



Elucidating the role of ligands on the adsorption mechanisms of Zn in various mineral systems using XAFS spectroscopy

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Naturally occurring ligands such as humic acid, siderophores and phosphate play a crucial role in controlling the mobility of heavy metals within the soil environment. The nature of influence of these ligands is likely dependent on their interaction with heavy metals as well as with soil mineral surfaces. In this study, X-ray absorption fine structure (XAFS) spectroscopy, which is able to determine coordination chemistry of absorbing element, was used to investigate the impact of ligands on Zn adsorption mechanisms by soil minerals. Common soil minerals were selected for the study. The ligands investigated are phosphate, citrate, humic acid and siderophore. Zinc adsorption onto the minerals was conducted at pH 7.5 with a 1:1 Zn to ligand molar ratio over a period of 24 hours and under N₂ atmosphere. XAFS data were collected in fluorescence mode at the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge, Louisiana. Data reduction was conducted using ATHENA and EXAFS data analysis using ARTEMIS. EXAFS spectral analysis revealed that upon adsorption, Zn forms tetrahedral coordination with first shell oxygen atoms both in the presence and absence of ligands. The investigated ligands had no impact on the first shell coordination sphere of Zn at the selected pH and Zn: ligand molar ratio. EXAFS fitting results also revealed that Zn adsorbs to mineral surfaces forming inner sphere complexes, and the formation of a Zn surface precipitate was also evident in selected mineral-ligand systems. The impact of ligands on the second neighbor coordination shell was dependent on the mineral surface and ligand. In the case of the ferrihydrite mineral, the presence of phosphate, citrate and humic acid generally decreased the number of second neighbor Zn and Fe atoms surrounding Zn, but inner sphere complexes and surface precipitates were still evident. In the case of gibbsite, a precipitate of Zn and P formed on the mineral surface in the presence of phosphate. In the presence of citrate, a Zn-citrate complex was also found on the surface of gibbsite. Overall, the impact of ligands on the adsorption mechanisms of Zn was dependent on the nature of ligand and type of mineral surface.