The Argonne National Laboratory Subsurface Biogeochemical Research Program SFA: Wetland Hydrobiogeochemistry

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Project: Argonne Wetland Hydrobiogeochemistry SFA

Project Website: https://doesbr.org/documents/ANL_SFA_flyer.pdf
https://www.anl.gov/bio/project/subsurface-biogeochemical-research

Project Abstract: Within wetlands, movement of water and biogeochemically catalyzed transformations of its constituents determine the mobility of nutrients and contaminants, emission of greenhouse gasses into the atmosphere, carbon (C) cycling, and the quality of water itself. The long-term objective of the Argonne *Wetland Hydrobiogeochemistry* Scientific Focus Area (SFA) is the *development of a mechanistic understanding and ability to model the coupled hydrological, geochemical, and biological processes controlling water quality in wetlands and the implications of these processes for watersheds commonly found in humid regions of the United States.* The Argonne *Wetland Hydrobiogeochemistry* SFA focuses research on a riparian wetland within Tims Branch at the Savannah River Site. Tims Branch contains riparian wetlands representative of those commonly found in humid regions of the Southeast that have C-rich soils and high Fe content. However, it is unique in that parts of the watershed received large amounts of contaminant metals and uranium as a result of previous industrial-scale manufacturing of nuclear fuel and target assemblies. Understanding the function of wetlands in relation to hydrologic exchange, including the concentration of nutrients and contaminants within the soluble and particulate components of groundwater and surface waters addresses the goal of the ESS Program to *advance a robust, predictive understanding of watershed function*.

Biogeochemical Dynamics of Fe and U in Fe Flocs in Tims Branch, Savannah River Site under Oxic/Anoxic Cycling

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Project Abstract: The Argonne *Wetland Hydrobiogeochemistry* SFA studies are centered on a riparian wetland field site within Tims Branch at the Savannah River Site and are focused on hydrologically driven biogeochemical processes within three critical zones: *sediment, rhizosphere,* and *stream*. The dynamic nature of the processes occurring within the *stream* zone is illustrated by the formation of flocs, which are multicomponent assemblages of microbes, minerals, and non-living organic matter that are often found in freshwater ecosystems, including wetlands. Abundant orange and reddish-brown flocs have been repeatedly observed along gaining sections of Tims Branch, where anoxic groundwater containing Fe(II) contacts oxygenated stream water. Analysis of these flocs by ICP-OES and XAFS spectroscopy revealed that the flocs contain high levels of Fe (8–17 wt%)—primarily in the form of ferrihydrite and lesser amounts of lepidocrocite and Fe-organic complexes as determined by Fe K-edge EXAFS spectroscopy—P (2–4 wt%) and S (1–3%). The flocs also contain 155–600 ppm U in the form of a U(VI) oxyhydroxide phase, as indicated by U L_{III}-edge EXAFS analysis. Flocs can undergo microbially mediated cycling of redox active elements such as Fe and U. Laboratory microcosm studies show that the transition from oxic to anoxic conditions leads to the reduction of Fe(III) to Fe(II) and U(VI) to non-uraninite U(IV); following a return to oxic conditions, Fe(II) and U(IV) oxidize back to Fe(III) and U(VI). Given that Fe flocs are frequently observed in a broad range of wetland environments, our studies of Fe floc biogeochemistry in Tims Branch and its potential impact on U speciation and transport expand our understanding of their role in the speciation and cycling of trace elements in wetlands, which in turn can lead to more robust modeling of trace element behavior in aquatic and terrestrial environments.

Watershed-Scale Hydrobiogeochemical Properties that Cause Contaminant Hot Spots

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Project: Argonne Wetland Hydrobiogeochemistry Science Focus Area (SFA)

Project Website: https://ess.science.energy.gov/anl-wetland-sfa/

Project Abstract: Argonne's Wetland Hydrobiogeochemistry SFA is a multi-scale study of the hydrobiogeochemical processes governing water quality at a uranium (U) contaminated wetland located on the Savannah River Site, Aiken, SC. The objective of this study was to determine hydrological, soil, and topographical properties that influence U concentration distribution along an 8 km reach. The general approach was to create U concentration maps, collect and characterize soil cores for U properties, and then use flow models to test various hypotheses to explain the presence of multi-hectare-sized hot spots of U. Using walk-over gamma mapping techniques, the area previously surveyed was expanded another 30% to ~40 hectares. Based on 400,000 gamma spectra and 10 soil cores, it was determined that 94% of the originally released 43,500 kg U remain in the wetland, mostly in five hot spots. The furthest hot spot (9 ha) was 8 km downstream of the source term and accounted for 11% of the detected U. Uranium soil concentrations in this hot spot were as high as 2000 mg/kg and were near perfectly correlated to organic matter and iron concentrations. A hydrological and contaminant transport model was calibrated and validated against measured data. It showed that the hot spots are located only in marshy wetlands, as opposed to uplands, and in areas where stream energy is or was extremely low, such as former ponds. Modeling results suggest that stream particles are responsible for much of the U transport in this system. Surprisingly, few U-rich particles could be found in sediments recovered from the hot spots using autoradiography followed by SEM/EDX techniques. The few hot particles that were found contained 12 to 16 wt% U. Together these results demonstrate that wetlands can be highly effective at immobilizing U for more than 50 years. Furthermore, contaminant reconcentration occurs only in areas where the hydrological conditions as well as sediment biogeochemical conditions are conducive. Results from this meter-to-hectare scale study are being combined with on-going laboratory gram-scale and spectroscopic molecular-scale studies to inform a model to predict water quality in wetlands.

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

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Project: Argonne Wetland Hydrobiogeochemistry Science Focus Area

Project Website: https://ess.science.energy.gov/anl-wetland-sfa/
https://www.anl.gov/bio/project/subsurface-biogeochemical-research

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.