

Coupled Hydrological and Geochemical Processes Governing the Fate and Transport of Radionuclides and Toxic Metals in the Hanford Vadose Zone

M.A. Mayes^{1*}, P.M. Jardine¹, S.E. Fendorf², M.N. Pace¹, X. Yin¹, T.L. Mehlhorn¹, and J.M. Zachara³
*mayesma@ornl.gov. ¹Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008 MS-6038, Oak Ridge, TN 37831. ²Department of Geological and Environmental Sciences, Stanford University, Palo Alto, CA 94305. ³Environmental and Molecular Science Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352.

Introduction

At the Department of Energy Hanford Reservation, near Richland, WA, plutonium production during the cold war era has resulted in the generation of large quantities of high level radionuclides and toxic metals. The primary method of disposal was underground burial within high-capacity single- and double-shelled steel tanks (“tank farms”). Approximately 1 million gallons of the waste are known to have leaked into the deep (70 m) vadose zone of this semi-arid region [1]. Observed migration of radionuclides has been characterized as “accelerated,” because the distribution of highly reactive radionuclides (e.g., ¹³⁷Cs) is significantly wider and deeper than expected [2]. This suggests that there is still considerable uncertainty regarding the mechanisms of contaminant transport in the vadose zone.

The goal of our research is to provide an improved understanding and predictive capability of the coupled hydrological and geochemical mechanisms contributing to the transport of radionuclides and toxic metals beneath the Hanford tank farms. Our approach is to perform a suite of experiments ranging from novel surface interrogation techniques (e.g., XAS) to miscible displacement experiments on disturbed and undisturbed sediments from the Hanford, Plio-Pleistocene, and Ringold Formations. Our objectives are (1) to 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 (i.e. ^{235/238}U, ¹³⁷Cs, ⁹⁰Sr, ⁶⁰Co, and Cr(VI)) in heterogeneous, laminated sediments, (2) to quantify the rates and mechanisms of radionuclide and toxic metal interaction with the solid phase under various hydrologic conditions, and (3) 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. Our results are expected to contribute to the overall conceptual understanding and quantitative modeling needs associated with radionuclide transport in the Hanford vadose zone.



FIGURE 1

Materials and Methods

Large undisturbed sediment columns (0.25 m dia x 0.25 m length) were acquired within the Hanford, Plio-Pleistocene, and Upper Ringold formations using a rotary coring apparatus equipped with diamond bit core barrels attached to a track-mounted hydraulic motor (Fig. 1). The Upper Ringold Formation, which comprises the lower 11 m of the vadose zone, consists of fine-grained, semi-consolidated, laminated silts and sands deposited within a lacustrine environment [3]. The Plio-Pleistocene Unit (thickness ~ 12 m) is a consolidated, calcite-cemented deposit composed of riverine lithic and ash fragments (Fig. 1) [4]. The Hanford Formation, which comprises the upper 45 m of the vadose zone, is a coarse- to fine-grained, heterogeneous, unconsolidated sand which was deposited as a result of cataclysmic floods during the most recent glacial period (Fig. 2) [3]. Detailed characterization efforts have shown that the core materials have nearly identical physical and geochemical characteristics as sediments beneath the 200-West Area of the Hanford tank farms [5]. Undisturbed cores were obtained parallel to lithological layering (horizontally) and perpendicular to lithology (vertically) (Fig. 2). Using an unsaturated flow technique (Fig. 3), the fate and transport of radionuclides and toxic metals are being investigated at a variety of water contents in the undisturbed cores.

Multiple nonreactive tracers have been used to identify nonequilibrium mass transfer resulting from purely physical processes, e.g., diffusional exchange between relatively immobile regions and preferential flow paths. Three nonreactive tracers Br^- , pentafluorobenzoic acid (PFBA), and piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) were used, which differ only in their free water molecular diffusion coefficient, thus physical nonequilibrium may be inferred by observed separation of the tracers [6, 7]. Further, the dependence of nonequilibrium processes upon water content has been tested by performing transport experiments at multiple pressure heads. This unsaturated flow technique reproduces fate and transport in select pore regimes, thereby isolating hydrological mechanisms operative at different water contents.



FIGURE 2



FIGURE 3

The transport of reactive contaminants may also be influenced by geochemical processes which are a function of the degree of physical nonequilibrium. Therefore, extensive geochemical investigations of radionuclide-sediment interactions have been performed. Samples of sediments with varying mineralogy and hydrologic characteristics (e.g., grain size) were acquired from within the sedimentary units of the various subsurface formation types. The transport of radionuclides was characterized by performing equilibrium and kinetic adsorption isotherms and miscible displacement experiments under a variety of experimental variables (e.g., ionic strength, pH, variable flux). Geochemical interactions with surface mineralogy were identified using a variety of surficial interrogation techniques (e.g., XAS, Mossbauer spectroscopy). The combination of hydrologic and geochemical techniques will allow us to establish the connection between sorption of radionuclides and variant hydrologic regimes resulting from differential water contents.

