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Solute Transport and U(VI) Reactivity in Natural Heterogeneous Sediments

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Melanie A. Mayes
August 2006

Dedication

To Kevin

Acknowledgements

I owe a great many people the most sincere thank you for their support, their encouragement, and their contributions to this dissertation. I am profoundly humbled by the faith each of these people have placed in me. I want to thank Gray Dean for his encouragement, patience, and for the sacrifices he has endured as a result of this endeavor. To my parents, John and Erma Mayes, who unflinchingly encouraged me to make my own pathway in this world. Many thanks also to my sister and good friend, Karen.

I would like to thank my entire committee for their willingness to help me. I deeply appreciate the confidence placed in me by Phil Jardine to lead our research, and thank him for his encouragement and support at ORNL. I want to thank Larry McKay for his support and efforts as committee co-chair, for the high quality of his classes at UT, and for sharing his scientific approach with me. I want to thank Ed Perfect for his contributions to our recently-funded DOE proposal, and to acknowledge the importance of receiving funding to pursue the questions generated from this research. I thank Jaehoon Lee for taking the extraordinary effort to teach a special problems class in Environmental Soil Physics.

The work presented here as my own was in reality the result of a multi-year effort by a large team of people. I want to thank Xiangping Yin for her excellent analytical and experimental expertise, and acknowledge her hard work and dedication to this research. I

want to thank Tonia Mehlhorn for sharing her knowledge and her professional advice on many aspects of this research. Further, I want to thank her for the friendship and support she has shared with me, and to acknowledge that I might not have retained my sanity without it. I want to thank Molly Pace for her contributions and for the opportunity to work with her. I want to thank Royce Dansby-Sparks, who helped to begin the work on the 200 East Area sediments that will ultimately resolve many questions posed by this research.

I would like to also extend my gratitude to the Environmental Sciences Division at Oak Ridge National Laboratory. It has been a great pleasure to work there for the past 10 years, and I am grateful for this experience. This dissertation would certainly not have happened without their support and encouragement. I would like to thank the Department of Earth and Planetary Sciences at The University of Tennessee. I am grateful their support over many years and I appreciate having had the opportunity to study there.

Finally, I would especially like to thank the funding agencies that have supported me and my research. The Department of Energy's Office of Science through the Environmental Management Science Program has provided over six years of support for my science. I would like to extend a personal thanks to Program Managers Roland Hirsch and Mark Gilbertson. I would like to acknowledge Frederick M. Mann and Frank J. Anderson of the Tank Farm Vadose Zone Group and CH2M Hill Hanford Group, Inc. for providing support for the IDF experiments. It has been a great pleasure to be engaged with the

Hanford site contractors and to be able to provide data and discussions to people involved with remedial efforts. Finally, I would like to acknowledge the fellowship kindly provided to me by the Waste Management Research Education Institute at The University of Tennessee.

Abstract

The primary goal of this research was to determine the relationship between sedimentary geology and solute transport parameters. The overall hypothesis was that the transport of reactive and nonreactive solutes can be predicted using observable sedimentary depositional characteristics. The objective was to test this hypothesis by performing a variety of quantitative transport experiments in intact layered sediment samples. In this study, I used natural materials to explore 1) how mineralogical composition influenced the fate and transport of uranium(VI), 2) the relationship between heterogeneous sedimentary layering and preference for direction of flow, and 3) the mechanisms of solute transport in a partially-saturated cross-bedded sand. In Chapter 2, uranium(VI) sorption to siliciclastic and carbonate sediments was quantified using batch isotherm, kinetic, and miscible displacement experiments. Uranium(VI) sorption was small ($K_d < 1$), most likely due to the formation of stable anionic and neutral $U(VI)-CO_3$ complexes and competition for sorption sites by dissolved carbonate. Sorption to carbonate-containing sediments was consistently greater than to siliciclastic sediments. Selective extractions and kinetic studies suggested that $U(VI)$ may have co-precipitated with calcite in carbonate sediments, while X-ray absorption spectroscopy suggested that $U(VI)$ reversibly adsorbed to iron oxides and clay minerals in siliciclastic sediments. In Chapter 3, saturated miscible displacement was applied to intact flow bedding parallel (pb) and flow across bedding (xb) samples from six different sedimentary facies. Hydraulic and transport parameters varied over 4 orders of magnitude. Hydraulic and transport

parameters (dispersivity, hydraulic conductivity) were slightly anisotropic, i.e., varied with direction of flow with respect to sedimentary bedding. Anisotropy increased predictably with the proportion of fine-grained material, suggesting that flow and/or solute transport across fine-grained beds may have been restricted in comparison to parallel to bedding. In Chapter 4, solute transport in partially-saturated, fine-grained and cross-bedded sediments was influenced by local-scale perching associated with flow across sedimentary layering. The arrivals of the wetting front and nonreactive tracers were concurrent, but the elution of tracers occurred well before the cores became fully saturated. This was suggestive of preferential flow, but changes in the volume of water inside the cores prevented the confirmation of such mechanisms. A reversed pattern of multiple nonreactive tracers was observed, which was characteristic of flow through restrictive media, i.e., media with low hydraulic conductivity. Overall, these results provided quantitative evidence to relate subsurface geology and contaminant transport. My findings will improve the conceptual and quantitative understanding of flow and transport in vadose zones composed of complex layered sediments.

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List of Symbols

Symbol	Units	Definition
α	T^{-1}	Mass transfer coefficient
λ	L	Dispersivity
D	$L^2 T^{-1}$	Dispersion coefficient
θ	$L^3 L^{-3}$	Volumetric water content
ρ	$M L^{-3}$	Dry bulk density
P	Dimensionless	Peclet number
R	Dimensionless	Retardation coefficient
v	$L T^{-1}$	Mean pore-water velocity

List of Abbreviations

Abbreviation	Definition
2-site	2-site chemical nonequilibrium model
200E	200 East Waste Management Area
200W	200 West Waste Management Area
Br	Bromide
BTC	Breakthrough curve
CDE	Convective-dispersive equation
CoEDTA	Cobalt-Ethylenediaminetetracetate complex
ERDF	Environmental Restoration Disposal Facility (200W)
HC	Hanford Coarse sediment
HD	Hanford Clastic Dike sediment
HF	Hanford Borrow Pit sediment
HI	Hanford Interbeds sediment
HL	Hanford Laminated sediment
IDF	Integrated Disposal Facility (200E)
MIM	Mobile-immobile model
MNRT	Multiple nonreactive tracers
PFBA	Pentafluorobenzoic acid
PIPES	Piperazine-1, 4-bis(2-ethanesulfonic acid)
PPU	Plio-Pleistocene Unit sediment
RL	Ringold Laminated sediment
RX	Ringold Cross-bedded sediment
U(VI)	Uranium(VI)
WMA	Waste Management Area
XAS	X-ray absorption spectroscopy

Chapter 1. Introduction

1.0 Solute Transport in Natural Sediments

The hydraulics of subsurface sediments is strongly influenced by original sedimentary structures, including thickness and continuity of beds, grain size, and grain size distribution. These factors affect the pore size, pore diameter, and pore connectivity of water flow paths. Within an individual sedimentary bed, pore size and pore size distribution depend upon the following depositional factors: 1) packing (bulk density), 2) breadth of particle size distribution (polydisperse v. monodisperse), 3) shape of particles, 4) cementing materials, and 5) structure/weathering/post-depositional modification.

Within groups of sedimentary beds, flow is affected by the range, variation, and connectivity of the hydraulic conductivity of individual layers. For instance, within a homogenous group of layers, the distribution of hydraulic conductivities or pore-water velocities in those layers is relatively narrow. Within a heterogeneous group of layers, the distribution of velocities is relatively wide. A narrow distribution of water velocity is similar to the idealized “piston-flow” model, in which an applied solute evenly displaces the solute occupying a given volume of pores in a soil or sediment. These conditions are readily modeled and solute transport is generally predicted with some degree of accuracy.

A wider variation in pore-water velocities may cause solute transport to be affected by so-called “preferential” transport processes. In preferential transport, some of the water-

containing media may be partially or completely bypassed. Bypass may be associated with fractures, macropores, heterogeneous sedimentary layering, and/or partially-saturated conditions. The flow regime becomes generally isolated to regions of higher conductivity, and regions of low conductivity may only have limited interaction with the overall flow regime. Sometimes such interaction may be sufficiently inhibited as to occur by diffusion rather than by advection (Jardine et al., 1988, 1993a,b). These types of scenarios result in physical nonequilibrium between relatively mobile and relatively immobile flow regimes. These conditions may or may not be readily modeled, due to uncertainties about the degree of heterogeneity in the sediments, the effects upon the flow regime, and the scales over which the processes are important. Preferential flow can occur in both saturated and unsaturated systems, but the pore regime(s) acting preferentially will change as a function of water content.

1.1 Directionality in the Flow Regime

Mayes et al. (2003) and Pace et al. (2003) presented a technique to investigate the distribution of pore-water velocities in layered sediments. Intact samples of sediments were taken in the horizontal and vertical directions and submitted to miscible displacement experiments using nonreactive tracers. This technique allows quantification of hydraulic transport parameters both parallel to sedimentary bedding (pb) and across sedimentary bedding (xb). Thus, in the horizontal or pb direction, the experiments measured the distribution of pore-water velocities and hydraulic conductivities of a group of sedimentary layers. In the vertical or xb direction, the experiments measured the

effects of averaging the distribution of pore-water velocities of a group of sedimentary layers. Experiments were performed under saturated and partially-saturated conditions to determine changes in the distribution and average of pore-water velocities as a function of saturation. This type of information is needed in order to adequately predict anisotropic flow in partially-saturated, layered sediments (Khaleel et al., 2002).

1.2 Solute Transport in Layered, Partially-Saturated, Porous Sediments

With decreasing water content, changes occur in the distribution of pore-water velocities in sedimentary layers. The physical and to some extent the chemical characteristics of adjacent sedimentary beds will influence the moisture content. For example, fine-grained materials tends to retain water and conduct flow under conditions where coarse-grained sediments are dry and are therefore virtually nonconductive. When water is introduced into a partially-saturated system, such as from a leaking underground storage tank, the water may be diverted laterally through the more conductive fine-grained materials (Fig. 1.1) (Serne et al., 2004a,b). Because underlying sediments may be partially or completely bypassed, this phenomenon is a type of preferential flow, which is referred to as tension-driven anisotropic flow or anisotropic lateral flow (Yeh et al., 1985a,b).

