

# Cryptic sulfur cycling coupled to iron and carbon cycling in dynamic riparian wetland environments

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Hyporheic zones, where oxic surface water and anoxic groundwater mix, are characterized by dynamic redox gradients that promote hotspots and hot moments of biogeochemical processes. Changes in environmental conditions (e.g., major precipitation events or wetting/drying cycles) and anthropogenic inputs of excess nutrients or contaminants can further influence the activity of hyporheic zones in ways that are not fully understood or easily predicted. In freshwater wetland and stream hyporheic zones, carbon (C) turnover and fate is heavily influenced by the biogeochemical cycling of iron (Fe). “Hidden” or “cryptic” sulfur (S) redox processes may be further coupled to these Fe and C cycles. S biogeochemical cycling is not well constrained in freshwater systems but can include the production of reactive intermediate S species coupled with Fe(III) reduction and methane oxidation, thus supporting higher rates of sulfur biogeochemical cycling than otherwise expected in these low sulfate environments. To better understand Fe-S-C biogeochemical cycling in a freshwater wetland and stream hyporheic zone experiencing dynamic flux conditions, we used field-based approaches including continuous surface- and ground-water level and flux measurements and seasonal sampling of water and sediments for metagenomic and geochemical analyses combined with reactive transport modeling using the PFLOTRAN code that incorporates “cryptic” S cycle reactions. Analytical results using X-ray absorption spectroscopy showed anoxic sediments dominated by both inorganic and organic intermediate S species and shotgun metagenome sequencing revealed an abundance of sulfur and thiosulfate oxidation genes, particularly in fully inundated areas experiencing predominantly upward hyporheic flux. Preliminary model scenarios further show the dominance of anaerobic sulfide oxidation under upwelling conditions compared to downwelling for driving Fe-S-C cycling. It is suspected that porewater aqueous or colloidal Fe(III), likely stabilized by organic matter, helps fuel a cryptic S cycle. Results from this study will be valuable for predicting coupled and “cryptic” biogeochemical cycling in riparian wetlands under global change scenarios.