Results and Discussion

Hydrologic processes are influenced by sediment layering and antecedent water content in the three sedimentary units which comprise the 70 m vadose zone beneath the tank farms. Dominant hydrologic processes were identified in the undisturbed cores [6, 7, 8], and our future research focusses on the implications of these processes on the geochemical transport of radionuclides and toxic metals. This paper will briefly describe observed hydrologic transport processes and discuss the implications with reference to geochemical transport processes.

A propensity for lateral flow is suggested within the Ringold Formation where sediments are fine-grained and strongly horizontally-bedded. The observations of similar breakthrough patterns and no tracer separation, regardless of saturation, in horizontal cores of this media supports this assertion (Fig. 4). The absence of tracer separation suggests that the formation of immobile water and preferential flow were minimal. This was likely a result of desaturation of coarse-grained beds and the subsequent restriction of flow to finer-grained bedding. Desaturation of specific beds resulted in the formation of capillary barriers, which prevented exchange between pore regions and eliminated physical processes of

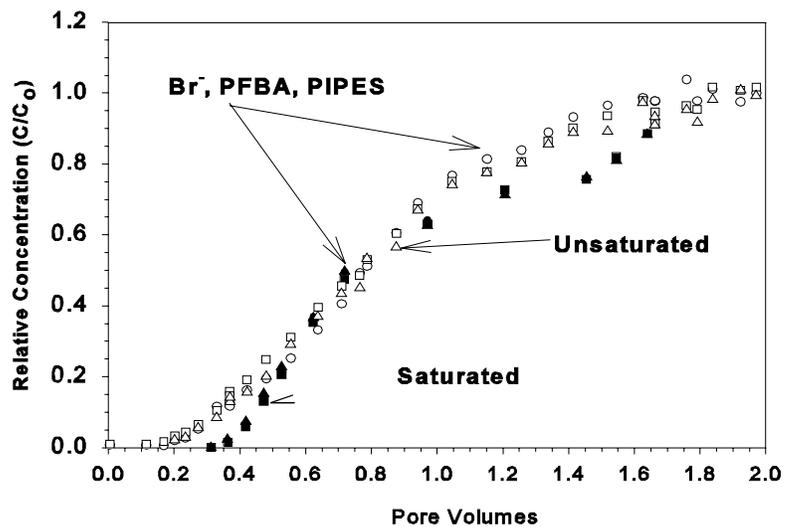


FIGURE 4

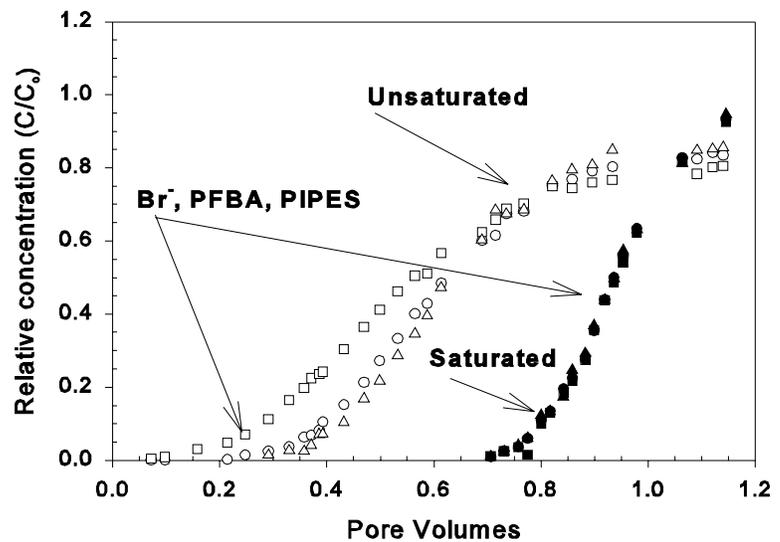


FIGURE 5

nonequilibrium. This mechanism of lateral flow may contribute to enhanced transverse spreading of wastes being released from the tanks.

When flow was required to cross lithologic discontinuities, the formation of capillary barriers in desaturated coarse layers inhibited stable vertical flow, thus resulting in the development of perched water and preferential finger flow. The observation of earlier tracer breakthrough with decreasing water content, and separation of the nonreactive tracers support these hypotheses (Fig. 5). This was observed in vertical cores composed of alternating coarse and fine layers, and in horizontal cores composed of strongly cross-bedded material in the Hanford and Ringold formations [6, 7]. The observance of immobile water as inferred by tracer separation is significant, because large pockets of immobile water may impede the vertical migration of waste being released from the Hanford tanks. Further, physical nonequilibrium has the potential to affect rate-dependent geochemical reactions during reactive contaminant transport.

