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Title: Quantification of Hydrological, Geochemical, and Mineralogical Processes Governing the Fate and Transport of Uranium over Multiple Scales in Hanford Sediments

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Research Objective

A long-term measure of the DOE Environmental Remediation Sciences Division is to provide sufficient scientific understanding to allow a significant fraction of DOE sites to incorporate coupled biological, chemical, and physical processes into decision making for environmental remediation and long-term stewardship by 2015. Our research targets two related, major obstacles to understanding and predicting contaminant transport at DOE sites: the heterogeneity of subsurface geologic media, and the scale dependence of experimental and modeled results.

The objective of our research is to provide validated reactive transport and scaling theories that can be applied to existing field-scale contaminant fate and transport data from the DOE Hanford site. Our approach is as follows:

1. Separate quantification of unsaturated hydraulic, geochemical, and mineralogical factors influencing the transport of uranium within the scale of individual sedimentary layers of intact sediments.
2. Application of numerical, composite medium, and fractal approaches to compute effective "up-scaled" coupled hydraulic and reactive transport parameters for heterogeneous media consisting of one or more layers.
3. Application of the up-scaled parameters to U(VI) transport through progressively larger scales of intact samples consisting of multiple sedimentary layers, in which uranium transport is influenced by anisotropic flow and geochemical and mineralogical variations between sedimentary beds.

In the Hanford vadose zone, contaminant sequestration appears to be correlated to sedimentary layers having fine grain size and higher moisture content. Pore-scale interactions between adjacent, heterogeneous layers of different moisture contents therefore determine the extent of lateral versus vertical flow. Contaminant mobility is also influenced by heterogeneities in the mineralogy and geochemistry of these adjacent layers. This combination of processes results in the heterogeneous subsurface distribution of contaminants at Hanford which is not adequately explained or predicted using current conceptual and numerical models.

Our experimental research targets both layer-scale and composite, e.g., multi-layer, interactions in order to better understand the transport of uranium(VI) through a natural heterogeneous, partially-saturated system. Our modeling strategy will provide validated approaches for applying layer-scale coupled hydraulic and reactive transport parameters to progressively larger and increasingly complex geologic systems. The end-product of this study will be a solid scientific basis for modeling and up-scaling contaminant transport in the vadose zone. Our results will be directly applicable to emerging data on subsurface contaminant distributions due to the investments by DOE into the Hanford Tank Farm Vadose Zone Project. If in fact contaminants are immobilized within the vadose zone, our proposed research, in combination with additional in situ investigations, could potentially save billions of dollars in remediation and clean-up costs. In the event of increased risk, however, our dataset will provide quantitative scientific information to test remedial strategies based upon geochemical or biological manipulations of mobile contaminants in the subsurface.

Research Progress and Implications

In our previous research supported by EMSP (Project ERKP621 by Jardine and Fendorf) and on-going research supported by the Tank Farm Vadose Zone Project (managed by CH2M Hill Hanford Group), we investigated the transport of U(VI) through intact, partially-saturated samples in which flow is either parallel to or perpendicular to bedding. Our initial efforts have focused on the interpretation, modeling, and up-scaling of these results. Dispersivity is generally greater when flow is parallel to beds versus when flow is perpendicular to beds, particularly under partially-saturated conditions (Mayes et al., in prep, a,b). These effects appear to be more important in relatively heterogeneous versus relatively homogenous subsurface media (Mayes et al., in prep, a). Local-scale perching induced by flow across certain sedimentary layers appears to increase the retention of contaminants (Mayes et al., in prep, c). We conclude that flow will be promoted in the lateral rather than the vertical direction due to the influence of natural sedimentary heterogeneities, which implies that heterogeneity must be incorporated into modeling and up-scaling strategies to adequately predict contaminant transport.

Hydraulic factors influencing the transport of uranium within individual sedimentary beds of intact sediments are being quantified using the new Ultra Rock Core Centrifuge (URC) at the University of Tennessee (UT), purchased with the support of the National Science Foundation. The URC has been used for decades in the oil industry to determine the capillary pressure-saturation curve and unsaturated hydraulic conductivity. The URC, however, has not been previously applied to environmental problems, and it is being subjected to a rigorous testing program using well-characterized Berea sandstone samples and Hanford sediment samples from Mayes et al. (in press; in prep, a,b,c). The new URC method is being validated by comparison with traditional pressure-cell methods and the widely-used unsaturated flow apparatus (UFA). Subsequently, the URC will be used to compute effective hydraulic properties for multiple sedimentary beds and these predictions will be compared with new and previously published hydraulic measurements made on large undisturbed cores (e.g., Mayes et al., in press; in prep, a,b,c).