As water is continually supplied to the sediments, the plume may expand in the lateral direction due to capillary forces and/or it may pool in localized areas of lower elevation,

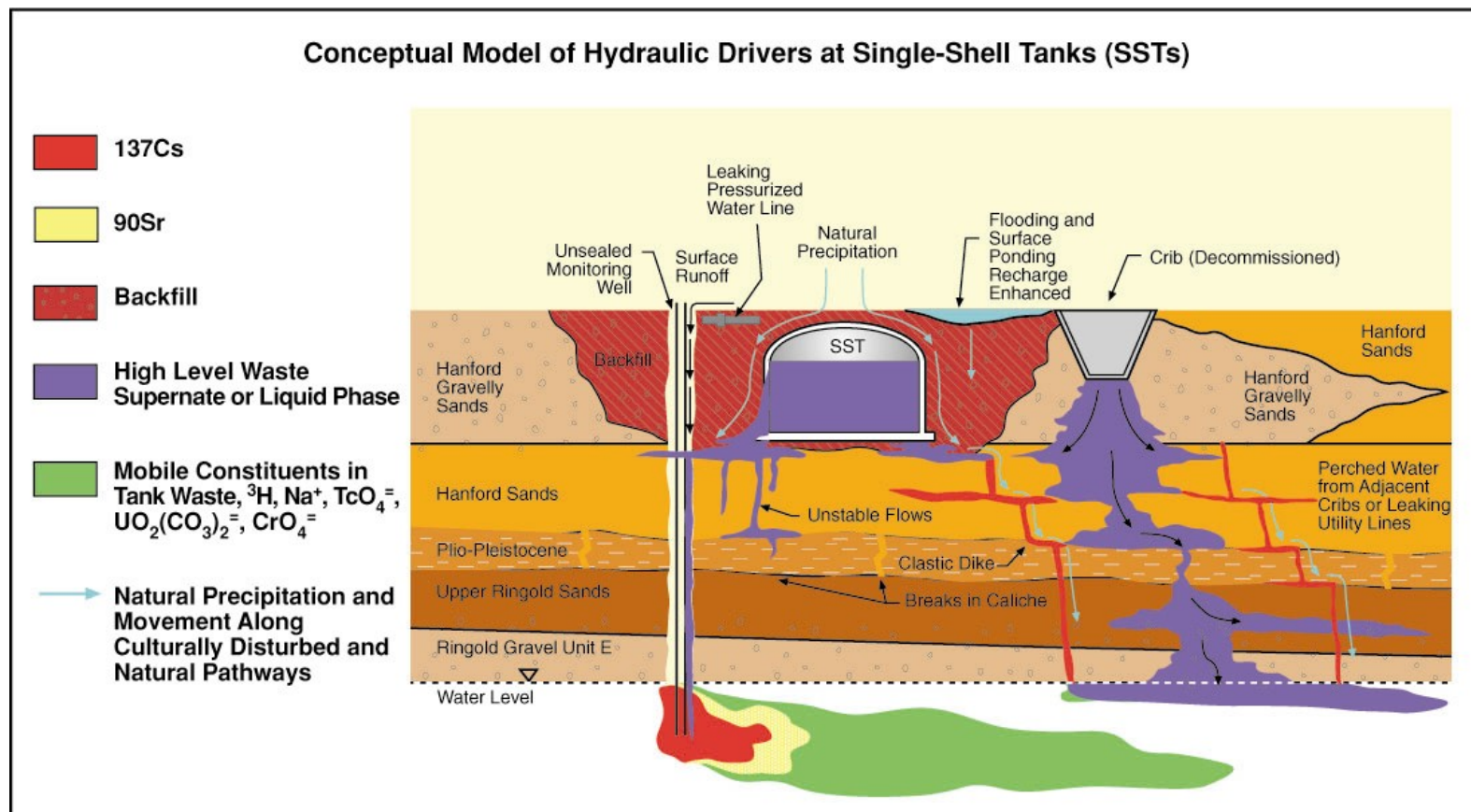


Figure 1.1 Conceptual model of preferential hydraulic processes in layered unsaturated sediments. Source: DOE, 1999.

such as in ripples, troughs, or in sloping sedimentary beds (Fig. 1.1). Such perching may allow the capillary barrier, or water-entry pressure, of underlying dry sediments to be exceeded and permit vertical transport of the plume. Because the unsaturated hydraulic conductivity of the overlying fine layers is low, the supplied infiltration rate will be insufficient to sustain flow in underlying coarse layers. Coarser-grained sediments would only be conductive at a higher water content producing a greater unsaturated conductivity. Therefore, the flow regime will split into isolated fingers of higher water contents in which flow can be physically sustained (Hillel and Baker, 1982). Such fingers are highly unstable and propagate rapidly in the vertical direction. This phenomenon is referred to as unstable vertical finger flow (Fig. 1.1).

Finally, embedded lenses of materials of different conductivity may induce so-called funnel flow. This mechanism tends to divert flow through or around the heterogeneity, resulting in a funneling or focusing of the flow pathways towards the edge of the feature (Kung, 1990a,b). Fine-grained lenses embedded within coarse sediments may either attract flow into the lens or divert flow to the edge of the lens, depending on the antecedent moisture conditions. Similarly, coarse lenses embedded in fine materials may either attract flow into or divert flow around the lens. Regardless, a funnel-shaped preferential pathway may be formed that effectively conveys solutions to greater depths.

The solute transport processes described above are localized responses to natural heterogeneity of horizontal sedimentary layering. Pore-scale interactions between adjacent sedimentary bedding or units will ultimately determine the type of flow regime

described above. In the subsurface, plume migration may involve all three preferential flow processes, as well as non-preferential “piston” flow. Contaminant transport is dependent upon where flow occurs, and therefore upon the physical characteristics of individual sedimentary beds and their antecedent moisture contents. Unfortunately in the subsurface neither of these is generally known with any degree of certainty.

1.3 Influence of Sediment Mineralogy

Mineralogical heterogeneities between adjacent sedimentary beds or units may influence contaminant transport by chemical and/or coupled physical and chemical interactions. Consider the case of a limestone or clay layer embedded within a sequence of sandy siliciclastic sediments. The heterogeneous layer may result in transport of contaminants or solutes that are influenced by coupled physical and geochemical processes. The textural physical characteristics of an embedded heterogeneous layer may influence the flow regime, but the chemical characteristics may change the type or rate of interfacial geochemical reaction. For example, uranium(VI) is known to sorb to iron oxides, clays, and calcite, which are components of natural sedimentary deposits. The surface reaction in iron oxides and clays is inner-sphere adsorption (Bostick et al., 2002), while in calcite the surface reaction is predominantly precipitation (Carroll and Bruno, 1991). In heterogeneous sediments, all three reactions may occur simultaneously, but the relative importance will depend upon the proportion of each mineral in the sediments. Because preferential flow processes will determine *where* flow occurs, the flow regime may

ultimately dictate contaminant reactivity. Coupled hydrological and geochemical processes are the most difficult to predict in subsurface materials.

1.4 Goals, Objectives, and Hypotheses

The primary goal of this research is to determine the relationship between sedimentary geology and solute transport parameters. The overall hypothesis is that the transport of reactive and nonreactive solutes can be predicted using observable sedimentary depositional characteristics. The objective is to test this hypothesis by performing quantitative transport experiments in intact layered sediment samples. In this study, I use natural materials to explore 1) how mineralogical composition influences the fate and transport of uranium(VI), 2) the relationship between heterogeneous sedimentary layering and preference for direction of flow, and 3) the mechanisms of solute transport in a partially-saturated cross-bedded sand.

Chapter 2: Comparing the Fate and Transport of Uranium(VI) in Siliciclastic and Carbonate Sediments

The goal of Chapter 2 was to determine the influence of sediment mineralogy upon the fate and transport of U(VI). The geochemistry of U(VI) at neutral pH is strongly influenced by the presence of dissolved calcium and carbonate, resulting in the formation of several U(VI)-CO₃ and Ca-U(VI)-CO₃ complexes. I hypothesized that the reactivity of U(VI) might be different in siliciclastic versus carbonate sediments because of the spontaneous formation of either surface- or solution-phase Ca-U(VI)-CO₃ complexes in

the latter sediment. The objective was to determine the rate and mechanisms of U(VI) sorption in siliciclastic and carbonate sediments using a series of kinetic, batch, and displacement experiments.

Chapter 3: The Influence of Heterogeneous Sedimentary Layering Upon the Saturated Transport of Solutes

The goal of Chapter 3 was to determine the relationship between heterogeneous sedimentary layering and anisotropy of the flow regime. In this paper I hypothesized that sedimentary heterogeneities, such as interbedded fine-grained layering, were responsible for directionality in the saturated flow regime. The objective was to compare transport parameters in intact flow bedding-parallel (pb) and flow cross-bedding (xb) samples from a variety of sedimentary facies. A variety of quantitative solute transport techniques were applied in order to determine the anisotropy of the flow regime. Solute transport parameters and anisotropy were subsequently interpreted in terms of sedimentary bedding characteristics such as grain size and the presence or absence of interbedded heterogeneous layers.

Chapter 4: Solute Transport in Partially-Saturated, Layered Fine Sediments

The goal of Chapter 4 was to determine the mechanisms influencing solute transport under unsaturated conditions in fine-grained layered sediments. Previous work had observed preferential flow and perching in the sediments and concluded that the mechanism was unstable finger flow. I hypothesized that the sediments were too fine-grained and too wet for finger flow, but that some other mechanism(s) were responsible

for the appearance of preferential flow. The objectives of this research were to determine the moisture conditions under which perching and/or preferential flow occurred, and to determine the responsible mechanism(s).

