Mesoscale Coupled Transport and Biogeochemical Effects on Reduction of U(VI) and NO_3^- as Co-contaminants in Natural Sediments and Soils

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As fluids in subsurface environments are not well mixed, even at relatively small scales, the subsurface can be categorized into advective and diffusion-limited domains. Information is lacking concerning local, diffusion-limited processes that arise from small-scale variations in permeability, preferential flow paths, and soil/sediment structure. The primary objective is to study the coupled transport and biogeochemistry of U(VI) and NO_3^-. The redox reactions of these co-occurring contaminants are investigated in realistically heterogeneous model systems. We emphasize direct measurements within diffusion-limited domains at the mesoscale (defined as the typical diffusion-limited scale, ranging from about 10^{-4} to 10^{-1} m). It is within these diffusion-limited domains that large gradients in microbial activity, chemical potentials, reaction rates, and transport rates can coexist. Thus, dynamics at this mesoscale can control redox-dependent biotransformations in nature.

Part 1. Effects of pH and carbon on bioreduction of NO_3^- and U(VI) (FRC Area 3 sediment and groundwater high in nitrate). Rates of NO_3^- and U(VI) reduction in response to organic carbon amendments are under investigation. Due to the carbon concentration required to complete denitrification, we are investigating the efficacy of a commercially available slow-releasing polylactate form of carbon (Regenesis HRC) as well as a rapid release version of the same product (Regenesis HRC Primer). We are following microbial activity through analysis of gas headspace CO_2, CH_4, N_2O, and H_2. Upon complete reduction of NO_3^- and U(VI) we will destructively sample sediment/solution and extract DNA to determine changes in microbial community composition in response to each treatment.

Part 2. Diffusion-limited U(VI) biogeochemical transformation (FRC background area sediments). Measurements include U oxidation state determination by micro-XANES spectroscopy, soluble U (kinetic phosphorimetry) redox potential profiling, microbial activity, and microbial community analysis. Column experiments of 2 types are in progress. The first examines the U contamination process, with U(VI) diffusion into soil columns at different levels of initial organic carbon and microbial activity. Strong retardation of the U(VI) diffusion front in initially reducing sediments has been found to persist even after nearly 1 year without resupply of organic carbon. The second set of experiments focus on bioremediation of previously contaminated sediments, with organic carbon solutions diffusing into columns already containing U(VI). Significant U(VI) reduction has occurred only in columns supplied with high levels of organic carbon.

Part 3. U(IV) reoxidation in subsurface environments that revert to oxygenated conditions (FRC Area 2 sediments). These experiments will evaluate long-term stability of previously bioreduced U. In step 1, FRC Area 2 sediments containing 200 ppm U, initially primarily as U(VI), were packed into columns and infused with lactate solutions to accelerate reduction. Supporting measurements include analyses of U concentrations in effluents, in situ determination of sediment U(VI):U(IV), redox potential profiling, and pore-water chemical analyses. This step is near completion. In subsequent steps, columns will be exposed to oxygenated waters under flow-through or diffusion conditions, with sediment and solution U(VI) concentrations monitored to determine reoxidation rates.