

## **Quantifying Cumulative Effects of Coupled Organic Matter and Nitrogen Cycling in River Corridors across the Columbia River Basin**

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*This element of the PNNL SFA seeks to quantify the cumulative effects of river corridor hydrologic exchange flows (HEFs), dissolved organic matter (DOM) chemistry, and microbial activity on biogeochemical cycling, water quality, and contaminant mobility across the Columbia River Basin (CRB) under both baseline and disturbance conditions.* River corridors play important roles in organic matter and nitrogen cycling and removal of excess nutrients. At basin scales, the incorporation of hydrologic connectivity and molecular information on microbiome structure (i.e., species composition and distribution of enzyme-encoding genes), microbial expression, and metabolomes will greatly improve a river corridor model (RCM) in capturing distinct water quality signatures in connection to variations in land use, hydrogeology, climate, and disturbances.

We have developed a multi-rate mass transfer (MRMT) RCM, SWAT-MRMT-R, to account for biogeochemical effects of HEFs within river corridors, resolving reactions that occur in both the surface water column and the hyporheic zones. Applying this RCM along the Hanford Reach has led to the new understanding that (1) traditional transient storage model that uses a single exchange coefficient overestimates denitrification in river corridors compared to MRMT; and (2) the locations of  $\text{NO}_3^-$  entering the river has a significant impact on nitrate retention and reduction due to spatial variability of HEFs.

We will enhance the mechanistic foundation of the RCM by linking dynamic river flow processes and heterogeneous terrestrial inputs with variable temperatures and reaction kinetics informed by molecular properties to investigate water, energy, and solute fluxes between the river-groundwater interface. Our RCM will provide the flexibility to leverage distributed molecular data from WHONDERS. We will tightly integrate modeling with experiments to advance the predictive understanding of the river corridor biogeochemistry; Initial model outputs will be used to focus field and laboratory experiments on biogeochemical hot spots and hot moments, which will then be used to refine mechanistic process representations (e.g., reaction network and kinetics) and parameterizations of RCM. The new RCM will enable the basin-scale predictions of cumulative effects of biogeochemical reactions influenced by HEFs, DOM chemistry and microbes, and will significantly improve the current state-of-the-art model that only estimates the reaction potentials. It will allow us to address questions like which watershed characteristics control spatial/temporal variations in river corridor biogeochemistry and how river corridors mediate watershed responses to disturbances. Beyond CRB, our approach can be generalized and applied to other basins facing environmental disturbances and water challenges with national significance.