1.5 Approach

Many studies in the literature use disturbed sediments that do not retain the specific physical or chemical characteristics of subsurface sediments. Therefore, such studies cannot resolve the preferential hydrologic or coupled hydro-geochemical processes that result from pore-scale interactions between adjacent sedimentary bedding or sedimentary units. My approach used intact sedimentary materials taken in vertical (flow crosses bedding, xb) and horizontal (flow is parallel to bedding, pb) orientations. This method facilitated the comparison of flow through adjacent sedimentary beds in pb cores with flow across sedimentary bedding in xb cores.

Many studies also extract sediment from a single location or borehole and attempt to draw hydrological or geochemical conclusions that are relevant to much larger spatial scales. Determining the chemical or physical transport properties of one sediment type will not provide sufficient understanding to apply appropriate remedial solutions. Instead an integrated approach was taken in which different sedimentary units were investigated using similar methods. There was a compromise in precision, because only a few samples would be taken from each unit. However, comparing results from identical experiments in sedimentary units will provide more overall information on general

themes, such as the influence of interbedded fines, mineralogy of sediments, or the degree of anisotropy under saturated conditions. Chapters 2 and 3 take this approach.

Chapter 4, however, takes a more detailed approach towards hydrologic processes occurring in one type of sediment. This follows similar studies by Pace (2005), which examined in detail hydrological and geochemical processes occurring in a single sedimentary unit.

Chapter 2. Comparing the Fate and Transport of Uranium(VI) in Siliciclastic and Carbonate Subsurface Sediments

1.0 Abstract

The objective of this study was to determine the influence of siliciclastic versus carbonate sediments on the fate and transport of uranium(VI). U(VI) was applied either as anionic U-CO_3 complexes or as a neutral Ca-U-CO_3 complex. Sorption in all sediments was enhanced when U(VI) was applied as the Ca-U-CO_3 versus U-CO_3 complex, suggesting that the Ca-U-CO_3 complex was not naturally formed in any of the sediments. Kinetic, isotherm, and miscible displacement experiments in repacked sediments demonstrated the higher sorption capacity of carbonate versus siliciclastic sediments. Sorption onto all sediments was completely reversible under short residence times. Selective extraction experiments suggested that calcite was the most probable sorbent of U-CO_3 in the PPU, and evidence suggested that U may have precipitated over longer timeframes. Differences in surface area significantly influenced the extent of U(VI) sorption for all sediments. X-ray absorption spectroscopy confirmed that U-CO_3 formed inner-sphere ternary complexes with iron oxides and edge sites of phyllosilicates in siliciclastic sediments. This study provided an integrated perspective on the fate and transport of U(VI), investigating the influences of mineralogy, geochemical speciation, and mechanisms of U(VI) attachment upon natural, heterogeneous sediments.

1.1 Introduction

1.1.1. Geology of the Hanford Subsurface

Subsurface disposal of uranium is a widespread problem within the U.S. Department of Energy (DOE) weapons complex and at former mining sites throughout the world. Several areas of the DOE's Hanford Reservation in eastern WA have experienced discharge of nuclear processing waste from tanks, cribs, and underground storage tanks into the vadose and underlying saturated zones. The vadose zone in the Hanford Plateau is predominantly comprised of a thick (~70 m) sequence of Pleistocene-age Hanford flood deposits of unconsolidated, horizontally-bedded sands, silts, and gravels (Bjornstad, 1990; DOE, 2002a). Below the Hanford is a partially-cemented layer of caliche or calcrete (2-30 m thick), which has been referred to as the Plio-Pleistocene and/or Cold Creek Unit (Slate, 2000; DOE, 2002a). The caliche formed by periodic subaerial exposure during a relatively sediment-starved period, resulting in extensive pedogenic cementation by calcium carbonate (Slate, 2000). Beneath the caliche resides the Miocene-Pliocene age Ringold Formation, a mostly unconsolidated sedimentary formation deposited by lacustrine and fluvial depositional processes (Bjornstad, 1990; Lindsay and Gaylord, 1990; Lindsay, 1995). The water table is typically located within the Ringold, with the caliche forming an approximate boundary between vadose and saturated zones (Slate, 2000).

The textural properties of the three geologic units are important in governing water and contaminant transport in the Hanford vadose zone. For unsaturated, horizontally-layered subsurface sediments, finer-grained layers tend to prevent steady-state vertical infiltration, resulting in perched water and anisotropic lateral flow (Gee and Ward, 2001; Pace et al., 2003, 2005; Pace, 2005; Mayes et al., 2003). Finer-grained layers in the Hanford flood deposits in the vadose zone often have higher water contents and greater contamination than nearby coarser-grained layers (Serne et al., 2002a,c,d,e; Knepp, 2002; DOE, 2002b). The Plio-Pleistocene Unit (PPU), in particular, is associated with increased moisture contents, perched water, and higher levels of ^{99}Tc , NO_3^- , and U contamination (Conrad and DePaulo, 2000; Serne et al., 2002a, 2004a,b; Knepp, 2002; DOE, 2002b). Widespread and occasionally unexplained contamination in the PPU suggests that the unit exerts regional control over contaminant mobility (Knepp, 2002; DOE, 2002b). The caliche layer is in sharp textural contrast to the surrounding unconsolidated, siliciclastic sediments, due to its extensive cementation, high bulk density (up to 2.4 g cm^{-3}), and high CaCO_3 content (6-67%) (Slate, 2000). Thus, increased moisture and contamination are consistent with the physical properties of the PPU in comparison to the overlying unconsolidated Hanford. This pattern has been observed in numerous contaminated boreholes in the 200W Waste Management Area (WMA) (DOE, 2002b). The underlying Ringold Formation is comprised of thick sequences of unconsolidated mud, sand, or gravel layers (Bjornstad, 1990; Lindsay and Gaylord, 1990).

1.1.2. Uranium(VI) Geochemistry

The heterogeneities of subsurface media, the complex history of past waste releases, and the complicated geochemistry of uranium each contribute to uncertainties regarding future migration of uranium plumes at Hanford. Precipitated U in contaminated sediments exists primarily as sodium boltwoodite, a uranophane-type mineral consisting of sodium, uranyl and silicate (Catalano et al., 2004), even though U in adjacent porewaters was dominantly uranyl carbonate complexes (Wang et al., 2004; Liu et al., 2004). It is probable that this configuration was more related to the history of tank waste releases in which hot, caustic $\text{NaNO}_3/\text{NaOH}$ solutions dissolved and reprecipitated subsurface sediments, resulting in the precipitation of uranyl silicates (Wang et al., 2004). In contrast, current U mobility is influenced by equilibrium with subsurface sediments typically containing 1-2% CaCO_3 (Kaplan et al., 1998; Knepp, 2002; DOE, 2002b; Wang et al., 2004; Liu et al., 2004). Further, the U plume analyzed by Wang et al. (2004) and Catalano et al. (2004) is suspected to be currently migrating, and the risks posed by this plume are related to current speciation rather than past waste releases (Liu et al., 2004). It is likely that current and future migration of uranium is tied to the formation of stable aqueous carbonate complexes, even where the carbonate content of sediments and porewaters is minor (Bargar et al., 1999, 2000).

Recent studies on the speciation of U(VI) under conditions of neutral pH have identified a previously unknown aqueous uranyl-carbonate complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (Bernhard et al., 1996, 2001; Geipel et al., 1997; Kalmykov and Choppin, 2000). Until recently,

geochemical speciation calculations predicted the formation of several similar anionic, uranyl-carbonate complexes, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ at these pH (Waite et al., 1994; Bernhard et al., 1996; Gerner et al., 2001a, b; Davis et al., 2003). It is now believed that the neutrally-charged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complex dominates U speciation in the presence of millimolar concentrations of aqueous Ca^{2+} at neutral pH (Bernhard et al., 1996, 2001; Geipel et al., 1997; Kaplan et al., 1998; Kalmykov and Choppin, 2000; Brooks et al., 2003; Zheng et al., 2003; Wang et al., 2004). The “new” dicalcium-uranyl-carbonate complex therefore represents a significant shift in our understanding and modeling of U(VI) transport at many radionuclide disposal sites. The existence of this complex, in addition to the suite of anionic uranyl-carbonate complexes, in contaminated Hanford porewaters is specifically supported by the laser-induced fluorescence study of Wang et al. (2004). Further, Brooks et al. (2003) observed that the formation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complex inhibits the ability of dissimilatory metal-reducing bacteria to enzymatically reduce U(VI) to U(IV), which is one of several promising remedial strategies for U-contaminated environments. Throughout this paper, the neutrally-charged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complex will be generically referred to as the “Ca-U-CO₃” complex, while the suite of anionic complexes ($\text{UO}_2(\text{CO}_3)_2^{2-}$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$) will be referred to as the “U-CO₃” complex(es).

1.1.3. Hypotheses, Goals, and Objectives

We hypothesized that the reactivity of U(VI) might be different in siliciclastic versus carbonate sediments because of the formation of either surface- or solution-phase Ca-

U(VI)-CO₃ complexes in the latter sediment. The goal of this study was to determine the influence of sediment mineralogy upon the fate and transport of U(VI) through siliciclastic (Hanford and Ringold) and carbonate (Plio-Pleistocene Unit) sediments. U(VI) was applied as an anionic U-CO₃ complex and as a neutral Ca-U-CO₃ complex. The objective was to compare U(VI) reactivity in siliciclastic and carbonate sediments using a series of kinetic, batch, and repacked column experiments.

1.2 Materials and Methods

1.2.1. Sample Collection and Characterization

Samples were collected from several places on the DOE's Hanford Reservation. Bulk samples of the Upper Ringold Formation (RL and RX) and the Plio-Pleistocene Unit (PPU) caliche were collected from the White Bluffs area (Mayes et al., 2003, 2005a). The RL samples are fine-grained, horizontally-bedded, laminated silts and sands that were deposited in a lacustrine environment (Mayes et al. (2003) referred to the RL samples as "US/S"). The RX samples are fine-grained and structurally consist of cross-beds and climbing ripples (Mayes et al. (2003) referred to the RX samples as "LS"). The PPU samples are very cemented and appear to be very similar to those of the Cold Creek Unit underlying the 200W WMA (Slate, 2000; DOE, 2002a).

