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 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 using dissolved oxygen sensors across 2nd-7th order streams in the YRB. Site locations were selected using a multi-iteration ModEx approach. The team identified system features that had the strongest influence over model predictions of river corridor hydrology and biogeochemical rates (e.g., aerobic respiration and denitrification). These model-relevant features were then used to parse the YRB into different classes using machine learning algorithms. In turn, field sites were selected to span the identified classes while accounting for logistical constraints inherent to *in situ* sensor deployments (e.g., land ownership). The full set of selected sites span four sub-basins in the YRB and are distributed across two complementary efforts that each focus on longer time series (multiple months) or spatial variation at a shorter time scale (1 week). The temporal component includes six sites distributed across stream orders and biomes from low order montane settings to high order lowland river settings and coincide with other agencies' gauging installations. The spatial component includes ~28 sites distributed more broadly across the YRB to maximize environmental breadth and provide opportunities to evaluate common patterns and context dependencies. Outcomes of the sensor deployments will be compared to model predictions for the contributions of sediments to river corridor respiration. Deviations between observations and model predictions will be studied to help guide model refinements through modifications to process representations and/or parameterizations. Sensor deployments are awaiting permit approvals and to provide longer-term context and model-relevant data, the model and measurement teams worked together to identify water chemistry variables most important for model evaluation. Selected variables span standard measurements (e.g., organic C concentration, ion chemistry, carbonate/bicarbonate speciation) and less standard measurements (e.g., FTICR mass spectrometry), all of which can be used to drive and/or evaluate reaction networks in the dynamic basin-scale models used by the SFA. Water chemistry samples are currently collected weekly at the six temporal study locations.