

ANNUAL REPORT, YEAR 2

Fate and Transport of Radionuclides Beneath the Hanford Tank Farms: Unraveling Coupled Geochemical and Hydrological Processes in the Vadose Zone

Purpose and Objectives

The overall goal of this research is to provide an improved understanding and predictive capability of coupled hydrological and geochemical mechanisms that are responsible for the accelerated migration of radionuclides in the vadose zone beneath the Hanford Tank Farms. The study is motivated by the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of multiple contaminants at the Hanford site. Our objectives are to (1) provide an improved understanding of how lithological discontinuities within the sediments influence the propensity for preferential flow and matrix diffusion at different water contents, (2) quantify the significance of downward vertical advection, lateral spreading, and physical nonequilibrium processes on radionuclide transport under variable hydrologic conditions, and (3) quantify the rates and mechanisms of ^{137}Cs , $^{235/238}\text{U}$, and ^{99}Tc interaction with the solid phase under various hydrodynamic conditions and to determine how physical heterogeneities (i.e. stratification, pore regime connectivity) influence the retardation and degree of geochemical nonequilibrium during contaminant transport.

Progress and Relevance to EM Needs

Our approach involves (1) field-relevant, long-term unsaturated flow and transport experiments in undisturbed Hanford sediments, (2) multiple tracer strategies for quantifying preferential flow and nonequilibrium mass transfer processes at various water contents, and (3) a variety of novel surface spectroscopic techniques to quantify the distribution and chemical environment of contaminants as a function of sediment lithology and water content.

Detailed investigations of uranyl sorption have been performed for a range of soil solids. Iron (hydr)oxides including ferrihydrite, goethite, and hematite sorb uranium(VI) strongly under neutral to slightly basic conditions. Dissolved carbonate complexes form under strongly alkaline conditions, leading to desorption of uranium. A variety of surface complexes have been postulated, although recent spectroscopic data suggests that uranium carbonate ternary complexes may be the principal surface species.

Mechanistic investigations of uranyl sorption on heterogeneous soils and sediment are complicated by the presence of multiple minerals, biological activity, and organic matter. In these systems, the chemical and microbial processes can reduce uranium to form insoluble U(IV) and mixed-valence oxides. Uranyl precipitates including uranyl phosphates, hydroxides, and carbonates can form in oxic, highly

contaminated soils and sediments. Under aerated soil conditions and neutral or higher pH, uranyl carbonate complexes dominate and limit sorption.

Uranyl surface species and their sorption mechanism have largely been determined through surface complexation modeling; direct identification of uranium surface complexes on soils and sediments has been less common. Accurately determining the surface structure of U is vital to determine the fate of this hazardous element in the environment. Strong sorption complexes and surface precipitates are the least labile and thereby decrease uranium bioavailability and transport. X-ray absorption spectroscopy (XAS) provides an *in-situ*, element-specific probe of the local structure of the surface complex, and with it the principal sorption mechanisms. Accordingly, in this study we used XAS to determine the sorption mechanism of uranyl on several soils and sediments that are associated with uranium contamination. A detailed understanding of the sorption mechanism will provide insight into its stability, and thus its transport and bioavailability. It will also help to determine the principal soil minerals that control uranium sorption.

A mechanistic understanding of uranium sorption in natural soils and sediments is useful for determining its transport and bioavailability in the environment. X-ray absorption spectroscopy (XAS) was used in conjunction with transport studies to determine the mechanisms by which uranium(VI) sorbs to three heterogeneous subsurface media (Fig. 1). Ternary complexes of uranyl carbonate or uranyl phosphate are the dominant surface species in these systems and appear to exist as disordered phases on iron (hydr)oxides and possibly aluminosilicates. The complexes are a composite of inner- and outer-sphere, with the former being dominant. Most of the uranium(VI) retained on these solids is relatively labile due to the disordered nature of the inner-sphere complexes coupled with the presence of outer-sphere complexes. The reversibility of uranyl sorption on these subsurface media supports the spectroscopically inferred stability of the surface species.

