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

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Project Abstract:

Biogeochemical cycling in subsurface aquatic systems is driven by anaerobic microbial processes that employ metalloenzymes. 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. This project seeks to establish mechanistic links between trace metal availability and biogeochemical transformations in subsurface systems. Integrated field and laboratory studies of trace metal availability and biogeochemical processes were conducted in riparian wetlands in the Tims Branch watershed at the Savannah River Site, marsh wetlands at Argonne National Laboratory, and the streambed of East Fork Poplar Creek at Oak Ridge National Laboratory. The speciation of trace metals in wetland soils and stream sediments shows surprising consistency across the field sites. Dissolved metals also show consistent uptake behavior by the soils and sediments but form distinct species at each site. Geochemical controls on trace metal availability may thus be site-specific despite similar native solid-phase speciation and binding affinities. Maximum bioavailable concentrations of ~10 nM for Cu and ~40 nM for Ni and Co occur in the porewater of stream sediments, below optimal for biogeochemical processes. The addition of Cu stimulates N_2O reduction in stream sediments and riparian wetland soils but not in marsh wetland soils. Production of CH_4 in riparian wetland soils increases by 75% following addition of Ni but marsh wetland soils generate indistinguishable amounts of CH_4 after similar amendment. Metal limitations on biogeochemical processes thus vary in occurrence among subsurface aquatic systems despite low metal availability across sites. Redox fluctuations in wetland soils and stream sediments promote Co and Zn availability and inhibit Cu availability under anoxic conditions. Oxic conditions in stream sediments and anoxic conditions in riparian wetland soils increase Ni availability. Repeated cycling of redox conditions enhance Zn and Cu bioavailability but decrease Ni and Co bioavailability. Metal limitations on biogeochemical processes may thus differ between consistently anoxic systems and those that redox cycle.