

# **Coupled Geochemical and Hydrological Processes Governing the Fate and Transport of Radionuclides and Toxic Metals Beneath the Hanford Tank Farms**

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Project Objective: - Provide an improved understanding of how preferential vertical and lateral flow, and the formation of immobile water influence the transport of radionuclides and toxic metals in heterogeneous, laminated sediments. - Quantify the rates and mechanisms of radionuclide and toxic metal interaction with the solid phase under various hydrologic conditions. - Provide new insights into how physical and mineralogical heterogeneities (e.g. stratification, pore regime connectivity, mineral composition along flowpaths) influence contaminant retardation and the degree of geochemical nonequilibrium during transport. Background: The Hanford Site is located in the semi arid Pasco Basin of the Columbia Plateau in south central Washington State. The major geologic units of the vadose zone are the Hanford Formation which overlies the Ringold Formation. The Hanford Formation consists of fine to coarse grained sands and gravels deposited by the cataclysmic floods of the Pleistocene; embedded caliche beds are also found in the Hanford Formation. The Ringold Formation consists of semi consolidated clays, silt, pedogenically altered sediment, fine to coarse grained sands and gravel. The Plio Pleistocene Unit (sandy gravels) and early Palouse soil (eolian, loess containing) separate the two formations. The Hanford Formation generally lies above the water table except in the eastern (300 Area) and northern (100 Area) parts of the site. Ringold strata are typically below the water table except in the central (200 Area) of the site, where they comprise ~15% of the vadose zone material. The vadose zone sediments at the site are generally coarse (70-80% sand and gravel), oxic, low clay content (< 10%), and very low organic carbon (< 1%). Due to stratification the hydraulic conductivity is highly spatially variable. Nevertheless, the hydraulic conductivity for the Hanford Formation is thought to be one order of magnitude higher than for the Ringold Formation and horizontal conductivities are thought to be 100 times higher than vertical conductivities. Factors that are poorly understood in the general hydrogeologic framework include cross cutting features (clastic dikes, vertical fissures), discontinuities in strata, and the presence of unsealed or poorly sealed wells and boreholes. All these features add to the complexity of moisture flow at the site and may result in the rapid transport of contamination through the vadose zone to the groundwater with minimal interaction with sediments. Furthermore, perched zones of saturation (perched water tables) are known to form on top of low permeability soil lenses (clays, fine sediments), highly cemented horizons (e.g., caliche beds), and at the contact between a fine grained stratum overlying a coarse grained stratum. Mud sequences in the Ringold Formation and the low permeability Plio Pleistocene unit and early Palouse soil underlying the 200 Area represent major features that control the formation of perched water tables. Perched water is known to exist underneath active release sites (Fig. 1). These perched water tables can promote significant lateral contaminant transport, where flow could potentially intercept vertical fissures. They also lead to wetting front instabilities that promote preferential flow and transport via finger flow and funnel flow. All of these mechanisms can result in enhanced contaminant migration. Because of the great depth to the water table underlying much of the site (~100 m) and the semi arid climatic regime (16 cm average annual precipitation), contaminant migration to groundwater was considered to be a minor concern. Nevertheless, the direct disposal to soils of approximately 450 billion gallons of waste water (via cribs and trenches) raised the local water table nearly 30m and effectively invalidated transport predictions predicated on natural climatic recharge. Major groundwater mounds were created underneath the 200 Area, although reduction of waste disposal has led to declines in water table elevation. In addition, an incomplete understanding of the complex vadose zone hydrology resulted in inadequate model simulations. Sediment Geochemistry The Hanford Site sediments are neutral to slightly alkaline with a net negative charge on soil particles which promotes the sorption of cations but anion adsorption is not favored under these conditions. Hanford Site sediments cannot be meaningfully differentiated based on chemical characteristics, with the exception of the ion exchange capacity, which is related to the fraction of fine grained sediments.

