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Spatiotemporal Variation in Organic Matter Chemistry in Global Rivers Modulates Biogeochemistry

James Stegen^{1*}, Emily Graham¹, Vanessa Garayburu-Caruso¹, Rosalie Chu¹, Bob Danczak¹, Amy Goldman¹, Hyun-Seob Song¹, Nikola Tolic¹, Jason Toyoda¹, WHONDRS Consortium, and the SFA Team

¹ Pacific Northwest National Laboratory, Richland, WA

Contact: james.stegen@pnnl.gov

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This element of the PNNL SFA seeks to understand spatiotemporal variation in organic carbon chemistry and its influences on river corridor biogeochemical function. Dissolved organic matter (DOM) chemistry is emerging as a strong influence on biogeochemical cycling in river corridors. However, reactive transport models do not currently consider chemical properties of DOM, indicating a significant structural gap that limits our ability to predict integrated hydro-biogeochemical function. To enable the incorporation of DOM chemistry into reactive transport models, we are (1) characterizing spatiotemporal patterns in DOM chemistry, (2) revealing mechanisms that underlie subsequent influences on river corridor biogeochemistry, and (3) developing new representations of DOM chemistry that can be incorporated into numerical models.

We present integrated research that addresses spatiotemporal characterization, mechanistic insight, and model representation of DOM in river corridors. We established a global research consortium (WHONDRS) to advance cross-system characterization of patterns in DOM chemistry and integrated hydro-biogeochemical function of river corridors. One WHONDRS effort characterizes temporal dynamics of DOM in surface and pore water under sustained high-frequency river stage fluctuations. Using new cheminformatics approaches inspired by ecological theory, this effort is revealing the spatiotemporal organization of model-relevant attributes of DOM chemistry and their relationship to biogeochemical dynamics. To evaluate the mechanisms underlying biogeochemical impacts of DOM chemistry, we paired laboratory experiments with new biogeochemical modeling approaches that account for thermodynamic and microbial regulation of respiration. Aerobic sediment slurries revealed that transitioning from C-limited to C-replete conditions was associated with a transition from thermodynamic regulation of respiration to limitation by organic N. These results point to interactions among thermodynamics, C concentration, and organic N availability as key controls on respiration rates in river corridors. In addition, these results challenge classical theory that discounts the relevance of DOM thermodynamics under aerobic conditions. To better understand the contradiction between theory and experimental outcomes we developed a numerical model to investigate the biogeochemical role of DOM chemistry in aerobic environments. The model revealed that thermodynamically favorable DOM promotes mineralization of less favorable DOM. Model outcomes therefore provide additional support to the inference that thermodynamic properties of DOM influence biogeochemical rates under aerobic conditions. This suggests the need to reconsider classic theory and revise models accordingly. Collectively, we are providing the data, field instrumentation, mechanistic knowledge, and theory to integrate DOM chemistry with hydrology to enhance predictive understanding of hydro-biogeochemical function in river corridors.