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Organic Carbon Thermodynamics Elucidate Spatiotemporal Mechanisms Governing Hyporheic Zone Biogeochemical Cycling

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This element of the PNNL SFA has contributed to a predictive understanding of river corridor hydrobiogeochemical function by revealing processes governing the oxidation of organic carbon (OC) in the hyporheic zone. Groundwater-surface water mixing zones (i.e., hyporheic zones) exhibit enhanced biogeochemical cycling, and strongly influence river corridor function. Processes governing biogeochemical cycling in these zones remain a crucial uncertainty in watershed-scale process models. To reveal governing processes we combined ultra-high resolution OC characterization, geophysical monitoring, microbial ecology, and biogeochemical assays to determine novel processes associated with the concept of ‘priming’ and how those processes are influenced by (i) riparian vegetation and (ii) hydrologic mixing in the Columbia River hyporheic zone. Here, priming occurs when microbial oxidation of thermodynamically unfavorable OC is fueled by the addition of more bioavailable OC.

Field surveys of sediment-associated OC (and related biogeochemical data) conflicted with priming expectations. We found that inputs of thermodynamically favorable OC protected thermodynamically unfavorable mineral-bound OC. We also found that riparian vegetation shifted biochemical pathways that drive the oxidation of OC. Further, despite the respective oxidation of water-soluble vs. mineral-bound OC pools in dense and sparsely vegetated areas, thermodynamically favorable OC was preferentially depleted in both areas. This suggests universal thermodynamic principles underlie biogeochemical cycling in the hyporheic zone.

In contrast, field surveys of pore water were consistent with priming. Groundwater contained thermodynamically favorable OC at low concentrations while surface water contained thermodynamically unfavorable OC at higher concentrations. As such, OC oxidation was concentration-limited in groundwater and thermodynamically-limited in surface water. When groundwater mixes with surface water, thermodynamically favorable OC in groundwater primes the oxidation of less favorable OC in surface water. We also show concomitant shifts in microbial communities and OC biochemical transformations. These results provide a mechanistic foundation for modeling hyporheic zone biogeochemistry under dynamic mixing.

The contrasting results from sediment-associated vs. pore water OC align with equivocal results in the literature regarding priming effects in aquatic habitats. This highlights the paucity of knowledge related to processes linking OC speciation to hyporheic zone biogeochemical function. Our studies do, however, provide conceptual hypotheses that will be pursued through an iterative model-experiment approach in the next triennial period of the PNNL SFA. Resulting process-based understanding will be used to inform reactive transport models and, ultimately, the development of a process-based watershed modeling framework.