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

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Project Abstract:

Whether of natural or anthropogenic origin, the fate and transport of metal nutrients and contaminants in soils and sediments is controlled by a complex network of biogeochemical reactions coupled with hydrologic processes. Dissolved organic matter (DOM) exerts a major control on metal mobility in surface and subsurface systems, albeit one that is poorly understood. Divergent OM transformation pathways drive variation in the chemical composition of DOM across watersheds. Yet, how this variation influences the functional composition and metal binding properties of DOM remains largely unexplored, although it may be a primary determinant of dissolved metal concentrations and migration.

The overarching goal of our project is to determine the effect of redox conditions resulting from differing hydrologic regimes on formation and transport of soluble metal-organic complexes. To meet our research goal, we are using a combination of field measurements and laboratory experiments to examine the relationships between redox conditions, functionality of dissolved organic matter, and metal speciation (specifically examining metal-ligand complexes). Continuous monitoring of floodplain biogeochemical conditions through climatic extremes at East River provide a unique look at metal-OM complexes. We have developed novel methods to separate, quantify, and characterize organic-metal complexes in natural DOM that pair with field experiments comprising floodplains having systematic variation in biogeochemical conditions. We evaluated the role of column chemistry and solvent composition on separation and recovery of complexes of metals ranging in binding preferences (Al, Fe, Co, Ni, Cu, Zn, Cd, Pb) with NOM. We are also developing a comprehensive computational approach for molecular characterization of metal-organic species, which merges LC-coupled high resolution (HR) mass spectrometry and ICP-MS analysis. We are employing these methods to characterize metal-organic species in soils from the East River and Savannah River watersheds. Our findings illustrate changes in binding preference of DOM from differing redox environments for Cd and Ni, metals having contrasting ligand preferences. Specific ligand selectivity and exchange changes depending on the environmental biogeochemical conditions. Our work is advancing a process-based understanding

of metal fate and transport within watersheds, focusing principally on the dynamic hydrologic states of floodplains. Ultimately, our work is helping to advancing a robust predictive understanding of how hydrologic changes in watersheds affect water quality and inorganic element/contaminant loading.