

Reactive transport modeling of Fe-S-C cycling: investigating the impacts of dynamic hydrologic conditions at a riparian wetland

ZIXUAN CHEN¹, SAMANTHA PEREZ², G.-H. CRYSTAL NG¹, CARA M SANTELLI¹, DANIEL I. KAPLAN³, SHREYA SRIVASTAVA¹, CARLA ROSENFELD⁴ AND KENNETH M. KEMNER⁵

¹University of Minnesota - Twin Cities

²University of Minnesota

³University of Georgia

⁴US EPA

⁵Argonne National Laboratory

Presenting Author: chen7452@umn.edu

Wetlands play a crucial role in enhancing water quality by transforming nutrients and organic substances, influencing the global carbon cycle and greenhouse gas emissions, and retaining metals. Iron (Fe) “flocs” in wetlands are of particular interest because they can immobilize toxic metals such as uranium (U). We hypothesize that the presence of these flocs highly depends on Fe interactions with carbon (C) and sulfur (S) in the hyporheic zone, where groundwater and surface water mix in the sediment bed. S cycling is often overlooked in freshwater systems with low sulfate concentrations – spatiotemporally dynamic water fluxes promote fast redox cycling, such that net changes in S species are challenging to observe. However, our previous work has emphasized the importance of “cryptic” S reactions behind these “hidden” Fe-S-C cycles, with a focus on two particular pathways: 1) anaerobic sulfide reoxidation (ASR) likely coupled to Fe³⁺ reduction to replenish porewater sulfate (SO₄²⁻), and 2) anaerobic oxidation of methane (AOM) coupled to sulfate (SO₄²⁻) reduction to moderate porewater methane (CH₄) while methanogenesis buffers H⁺-consumption by Fe³⁺ reduction. In the current work, to better understand the importance of dynamic hydrologic flux on hyporheic zone Fe-S-C biogeochemical cycling, we carried out reactive transport simulations with PFLOTRAN based on field measurements and geochemical and microbial analysis for the Tims Branch site, part of the DOE’s Wetland Hydro-Biogeochemistry Science Focus Area. Our model results highlight the critical role of “cryptic” S cycling in wetlands in increasing Fe²⁺ and moderating CH₄ porewater concentrations. Comparing the model under three hydrologic flux scenarios, constant flux, regularly alternating flux direction, and field-based dynamic flux, we found that when dynamic hydrologic fluxes include alternating directions, this can facilitate increased Fe²⁺ concentrations at different sediment depths. This has important implications for contaminants, because when such an increase in Fe²⁺ occurs at the sediment surface, iron “flocs” are likely to form in surface waters. Our research sheds light on the impacts of dynamic hydrological settings on Fe-S-C cycles critical to carbon budgets and heavy metal mobilization.