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Interactions Between Organic Carbon Concentration, Chemistry, and Thermodynamics Govern Elevated Metabolism in the Columbia River Hyporheic Zone

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This element of the PNNL SFA seeks to understand the role of organic carbon chemistry in regulating aerobic respiration and to inform reactive transport models used in predictions of watershed-scale function. Organic carbon (C) metabolism is key to conceptualizing and parameterizing controls on biogeochemical cycling within reactive transport and watershed models. In particular, subsurface groundwater-surface water mixing (hyporheic) zones contain hotspots of enhanced metabolism that contribute substantially to river corridor function. Despite considerable research on biogeochemical reactions in the hyporheic zone, we still have a poor understanding of their governing processes. Previous work has shown a dependence of hyporheic biogeochemical rates on mixing of groundwater- (GW) and surface water- (SW) associated organic C pools with distinct chemistries. Based on these observations, we hypothesize that comparatively low metabolism in GW and SW independently are due to concentration limitation in GW (despite favorable C thermodynamics) and thermodynamic limitation in SW (despite sufficient C concentration). When GW and SW mix, we hypothesize both limitations are overcome, resulting elevated respiration.

To test these hypotheses, we evaluated the response of hyporheic zone sediments from the Hanford 300A in central Washington to different concentrations of carbon substrates with various chemical attributes. Four C compounds (two amino acids and two organic acids, one of each with high and low thermodynamic favorability) were added to batch reactors at ambient, 10- (equivalent to SW concentration), and 30-fold GW C concentrations. Further, mixed treatments including amino acids with varying thermodynamics were used to evaluate priming influences on respiration. Oxygen consumption was measured using non-invasive fiber opticsensors. Results indicate stimulated respiration when amino acids of differing thermodynamics are present in approximately equivalent proportions. Associated changes in geochemistry and in C chemistry provide mechanistic knowledge of possible thermodynamic limitations. Our results also support field-based insights suggesting a role for N-bearing compounds in metabolism.

Our results are being used to develop biogeochemical reaction models that incorporate multiple C compounds as electron donors (Song et al. poster). These models have replicated a priming-like effect within narrow mixing conditions observed *in situ*. Further, we lead a global initiative studying hyporheic zone metabolism through standardized sampling and a newly-developed sensor rod through the Worldwide Hydrobiogeochemical Observation Network for Dynamic River Systems project (WHONDRS, Stegen et al. poster). Collectively, this work links into reactive transport models that inform ecosystem predictions in the Columbia River watershed.