Samples of laminated, slightly rippled and fine- to medium-grained Hanford flood deposits (HL) were collected from ~25 m depth in the Environmental Restoration

Disposal Facility (ERDF) in the 200W area of the Hanford Reservation (Pace et al., 2003). Detailed description of these samples can be found in Pace et al. (2003) (samples were referred to as “HH” and “HV”). Hanford samples (HF) used for X-ray absorption spectroscopy were collected from the Borrow Pit, which is located below the White Bluffs across the Columbia River from the 300 Area. Very little other information is available on the HF samples, and this manuscript assumes that the geochemistry of all Hanford flood deposits, as it applies to uranium sorption, is relatively similar.

Additional samples of the Hanford flood deposits were collected from ~11 m depth in the Integrated Disposal Facility (IDF) in the 200E area of the Reservation, including a clastic dike sample (HD), a coarse sand (HC), and a coarse sand interbedded with a silty matrix (HI). Description of all samples is available in Chapter 3. We also utilized well-characterized composite samples from two depths (46 m and 61 m) within exploratory borehole C3177 drilled into the proposed IDF (Horton et al., 2003). The borehole samples have been utilized by a number of researchers, and their inclusion here is to facilitate comparison of our results with those of others.

A variety of solid phase characterization techniques were applied to the samples (Table 2.1). The total carbon content was determined using standard dry combustion technique on bulk samples and on samples in which the inorganic carbon was removed by acid dissolution. The inorganic carbon was calculated by subtraction of the organic carbon from the total carbon. Total extractable Fe oxides were determined using the citrate-bicarbonate-dithionite (CBD) method (Loeppert and Inskeep, 1996). Surface area was

Table 2.1 Geochemical characterization of selected Hanford area sediments.

<i>Sediment</i>	<i>TIC</i> (wt. %)	<i>TOC</i> (wt. %)	<i>Fe</i> (g kg ⁻¹)	<i>SA</i> (m ² g ⁻¹)
¹ HL	0.22	0.02	4.90	6.13
² C3177: 46m	0.17	0.03	5.68	3.52
² C3177: 61m	0.14	0.04	6.80	5.30
³ PPU	2.68	0.32	1.61	12.9
³ RL	0.26	0.02	7.49	9.11

¹Pace et al., (2003), ²Horton et al. (2003), ³Mayes et al. (2005b).

TIC = total inorganic C, TOC = total organic C, Fe = total iron oxides by CDB (citrate-dithionite-bicarbonate) method, SA = surface area by nitrogen displacement and BET (Brunauer, Emmet and Teller) method.

measured using N₂ and the Brunauer, Emmet and Teller (BET) method (Greg and Sing, 1982). Mineralogy was determined on bulk sediments and on sand, silt and clay fractions isolated using the bouycous hydrometer method (Gee and Bauder, 1986). Bulk, sand and silt fractions were ground in a mortar and pestle and then back-filled into X-ray diffraction (XRD) mounts. Clay (<2µm) and fine clay (<0.2 µm) fractions were oriented using the filter-membrane peel technique (Drever, 1973). XRD analyses were performed on a Scintag XDS 2000 diffractometer (40 kV, 35 mV) equipped with Co-K α radiation. Sand and silt fractions were examined by scanning electron microscope with energy dispersive X-ray analysis. The clay fractions were also examined using transmission electron microscopy, differential thermal analysis, and thermogravimetric analysis. Thin sections were prepared by impregnation with Hillquist C-D epoxy (Denver, CO), and analyzed using plane- and cross-polarized light transmission on an optical microscope. Characterization of the C3177 sediments was obtained from Horton et al. (2003), with the exception of total iron oxides which were determined in our lab.

1.2.2. Uranium(VI) Geochemical Speciation

Uranium speciation modeling was calculated using the React module in The Geochemists Workbench (Bethke, 1994). U(VI) formation constants were obtained from the database of Grenthe et al. (1992) and Bernhard et al. (2001), as modified by S.C. Brooks of ORNL. All U(VI) experiments were conducted using a maximum concentration of 8.4 e-5 M U as UO₂(NO₃)₂. Influent pH was adjusted to the native sediment pH (8) using NaHCO₃ in equilibrium with a 1% CO₂(g) headspace. All experiments were conducted

at a total ionic strength of 0.1 M using a matrix of NaNO₃ or NaCl. The ionic strength and carbonate concentrations are appropriate for vadose zone porewater solutions (Serne et al., 2002b; Knepp, 2002), and are enriched compared to groundwater solutions (Kaplan et al., 1998). Speciation modeling suggested that the 1% CO₂(g) headspace resulted in the formation of a dominant anionic U(VI)-carbonate complex, UO₂(CO₃)₃⁴⁻ at pH 8 (Fig. 2.1a). Similar results have been obtained by numerous researchers (e.g., Waite et al., 1994; Bernhard et al., 1996; Kaplan et al., 1998; Barnett et al., 2000; 2002; Davis et al., 2003; Brooks et al., 2003). Throughout this paper, this geochemical speciation will be simplified and referred to as the “(anionic) U-CO₃ complex”.

Additions of Ca²⁺ ranging from 0-0.02 M Ca as CaCl₂·2H₂O were also investigated in selected kinetic batch experiments. The addition of Ca²⁺ resulted in the formation of the neutral Ca₂UO₂(CO₃)₃ complex at pH 8 (Bernhard et al., 1996, 2001; Geipel et al., 1997; Kaplan et al., 1998; Kalmykov and Choppin, 2000; Brooks et al., 2003; Zheng et al., 2003). Above 0.002 M Ca, this complex completely dominates U(VI) speciation (Fig. 2.1b). Throughout this paper, this geochemical speciation will be simplified and referred to as the “(neutral) Ca-U-CO₃ complex”.

Uranium analyses were completed using either a Kinetic Phosphorescence Analyzer (KPA) (Chemchek Instruments, Richland, WA) or a Perkin-Elmer ELAN 6100 ICP/MS (Perkin-Elmer Instruments, Shelton, CT). Throughout the paper it is assumed that U is equivalent to U(VI), which has been experimentally verified for many samples and is

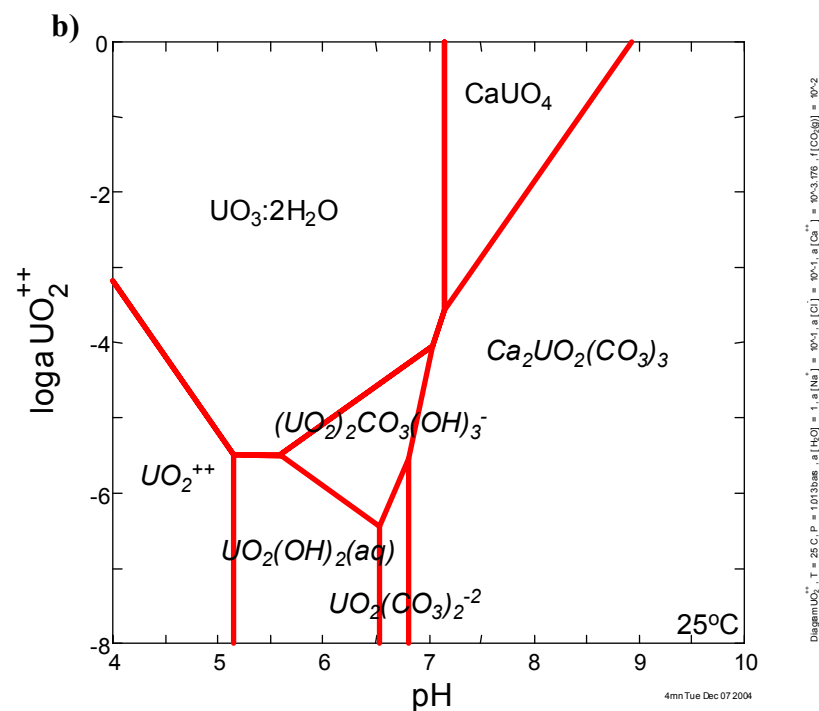
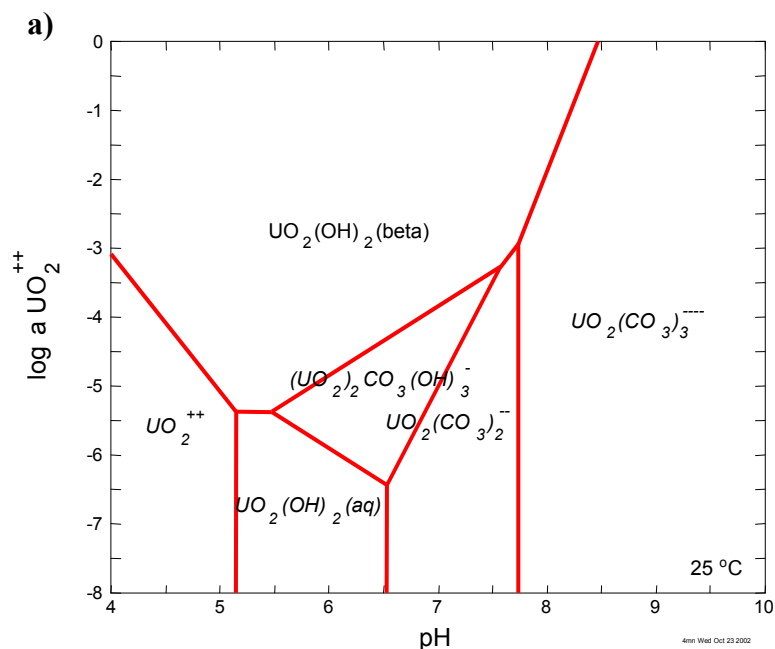


Figure 2.1 Speciation of aqueous U(VI). Experimental conditions were 25 °C, 1.013 bars pressure, $p\text{CO}_2(\text{g}) = 10^{-2}$, in 0.1 M NaCl. a) in the absence of Ca, and b) in the presence of $10^{-3.17}$ M Ca. Aqueous species are indicated by italic font, and solid species are indicated by normal font.

expected, given the pH and Eh conditions of these experiments which are not conducive to the formation of aqueous or precipitated U(IV).

