Hydrobiogeochemical Variability: Mechanisms Governing Reaction- to Basin-Scale Hydrobiogeochemical Regimes

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Project Abstract: *This element of the PNNL River Corridor SFA seeks to identify places/times across the Yakima River Basin (YRB) in which sediment-associated metabolism strongly influences active channel biogeochemistry, and to reveal drivers of underlying molecular properties.* To represent processes governing river corridor biogeochemistry in predictive models, we need to understand how and why biogeochemical contributions from sediment-associated organisms vary through space/time; such contributions vary from 3-96% of respiration. Recent RCSFA work predicts spatial variation in sediment contributions to respiration. To evaluate these predictions, we are deploying sensor systems across 2nd-7th order streams in the YRB. Site locations were selected using a multi-iteration ModEx approach. Sites span four sub-basins in the YRB and are distributed across multiple complementary efforts that each focus on time series (discussed here) or spatial variation (discussed in a separate presentation). The temporal component includes 6 sites distributed across stream orders and biomes from low order mountain settings to high order lowland rivers adjacent to agricultural and urban areas, coinciding with other agencies' gauging installations. The 6 sites have been visited every 1-2 weeks starting in April 2021 to collect *in-situ* measurements and water samples for standard measurements (e.g., organic C concentration, ion chemistry, carbonate/bicarbonate speciation) and less standard measurements (e.g., FTICR mass spectrometry), to provide model-relevant data. Initial analysis of the FTICR data indicates that many organic matter characteristics vary with catchment area. Specifically, both organic matter functional diversity, as it relates to biodegradability, and the potential for varied biogeochemical organic matter transformations increased with increasing catchment area. Starting in November 2021, preliminary deployments of automated dark-bottle incubation systems (autochambers) were initiated. These autochambers are designed to estimate the fraction of system respiration from sediments by measuring the difference between water column and ecosystem respiration rates in the river corridor. These are novel sensor systems, and the initial deployments are designed to generate time-series data and test/improve system function and reliability prior to larger-scale deployments. Data reduction and QA/QC has been developed and employed to generate sensor-based datasets. Lab analysis of samples is completed as samples are generated, and QA/QC is ongoing. These sensor- and sample-based time series will be used to drive and evaluate reaction networks in the dynamic basin-scale models used by the RCSFA.