

A BENEFICIAL TRANSFORMATION OF URANIUM IN GROUNDWATER

Uranium is an all-too-common groundwater contaminant found at nuclear sites in the U.S. and worldwide. The advantages of bioremediation for removing contaminants from difficult-to-access environments, such as groundwater systems, are many. But to be sure that bioremediation is effective, the impact of biogeochemical processes on contaminant speciation must be understood. Research at the MR-CAT 10-ID beamline at the APS shows that the reduction of highly mobile aqueous hexavalent uranium (U^{VI}) to insoluble tetravalent uranium (U^{IV}) under oxygen-deficient conditions by the addition of an electron donor, or by modifying the environment to promote bacterial growth (biosimulation) can bring the uranium concentration in groundwater to below the U.S. Environmental Protection Agency maximum allowed level for drinking water.

10-ID • MR-CAT • Chemistry, environmental science, materials science • Diffraction anomalous fine structure, microfluorescence (hard x-ray), small x-ray absorption fine structure, x-ray absorption fine structure • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users

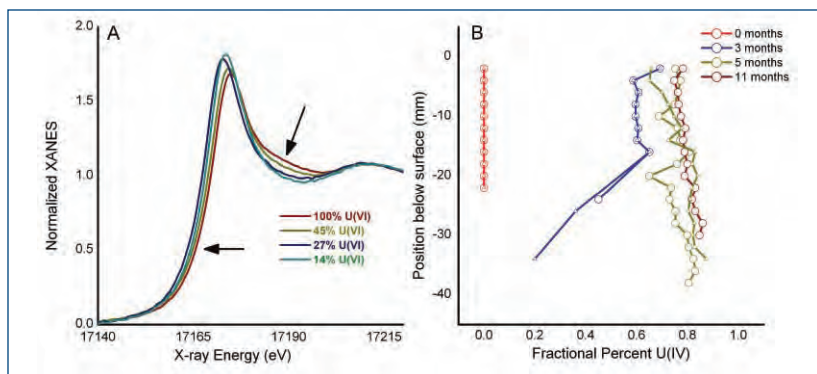


Fig. 1. Photograph (right) of microcosm at T11 and (above) U L_3 -edge XANES spectra for microcosm 1 (O) and microcosm 2 (Δ) as the microcosms aged from T0 to T11. (A) Evolution of the U spectra, with percentage of U^{VI} (based on linear combination fitting), with the remainder as U^{IV} . Arrows point in the direction of more U^{IV} . (B) Percentage of U^{IV} (based on linear combination fitting of the XANES spectra), with depth below the groundwater-sediment interface at 0 mm. Uncertainty is approximately 10%. (Figures this page ©2010 American Chemical Society)

The reduction of U^{VI} to U^{IV} occurred by two processes: Initial U^{VI} complexed by C- and P-containing ligands was transformed to U^{IV} in uraninite and associated with Fe-containing ligands, while Fe^{III} and sulfate was reduced by microbes.

Monitoring the spatial and temporal changes in the biogeochemistry of a sediment requires an analytical technique that does not disturb the sample. In this study, the researchers from Argonne, Stanford University, Michigan State University, and Oak Ridge National Laboratory (ORNL) monitored uranium, iron, and the microbial community in a sediment and groundwater sample from well FW026 at the Y-12 National Security Complex in Oak Ridge, Tennessee. A 1 mm \times 1 mm x-ray beam was used to probe the sediment depth profile for uranium and iron valence state and speciation within static microcosms, allowing analyses in sediment columns without disturbing them. X-ray fluorescence is used to map the distribution of U within the microcosm. Uranium x-ray absorption near edge structure measurements revealed two processes transforming U^{VI} to U^{IV} (Fig. 1). Extended x-ray absorption fine structure measurements determined the speciation of the uranium during transformation.

Analyses began five days after creating the microcosms (Time 0 (T0)) at the MR-CAT beamline. Samples were analyzed again at 3 months (T3), 5 months (T5), and 11 months (T11).

Changes in biogeochemistry mirrored visual changes within the sample. At T0 the entire sediment was a uniform yellow-tan with only U^{VI} present. By T3, bioreduction had turned the top layer and several regions within the sediment black. U^{IV} totaled 75% of uranium in the topmost layer and decreased at greater depths. At T5 and T11 the U^{IV} concentration of $80\% \pm 10\%$ was distributed evenly. Iron reduction, like uranium reduction, began at the top and progressed down the sediment profile. The uranium species changed, from U^{VI} in monodentate P ligands (U^{VI} -P) and bidentate C ligands (U^{VI} -C) at T0 to uranium associated with iron and with U^{IV} in the form of uraninite by T11.

The relative abundances of different bacterial phylogenetic groups revealed that the maximum phylogenetic diversity and most even relative abundances were at T0. Aqueous sulfate was completely consumed by T5, after which the population of sulfate-reducing bacteria decreased. Bacterial groups not dependent on sulfate then increased and were dominant at T11. Not all bacterial groups tracked the changes in electron donor and acceptor abundances, suggesting that other factors affected microbe abundances, including differences in sediment chemistry, and biological factors such as competition and commensalism between species and predation by viruses.

In the year-long experiment, U^{IV} only reached 82%. The authors specu-



late that the remaining U^{VI} is unavailable for reduction because it is sequestered within the sediments. Since the sediments have been exposed to the uranium-contaminated groundwater at ORNL for over 50 years, the sediments have had time to incorporate uranium into their internal structure. To be sure that this method of bioremediation will be effective, researchers must determine that this U^{VI} is stable and will remain sequestered under other geochemical conditions. — Dana Desonie

See: Shelly D. Kelly^{1*}, Wei-Min Wu², Fan Yang³, Craig S. Criddle², Terence L. Marsh³, Edward J. O'Loughlin¹, Bruce Ravel^{1**}, David Watson⁴, Philip M. Jardine⁴, and Kenneth M. Kemner¹, "Uranium Transformations in Static Microcosms," *Environ. Sci. Technol.* **44**, 236 (2010).

DOI:10.1021/es902191s

Author affiliations: ¹Argonne National Laboratory, ²Stanford University, ³Michigan State University, ⁴Oak Ridge National Laboratory. Present address.: [†]EXAFS Analysis, ^{**}Brookhaven National Laboratory/National Institute of Standards and Technology

Correspondence:

*dr.sdkelly@gmail.com

This work was supported under contract DE-AC02-06CH11357 by the U.S. Department of Energy (DOE) Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Program. MR-CAT operations are supported by the DOE and the MR-CAT member institutions. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.