**Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones**

Jeffrey G. Catalano[1]*, Daniel E. Giammar[1], Jinshu Yan[1], Neha Sharma[1], Elaine D. Flynn[1], Grace E. Schwartz[2], Scott C. Brooks[2], Pamela B. Weisenhorn[3], Kenneth M. Kemner[3], Edward J. O'Loughlin[3], Daniel I. Kaplan[4]

[1]Washington University, Saint Louis, MO
[2]Oak Ridge National Laboratory, Oak Ridge, TN
[3]Argonne National Laboratory, Argonne, IL
[4]Savannah River National Laboratory, Aiken, SC

**Contact:** catalano@wustl.edu

**Project Lead Principle Investigator (PI):** Jeffrey G. Catalano

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**Project Abstract**:

Biogeochemical cycling in subsurface aquatic systems is driven by anaerobic microbial processes. Many of the organisms involved mediate these processes using metalloenzymes that require trace metals as key reactive centers. Pure culture studies reveal that low availability of trace metals may inhibit methanogenesis, mercury methylation, and reduction of $N_2O$ to $N_2$ during denitrification. However, whether such limitations occur in natural subsurface aquatic systems is currently unclear. If present, such limitations are likely controlled by trace metal speciation as this directly impacts bioavailability. This project seeks to establish mechanistic links between trace metal availability and biogeochemical carbon, nitrogen, and mercury transformations in subsurface systems. Integrated field and laboratory studies of trace metal availability and biogeochemical processes are underway at riparian wetlands in the Tims Branch watershed at the Savannah River Site and marsh wetlands at Argonne National Laboratory, both in collaboration with the Argonne Wetland Hydrobiogeochemistry SFA, as well as the streambed of East Fork Poplar Creek (EFPC) at Oak Ridge National Laboratory in collaboration with the ORNL Mercury SFA. Solid-phase trace metal (Co, Ni, Cu, Zn) concentrations in the soils and sediments at these sites are one-half to one-tenth of crustal averages. The overlying surface waters have dissolved trace metal concentrations roughly an order of magnitude below optimal levels for microbial processes. These observations suggest that our field sites will display metal-limited biogeochemistry. Despite the distinct physical settings under investigation, the speciation of trace metals in the wetland soils and stream sediments varied little, suggesting broadly universal controls on metal availability in subsurface aquatic systems. While the wetland soils and stream sediments displayed similar trace metal uptake behavior, added metals surprisingly formed different species at each site. Cobalt addition to stream sediments did not produce a clear impact on mercury methylation, but further studies are needed to examine longer incubation times. Ongoing incubations of wetland soils and stream sediments are investigating whether the addition of nickel and copper stimulate methanogenesis and $N_2O$ reduction, respectively.