Poster #22-30

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

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BER Program: SBR
Project: University Award

Aquatic ecosystems display strong coupling between hydrologic conditions and the cycling of carbon, nitrogen, and other major elements as well as trace metal micronutrients and contaminants. In many such systems, sharp redox gradients can produce spatially-varying regions of biogeochemical activity. The biogeochemistry of subsurface zones of aquatic systems has been widely explored from the perspective of redox conditions, substrate availability, and thermodynamic controls on metabolic processes. However, an additional yet under-examined constraint is the availability of trace metal micronutrients. An array of metalloenzymes are essential to many biological pathways associated with microbial carbon and nitrogen cycling and mercury methylation. Laboratory studies using isolate microorganisms have demonstrated that low metal availability inhibits key biological pathways, but similar limitations in natural and human-impacted systems have not been widely investigated. The project thus seeks to establish whether aquatic systems display trace metal limitations on biogeochemical carbon, nitrogen, and mercury transformations. We hypothesize that solid-phase speciation is the primary control on metal availability and that biogeochemical processes utilizing a pathway containing a single, metal-bearing enzyme are most susceptible to metal limitations. This project integrates field and laboratory studies of trace metal availability and biogeochemical processes occurring in wetland soils and hyporheic zone sediments. Our primary field sites include a riparian wetland 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 hyporheic zone of East Fork Poplar Creek (EFPC) at Oak Ridge National Laboratory in collaboration with the ORNL Mercury SFA. These studies are supplemented by work in marsh wetlands at Marais Temps Clair Conservation Area near St. Louis, MO. In the first half- year of this project, our efforts have focused on key initial tasks. Preliminary measurements showed that the addition of nickel to incubations of marsh soil increased methane production by a factor of 10. We have pursued similar studies using stream sediments from EFPC to explore whether cobalt addition affects mercury methylation. No clear trend was observed, but future work will examine longer incubation times. Soil, sediment, and water sampling at both the EFPC and marsh wetlands at Argonne have investigated the controls on trace metal availability. Planned sampling at the Tims Branch riparian wetland along with incubation experiments using materials from all field sites will further assess the impact of trace metal availability on biogeochemical cycling.