1.2.3. Experimental Methodology

Batch isotherm experiments were conducted using 4 ml of solution and 2 g of sediment in 30 cm³ polypropylene centrifuge tubes that were placed on a rotary shaker in a glovebox containing an atmosphere of 1% CO₂(g). The solution:solid ratio was chosen to most closely mimic subsurface conditions in which water content is low. In addition, the low ratio minimizes calcite dissolution observed under high solution:solid ratios (Zheng et al., 2003). PPU sediments were obtained by crushing the consolidated caliche rock to pass through a 2 mm sieve using a mortar and pestle. Hanford and Ringold samples utilized were those which passed through the 2 mm sieve without treatment. The isotherm (batch) experiments were conducted for 72 h using different initial concentrations of U ranging from 0 – 8.4 e-5 M. The kinetic experiments were identical to the isotherm experiments, except they were conducted using only the highest concentration of U and samples were collected as a function of time ranging from 0.02 – 45 d. Batch isotherms were duplicated for each concentration of U, and kinetic experiments were not duplicated. Control (blank) samples were collected from the influent reservoir at the same time as sediment-containing samples. One experiment was conducted (in duplicate) in which the solid:solution ratio was changed by varying the mass of PPU solid added from 0.1 g to 2 g. This experiment was conducted using the highest concentration of U, 4 ml of solution, and collection at approximate equilibrium (7d). All samples were

centrifuged at 2500 rpm for 15 min and decanted into two separate vials, one of which was immediately used to determine pH, and the other was acidified to pH 2 for later analyses.

In three kinetic experiments, simple, selective extraction techniques were applied to sediment samples before measuring U sorption. Only one extraction technique was applied per experiment, and a control experiment was performed with sediments in which no extractions were applied. Organic matter was removed using 30% H₂O₂, carbonate was removed using buffered Na-acetate (Grossman and Millet, 1961), and Fe-oxide was removed using the citrate-dithionite-bicarbonate (CDB) method (Loeppert and Inskeep, 1996). Two g of sediment were used for each extraction sample to duplicate the quantity of soil utilized in all other experiments. Following extraction, the sediments were rinsed 5-6 times using 0.01 M NaCl to remove any entrained extractant solutions. The samples were then dried at 40°C to remove porewater which would dilute the added concentration of U in the subsequent sorption experiments. The control samples were rinsed and dried following the same methods as the extracted samples. Samples were not run in duplicate, and were collected as a function of time from 0.04-15 d. Sample collection and preparation followed the methods described above.

Repacked saturated miscible displacement experiments were conducted using an Omnifit chromatography column 1 cm diameter x 4.5 cm length (Bio-Chem Valve/Omnifit, Cambridge, UK). Influent solutions were delivered from a pressurized vessel containing 1% CO₂(g) headspace using a Deltec 3000 Modular Infusion System (SIMS Deltec, Inc.,

St. Paul, MN). Effluent was collected as a function of time in pre-acidified tubes on an Isco Retriever II fraction collector (Lincoln, NE). The transport experiments were conducted as follows. The matrix solution (NaCl or NaNO₃) was delivered to the column bottom until a steady-state flux was achieved. At this time, delivery of the influent solution (also pH 8) was initiated minimizing interruption in flow. The influent solution consisted of the nonreactive tracer NaBr (2 e-3 M) and U(VI) (8.4 e-5 M), and matrix component such that the total ionic strength of influent and matrix were both 0.1 M. After the desired pulse of influent was applied, the matrix solution was again delivered to the column minimizing interruption in flow. The matrix solution was terminated when the concentration of tracers dropped below 2% of influent. Analyses of nonreactive tracer Br was accomplished via UV detection (190 nm) in a low-pressure liquid chromatography system using the AS9-HC anion exchange column (Model DX-600, Dionex Corp., Sunnyvale, CA).

1.2.4. X-Ray Absorption Spectroscopy

X-ray Absorption Spectroscopy (XAS) was utilized to determine the chemical environment of adsorbed uranium species, generally following the methods of Bostick et al. (2002). XAS was performed at the Stanford Synchrotron Radiation Laboratory on beamlines 4-2 or 4-3. The storage ring operated at 3.0 GeV and at currents between 50 and 100 mA. Spectra were taken with a Si(220) double-crystal monochromator with an unfocused beam. Incident and transmitted intensities were measured with 15-cm N₂-filled ionization chambers. Sample fluorescence was measured with a multi-element Ge

detector oriented 45° off the sample and orthogonal to the incident radiation. The beam was detuned ~50% to reject higher-order harmonic frequencies and to prevent detector saturation. X-ray absorption spectra were collected from -200 to +1000 eV about the L_{III}-edge of U(17 166 eV). At least 5 spectra were collected for each sample and averaged for analysis. Internal calibration was achieved with uranyl nitrate between the second and third ionization chambers; its inflection point was set at 17 176 eV.

1.2.5. Quantification of Experimental Parameters

The transport of nonreactive tracers and/or U was modeled using the convective-dispersive equation (CDE) (Toride et al., 1999). This modeling is designed to provide simple parameters to quantitatively describe nonreactive and reactive transport, such as dispersion (D) and retardation (R) coefficients, where $R = 1 + K_d \rho_b / \theta$, and K_d ($L^3 M^{-1}$) is the linear distribution coefficient, θ ($L^3 L^{-3}$) is the volumetric water content, and ρ_b ($M L^{-3}$) is the bulk density. The linear distribution coefficient K_d represents the slope of a linear adsorption isotherm. Description of this widely-used modeling strategy is available and will not be explored here in detail. Note that this modeling effort is not designed to provide a mechanistic understanding of reactive or nonreactive transport. Uranium transport is generally modeled quantitatively using surface-complexation modeling (e.g., Waite et al., 1994; Barnett et al., 2002; Davis et al., 2003), but this is beyond the scope of this manuscript. When the isotherm was nonlinear, the Freundlich equation was used to describe the partitioning between the solid and solution phases. The amount of U sorbed at equilibrium ($[U]_{sorb}$) is described by $[U]_{sorb} = K_f ([U]_{soln})^n$, where

K_f is the nonlinear distribution coefficient and n is the dimensionless Freundlich parameter ($n < 1$).

1.3 Results and Discussion

1.3.1. Sediment Mineralogy

Thin section analysis suggests that the mineralogy of the PPU was quite simple, consisting of pedogenic CaCO_3 , amorphous silica (Si_{am}) and quartz rock fragments (Fig. 2.2a, b). Calcite (CaCO_3) was the primary matrix mineral in Fig. 2.2a, exhibiting a characteristic “popcorn” structure, indicating secondary growth into void spaces (Retallack, 1997; Slate, 2000). Amorphous silica (Si_{am}) was the primary matrix mineral in Fig. 2.2b, which is probably related to the alteration of volcanic ash (Retallack, 1997), considering the proximity of Hanford to the Columbia River flood basalts and the Cascade Range. Calcite thinly coats void spaces within the Si_{am} matrix regions, indicating their later formation on this sample. X-ray diffraction (XRD) analyses confirmed only the presence of calcite minerals (Fig. 2.2c). Selective extraction results (Table 2.1) also suggested a high proportion of calcite. If the assumption is made that all TIC is associated with calcite, the PPU is ~25% calcite, whereas the RL and HL are ~3% (Table 2.1). Such levels are typical for these units in the Hanford subsurface (Slate, 2000; DOE, 2002a; Horton et al., 2003).

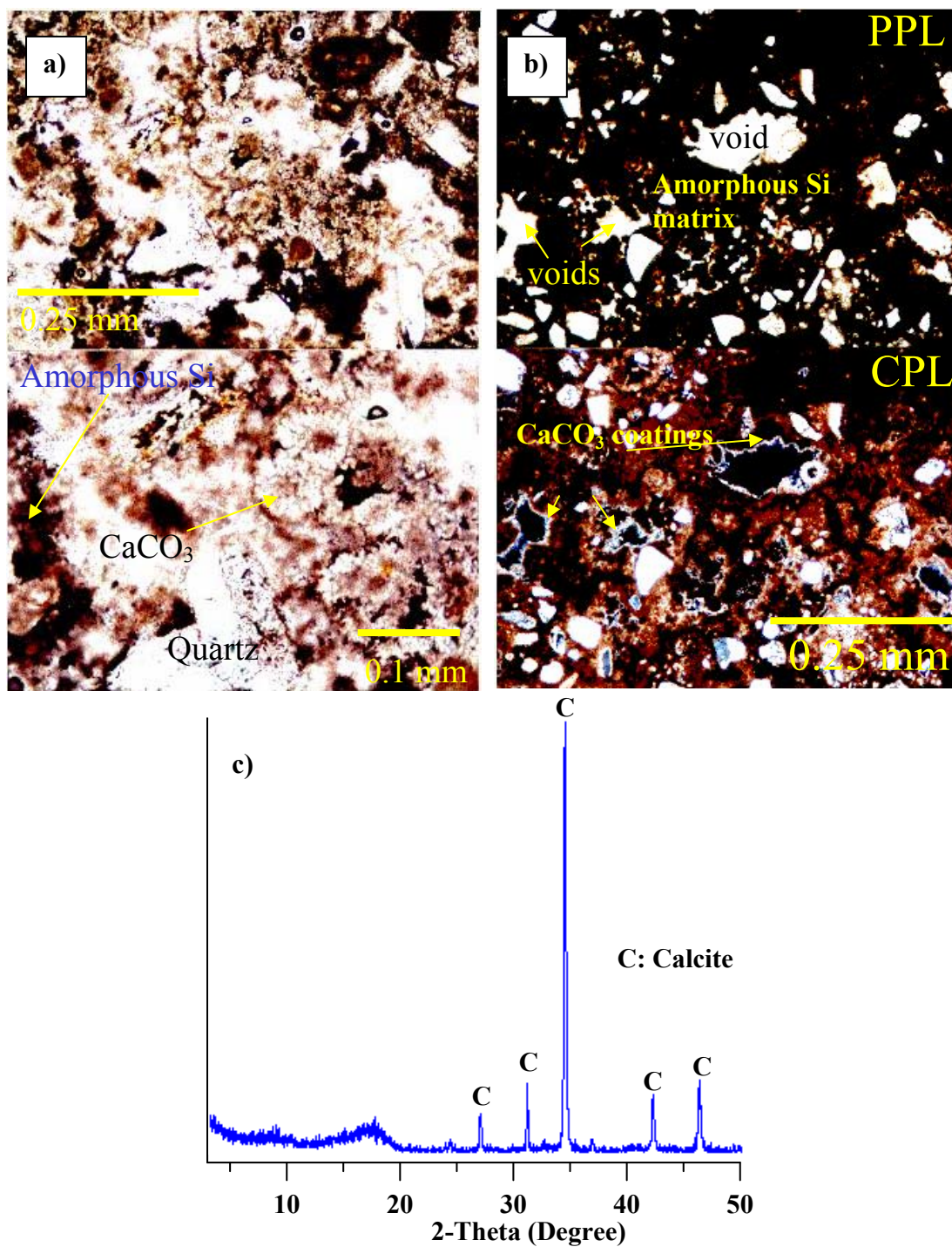


Figure 2.2 Mineralogy of Plio-Pleistocene Unit (PPU). a) Thin section rich in calcite, in plane-polarized light (PPL) on top, and cross-polarized light (CPL) on bottom, b) Thin section rich in amorphous silica showing calcite coatings, with PPL on top, and CPL on bottom. Magnification is equivalent for PPL and CPL. c) X-ray diffraction pattern of bulk PPU sample showing calcite (C).

