technique of X-ray absorption spectroscopy and chemical extractive fractionation.

In a model experiment the samples taken in Calcic Chernozem were artificially contaminated with higher portion of $Zn(NO_3)_2$ (2000 mg/kg). The metal were incubated in soil samples for 2 year. The samples of soil mineral and organic phases (calcite, kaolinite, bentonite, humic acids) were saturated with Zn^{2+} from a solution of nitrate salts of metal. The total content of Zn in soil and soil various phases was determined using the X-ray fluorescence method. Extended X-ray absorption fine structure (EXAFS) Zn was measured at the Structural Materials Science beamline of the Kurchatov Center for Synchrotron Radiation. Sequential fractionation of Zn in soil conducted by Tessier method (Tessier et al., 1979) which 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). This methodology has so far more than 4000 citations (Web of Science), which demonstrates the popularity of this approach.

Much Zn compounds are contained in uncontaminated soils in stable primary and secondary silicates inherited from the parental rocks (67% of the total concentrations in all fractions), which is a regional trait of soils in the fore-Caucasian plain.

Extracted fractionation of metal compounds in soil samples, artificially contaminated with Zn salts, indicates the priority holding of Zn^{2+} ions by silicates, carbonates and Fe-Mn oxides. The Zn content significantly increases in the exchangeable fraction. Atomic structure study of the soil various phases saturated with Zn^{2+} ion by using (XANES) -ray absorption spectroscopy allowed the determination of mechanism of metal ions interaction with soil phases and the resulting types of chemical bonds. Interaction with soil components modifies the electron structure of the metal ions themselves. The soil contamination with Zn is accompanied by decreasing the stable connection between metal and soil components. Interacting with humic acids in chernozem, the Zn^{2+} ion is coordinated by functional groups and ligands and forms unstable outer-sphere complexes. Zinc included into octahedral structures of layered minerals and hydro(oxides) can be inner-and outer-sphere adsorbed. The Zn^{2+} ions enable to replace Ca^{2+} ions in octahedral positions being coordinated with carbonate ions as ligands, thus forming absorbed complexes at the surface of mineral calcite.

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