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Mesoscale Coupled Transport and Biogeochemical Effects on Reduction of U(VI) and NO₃⁻ as Co-contaminants in Natural Sediments and Soils

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Since 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 on local, diffusion-limited processes that arise from small-scale variations in permeability, preferential flow paths, and soil/sediment structure. The primary objective of this research is to study coupled transport and biogeochemistry of U(VI) and NO₃⁻. 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 (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, the dynamics at this mesoscale can control redox-dependent biotransformations in nature.

Diffusion-limited U biogeochemical transformations. Measurements include determinations of U oxidation state (micro-XANES spectroscopy), soluble U, redox potential profiles, microbial activity, and microbial communities. Strong retardation of the U(VI) diffusion front in initially reducing sediments has been found to persist even after nearly two years without resupply of organic carbon. In oxidizing soils, U(VI) diffusion was relatively rapid under both acidic and slightly alkaline conditions because of relatively weak sorption. The strength of U(VI) sorption can be orders of magnitude less at high concentrations typical of initial waste sources.

U(VI) sorption in soils containing calcium carbonate. Calcite is a common component in slightly alkaline soils and sediments. However, the impact of calcite on U(VI) sorption in whole soil systems (as opposed to model systems comprised of single mineral phases) has not previously been evaluated. We found substantial suppression of U(VI) sorption at neutral to slightly alkaline pH, and showed that the depressed level of U(VI) sorption is fairly well accounted for by the stability of aqueous Ca₂UO₂(CO₃)₃, identified by Bernhard et al. [1].

Long-term stability of in situ microbially reduced U(IV). 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 included analyses of U concentrations in effluents, in situ determination of sediment U(VI):U(IV), redox potential profiles, pore water chemical analyses, microbial activity, and microbial community structure. Nearly complete U reduction was achieved by about 90 days, with effluent U concentrations decreased from initial values in excess of 1,000 ppb down to less than 5 ppb. However, continued organic carbon infusion and monitoring (over 500 days) revealed substantial U remobilization, with later effluent U concentrations exceeding 300 to 500 ppb. Net U reoxidation within the soil columns was supported by micro-XANES analyses. The remobilization of U was attributed to in-situ production of biogenic carbonate which shifts equilibrium towards stable U(VI) carbonate species. A shift in bacterial community structure was observed in the re-oxidation stage (relative to the earlier reducing stage). Thus, in some cases, reduction-based U immobilization can be transient and unreliable. This result also demonstrates the need for experiments that address long-term stability of in situ strategies for remediating actinide and metal contaminants.

1. G. Bernhard, G. Geipel, T. Reich, V. Brendler, S. Amayri, H. Nitsche. 2001. *Radiochim. Acta* 89, 511.