Mineralogy observed in the Hanford (HL) and Ringold (RL) formations was more complex. Examination of RL in thin section revealed typical siliciclastic sedimentary bedding consisting of quartz, mica, feldspar, and prominent Mn- and Fe-oxide staining along bedding planes associated with clays (Fig. 2.3a). Such staining was visible with the naked eye in the Ringold (Mayes et al., 2003). All Hanford and Ringold sediments exhibit significant levels of Fe-oxides (Table 2.1). The mineralogy of the sand and silt fractions of RL and HL (Pace et al., 2003) samples revealed the predominance of quartz with lesser amounts of plagioclase, mica, and chlorite (Fig. 2.3b). XRD analysis of handpicked mica from the sand fraction from both formations showed that the mica was biotite and HIV in HL sediment (Pace et al., 2003) and muscovite, vermiculite, and HIV in RL sediment. Bulk C3177 borehole sand- and silt-sized sediments contained quartz, feldspar (both plagioclase and alkali-feldspar), and lesser amounts of mica, chlorite, and an amphibole (Horton et al., 2003). Clay mineralogy of C3177 sediments consisted of illite, smectite, chlorite, and kaolinite.

1.3.2. Adsorption and Transport of U-CO₃ Complex

Equilibrium adsorption isotherms were obtained for six samples of the Hanford flood deposits using the anionic U-CO₃ complex (Fig. 2.4a). Reaction with the solid phase was minimal, resulting most in distribution coefficients (K_d) < 1 (Table 2.2). The solutions were buffered with dissolved carbonate, resulting in complete complexation of uranyl within an anionic carbonate complex (Fig. 2.1a). Consequently, decreased reactivity was

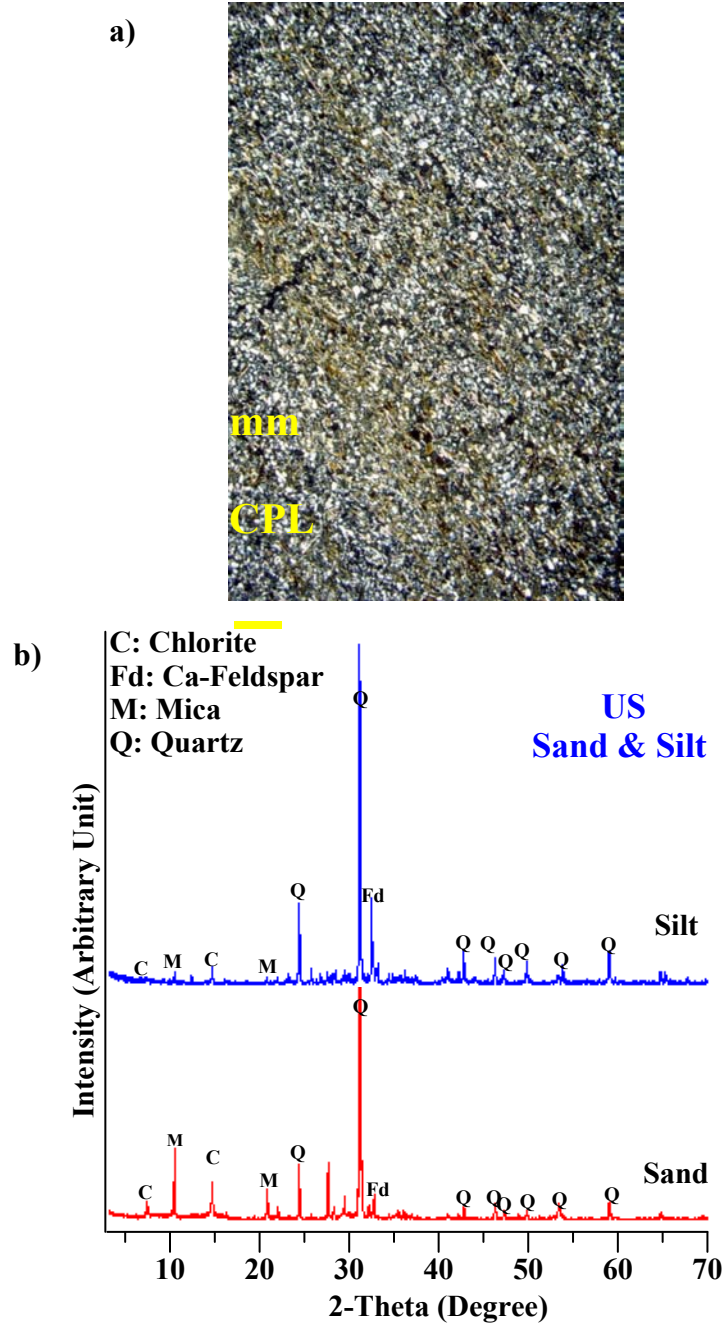


Figure 2.3 Mineralogy of Ringold Laminated (RL). a) Thin section in cross-polarized light, and b) X-ray diffraction pattern of silt and sand fractions showing chlorite (C), Ca-feldspar (Fd), mica (M), and quartz (Q).

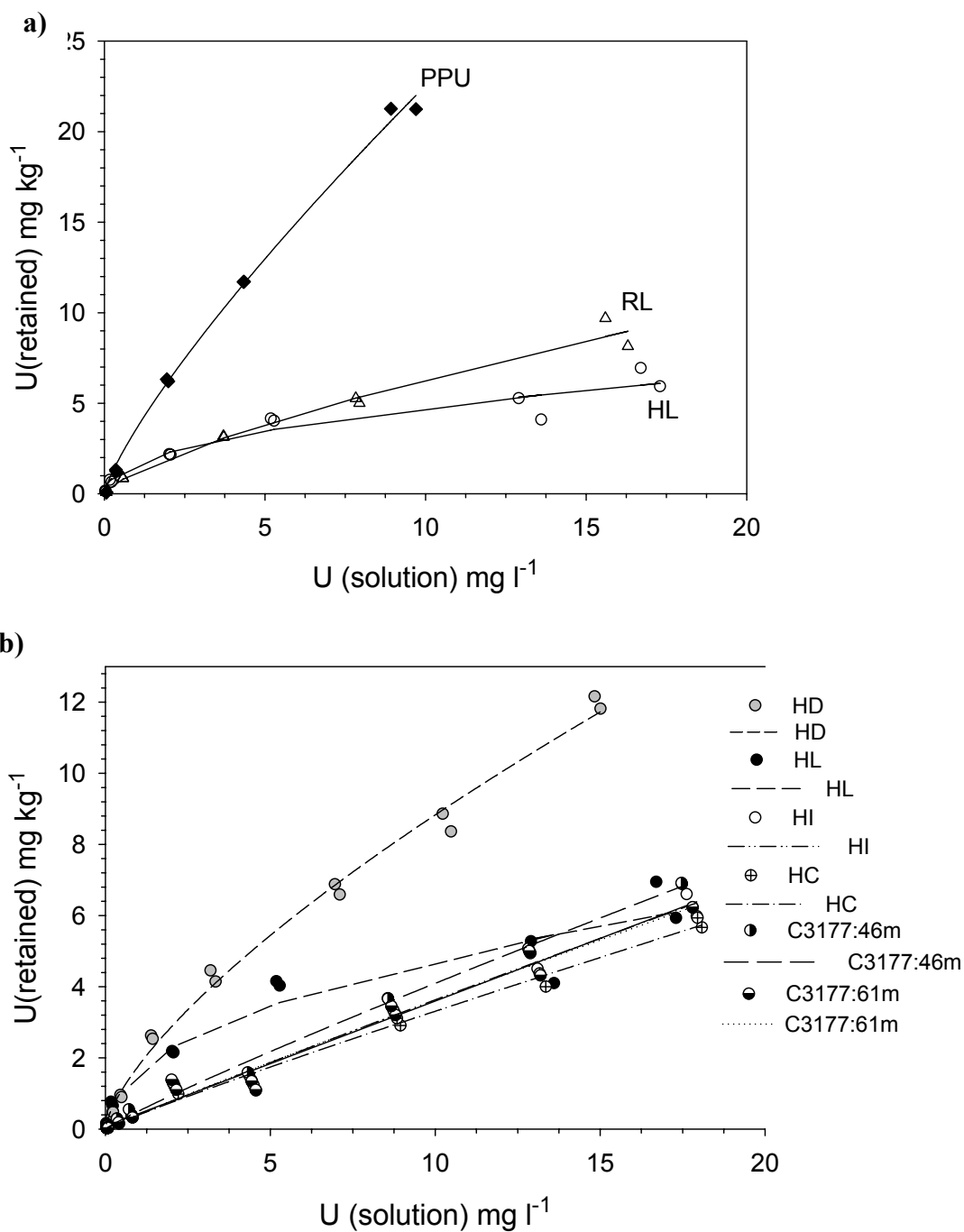


Figure 2.4 U(VI) isotherm. Experimental conditions were $I = 0.1$ M, $p\text{CO}_2(\text{g}) = 10^{-2}$, $0 - 8.4 \times 10^{-5}$ M U(VI), 2g:4mL, 0 M Ca, for 72 h. a) Isotherms with Freundlich fits on PPU, RL, and HL samples b) Isotherms on Hanford flood deposits used Freundlich equation for HD and HL, and linear equation for HI, HC, and both C3177 samples.