Underneath the 200 Area, smectite is the dominant 2:1 phyllosilicate in the clay fractions from the Hanford and Ringold Formations. Illite and its weathering products vermiculite and chlorite are common on the Hanford and Upper Ringold. Smectite concentrations decrease with depth whereas the concentrations of illite, vermiculite, and chlorite increase with depth (Amonette, PNNL, unpublished data). These 2:1 phyllosilicates confer to the soil a large capacity for  $^{137}\text{Cs}$  sorption. In fact, direct waste disposal to the soil was based on the assumption that the geochemical capacity for retaining contaminant solutes was more than adequate to prevent waste migration through the subsurface. This assumption has proven to be overly optimistic. Waste Disposal to Soils at the Hanford Site Enormous quantities of radioactive, chemical, and mixed wastes were generated at the Hanford Site. Solid wastes were typically disposed of via on site burial, while liquid wastes were discharged to shallow subsurface cribs, French drains, trenches and injection wells. Most liquid waste discharges have ceased along with most production activities in the past decade, nevertheless, relatively mobile radionuclides such as  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , U, and  $^3\text{H}$  have contaminated the aquifer beneath the site. Groundwater plumes exist below a significant fraction of the site, and concentrations of  $^3\text{H}$ ,  $^{129}\text{I}$  and U in the Columbia River, which bisects the site, are significantly higher below the site than above. Of particular concern is contaminant transport below the single shell tanks in the 200 West Area. Contaminants have entered the subsurface below these tank farms due to leaks and spills. U contamination has been detected up to depths of 30 m below the U Tank Farms in the 200 West Area (DOE, 1997). The detection of significant  $^{137}\text{Cs}$  transport beneath the tanks and the presence of  $^{99}\text{Tc}$  in the groundwater fundamentally altered the long held assumptions that the tanks wastes were not mobile and therefore did not pose a significant risk. These observations prompted a call for a reevaluation of contaminant transport in the vadose zone (DOE, 1998). Although the accelerated transport of  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$ , and  $^{235/238}\text{U}$  within the vadose zone beneath the 200-West Area Tanks has been recognized, the mechanisms responsible for the vertical migration of the radionuclides is unclear. Fundamental experimental research is needed that will improve the conceptual understanding and predictive capability of radionuclide migration in the Hanford tank-farm environment. Since geochemical reactions are directly linked to the system hydrodynamics, coupled geochemical and hydrological processes must be investigated in order to resolve the key mechanisms contributing to vadose zone and groundwater contamination at Hanford. Status: 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. (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. This suggested that physical nonequilibrium conditions were not occurring during lateral flow in these sediments. (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. Significant findings regarding geochemical processes in sediments beneath the tanks: (1) Batch and repacked column studies have shown that U, Cs, and Sr can be strongly bound to the various sediments beneath the tank farms even under conditions where the solid phase pH is as high as 8.4. However, when U-CO<sub>3</sub> species dominant the system, sorption reactions become increasingly less important and U remains highly mobile. Sediment samples from the Ringold formation (White Bluffs) and Hanford formation (ERDF and ILAW sites) have been shown to effectively dissociate Sr-EDTA complexes and reduce mobile Cr(VI) to sparingly soluble Cr(III). These findings are important since they show geochemical reactions can help impede the migration of Sr and Cr through the Hanford vadose zone. However, the Ringold and Hanford sediments were also found to effectively oxidize Co(II)EDTA to Co(III)EDTA. The adverse environmental implications of this reaction is that Co(III)EDTA is an extremely stable complex that enhances its mobility in subsurface environments. (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 assess 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. We have recently been investigating the attenuation of chromium within Hanford sediments. Using a unique

