

SLAC SFA: Mechanistic linkages between floodplain critical element and contaminant redox cycles

Program Affiliation: Subsurface Biogeochemical Research

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Organic-rich sulfidic sediments in the uranium-contaminated floodplain at the DOE site in Rifle, Colorado, exhibit U(IV) concentrations 100-fold higher than the local background. Our prior studies led to the hypotheses that: 1) these naturally reduced zone (NRZ) sediment bodies are general features of floodplains and *regionally* accumulate uranium in the upper Colorado River Basin (CRB); 2) NRZs are regionally important regulators of biogeochemical critical element (BCE, e.g. C, N, S, Fe) cycling, and 3) Uranium fate is tightly linked to BCE redox cycling in NRZs. The SLAC-SFA is investigating the validity of these hypotheses through in-depth molecular analyses of BCE and contaminant chemistry in sediment cores at fine spatial resolution.

In the past year, we have completed new NRZ sediment and pore water sampling activities at Rifle, Naturita, and Grand Junction CO; Shiprock, NM; and Riverton, WY. This work has confirmed that NRZs are common features of these floodplains and that they harbor large U and organic C inventories. Using spectroscopic methods (including X-ray absorption spectroscopy, Mössbauer spectroscopy, X-ray diffraction, and Fourier transform ion cyclotron resonance mass spectrometry) combined with chemical extraction and U isotopic signatures, we have established and compared depth profiles of detailed speciation information for U, Fe, S and C from all five floodplains. This work shows that there is an overall regional inverse correlation between the nominal oxidation state of carbon (NOSC) and increasing sulfide and U content, providing a mechanistic molecular explanation for the tight coupling between U, S and C cycling within NRZ sediments. The NOSC of soluble organic compounds in U-enriched NRZs is close to or below the thermodynamic limit for microbial respiration with sulfate as the terminal electron acceptor, indicating that U is retained here because of its higher thermodynamic favorability in supporting microbial respiratory growth. Combined with sediment pore water and microbial respiration data, this information is allowing us to construct a regional conceptual model of the ecosystem biogeochemical functions of NRZs in upper CRB floodplains.

To develop a more detailed mechanistic understanding of the links between organic matter decomposition and different element cycles, we are further examining the syntrophic coupling of fermentation to anaerobic respiration on solid phase substrates. This work is providing essential knowledge about the relevance of carbon substrate chemistry, spatial separation and electron acceptor availability for the rate and mode of coupled, microbially mediated redox transformations.