Mesoscale Biotransformation of Uranium

Tetsu Tokunaga[1], Jiamin Wan[1], Terry Hazen[1], Mary Firestone[1,2], Eoin Brodie[1], Zuoping Zheng[1], Joern Larsen[1], and Don Herman[2]

[1]Lawrence Berkeley National Laboratory, Berkeley, CA;
[2]Univ. of California, Berkeley, CA

Two outstanding issues central to the success of reduction-based in situ uranium bioremediation are the long-term stability of bioreduced U(IV), and the extent of U reduction achievable in transport-limited regions that comprise most of the subsurface. These critical concerns are being addressed through series of long-term column experiments.

Long-term Stability of In situ Microbially Reduced U(IV). Although previous short-term experiments on microbially mediated U(VI) reduction have supported the prospect of immobilizing the toxic metal through formation of insoluble U(IV) minerals, our longer-term (17 months) laboratory study showed that microbial reduction of U can be transient, even under sustained reducing (methanogenic) conditions. FRC Area 2 sediments containing 200 mg kg^{-1} U, at first primarily as U(VI), were packed into columns and infused with lactate solutions to accelerate reduction. Uranium was reduced during the first 60 days, but later (100 to 500 days) reoxidized and mobilized, even though a microbial community capable of reducing U(VI) remained active. Microbial respiration caused increases in (bi)carbonate concentrations and formation of very stable uranyl carbonate complexes, thereby shifting U(IV)/U(VI) equilibrium to much more reducing potentials. Fe(III) and Mn(IV) are likely terminal electron acceptors for U reoxidation. Thus, U remediation by organic carbon-based reductive precipitation can be problematic in sediments and groundwaters with neutral to alkaline pH, where uranyl carbonates are most stable. Our research is now focusing on biogeochemical conditions that can sustain U(IV) solid phases in the presence of carbonate.

Uranium Reduction in Sediments under Diffusion-Limited Transport of Organic Carbon. Delivery of organic carbon (OC) into contaminated sediments for stimulating U reduction is diffusion-limited in less permeable regions that comprise most of the subsurface. In order to study OC-based U reduction in diffusion-limited domains in sediments, Oak Ridge and Altamont soils were treated with $UO_2(NO_3)_2$ [U(VI) concentration ≈ 320 mg kg^{-1}], packed into columns, then hydrostatically contacted with tryptic soy broth solutions. Thus, OC was mineralized while diffusing into initially oxidizing soils. Even at average OC supply rates of 1 μmol OC (g soil)$^{-1}$ day^{-1}, the U reduction zone extended only about 40 mm into the soil columns. Spatial distributions of redox potentials, U oxidation state, and microbial communities were well correlated. Stratification of a reduced U(IV) zone over an oxidizing U(VI) zone persisted over 600 days because the OC supply was diffusion-limited and completely oxidized within the thin zone immediately adjacent to its point of application. These results show that low U concentrations in groundwater samples from OC-treated sites are not necessarily indicative of pervasive U reduction.