

***In Situ* Studies of Metal Speciation in the Environment**

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Pollution from heavy metals is a significant threat to the environment. The mobility of metals in sediments depends critically on the way in which they are chemically bound in the soils. When attempting to characterize chemical speciation, it is preferable to perform the studies in a manner that is least disruptive to the sample. For this reason, *in situ* x-ray absorption spectroscopy was used to characterize the speciation of Zn in sediments obtained from the DePue Wildlife Management Area in Illinois.

Soil sample cores were extracted from a number of locations on the site. The cores were measured *in situ* on the MR-CAT beamline 10-ID. The results revealed a number of mineral forms and Zn adsorbed to clays and synthetic amorphous precipitates of hydrous ferric oxides (HFO).

The spectra were modeled as linear combinations of spectra of the various standards using several methods implemented as Mathematica notebooks: linear least squares fitting using singular value decomposition (SVD) and principal components analysis (PCA), nonlinear least squares fitting with constraints, and linear programming with constraints. We found that the most reliable methods were the ones with built-in positivity and normalization constraints.

The results indicate that Zn is primarily bound to montmorillonite clay and HFO, with only small fraction of other species. The apparent fraction of Zn bound to HFO is surprisingly high, given the much higher concentration and specific surface area of HFO relative to the clay. The reasons for this are a subject of further investigation. The ligands to the Zn were principally oxygen with no evidence of substantial sulfur coordination. Despite large variations in concentration with depth, only very small differences in chemical speciation were observed versus depth or position on the site.

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