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Iron Flocs as Biogeochemically Dynamic Reservoirs of Uranium in Tims Branch Wetlands, Savannah River Site

Edward O'Loughlin,1* Maxim Boyanov,1,2 Daniel Kaplan,3 Kent Orlandini,1 Pamela Weisenhorn,1 and Kenneth Kemner1

¹ Argonne National Laboratory, Argonne, IL;

² Bulgarian Academy of Sciences, Sofia, Bulgaria;

³ Savannah River National Laboratory, Aiken, SC;

Contact: oloughlin@anl.gov

BER Program: SBR Project: Argonne Wetland Hydrobiogeochemistry SFA Project Website: <u>https://doesbr.org/documents/ANL_SFA_flyer.pdf</u> https://www.anl.gov/bio/project/subsurface-biogeochemical-research

The Argonne Wetland Hydrobiogeochemistry SFA studies wetland hydrobiogeochemistry centered on a riparian wetland field site within Tims Branch at the Savannah River Site. Research is 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 presence 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 at multiple locations along Tims Branch. Analysis of these flocs by ICP-OES and XAFS spectroscopy revealed that the flocs contained high levels of Fe (9.7%)—in the form of ferrihydrite (83%) and lepidocrocite (17%) as determined by Fe K-edge EXAFS spectroscopy—P (2.7%), S (1.2%), and Al (0.4%) on a dry mass basis. The flocs contained 320 ppm U and preliminary U L_{III}-edge EXAFS analysis indicates that it is U(VI) in the form of a U oxyhydroxides phase. The concentration of U in floc material was 5.5 times greater than the highest concentration of acid-extractable U in streambank sediments collected at the same time as the floc, indicating the potential importance of flocs in controlling U transport at the site. The stability of flocs varies over time and is dependent on a multitude of physical, chemical, and microbiological processes within the floc and the surrounding water; however, the specific factors controlling the frequency and locations of floc formation and dispersion in Tims Branch are unknown and the focus of current studies. In addition, flocs 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 likewise 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. The results of our initial studies of Tims Branch flocs suggests that they represent a significant, previously unidentified reservoir of potentially mobile U, and as such are the focus of further investigation. Given that iron flocs are frequently observed in a broad range of wetland environments, our studies of iron floc formation in Tims Branch and their impact on U speciation and transport expands our understanding of their role in the speciation and cycling of trace elements in wetlands.