Table 2.2 Freundlich and linear parameters describing the sorption of U(VI).

<i>Sediment</i>	<i>Source</i>	<i>Freundlich parameters</i>			<i>Linear parameters</i>		
		K_f	n	r^2	K_d	<i>intercept</i>	r^2
HL	ERDF	1.67	0.455	0.975	0.338	0.786	0.940
HI	IDF	0.399	0.960	0.992	0.352	0.078	0.992
HC	IDF	0.392	0.927	0.995	0.315	0.104	0.994
HD	IDF	1.768	0.699	0.997	0.785	0.677	0.988
C3177: 150'	IDF	0.500	0.913	0.996	0.387	0.142	0.997
C3177: 200'	IDF	0.409	0.946	0.991	0.350	0.071	0.991
PPU	White Bluffs	3.594	0.797	0.998	2.295	0.607	0.986
RL	White Bluffs	1.19	0.723	0.993	0.552	0.430	0.983

K_f = Freundlich distribution coefficient, n = non-dimensional Freundlich parameter, K_d = linear distribution coefficient.

observed in comparison to carbonate-free solutions in which the uranyl cation, UO_2^{2+} , might dominate aqueous speciation (Carroll and Bruno, 1991; Carroll et al., 1992; Waite et al., 1994; Kaplan et al., 1998; Barnett et al., 2000, 2002; Zheng et al., 2003). In addition, it is likely that competition for sorption sites occurred between the negatively charged U-CO_3 complex and dissolved carbonate (CO_3^{2-}) (Zachara et al., 1993; Kaplan et al., 1998; Barnett et al., 2000, 2002). The linear distribution coefficients (K_d) in Table 2 are within the range of those in simulated vadose zone porewater solutions containing high levels of CO_3^{2-} , which are typically $0 - 1 \text{ cm}^3 \text{ g}^{-1}$ (Serne et al., 2002b; Knepp, 2002). Simulated groundwater solutions, in which the carbonate concentration and total ionic strength are lower, tend to have higher K_d , ranging from $1 - 7 \text{ cm}^3 \text{ g}^{-1}$ (Kaplan et al., 1998; Gamedainger et al., 2001a, b; Serne et al., 2002b). This suggests that the chemistry of vadose zone porewater solutions is not conducive to the retention of U(VI).

The uranium isotherm appeared to be linear for some sediments, and nonlinear for others (Fig. 2.4). The Freundlich equation was appropriate for more reactive PPU, RL, and HD samples and the relatively nonreactive HL sample, as evidenced by n values significantly less than unity (Table 2.2). The linear K_d approach appeared to be appropriate for most of the less reactive samples (HC, HI, C3177). Consequently, both nonlinear and linear parameters are provided for comparison in Table 2.2. Figure 2.4 only showed the best fit, which was the Freundlich equation for HL, HD, RL, PPU and the linear equation for HC, HI, C3177. In general, Fig. 2.4b indicates variation in the sorption capacity of the Hanford flood deposits for U, and it is hypothesized that a relationship between grain size and/or surface area might be responsible. The more reactive HL and HD sediments are

generally more fine-grained than the less reactive samples (Chapter 3), an observation which is consistent with the transport results of Gamerding et al. (2001a, b).

Comparison of HL with two other relevant geologic units, the Plio-Pleistocene (PPU), and Ringold (RL) provided additional insight into the mobility of U throughout the Hanford subsurface. The isotherms of the HL, PPU and RL samples in the presence of U-CO₃ are shown in Fig. 2.4b. The capacity of PPU for U was greater and the isotherm more linear than RL and HL (Table 2.2). The degree of U sorption onto the PPU was not expected, since the mineralogy consisted of carbonate and amorphous silica (Fig. 2.1), and the Fe-oxide content was quite low (Table 2.1). The sorption capacity of carbonates is known to be considerably less than that of Fe-oxides (Milton and Brown, 1987), but it was observed by Zachara et al. (1993) that calcite may become the dominant sorbent when its site concentration exceeds that of Fe-oxides. Consequently, it is possible that different mineralogic components might govern sorption in the PPU versus the RL and HL.

Large differences were observed between U retention in our RL samples ($K_d = 0.55$) and the Ringold samples of Barnett et al. (2000) ($K_d = 480$). Differences in iron-oxide content, pH conditions, and CO₃²⁻ concentration each contributed to this variation. In the previous study, the Ringold contained approximately 4 times the amount of Fe-oxides as RL and had a native pH of 6.8 (Barnett et al., 2000). The previous Ringold was collected from a localized zone highly enriched in Mn- and Fe-oxides referred to as a “Fe-Mn stringer,” whereas the RL sample was more representative of the Ringold Formation as a

whole (Mayes et al., 2005b). Determination of the pH adsorption edge found that maximum U(VI) sorption occurred between pH 5 and pH 7, while a precipitous drop in adsorption occurred above pH 7 (Barnett et al., 2000). By pH 8, which is analogous to the present study, sorption had dropped to < 5% of the influent concentration (Barnett et al., 2000). The steep edge feature was attributed to the pH-dependent solubility of calcite and the subsequent formation of stable anionic U-CO₃ complexes, which are consistent with the results of Zheng et al. (2003). In addition, U(VI) sorption was also inversely related to pCO₂. Less sorption was observed at pCO₂ = 10^{-3.5} versus pCO₂ = 10⁻² due to competition with dissolved carbonate (Carroll and Bruno, 1991; Waite et al., 1994, Barnett et al., 2000, 2002; Serne et al., 2002b). Barnett et al. (2000) utilized the lower pCO₂ while the present study utilized the higher pCO₂, thereby contributing to decreased sorption observed here, which is consistent with vadose zone porewater conditions at Hanford (Serne et al., 2002b).

Short-term transport experiments were conducted using U-CO₃ and repacked sediments of HL, PPU, and RL (Fig. 2.5, Table 2.3). Minimal retardation of U was observed in the HL and RL sediments, whereas U was more retarded ($K_d \sim 0.27$) in the PPU (Table 2.4). The transport K_d is an order of magnitude lower than from batch experiments (Table 2.2). This was expected since the experiments were conducted with very short residence times (2 h) in order to effectively isolate short-term retention processes. The Br and U data for both RL and HL sediments are sparse and resulted in failure of the CDE model. Regardless, it was clear that the breakthrough of U and Br in HL and RL were nearly coeval, implying little sorption and K_d approaching zero (Fig. 2.5). Transport results are

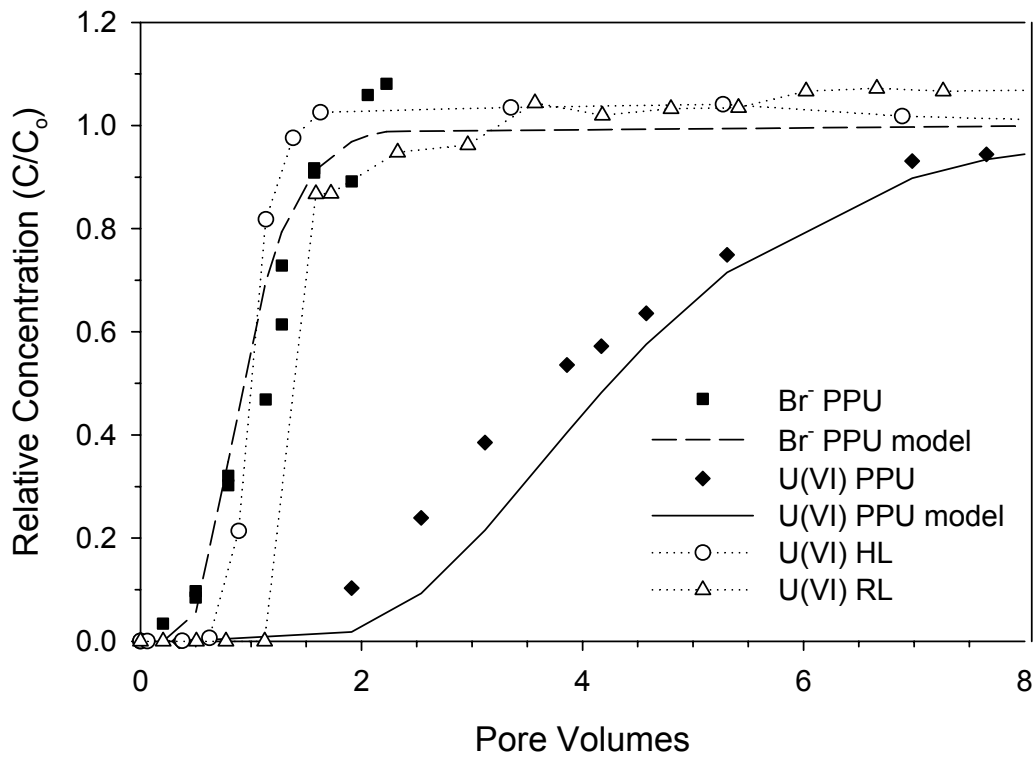


Figure 2.5 U(VI) transport experiment in repacked sediments. Breakthrough curves showing observed Br for PPU experiment (squares), observed U(VI) (triangles, RL; circles, HL; and diamonds, PPU), and PPU experiment modeled with convective-dispersive equation (lines). Experimental conditions were $I = 0.1$ M, $p\text{CO}_2(\text{g}) = 10^{-2}$, 8.4×10^{-5} M U(VI), 0 M Ca in repacked sediments.

Table 2.3 Physical parameters for miscible displacement experiments.

