

# Laboratory and Field Studies of the Redox Dynamics of Fe and U in Fe Floccs in Riparian Wetlands within the Tims Branch Watershed, Savannah River Site, USA

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Discharge of metallurgical process wastewater containing U and co-contaminants (Ni, Cr, Zn, Pb) from a former nuclear material production facility (M-Area at the Savannah River Site) led to extensive contamination of downstream wetlands along Tims Branch. Abundant orange and reddish-brown floccs have been repeatedly observed along gaining sections of Tims Branch, where anoxic groundwater containing Fe(II) discharges into oxygenated stream water. These 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), and are effective scavengers of P (2–4 wt%), U (32–600 ppm), and trace metals. The floccs initially form under oxic conditions. However, accumulation of floccs can lead to burial of older flocc material and the development of anoxic conditions. Furthermore, during periods of enhanced stream flow, accumulated anoxic flocc material can become resuspended in oxic stream water. Thus, biogeochemical processes and attendant changes in redox conditions within the floccs are likely to affect the speciation of redox active constituents (e.g., Fe and U), and potentially the bioavailability of nutrients such as P. Our laboratory microcosm studies of floccs show that the transition from oxic to anoxic conditions leads to reduction of Fe(III) to Fe(II) and U(VI) to non-uraninite U(IV), as determined by XAFS analysis; following a return to oxic conditions, Fe(II) and U(IV) oxidize back to Fe(III) and U(VI). XAFS analysis along the depth profile of accumulated flocc material collected in Tims Branch shows a progressive reduction of Fe(III) to Fe(II) and U(VI) to U(IV) with depth, consistent with the observed decrease in redox potential and analogous to the behavior of Fe and U during redox manipulations in our microcosm study. 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.