The migration of trace elements in the environment is dependent on the chemical species which dominate under given geochemical conditions. The mobility can be enhanced or retarded by altering the oxidation state or forming soluble organic ligand-metal ion complexes. This work examines three case studies to evaluate the impacts of these changes in chemical speciation on the transport of trace elements through soil. Our approach seeks to characterize the time and length scales over which non-equilibrium states are maintained by rate-limiting (or rate-enhancing) reactions between radionuclides and co-reactants due to interactions between physical mass-transfer processes (i.e., flow, advection, diffusion) and (biogeo)chemical reactions.

Neptunium and technetium transport in field lysimeter studies has demonstrated enhanced mobilization of Np and Tc due to oxidation of Np(IV) to Np(V) and Tc(IV) to Tc(VII). Solid NpO$_2$(s) and Tc amended cementitious waste form samples were deployed in field lysimeters for up to 2 years. The effluent concentrations of Np and Tc were continually monitored and after retrieval from the field, the lysimeters were destructively sampled to determine the solid phase concentrations of Np and Tc as a function of depth in the lysimeter. The retrieved solid phases indicated surficial oxidation of NpO$_2$(s) along grain boundaries and leaching of Tc from corrosion rinds of the cementitious waste form. Both processes are controlled by redox gradients between the soil pore water and the waste forms. Complimentary laboratory testing has evaluated the rate and extent of source term oxidation and demonstrated that strong reducing gradients downgradient of the source can reduce Tc(VII) to immobile and insoluble Tc(IV). These measurements are enabled by the development of real-time, in-situ radioisotope monitoring techniques by our team.

A second mechanism by which the mobility of ions can be altered is through complexation with organic ligands. This work has examined the influence of nutrient availability, plant roots and plant root exudates on preferential water flow through field lysimeters and dissolution of uranyl phosphate minerals through formation of soluble U(VI)-ligand complexes. Results indicate that less soluble phosphate sources lead to enhanced plant exudate production which in turn enhances uranium solubility and mobility. These results were verified using flow-through batch reactor experiments examining the dissolution of uranyl phosphate by citric acid (a common phytosiderophore). Ongoing field lysimeter experiments with and without plants are examining these processes on larger spatial and temporal scales.

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