Geochemical and mineralogical factors influencing the transport of uranium(VI) within individual sedimentary beds are being determined by relating speciation to mobility. The primary control on U(VI) speciation appears to result from the dissolution of solid-phase calcite and liberation of Ca^{2+}. At ORNL and Stanford, we are investigating the influence of calcite and Ca^{2+} on the speciation, sorption, and transport of U(VI). We have prepared a proposal to quantify U(VI) speciation using cryogenic laser-induced fluorescence spectroscopy at the Environmental Molecular Sciences Laboratory, and we have designed experiments to relate these results to U(VI) mobility. In related ERSP work, the Stanford University group has submitted a spectroscopic study investigating the influence of Ca and Fe on bacterial reduction of U(VI) (Stewart et al., accepted). Stanford will extend this work to determine the influence of particle size and mineralogy upon the sorption of U(VI).

We are applying a variety of numerical, composite medium, and fractal approaches to compute effective "up-scaled" coupled hydraulic and reactive transport parameters from the layer-scale to the multilayer-scale. The composite medium approach is based upon changes in effective hydraulic conductivity and direction of flow (i.e., anisotropy) as a function of saturation. Lateral flow in heterogeneous sands is scaled as a weighted arithmetic mean and vertical flow is scaled as a harmonic mean. In essence, flow across heterogeneous bedding becomes limited by the sediment having the lowest conductivity, while flow parallel to heterogeneous bedding is most closely approximated by that of the sediment having the highest conductivity. Initial efforts at ORNL using a combined numerical/composite medium approach seem to suggest an unrealistic bias towards flow in the lateral (horizontal) direction. Preliminary results at UT for composite medium upscaling in a Cantor bar model comprised of two contrasting sediments with a fractal size distribution of layers indicate that anisotropy varies dramatically with water content (Leão et al., 2006; Leão and Perfect, 2006). The highest anisotropy ratios occur at very high or very low water contents depending upon the textural contrast between the layered sediments. The advantage of using the Cantor bar model in this context is that the effective unsaturated hydraulic conductivity function is defined in terms of parameters that can be obtained from independent measurements of the geometry of layered systems. A multifractal extension of this approach is being explored that allows for sediments with a wide range of textural contrasts rather than only two textures.

Planned Activities

The processes we are investigating are a result of the pore structure of natural, layered sediments, therefore we will collect a large, intact, meter-scale block of Hanford sediments from the 200 West Area this winter. A statistical distribution of representative samples will be collected in order to characterize the entire block in terms of water content and particle-size. The block will be transferred to ORNL where each layer will be instrumented with solution sampling probes, TDR, and tensiometers. U(VI) and a suite of nonreactive tracers will be applied to the block and their distribution as a function of time will be sampled within each layer, generating both layer-scale and composite (multi-layer) transport parameters. Intact and disturbed samples at the layer scale will be used to quantify the hydraulic parameters using the URC, and the geochemical and mineralogical environment of sorbed U(VI) at ORNL and Stanford. Our up-scaling approach will be verified by using transport parameters obtained from layer-scale datasets to predict composite transport in the large block sample. Once a scaling approach has been validated, it can be tested on observed field-scale contaminant transport scenarios.

Roles and Responsibilities

ORNL will perform the U(VI) transport experiments in small layer-scale and large multilayer-scale samples, reactive transport modeling, and up-scaling procedures. UT, through a subcontract, will quantify the hydraulics of the layer-scale samples, and will perform hydraulic modeling and fractal upscaling procedures. Stanford will determine the geochemical and mineralogical environment of U(VI) sorption using a variety of spectroscopic techniques.

Information Access

IN PREPARATION

Mayes, M.A., McKay, L.D., Jardine, P.M., Dansby-Sparks, R.N., Yin, X.L., Pace, M.N., and T.L. Mehlhorn. In preparation (a) (ready for submission). The influence of heterogeneous sedimentary layering on the saturated transport of nonreactive solutes.

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Mayes, M.A., Pace, M.N., Jardine, P.M., McKay, L.D., Perfect, E., and X.L. Yin. In preparation (c). The influence of water content and heterogeneity on the transport of U(VI) and Co(II)EDTA through partially-saturated intact sediments.

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