Title: **Deciphering controls on metal migration within floodplains: The critical role of redox environments on metal-organic complexes**

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Project: University Project

Project Abstract: Dissolved organic matter (DOM) has a major but poorly understood control over the mobility of metals in surface and subsurface systems. Variations in the chemical composition of DOM across watersheds, owing to divergent organic matter transformation pathways, have potentially important influences on metal mobility. An outcome that has largely remained unexplored, but which may have critical impacts on dissolved metal concentrations and associated migration, is variation in the functional composition of DOM.

The *overarching goal* of our project is to determine the effect of redox conditions resulting from differing hydrologic environments on formation and transport of soluble metal-organic complexes. To meet our research goal, we developed a method to separate and quantify organic- metal complexes in natural DOM. We evaluated the role of column chemistry and solvent composition on elution and recovery of complexes of metals ranging in binding preferences (Al, Fe, Co, Ni, Cu, Zn, Cd, Pb) with (i) Suwannee River NOM and (ii) Suwannee River Fulvic Acid. Further, we examined variations in organic ligand binding of Cd from the DOE-sponsored East River Watershed using LC-ICPMS. Floodplain sediment pore-water samples were collected from oxic and anoxic environments and reacted with Cd. We observed significant differences in the composition of Cd binding ligands. In the oxic samples, three distinct Cd peaks are observed at early retention times, indicating different polar species. In the anoxic sample, the polar species are far less abundant and nonpolar ligands are observed. These results lead us to posit that redox environment, controlled by hydrologic state, is a major control over the composition of organic ligands across different regions of the watershed, and is consistent with the recent findings on the broader composition of organic matter across redox zones.

Our work is advancing a process-based understanding of metal fate and transport within watersheds, focusing principally on the dynamic hydrologic states of floodplains, leveraging the Columbia River, East River and Savannah River watersheds as experimental testbeds. Ultimately, our work is helping to advance the SBR programs goal of developing a robust predictive understanding of how hydrologic changes in watersheds affect water quality and inorganic element/contaminant loading.