Coupled Cycling of Organic Matter, Uranium, and Biogeochemical Critical Elements Scientific Focus Area

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Advancing predictive understanding of uranium subsurface biogeochemistry, fate, and transport

Uranium is a contaminant of major concern in groundwater within the upper Colorado River Basin (CRB), where a large number of Department of Energy (DOE) legacy uranium mill sites are located. In fact, uranium is the most common radionuclide contaminant, except for tritium, at DOE sites. Anoxic, organic-enriched sediments known as naturally reduced zones (NRZs) are common within these sites and contain large amounts of accumulated uranium.

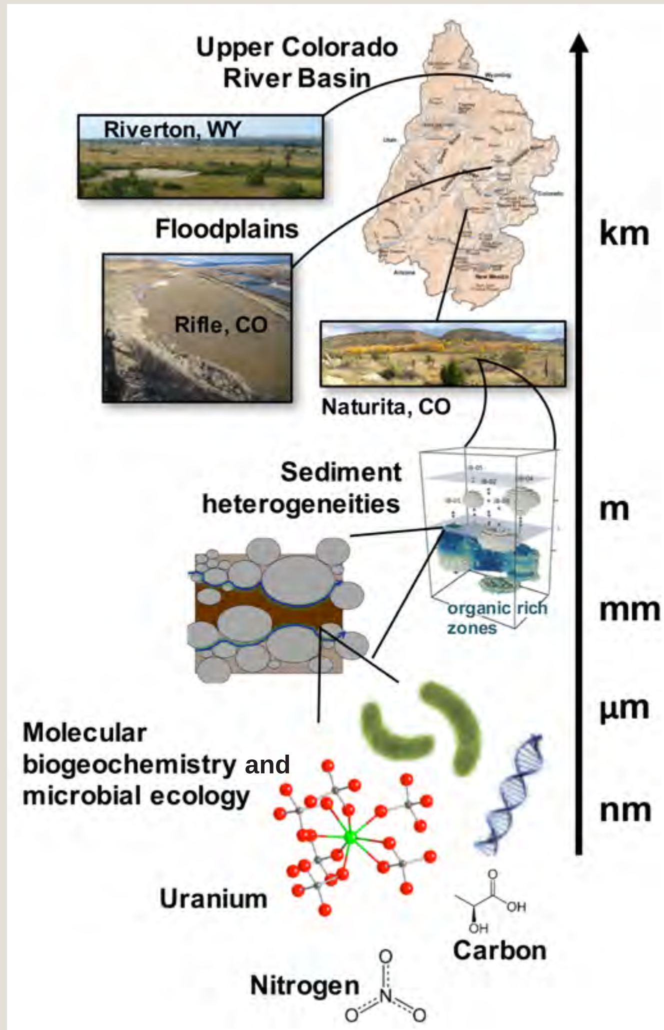
Recent research shows that these NRZs appear to be regionally important biogeochemical hotspots. Indeed, anoxic sediments are globally important repositories of uranium, organic carbon, and other biogeochemical critical elements (BCEs) including nitrogen, sulfur, and iron. These sediments also drive oxidation-reduction cycling of toxic contaminants including uranium, with strong implications for contaminant mobility. Drought can disturb anoxic sediments, causing them to become oxidized and to release their nutrient and contaminant loads, with significant impacts to connected ground and surface water systems. Seasonal fluctuations of the water table occur annually within the upper CRB, creating cyclical oxidizing aquifer conditions that can drive uranium and carbon release on a regional scale. At some upper CRB sites, uranium has accumulated in association with evaporite minerals in the unsaturated zone. In these locations, inundation by flooding can cause this uranium inventory to be released. There is concern that both NRZs and evaporite deposits are contributing to uranium plume persistence regionally or could do so in the future.

