

Biogeochemical Dynamics of Fe and U in Fe Floccs 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 floccs, 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 floccs have been repeatedly observed along gaining sections of Tims Branch, where anoxic groundwater containing Fe(II) contacts oxygenated stream water. Analysis of these floccs by ICP-OES and XAFS spectroscopy revealed that the floccs 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 floccs also contain 155–600 ppm U in the form of a U(VI) oxyhydroxide phase, as indicated by U L_{III}-edge EXAFS analysis. Floccs 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 floccs are frequently observed in a broad range of wetland environments, our studies of Fe flocc 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.