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

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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, $^{235/238}U$, 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.

This report summarizes 1.5 y of research for a 3 y project.

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.

A special-use permit to extract core from the White Bluffs was granted by the DOE-RL cultural resources agency. The White Bluffs was an ideal location for extracting Upper Ringold and Plio-Pleistocene core material since the physical and geochemical characteristics of these formations is nearly identical to those beneath the 200 West Area of the Hanford tank farms. Sediments from the Hanford Formation were acquired from another location. A rotary coring apparatus using a diamond bit core barrel was fabricated and mounted onto a backhoe so that cores could be obtained at any angle within the various formations. Undisturbed cores (0.3m diam X 0.3 m length) were obtained parallel to lithological layering (horizontally into the formation…see Fig. 1a) and perpendicular to lithology (vertically downward). The different core types served to quantify the significance of downward vertical advection versus lateral movement of contaminants due to tension-dependent anisotropy. In order to extract the cores from the formation, the annulus separating the formation from the core was filled with expandable foam and allowed to harden. The cores were then carefully removed from the formation by hand excavation. The rigid foam material not only maintained the integrity of the cores, it also contained an impression of the various sediment layers from the surrounding porous media, including Fe-oxide staining patterns. Thus, it was possible to infer the distribution of flow paths and mineralogical heterogeneities within the cores. A total of eight cores were obtained; three from the Upper Ringold sands (two horizontal, one vertical), three from the Upper Ringold sandy silts (two horizontal, one vertical), one angled core that cross-cut the Upper Ringold sands and silts, and one Plio-Pleistocene core. Bulk samples were obtained from each formation types as well as from the Hanford formation at a different location. The various cores were transported back to ORNL, where they were prepared for unsaturated flow and transport studies using a variety of nonreactive tracers and the contaminants of interest ^{137}Cs, $^{235/238}U$, and ^{99}Tc.

Using a modification of the unsaturated flow technique described by Jardine et al. (1993, SSSAJ), the fate and transport of multiple nonreactive tracers (Br, pentafluorobenzoic acid, and PIPES) and reactive radionuclides ^{134}Cs, $^{95/99}Tc$, and $^{235/238}U$ are being investigated at a variety of water contents reflective of a range of recharge rates common to the Hanford site (Fig. 1b). Nonreactive tracer studies have been initiated first in order to quantify any physical nonequilibrium processes that may exist in the sediments. Each nonreactive tracer differs only in its free water molecular diffusion coefficient. Thus, the tracers are ideal for assessing nonequilibrium mass transfer processes as a function of water content in the various media. In order to determine the inlet tracer flux at the column upper boundary at various degrees of unsaturation, small undisturbed cores (8 cm diam X 6.5 cm length) of the various sediment materials were also acquired and used to determine the water retention properties of the media. The water retention functions were modeled with the van Genuchten equation and was used to generate hydraulic conductivity vs. pressure head functions. Thus, the inlet tracer flux could be estimated for any given pressure head imparted on the various cores to create unsaturated conditions.

Significant findings regarding hydrologic processes in sediments beneath the tanks:

(1) The saturated and unsaturated hydraulic conductivity of cores acquired parallel to lithological layering was an order of magnitude more rapid than the conductivity of cores acquired perpendicular to lithological layering. Thus, lateral flow beneath the tank farms is a strong contributor to the spread of contaminants. Also, the conductivity of fine grained cores were an order of magnitude slower than core acquired in sandy media.

(2) The transport of the three nonreactive tracers at different degrees of unsaturation showed essentially no difference in breakthrough patterns when flow remained unrestricted along continuous lithological features as is the case for the horizontal cores (Fig. 1c). This suggested that physical nonequilibrium conditions were not occurring during lateral flow in these sediments. Thus matrix diffusion processes are not contributing to the attenuation of waste being released from the Hanford tanks allowing for more rapid transport rates beneath the tank farms.

(3) However, when flow is partially restricted by lithologic discontinuities as is the case for the vertical cores (e.g. alternating coarse and fine layers), perched water tables develop resulting in unstable wetting fronts and the prevalence of preferential flow. The early breakthrough and significant separation of tracer in the effluent suggest that large pockets of immobile water develop creating a condition of physical nonequilibrium between flowing domains and immobile domains. From a contaminant transport perspective this process is advantageous since the presence of large pockets of immobile water will significantly impede the vertical migration of waste being released from the Hanford tanks.

Once the physical processes have been deciphered, reactive radionuclides ^{134}Cs, $^{95/99}Tc$, and $^{235/238}U$ will be investigated at a variety of water contents. Our unsaturated flow technique will allow for fate and transport investigations in select pore regimes thereby isolating hydrological and geochemical mechanisms that are operative at different water contents. Currently we are conducting batch sorption experiments on the various sediments and using interfacial molecular techniques (x-ray absorption spectroscopy, hyperquenching fluorescence) to quantify the distribution and chemical environment of the sorbed contaminant species. Knowledge of the reaction mechanisms will serve to enhance our predictive capability of the observed contaminant transport experiments at the various hydrologic conditions.

