Effect of Organic Ligands on U and Fe Biogeochemistry in Wetland Sediments

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Project Abstract: The Argonne SFA (*Wetland Hydrobiogeochemistry*) studies the processes that govern elemental cycling and particle formation/transport at a DOE field site, the Tims Branch wetland at the Savannah River Site. The organic-rich sediments in this riparian ecosystem experience changing redox conditions that induce transformations of the major elements (C, Fe, P, S), as well as of several contaminants discharged during past operations at the site (Ni, Cr, Zn, Pb, U). Although laboratory studies have isolated some of the effects of redox transformations on speciation, unexpected behavior is sometimes observed in complex natural systems due to unanticipated interactions between the multiple constituents. We characterized a number of intact sediment cores by synchrotron x-ray spectroscopy to determine the elemental distribution and the speciation of Fe and U with depth. The valence of U was dependent on local saturation state. We found U(IV) predominantly in hydrated sediments, indicating the establishment of reducing conditions due to microbial activity. U was present in a form different from synthetic nano-uraninite (UO_2), indicating a significant influence of minerals and organic ligands on the speciation of U(IV) in wetland sediments. To better understand the effects of each, we carried out U(VI) bioreduction experiments with added clay minerals and/or organic ligands (citrate, EDTA, DFOB). Addition of clays alone did not change U(IV) speciation (i.e., uraninite formed). The presence of citrate resulted in a soluble U(IV) complex under all tested conditions. EDTA and DFOB also formed soluble U(IV) complexes, but in systems with Fe-containing clays, the U(IV) complex remained in the solids by interlayer uptake or as a bridging ternary complex. These results illustrate the intricate interdependencies between the constituents of contaminated sediments and provide information for the inclusion of corresponding reactions in transport models. Improved mechanistic models in turn lead to better predictions and policy decisions.