SLAC SFA: Characterization of Uranium and Biogeochemical Critical Elements in Organic-Rich Sediments

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A growing body of evidence suggests that organic-rich sediments help to control the behavior of uranium and biogeochemical critical elements ("BCEs", including C, N, P, S, and Fe) in contaminated floodplains in Western U.S. DOE legacy sites. Lenses of these sediments containing also reduced uranium, iron, and sulfur, are referred to as naturally reduced zones (NRZs), and interact with groundwater along extensive interfaces. Large stores of organic matter in NRZs have the potential to fuel microbial activity and biogeochemical cycling of metals and BCEs. Consequently, NRZs are of intense interest as moderators of uranium and BCE fate and transport - locally at Rifle - and regionally in contaminated floodplains throughout the upper Colorado River basin. Understanding the molecular-scale speciation of uranium and BCEs is of central importance to advancing SBR predictive capabilities of NRZ-uranium-BCE-floodplain interactions. The mechanistic linkages between organic matter and uranium species are believed to be particularly important.

In the past year the SLAC SFA has investigated the following specific questions relating to NRZs at the Rifle site: (i) What is the molecular-scale speciation of U(IV), C, and N? (ii) What is the age of carbon in the aquifer and, by inference, the depositional age of the NRZs? Also, (iii) is carbon being exported to the surrounding aquifer? This work showed that non-crystalline U(IV) was the dominant form of uranium in all sediments examined. NRZ sediments were found to be surprisingly youthful, about 200 years old. N and C speciation in NRZs was found to be similar to that in the surrounding sediments, suggesting that NOM is being exported from the NRZs. Moreover, abundant proteinaceous coatings on NRZ minerals suggest the presence of bacterially-derived biomass. These observations contribute to the evolving picture of NRZs as youthful and biologically active zones that influence the surrounding aquifer.

Decomposition of thawing Arctic soil organic matter (SOM) is also of intense interest because it releases large amounts of methane and CO_2. Iron is believed to play a critical role in regulating bacterial metabolisms and hence the CO_2/methane balance. In collaboration with NGEE Arctic investigators, we used XAS to examine the speciation of Fe and SOM in samples from the Barrow Environmental Observatory. These measurements show that "dissolved" Fe(III) is present as both colloids and complexes, and different SOM functional groups are dominant in mineral soil vs dissolved fractions. These results are helping to build the molecular-scale basis for process-based modeling of SOM.