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 are underway at 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. Diffusive gradients in thin films (DGT) probes identify maximum porewater concentrations in stream sediment of ~10 nM for Cu and ~40 nM for Ni and Co, suggesting that these systems display metal-limitations. N_2O reduction is stimulated by Cu addition to stream sediments and riparian wetland soils, but marsh wetland soils display no N_2O accumulation even at background levels of Cu availability, i.e., no Cu limitations were apparent. Riparian and marsh wetland soils show little to no enhancement in CH_4 production in response to increases in dissolved Ni concentrations. Redox fluctuation experiments demonstrate that anoxic conditions promote Ni and Co availability and inhibit Cu availability in riparian wetland soils. Similar metal availability trends were displayed by stream sediments during redox fluctuations except for Ni, which showed greater availability under oxic conditions. Ongoing studies continue to explore metal limitations on CH_4 production and how formation of FeS in wetland soils and stream sediments affects metal availability.