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ABSTRACT TITLE: Biogeochemical Investigations Across Oxidation-Reduction Boundaries at the Hanford Site SFA

ABSTRACT: The area near the Columbia River shore at the 300 Area comprises a complex system where microbial populations and associated activities are controlled by processes occurring across lithologic boundaries where contrasting nutrient availability and transport properties impose transitions in oxidation-reduction potential. While the regional hydrologic gradient is generally from surrounding uplands toward the Columbia River, seasonal and short-term changes in river stage cause fluctuations in the gradient such that the groundwater flow direction and velocity, and water table elevation are highly variable. Our focus here is on C, N, and elemental biogeochemical cycles across the contact zone between young (~15,000 years), highly-transmissive Hanford formation sediments; and older (~3.5 My), finer-grained Ringold Formation sediments that lie immediately below.

A series of passive multilevel samplers were deployed across known fine-to-coarse lithologic boundaries at the top and bottom of the Ringold Formation's uppermost mud. Deployment locations included two IFRC wells and three others in the extended 300 A monitoring network. Aqueous and dissolved gas samples were analyzed for the metabolically sensitive solutes O_2, NO_3^-, NO_2^-, SO_4^{2-}, Mn^{2+}, Fe^{2+}, HS^-, H_2, and CH_4. Sediment samples from above, within, and below the contact zone were analyzed for carbon forms, sulfur species, iron valence, mineralogy [including Fe(II) phases], pore scale physical features by x-ray tomography, and microbial community structure and function as determined by q-PCR assays and 16S gene sequencing.

Across the gravel-mud boundary from the Hanford to Ringold formations, the concentrations of SO_4^{2-}, Mn^{2+}, HS^-, NO_2^-, H_2, and CH_4 increased with depth, while the concentrations of O_2 and NO_3^- decreased. Dissolved ferrous iron and Mn^{2+} were present throughout the sampled Ringold formation. Mineralogic and chemical analyses revealed the presence of an abrupt redox transition zone (rtz) within the Ringold mud. Iron within ubiquitous phyllosilicates above the rtz was in the oxidized form, while Fe in deeper phyllosilicates was reduced and framboidal pyrite was present. Anaerobic metabolism, heterogeneously distributed within the fine portions of the Ringold formation, was catalyzed by relatively small but active microbial populations that consumed dissolved and solid-phase electron acceptors including nitrate, Fe(III), and sulfate. H_2 and CH_4 concentration gradients suggested that slow fermentation of detrital organic matter supplied electron donor that drove sequential electron donor consumption across the lithologic boundary. Concentration gradients imply transport from the Ringold to the Hanford formation that are likely responsible for system-scale maintenance of redox boundaries in the greater 300.