A Scientific Focus Area (SFA) led by SLAC National Accelerator Laboratory (SLAC) is studying biogeochemical controls on uranium and carbon release from upper CRB sediments. The project is supported by DOE's Office of Biological and Environmental Research (BER) as part of BER's Subsurface Biogeochemical Research (SBR) program. In this endeavor, the SLAC SFA is studying the regional occurrence, molecular speciation, and biogeochemical cycling of uranium, organic matter, and associated BCEs in relation to hydrological conditions. Several DOE legacy sites across a north-south transect in the upper CRB are being investigated. The goal is to identify, interrogate, and model critical processes in these subsurface ecosystems to improve BER's ability to predict earth system behavior and better anticipate the impacts of climate variability on uranium release and floodplain biogeochemical dynamics.

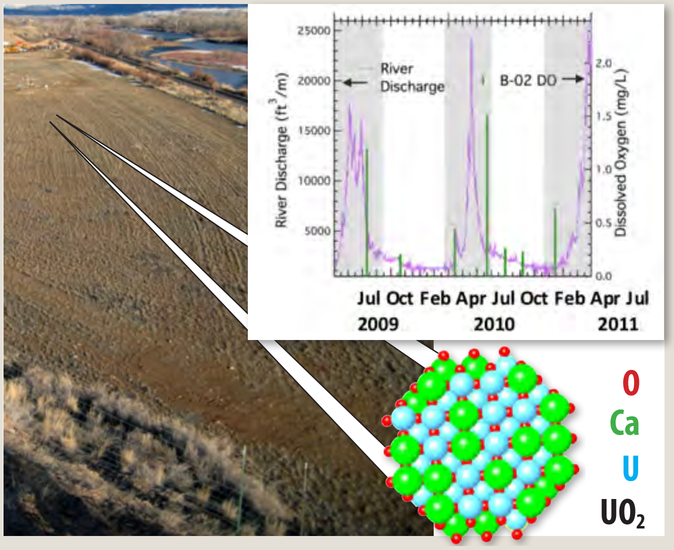
Key Knowledge Gaps

The SLAC SFA is investigating biogeochemical redox processes that control uranium, carbon, and BCE behavior in alluvial floodplains in the upper CRB and surrounding areas, emphasizing hot spots of microbial and geochemical activity in organic-enriched, redox-cycled sediments. Major scientific questions being addressed include:

- What are the physical, hydrological, and biogeochemical characteristics of NRZs and evaporite-rich sediments?
- What biological, kinetic, and thermodynamic factors control the speciation and behavior of uranium, organic carbon, and BCEs?
- How do NRZs interact with surrounding floodplain aquifers?
- What role does microbial nitrogen cycling play in mediating uranium redox cycling?
- What are the mechanisms and rates of uranium release to surrounding aquifers?



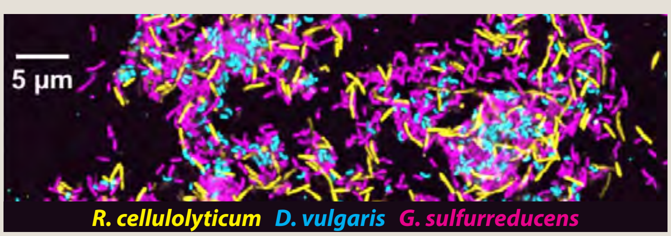
Biogeochemical Processes: Regional Context. *The SLAC SFA is building a systems-level understanding of the coupled cycling of uranium, organic matter, and BCEs by employing an integrated suite of approaches that link the molecular and pore scales to field and regional scales at sites across the upper CRB.*