integration of synchrotron based techniques inclusive of X-ray microprobe analysis in conjunction with micro-X-ray absorption spectroscopy and micro-X-ray diffraction, allows us to (1) map the distribution of Cr, (2) determine the valence state of Cr, and (3) determine its correlation to specific mineral constituents. Our analysis reveals that chromium is retained appreciably on via reduction from chromate to Cr(III) and that ferrous bearing primary minerals within the Hanford formation are responsible for reduction. Biotite and to a lesser extent ilmenite are the principal components leading to the attenuation of chromium through reduction of Cr(VI) and deposition of Cr(III). Our results reveal that chromium is reduced to Cr(III) and sequestered in localized domains proximal to ferrous bearing mineral phases. However, surface passivating layers, inclusive of ferric hydroxide coatings, arrest the reducing capacity of the mineral surface and thus lead to the unaltered transport of chromate through the sediments. Thus, it is critical that mineral surface remain in a reactive form in order to limit the transport of chromate. (3) Reactive transport of Sr, U, and Co(II)EDTA in undisturbed Hanford cores and U in undisturbed consolidated material of the Plio-Pleistocene unit have also been conducted. The Plio-Pleistocene unit was not conducive to either preferential vertical finger flow or to lateral flow, as no tracer separation (Br/PFBA/PIPES) was observed under our experimental conditions. The absence of distinct sedimentary bedding in the Plio-Pleistocene probably accounts for this observation. Our results therefore suggest that physical nonequilibrium processes will be minimal in the Plio-Pleistocene unit. Reactive transport of  $^{235}/^{238}\text{U}$  through the Plio-Pleistocene unit exhibited evidence of nonequilibrium, possibly influenced by kinetics or multi-site/multi-species reactivity. Sorption of  $^{235}/^{238}\text{U}$  was significantly enhanced under equilibrium conditions when compared to transport or flowing conditions, which suggests kinetic effects on sorption. Transport experiments were conducted in an atmosphere representative of subsurface conditions (1%  $\text{CO}_2$ ), which resulted in the formation of a stable uranyl-carbonate complex. Therefore, it is also likely that the large complex may have different affinities for subsurface sorption sites. Transport through the Plio-Pleistocene unit has demonstrated the presence of geochemical nonequilibrium while physical nonequilibrium processes were minimal, thus resulting in a greater understanding of the relevant mechanisms governing contaminant interactions in the Hanford subsurface. The transport of Sr and  $\text{U-CO}_3$  in the Hanford core shows strong and moderate reactivity, respectively which is consistent with batch and repack column studies and the transport of Co(II)EDTA shows complete oxidation to Co(III)EDTA. (4) Generation of Fe(II) reductant pools for chromium and uranium reductive attenuation are dependent on the host ferric mineral forms. We compared the reducing capacity, biomineralization, and microbial colonization of goethite and hematite to 2-line ferrihydrite under advective flow within a medium mimicking that of natural groundwater. Microbial reduction of 2-line ferrihydrite, goethite, and hematite was investigated using a number of columns performed in two main experimental studies. Introduction of dissolved organic carbon upon flow initiation results in the onset of dissimilatory iron reduction of all three Fe phases (2-line ferrihydrite, goethite, and hematite). While the initial surface area normalized rates are equivalent (ca. 10-11 moles Fe(II)/ $\text{m}^2 \text{g}^{-1}$ ), the amount of Fe(III) reduced and mechanisms of sequestration differ among the three iron oxide substrates. Following 16 d of reaction, the amount of Fe(III) reduced within the ferrihydrite, goethite, and hematite columns is 25, 5, and 1%, respectively. This trend in reduction is consistent among systems normalized to both total Fe(III) (ca. 10 mg  $\text{g}^{-1}$ ) or surface area for the goethite- (0.4  $\text{m}^2 \text{g}^{-1}$ ) and hematite-coated (0.5  $\text{m}^2 \text{g}^{-1}$ ) sand. Additionally, goethite and hematite illustrate a similar control on the fate of Fe(II), which differs appreciably from the sequestration and precipitation mechanisms within the ferrihydrite columns. While 83% of the Fe(II) produced in the ferrihydrite system is retained within the solid-phase, merely 17% is retained within both the goethite and hematite columns. Iron(II) sequestered within the solid-phase in the ferrihydrite column is dominantly present as the secondary precipitate magnetite. Conversely, no secondary precipitation was detected upon reductive dissolution of goethite and hematite, indicating that Fe(II) within the solid-phase exists largely as a complex on the oxide surfaces. Thus, the specific mineralogy of an aerobic environment will dictate the degree to which a reductive strategy will function in the reductive stabilization of heavy metals (e.g., chromium) and radionuclides (e.g., uranium and technetium).