

## Poster #22-27

**Savannah River Site Sediments: Biogeochemistry and U speciation**

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

The Argonne SBR SFA is focused on hydrobiogeochemical investigations of a wetland field site (Tims Branch at the Savannah River Site), which is representative of many riparian environments and unique in that it received large amounts of contaminant metals (Ni, Cr, Cu, Pb) and uranium (U) during the manufacture of fuel and target assemblies. The radiological contamination along Tims Branch was mapped using aerial and field-deployable detectors, and sediment cores were collected at locations with elevated U concentrations.

Sediment profiles consisted of organic-rich layers (OL) overlaying mineral layers (ML). Acid digestions indicated elemental content ranging from constituents of the native minerals (e.g., Mg, Al, K, Ca, and Ti) to legacy contaminants (e.g., Cr, Ni, Cu, Pb, and U). The OL was enriched in U ( $44.5 \pm 17.1$  ppm) relative to the ML ( $6.38 \pm 2.19$  ppm). Microbial community analysis (16S rRNA) showed a diverse microbial population, dominated by sequences from the phyla *Proteobacteria*, *Nitrospirae*, *Chloroflexi*, and others. Fe K-edge XANES indicated 13% Fe(II) in the unsaturated portion of the OL and 30% and 26% in the saturated portions of the OL and ML, indicating the presence of reducing conditions. U L<sub>III</sub>-edge XAFS spectroscopy indicated that in the unsaturated portion of the OL and in the ML, U was present as U(VI), whereas in the saturated portion of the OL >95% of the U was present as mononuclear U(IV) that rapidly oxidized when exposed to air. Oxic/anoxic incubations of the sediments with glucose indicated a facile and reversible transition between adsorbed U(VI) and mononuclear U(IV) species.

Previous studies at Tims Branch concluded that U(VI) is the predominant species; our new observations of variable U oxidation state with depth and location of the core—as well as the stabilization of mononuclear U(IV) species in the organic-rich layer—suggest that there are significant knowledge gaps in our understanding of the processes responsible for the mobilization of U. We also carried out experiments to understand the role of organic matter in the U(IV) species formed at the field site. Building on prior SFA work, we reduced TiO<sub>2</sub>- adsorbed U(VI) in the presence of humic acid (HA). The U(IV) speciation was determined by EXAFS spectroscopy, which suggested U(IV) complexation with the HA. Similarly, the siderophore DFOB was found to complex U(IV) following reduction of a U(VI)-DFOB complex adsorbed to NAu-2 clay. The mechanistic understanding provided by these results improve our ability to predict U transport using Reactive Transport Models.