

Biogeochemistry and Contaminant Speciation in Savannah River Site Sediments

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<https://www.anl.gov/bio/project/subsurface-biogeochemical-research>

Project Abstract: The Argonne SBR SFA project (Wetland Hydrobiogeochemistry) focuses on the study of molecular to core-scale processes at a DOE field site, wetlands associated with Tims Branch at the Savannah River Site. The site has characteristics typical of most riparian environments but is unique in that several contaminants (Ni, Cr, Zn, Pb, U) were discharged during past operations, providing an opportunity to study the effect of wetland processes on their long-term fate. Based on maps of the radiation distribution along Tims Branch, sediment cores were collected periodically at locations with elevated U concentrations. The in situ elemental distribution with depth was determined at 500-micron resolution by synchrotron x-ray fluorescence (XRF) spectroscopy on the intact cores, calibrated by acid digestion of subsamples. Results reveal that U is accumulated in the top 5-10 cm of the sediment at most locations, suggesting surface deposition and transport of contaminated particles. However, several locations showed U accumulation as deep as 25-30cm, suggesting porous media transport or burial. Correlations between some contaminants and mineral-specific elements (Fe, Ti) were observed. The in situ valence of U was determined using x-ray absorption spectroscopy (XANES) on the intact cores. Results show that in water-unsaturated sediments the predominant valence state is U(VI). In contrast, when U is present in water-saturated sediments the predominant valence state is U(IV), even within the 5-10cm layer that is close to the air-sediment interface. These results indicate a previously unappreciated importance of reduced U(IV) species controlling the mobility of U at this site. U L_{III}-edge EXAFS spectroscopy on sediment subsamples with high concentration of reduced U(IV) indicates that the reduced species is not mineralized uraninite (UO₂), but mononuclear U(IV) atoms associated with binding groups in the sediment. Comparisons to spectra obtained from defined mononuclear U(IV) species in laboratory reactors indicate that U(IV) in the sediment is not complexed to phosphate or carboxyl ligands, suggesting that U(IV) is not associated with organic material. The best spectral resemblance is to a mononuclear U(IV) species adsorbed on TiO₂, suggesting association of U(IV) with minerals in the sediment. Laboratory experiments indicate that Suwanee River humic acid is not able to complex U(IV) in co-precipitation experiments with U(IV). In contrast, the siderophore DFOB was found to complex U(IV) in the presence of reduced NAu-2 clay. The mechanistic understanding provided by these findings improve our ability to predict the transport of contaminants in natural environments using Reactive Transport Models.