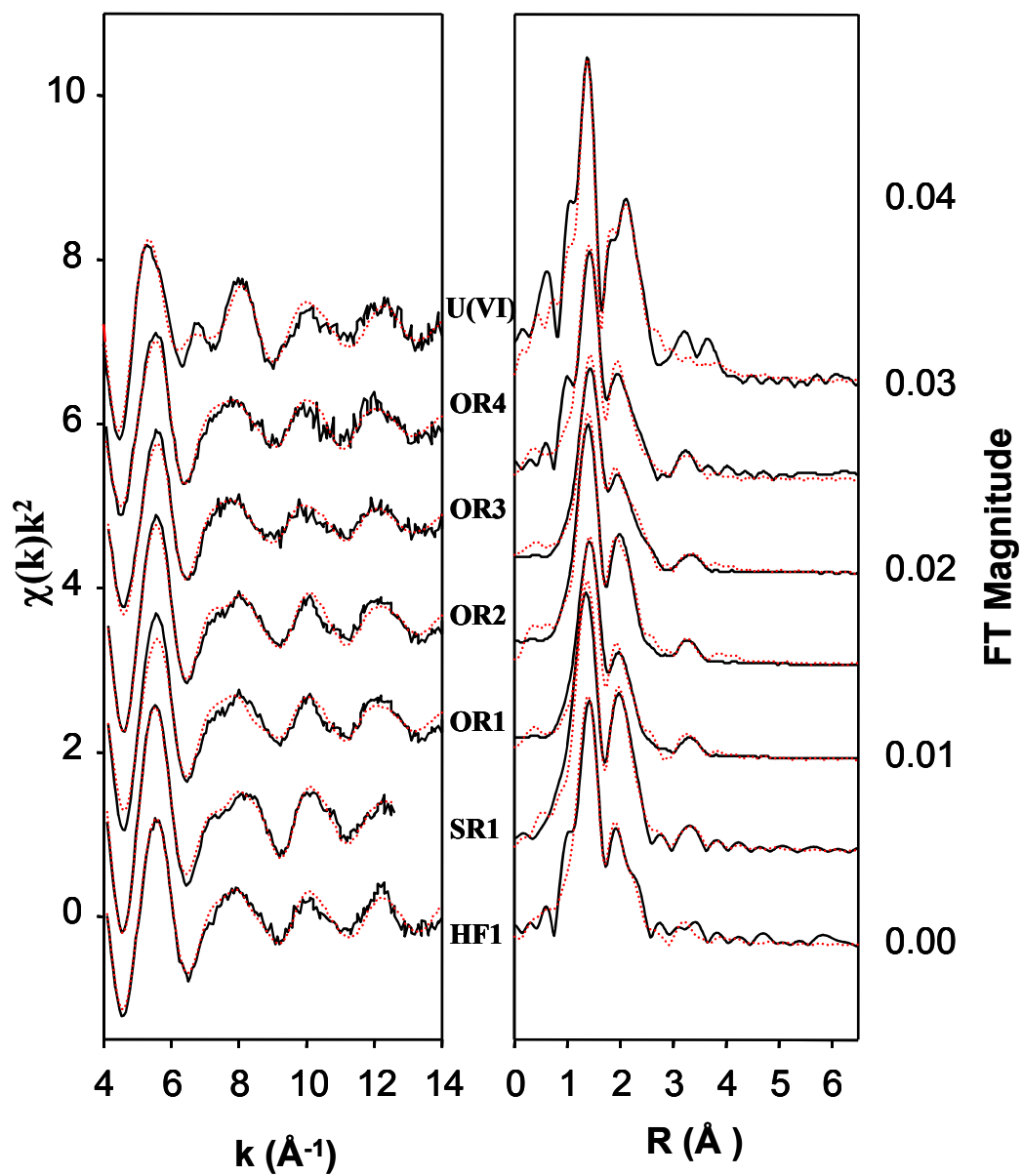


Figure 1. (A) The k^2 -weighted $\chi(k)$ U-L_{III} EXAFS spectra and (B) uncorrected radial structure functions for HF, SR, and OR subsurface media sorbed with U. The experimental data (solids lines) are fit (dotted lines) using the parameters described in Table 3.