The consolidated material of the Plio-Pleistocene unit was not conducive to either preferential vertical finger flow or to lateral flow (Fig. 6), as no tracer separation was observed under our experimental conditions. The absence of distinct

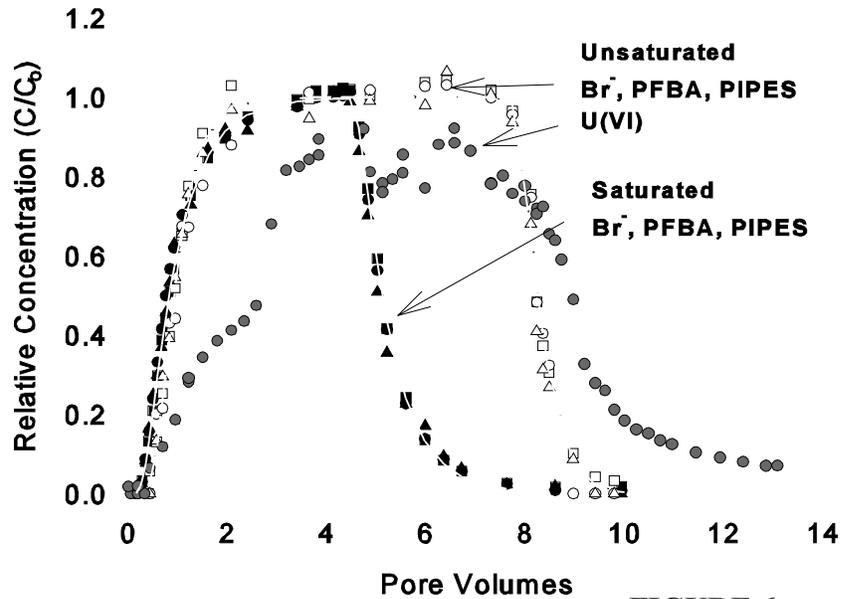


FIGURE 6

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 (Fig. 6). 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 [8]. Transport experiments were conducted in an atmosphere representative of subsurface conditions (1% CO_2), which resulted in the formation of a stable uranyl-carbonate complex [9, 10]. 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 direction of our future studies will focus on the identification of coupled physical and geochemical nonequilibrium processes which will likely be present during the transport of radionuclides through the large, undisturbed cores, as suggested by our hydrologic investigations. During miscible displacement experiments in packed columns, $^{235/238}\text{U}$ has exhibited kinetic effects in the Hanford and Ringold formations [11], therefore we expect that physical nonequilibrium processes may additionally affect the transport of radionuclides in the Hanford and Ringold undisturbed cores. Kinetic effects have also been observed in the transport of Cs through

the Hanford Formation, probably due to rate-limited migration of Cs into the interlayers of biotite micas, which are present only in the Hanford media. Further, coupled Cs and Sr transport has been observed to enhance this effect in the Hanford. The transport of Cr(VI) and Co(II)EDTA²⁻ are still under investigation. In summary, our approach should yield new insights regarding geochemical and surficial mechanisms of sorption and their dependence upon the physical and hydrologic characteristics of subsurface media.

References

1. U.S. D.O.E. 2002. Predecisional Draft.
2. Riley, R.G., and Zachara, J. M., 1992. USDOE DOE/ER-0547T. U.S. Dep. Of Energy, Washington, DC.
3. Bjornstad, B.N. 1990. PNNL-7336, Pacific Northwest National Laboratory, Richland, WA.
4. Slate, J.L. 2000. BHI-01203, Bechtel Hanford, Inc., Richland, WA.
5. Roh, Y., M.A Mayes, M.N. Pace, and P.M. Jardine. 200_. (In prep.).
6. Mayes, M.A., Jardine, P.M., Mehlhorn, T.L. , Bjornstad, B.N., Ladd, J.L. and Zachara, J.M . 2002. J. Hydrol. (In press).
7. Pace, M.N., Mayes, M.A., Jardine, P.M., Mehlhorn, T.L., and Zachara, J.M. 200_. Vadose Zone J. (Submitted).
8. Mayes, M.A., Pace, M.N., Jardine, P.M., Mehlhorn, T.L., Roh, Y., and Zachara, J.M. 2002. Soil Science Society of America National Meeting, Nov. 10-14, Indianapolis, IN.
9. Pace, M.N., Mayes, M.A., Yin, X., Jardine, P.M., and Zachara, J.M. 200_. (In prep.)
10. Bostick, B.C., M.O. Barnett, P.M. Jardine, S.C. Brooks, S.E. Fendorf. 2002. Uranyl surface species formed on subsurface media from DOE facilities. Soil Sci. Soc. Am. J. 66:99-108.
11. Pace, M.N., Mayes, M.A., Jardine, P.M., Yin, X., Mehlhorn, T.L., and Zachara, J.M. 2002. Soil Science Society of America National Meeting, Nov. 10-14, Indianapolis, IN.