

## **Hydro-Biogeochemical Reactivity of Subsurface Interfaces**

### **SLAC Floodplain Hydro-Biogeochemistry SFA Project Overview**

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**BER Program:** ESS

**Project:** SLAC Floodplain Hydro-Biogeochemistry SFA

**Project Website:** <https://www-ssrl.slac.stanford.edu/sfa/>

**Project Abstract:** Floodplains are large, hydrologically active landforms, enriched in organic carbon and containing abundant and diverse microbial communities. Subsurface interfaces within floodplains are extensive, and exhibit sharp redox and solute concentration gradients that support intense biogeochemical cycling of carbon, metal micronutrients (*e.g.*, Fe, Mn), and other solutes. The biogeochemical function of subsurface interfaces is controlled by intricate coupling between hydrological and biogeochemical processes. Yet, in spite of their importance, *our understanding of subsurface interfaces as nexuses of hydrological and biogeochemical process coupling is poor.*

The mission of the SLAC Floodplain Hydro-Biogeochemistry SFA is to develop conceptual and numerical process representations to describe the coupling between hydrological, biological, and geochemical (*i.e.*, “hydro-biogeochemical”) processes across subsurface interfaces in response to hydrologic perturbations such as onset of spring flooding and summer drought. To do so, we are studying: (i) meter-scale hydrological exchange flows and cm-scale ion transport across subsurface interfaces; (ii) changes in microbial community structure and diversity; and (iii) the molecular/electronic structures and reactivity of organic carbon- and iron-bearing colloids, which are exported across interfaces. These factors interact across spatial and temporal scales to produce biogeochemical hot spots and hot moments. We are accomplishing this program through integration of field observations and sampling, laboratory experiments, and hydrological and reactive transport modeling that contributes to IDEAS-Watersheds and the ESS modeling ecosystem.

We are focusing on two important types of interfaces that are abundant in floodplains, but which have received little research attention at molecular-to-system levels: (1) Interfaces between gravel bed alluvium and overlying organic- and metal-enriched soils, which are ubiquitous across the intermountain West, as exemplified by our field sites at Slate River, CO and Riverton, WY; (2) interfaces surrounding fine-grained sediment lenses embedded within coarse-grained aquifer material, which promote the establishment of reducing conditions in surrounding coarse and otherwise oxic aquifer material, altering groundwater compositions. This work is providing new and deeper mechanistic process representations of hydro-biogeochemical coupling within floodplains, their impact on water composition, and their responses to perturbations.

## **SLAC Floodplain Hydro-Biogeochemistry SFA: Reactivity, Structure, and Transport of Colloids and Particles Across Subsurface Interfaces**

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**Project Abstract:** Floodplains characteristically exhibit a multitude of juxtaposed soil layers with sharply contrasting physicochemical and hydrologic properties. Water movement across interfaces between these layers results in mixing of porewaters of distinctly different chemical compositions, stimulating a host of biogeochemical processes, including the production of colloids (operationally defined here as  $>0.15 \mu\text{m}$ ). Field observations from our Slate River, CO, field site show that Fe- and organic C-rich colloids form in fine-grained, primarily anoxic soils when oxic water from the gravel bed penetrates into the finer layers, and subsequently can be exported back across this interface when groundwater flow direction changes. Independently, laboratory observations using soils and sediments from our Riverton, WY, field site indicate that fine-grained, anoxic zones release colloids or particles such as active bacterial cells with substrates that stimulate the spread of reducing conditions into proximal coarse-grained zones. Thus, we hypothesized that colloidal transport across subsurface fine-anoxic and coarse-oxic interfaces drive downgradient biogeochemical reactions.

We have tested (and continue to test) this hypothesis through a suite of laboratory column and incubation experiments, coupled with reactive transport modeling. In addition, we are investigating the structure and composition of colloidal exports from fine-grained to coarse-grained zones and their stability, reactivity, interactions with the coarse-grained matrix, and transport properties. In the past year, we have discovered that the ratios of sulfide to initial Fe(III) and final Fe(II) to Fe(III) are key controlling factors for the size and stability of colloids forming in sulfidic zones. Further, our iterative coupling of laboratory experiments and reactive transport modeling has provided quantitative evidence that particulate/colloidal organic matter exports most likely include live microbial cells. Because these exports include active enzymes that facilitate the establishment of reducing reaction networks in an otherwise oxic environment, they constitute *exported reactivity*. These findings demonstrate that knowledge of the composition of material exchanges (solutes, colloids, particles, microbes) and their impact on biogeochemical reaction networks on both sides of the interfaces is critical for predicting larger-scale environmental processes (*e.g.*, greenhouse gas emissions, contaminant transport to ground- and surface waters).

## **SLAC Floodplain Hydro-Biogeochemistry SFA: Hydro-Biogeochemical Reactivity Across Interfaces in Riparian Floodplains Along Slate River, CO**

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**Project Abstract:** Interfaces between conductive gravel bed alluvium and overlying nutrient- and metal-enriched soils are ubiquitous in riparian environments of the intermountain West. These interfaces are laterally extensive zones where sharp redox gradients and intense microbial activity may substantially alter watershed-scale nutrient and metal micronutrient / contaminant availability. The biogeochemical function of these interfaces is controlled by intricate coupling between hydrological and biogeochemical processes. Yet, this coupling is poorly understood.

We investigated the relationship between hydrological transitions and biogeochemical responses in a representative riparian floodplain along the Slate River, Gunnison County, CO. Beaver dam construction adjacent to this site induced a massive hydrological perturbation in September 2019. Field measurements and hydrological modeling suggest that the onset of ponding and partial inundation reversed both horizontal and vertical flow directions in the shallow ( $\leq 2$  m) soils, leading to greatly increased downward infiltration of iron-rich *anoxic* porewater into the underlying gravel bed. In contrast, measurements and simulations suggest that, prior to dam construction, evapotranspiration (ET)-driven upward flow carried *oxic* water from the gravel bed into the overlying soil. A new site hydrologic model predicts that the hydrologic shift created an oxygen minimum zone ( $< 1$  mg/L) that is controlled by the balance between oxygen penetration and microbial respiration.

The increase in anoxic porewater adjacent to ponded sites is reflected in microbial community structure and diversity. For example, methanogenic archaea and sulfate-reducing bacteria are more abundant in these soils relative to their non-flooded counterparts. These observations imply significant changes in microbially-mediated biogeochemical cycling in soils impacted by flow reversal. We conclude that prolonged surface water impoundment and attendant increases in adjacent groundwater levels alter groundwater and nutrient flow vectors and fluxes, leading to redox zonation of the floodplain. Our model predicts that, proximal to ponded water, anoxic porewater and stable microbial communities persist. Enhanced downward export of anoxic porewater and nutrients into the conductive gravel bed occurs. Further from the river, the “distal zone”, where seasonal cycles dominate (as opposed to inundation), is influenced by ET and lateral recharge from inundated regions. Enhanced upward transport of oxic gravel bed groundwater into overlying anoxic soils also occurs in this zone. Our 2021 field program is focused on defining the boundary between these zones. These results provide a new model for understanding hydrologic-BGC controls over riparian floodplain function in the intermountain Western U.S.