Microbiological Controls on the Fate and Transport of Chelated Radionuclides: Multiscale Investigations in Unsaturated Structured Media

Scott C. Brooks
Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

The overall goal of this project is to provide an improved understanding and predictive capability of the mechanisms that allow chelate-degrading bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that vadose zone microbial activity can effectively consume chelating organic ligands, thus facilitating the immobilization of released metals and radionuclides via sorption and precipitation reactions. The central hypothesis of this study is: in structured soils and aquifers, the biodegradation of metal-chelating ligands is limited by the diffusive mass flux of contaminants from pores too small to be accessed by bacteria to larger pores where bacteria reside.

Our objectives are to (1) develop an improved understanding and predictive capability of the mechanisms governing the biodegradation of cobalt (Co)-NTA in unsaturated, structured media; (2) quantify the microbial and hydrologic conditions that influence the biodegradation of metal-chelating ligands for the purpose of contaminant containment and remediation in heterogeneous, structured media; and (3) provide integrated experimental and theoretical methodologies for the scale-up of biohydrogeochemical processes from the microscopic scale to the macrocosm (pedon) scale. Our approach involves the use of a variably saturated dynamic flow technique to quantify the biodegradation of $Co^{II}NTA$ as a function of pore class size in structured media and existing models that couple microbial and hydrogeochemical processes to conduct multiscale process and parameter upscaling studies. The experimental results will provide new insights concerning the relationship between the biodegradation of radionuclide-chelate complexes and the pore structure and hydrologic connectivity in heterogeneous subsurface environments. Further, these results will enhance our ability to upscale laboratory- and pedon-scale biodegradation processes to the field scale.

Our results to date demonstrate some of the complex biogeochemistry that influences the fate and transport of chelated metals and radionuclides. The interaction of $Co^{II}NTA$ with common soil minerals results in the rapid formation of a variety of highly stable oxidized products, including $Co^{III}NTA$, $(Co^{III}NTA)_2$, and two isomers of $Co^{III}(IDA)_2$. These products have been observed in batch systems and in column displacement studies using undisturbed cores of structured saprolite. The stoichiometry of reaction products is a function of soil properties (e.g., pH). There is no direct evidence for the formation of geochemical dissociation products such as $Fe^{III}NTA$ or $Al^{III}NTA$. Furthermore, Co(III) complexes exhibit a low affinity for the solid phase. Accordingly, Co injected into undisturbed cores (as $Co^{II}NTA$) exhibits more rapid transport with increasing pH, indicating that the mobile cobalt remains as an anionic ligand-metal complex during transport through the column. Bacterial strains that can degrade NTA and some metal-NTA complexes (e.g., $Co^{II}NTA$) cannot degrade NTA complexed with Co(III). This effect is presumably the result of the kinetic and thermodynamic stability of $Co^{III}NTA$. These observations illustrate some of the complex biogeochemistry that influence the fate and transport of chelated metals and radionuclides.
These observed oxidation reactions have far-reaching implications for the transport of Co-NTA in soils and groundwater. The Co(III) complexes have a lower affinity for the solid phase than the corresponding Co(II) complexes resulting in enhanced transport of cobalt. The Co(III) complexes are much more stable, effectively competing with geochemical dissociation reactions and the concomitant formation of surface reactive Co(II). The Co(III) complexes are resistant to biodegradation.