Microscale Metabolic, Redox and Abiotic Reactions in Hanford 300 Area Subsurface Sediments

Haluk Beyenal[1] (PI), Jim Fredrickson[2], Jeffrey S. McLean[3], Bin Cao[1,2], and Paul D. Majors[2]

[1]Washington State University, Pullman, WA; [2]Pacific Northwest National Laboratory, Richland, WA; [3]J. Craig Venter Institute, La Jolla, CA.

beyenal@wsu.edu, Jim.Fredrickson@pnl.gov, jmclean@jcvi.org, bcao@wsu.edu, Paul.Majors@pnl.gov

Collaborators: Kenneth M. Kemner, Bhoopesh Mishra, and Maxim I. Boyanov (Argonne National Laboratory, Argonne, IL); Matthew J Marshall, Liang Shi, David W Kennedy, Roslyn N. Brown, Yijia Xiong, Margaret F. Romine, Mary S. Lipton, Nancy G Isern (Pacific Northwest National Laboratory, Richland, WA)

The U.S. Department of Energy Hanford 300 Area (300A) site experiences periodic hydrologic influences from the nearby Columbia River as a result of changing river stage, which causes changes in groundwater elevation, flow direction and water chemistry. An important question is the extent to which the mixing of Columbia River water and groundwater impacts the speciation and mobility of uranium (U). This year, we designed experiments to mimic interactions among U, oxic groundwater or Columbia River water, and 300A sediments in the subsurface environment of Hanford 300A. The results revealed that U was immobilized by 300A sediments predominantly through reduction (80-85%) when the column reactor was fed with oxic, organic-amended synthetic groundwater (OA-SGW). The reduced U in the 300A sediments fed with OA-SGW was relatively resistant to remobilization by oxic Columbia River water. Oxic Columbia River water resulted in U remobilization (~7%) through desorption, and most of the U that remained in the 300A sediments fed with OA-SGW (~93%) was in the form of uraninite nanoparticles. These results revealed that: 1) the reductive immobilization of U through OA-SGW stimulation of indigenous 300A sediment microorganisms may be viable in the relatively oxic Hanford 300A subsurface environments and 2) with the intrusion of Columbia River water, desorption may be the primary process resulting in U remobilization from OA-SGW-stimulated 300A sediments at the subsurface of the Hanford 300A site.

In continuation of our work related to understanding how heavy metals interact with subsurface biofilms at the microscale, noninvasive nuclear magnetic resonance imaging (MRI) and spectroscopy (MRS) approaches were used to monitor spatiotemporal responses of live *S. oneidensis* MR-1 biofilms to U(VI) and Cr(VI). MRI and spatial mapping of diffusion in the biofilms revealed that, although the overall biomass distribution was not significantly altered upon exposure to U(VI) or Cr(VI), microenvironments in the biofilm matrix changed as indicated by localized changes (~ 20 microns) of water diffusivity in the biofilms, suggesting potentially important contaminant-induced changes in structural or hydrodynamic properties of biofilm matrix upon exposure to the metals. We also quantitatively demonstrate that the responses of cellular metabolism in biofilms interacting with environmental contaminants are spatially stratified, implying the possibility that the strategies for detoxification or adaptation utilized by cells in biofilms may be altered in response to the local microenvironments. Lastly, we developed a 2-dimensional mathematical model to predict substrate utilization and metabolite production rates in *Shewanella oneidensis* MR-1 biofilms as well as U immobilization by considering reduction and adsorption processes in the cells and in the extracellular polymeric substances (EPS). The model included the production of EPS using the experimental data we generated last year. The EPS bound to the cell surface and distributed in the biofilm were considered as bound EPS (bEPS) and loosely-associated EPS (laEPS), respectively. COMSOL® Multiphysics finite element analysis software was used to solve the model numerically. We used a custom designed biofilm reactor placed inside a nuclear magnetic resonance (NMR) micro-imaging and spectroscopy system, and monitored substrate utilization and metabolite production rates to compare model with experimental data.