Significant findings regarding geochemical processes in sediments beneath the tanks:

(1) Batch studies have shown that U and Cs are strongly bound to the various sediments beneath the tank farms even under conditions where the solid phase pH is as high as 8.4. Modeled partition coefficients for U were on the order of 10 to 15 cm^3/g corresponding to retardation coefficients of 35 to 50. Modeled partition coefficients for Cs ranged from 30 to 90 cm^3/g, with the Hanford formation exhibiting a significantly larger retention capacity for the Cs versus the Ringold formation. Ternary exchange isotherms for the U-Cs-Ca system showed limited competitive sorption effects suggesting independent mechanisms controlled U and Cs sorption. This is consistent with experimental evidence showing that U sorption is often controlled by subsurface Fe-oxides and Cs sorption is often associated with the interlayer spaces of 2:1 phyllosilicates.

(2) X-ray Absorption Spectroscopy (XAS) suggested that inner-sphere ternary carbonate complexes formed on Fe-oxides in sandy Ringold sediments while sorption of sheet silicates was the primary sorption mechanism in silty Ringold sediments. These data underscore the importance of understanding the sediment mineralogy to accurately access the fate and transport of uranium in the environment. The implications of the sorption reactions are that the downward vertical migration of U beneath the tank farms will be significantly slowed by interfacial geochemical sorption reactions.

Implications:

The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for Tank Farm restoration. By unraveling fundamental contaminant transport mechanisms in complex porous media, we will provide an improved conceptual understanding and predictive capability of a variety of vadose issues within the DOE system.

<u>Peer-reviewed manuscripts</u>:

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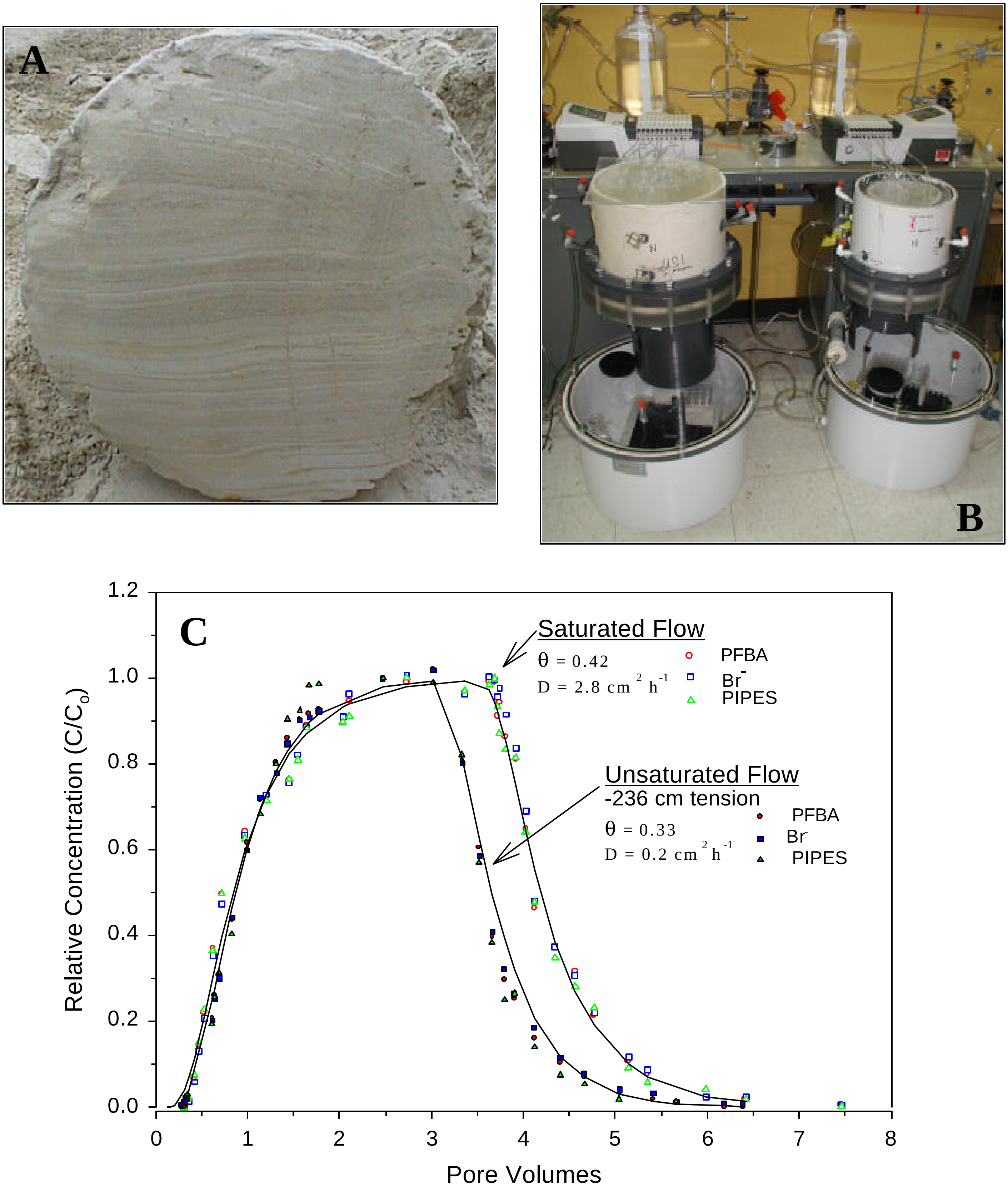

Figure 1 (A) The face of an undisturbed core that was acquired parallel to lithologic layering in the Ringold formation, (B) the unsaturated flow setup, and (C) an example of multiple nonreactive tracer breakthroughs at two different water contents for flow parallel to the bedding structure of the media.