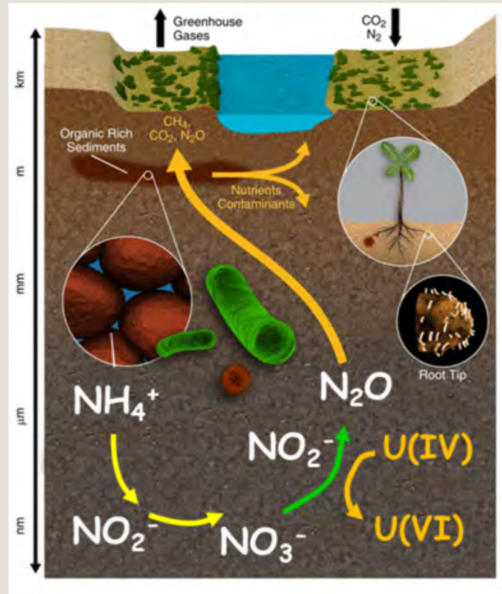
Hot Moments Control Uraninite Oxidation. ***(Top right)*** *Dissolved oxygen concentrations (green bars in graph) in the Rifle aquifer are briefly and sharply elevated in early summer when the Colorado River is at high-water stage (magenta curve). Uranium (IV) (represented by uraninite, UO_2) oxidation proceeds rapidly at these times and is negligible the rest of the year.* ***(Lower right)*** *Naturally abundant calcium (CA^{2+}) atoms (green) bond to uranium (U) sites at surfaces of UO_2 nanoparticles, retarding oxidation.*

Toward Integrative, Systems-Level Understanding

The biogeochemical properties (including molecular speciation) and hydrology of heterogeneous NRZ sediments control the fluxes of uranium, carbon, and BCEs within floodplains; yet, these properties are poorly understood at molecular to pore and field scales. The SLAC SFA is building a systems-level understanding of the coupled cycling of uranium, organic matter, and BCEs by employing an integrated suite of approaches that link the molecular and pore scales to field and regional scales at sites across the upper CRB. Investigations of the molecular characteristics and behavior of uranium in field materials and model experimental systems using sequential extractions; X-ray absorption spectroscopy; X-ray, electron, and isotope imaging; electrochemistry; and stable isotope techniques are furthering the understanding of which mechanisms control uranium interactions with groundwater under variable saturation and redox conditions. Molecular microbiology and microbial ecology techniques are providing information on microbial dynamics that mediate uranium redox cycling. This work is producing new process-level models necessary to understand the function and vulnerability of NRZ and unsaturated zone systems at floodplain to regional scales.



Bacterial Triculture. *Major microbial communities present in anoxic sediments are represented by the triculture of* Ruminiclostridium cellulolyticum *(fermentative bacterium capable of degrading cellulose),* Desulfovibrio vulgaris *(sulfate reducer), and* Geobacter sulfurreducens *(metal-reducing organism). Studies of uranium reduction in tricultures are showing how physical and biological conditions mediate uranium reduction.*



Nitrogen-Cycling Microbes. *Microbially mediated nitrogen cycling, particularly nitrification and denitrification, is a potentially important catalyst of uranium, sulfur, and iron oxidation in NRZ sediments.*

Regional Importance of NRZs

By adopting a regional perspective, a much larger array of behaviors can be observed than at a single site, enabling a deeper understanding of the biogeochemical functions and vulnerability of NRZs and unsaturated zone sediments to perturbations. For example, initial SFA research at the Rifle, Colorado, site led to the view that NRZs are permanently saturated and fine-grained sediment bodies. Examination of sites across the upper CRB, however, has expanded this model considerably. SLAC SFA research has found that a large fraction of NRZs occur within the zone of annual groundwater table fluctuations and thus are subject to major changes in saturation state annually and during the increasingly frequent droughts experienced in this region. Moreover, NRZs can be fine or coarse textured. Coarse-grained NRZs subject to groundwater fluctuation show the greatest biogeochemical activity and vulnerability to loss of uranium and organic carbon. These findings are advancing a conceptual understanding of the impacts of NRZs and evaporites on uranium plume persistence within the upper CRB, and further are providing new insights into methods for manipulating subsurface biogeochemical processes and remediation.

Contacts and Websites

Principal Investigator
John Bargar, bargar@slac.stanford.edu, 650.926.4949

BER Program Managers
Roland Hirsch, roland.hirsch@science.doe.gov, 301-903-9009
David Lesmes, david.lesmes@science.doe.gov, 301.903.2977
Paul Bayer, paul.bayer@science.doe.gov, 301.903.5324

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