

Title: 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. To accomplish this, 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. Groundwater and surface water level monitoring wells have been installed to provide hydrological context (e.g., gaining versus losing stream conditions) to the study sites within the watershed. 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.*

The overarching hypothesis of our research is that *hydrologically driven biogeochemical processes that create redox dynamic conditions from the nanometer to meter scales are a major driver of groundwater and surface water quality within riparian wetland environments.*

We identified three major components (focus areas) of the Tims Branch riparian wetland that represent critical zones containing hydrologically driven biogeochemical drivers, which control water quality: *sediment, rhizosphere, and stream.* Within these three focus areas, we identified two common thematic knowledge gaps that inhibit our ability to predict controls on water quality:

- (1) *In-depth understanding of the molecular-scale biogeochemical processes that affect Fe, C, and contaminant speciation within the wetland sediment, rhizosphere, and stream environments; and*
- (2) *In-depth understanding of hydrologically driven biogeochemical controls on the mass transfer of Fe, C, and contaminants within wetland sediment, rhizosphere, and stream environments.*

Holistically addressing hypotheses related to these two knowledge gaps organizes the SFA in its development of a hydrobiogeochemical conceptual model of the Tims Branch riparian wetland.

Hydrobiogeochemical Processes Impacting Uranium Speciation and Transport in Tims Branch, Savannah River Site

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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. As for many wetland environments, wetlands within Tims Branch are subject to both seasonal and episodic changes in hydrologic conditions affecting the degree of saturation, and thereby the redox state, of soils and sediments. The redox dynamic nature of these soils/sediments is driven largely by microbial activity that results in active biogeochemical cycling of major elements (i.e., Fe and S) as well as trace metals including U. Synchrotron x-ray spectroscopic measurements of sediment cores collected within the wetlands show a strong correlation between the degree of saturation and the redox state, as indicated by the valence of Fe and U, with Fe(III) and U(VI) predominant in unsaturated sediments and Fe(II) and U(IV) in saturated sediments. U(IV) in the saturated sediments is present as mononuclear U(IV) ions, that readily oxidize to U(VI) on exposure to air. The redox dynamic nature of the wetlands is also illustrated by the formation of iron-enriched flocs along gaining sections of Tims Branch, where anoxic groundwater containing Fe(II) contacts oxygenated overlying water. The flocs contain Fe (9.7% on a dry mass basis)—in the form of ferrihydrite (83% of Fe) and lepidocrocite (17%) as determined by Fe K-edge EXAFS spectroscopy—as well as P (2.7%), S (1.2%), and Al (0.4%). The flocs are effective scavengers of U, with concentrations ranging from < 0.05 ppm in uncontaminated areas to as high as 600 ppm in the contaminated area, depending on location. Furthermore, the concentration of U within the flocs was found to vary by an order of magnitude in response changes in streamflow due to episodic rain events, suggesting the potential importance of flocs in controlling U transport at the site. The stability of flocs varies over time and they can undergo microbially mediated cycling of

redox active elements such as Fe and S, the effects of which on U speciation within the flocs in situ is as yet unknown, as is the fate of U when the flocs degrade/disperse; however, preliminary microcosm studies indicate that floc-associated U(VI) is reduced to U(IV) when flocs are exposed to anoxic conditions.

Molecular to Core-Scale Biogeochemistry at Tims Branch Wetland, Savannah River Site

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Project: Argonne Wetland Hydrobiogeochemistry SFA

Project Website: https://doesbr.org/documents/ANL_SFA_flyer.pdf
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Project Abstract: The Argonne SFA project (*Wetland Hydrobiogeochemistry*) studies the processes that govern elemental cycling and particle formation/transport at the oxic-anoxic interfaces of a DOE field site, the Tims Branch wetlands at Savannah River National Laboratory. The variable redox nature of this riparian ecosystem creates conditions for the formation and dissolution of iron mineralization products, which can influence carbon and phosphorous balances, as well as the mobility of contaminants discharged during past operations (Ni, Cr, Zn, Pb, and U). Recognizing the potential value of using U as a sentinel for sediment redox state and particle-associated transport, the distribution of uranium along Tims Branch was mapped on the kilometer and meter scale using helicopter- and backpack-borne gamma detectors. Results show that 83% of the contamination released in the 1970s remains in the wetland and that the contamination accumulated in limited portions along the wetland where the stream had broadened and flow was slow. These results at the watershed scale not only quantify the longevity of contaminant sequestration, but also provide an idea of the hydrological as well as the biogeochemical factors responsible for sequestering elements/particles in riparian wetlands. To understand the influence of pore-scale wetland conditions on the molecular speciation of Fe and U, specific locations on the radiation maps were chosen for sediment coring. The elemental content and speciation with depth was determined in the intact cores at millimeter resolution by synchrotron x-ray spectroscopy. U accumulated in the top 5-10 cm of the sediment and correlated with Fe and the other contaminants, suggesting that the distribution was due to particle

deposition rather than precipitation from groundwater. The valence of U varied with depth and coring location, predominating as U(IV) in saturated sediments and as U(VI) in drier locations. Reduced U correlated with reduced Fe species and an increase in fermentative and metal-cycling bacteria, as well as with O₂ profiles observed at the site. U EXAFS spectroscopy revealed that the reduced U species are mononuclear U(IV) ions, rather than the UO₂ species predicted by models. To elucidate the speciation, we studied controlled systems with U(IV) bound to minerals and organic ligands (citrate, EDTA). The spectral comparisons suggested that sediment-associated U(IV) was bound to mineral surfaces. Our multiple-scale characterization results indicate a previously unappreciated importance of U(IV) species and particle transport at the site, which together with the observed redox variability over a few centimeters presents a challenge for modelling elemental speciation and transport.