<i>Media</i>	<i>L</i> <i>cm</i>	<i>r</i> <i>cm</i>	θ $cm^3\ cm^{-3}$	ρ_b $g\ cm^{-3}$	v $Cm\ h^{-1}$	<i>Pulse</i> <i>pv</i>
HL	4.5	0.5	0.44	1.70	1.95	20.85
PPU	4.5	0.5	0.37	1.67	2.19	59.30
RL	4.5	0.5	0.45	1.50	1.98	10.05

L = column length, r = column radius, θ = water content, ρ_b = bulk density, v = mean porewater velocity, pv = pore volumes.

Table 2.4 Transport parameters obtained from the application of the convective-dispersive equation (CXTFIT) to PPU experiment and the mass recovery of tracers.

<i>Sediment</i>	<i>Tracer</i>	<i>Recovery</i>	<i>D</i> ($cm^2\ h^{-1}$)	<i>K_d</i>	<i>r²</i>
HL	Br ⁻	0.97			
	U	1.03			
PPU	Br ⁻	1.01	0.77 ± 0.29	0.27 ± 0.03	0.993
	U	1.03	0.77 ± 0.29		0.983
RL	Br ⁻	1.00			
	U	1.10			

D = dispersion coefficient, and K_d = linear distribution coefficient, both obtained from application of CXTFIT.

similar to isotherms (Fig. 2.4) in that U was more effectively retained by the PPU sediment. Recovery of U(VI) for all three sediments was ~100% (Table 2.4), suggesting that the experiments measured short-term processes, most likely representative of adsorption (Giammar and Hering, 2001; Gamerdinger et al., 2001a,b). A large, intact, unsaturated PPU core (12,000 cm³) experiment with longer residence times (240 h) resulted in 90% recovery and a similar K_d as the repacked column (Table 2.4) (Mayes et al., 2005a). The similarity between the K_d from the large intact core and the small, repacked sediments shown here is surprising, and is most likely because the experiments in this study used ground PPU sediments that might have artificially increased the surface area in comparison to the consolidated intact rock core (Mayes et al., 2005a). The difference in mass recoveries, however, may suggest that the current experiments measured reversible, adsorptive processes, and that considerably longer time scales may be required for immobilization. Precipitation of U has been observed to be quite reversible in carbonate-rich solutions, but such reversibility is often subject to significant kinetic limitations (Serne et al., 2002b; Liu et al., 2004; Qafoku et al., 2005).

1.3.3. Mechanisms of U(VI) reactivity

X-ray absorption spectroscopy (XAS) was applied to Hanford (HF), RX and RL samples to determine the solid-phase speciation of adsorbed U, following the methods of Bostick et al. (2002). Uranyl-carbonate was found to adsorb as an inner-sphere ternary complex, and was associated with Fe-oxides for HF and RX sediments and the edges of 2:1 phyllosilicates for RL sediments (Fig. 2.6). Sorption onto Fe-oxides is consistent with

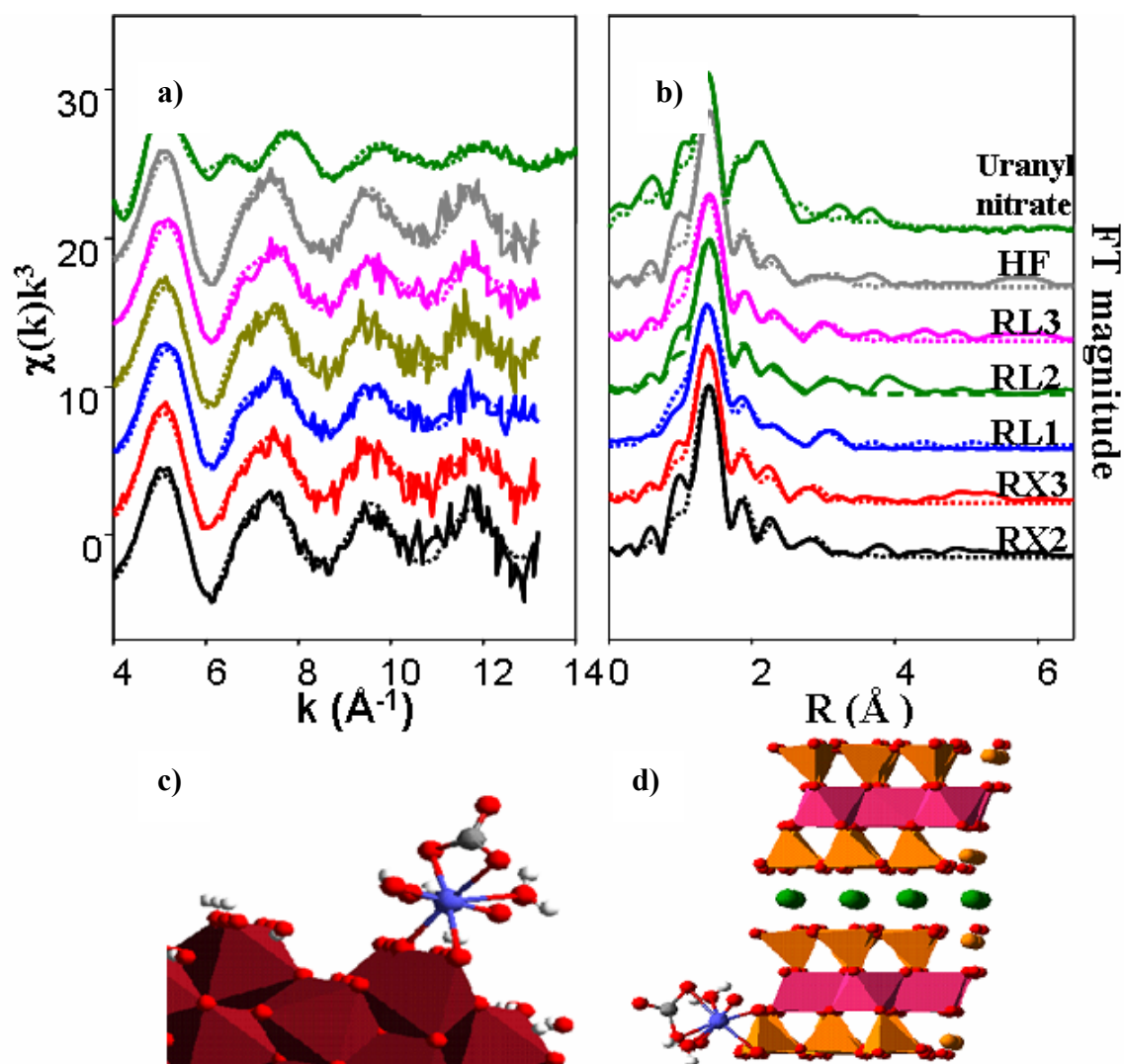


Figure 2.6 Results from x-ray adsorption fine structure spectroscopy (EXAFS). a) The k^2 -weighted $\chi(k)$ U-L_{III} extended EXAFS spectra, and b) uncorrected radial structure functions for uranyl nitrate, Hanford (HF), Ringold Laminated (RL1 – RL3), and Ringold cross-beds (RX1, RX3). The experimental data (solid lines) are fit (dotted lines) using parameters described in Bostick et al. (2002). FT = fourier transform, R = bond length. c) Model structure for U sorbed to Fe-oxides showing the formation of an inner-sphere ternary complex containing carbonate. The (110) face of goethite is used to illustrate the inner-sphere complex; outer-sphere complexes are not depicted, and d) Model structure for U sorbed to edge sites of 2:1 phyllosilicates showing the formation of an inner-sphere ternary complex containing carbonate.

previous results on the Ringold Formation (Barnett et al., 2000; Bostick et al., 2002), and other geologic media containing Fe (Waite et al., 1994; Bargar et al., 1999, 2000; Bostick et al., 2002). Bargar et al. (1999, 2000) further suggested that a metal bridge (uranium) was formed between the oxide surface hydroxyls and the carbonate complex. Sorption of the anionic U-CO_3 complex onto phyllosilicates in the RL samples, however, differs from results of Turner et al. (1996) in which UO_2^{2+} was observed to adsorb onto phyllosilicates in the absence of dissolved carbonate. Further, RL, RX, and HF are mineralogically similar, suggesting at least two possible mechanisms for U-CO_3 sorption in siliciclastic sediments. The similarity between the large intact core (Mayes et al., 2005a) and the small, repacked sediments shown here is surprising, and possibly suggests that the current experiments measured reversible, adsorptive processes, and that considerably longer time scales may be necessary for irreversible sorption. The mechanism of U sorption, therefore, remains somewhat uncertain for the PPU samples.

Comparison of the mineralogy of the sediments provided four mutually non-exclusive hypotheses to explain greater U retention in the PPU vs. lesser sorption in the HL and RL (Table 2.1). These hypotheses, with respect to the PPU, are: 1) high surface area leading to greater sorption onto generic or unknown mineral component(s), 2) higher organic carbon content leading to sorption of U onto organic matter, 3) higher calcite content leading to significant adsorption and/or precipitation of U onto calcite, and/or 4) higher calcite content leading to the formation of adsorbed or precipitated $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complex that has different affinity for the solid phase than the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex.

The third and fourth hypotheses warrant a bit more explanation. It is known that the extent and rate of U sorption onto calcite is generally much lower than onto Fe-oxides (Milton and Brown, 1987; Zachara et al., 1988, 1993; Carroll and Bruno, 1991; Carroll et al., 1992; Reeder et al., 2000). However, the high concentration of calcite and low concentration of Fe-oxides in the PPU suggest the possibility of sorption onto calcite, as suggested by Zachara et al. (1993). Further, the association of U with calcite might be a result of adsorption, precipitation, or both, as suggested by Bruno and Carroll (1991) and Carroll et al. (1992). It is for this reason that the more general terms “sorption” and “retention” are used throughout this manuscript. Finally, experiments shown in Figs. 2.4 and 2.5 utilized influent solutions consisting of the anionic U-CO_3 complex. In media composed of 25% calcite, it is possible that the neutrally-charged Ca-U-CO_3 complex might form in solution due to calcite dissolution, and/or on the solid phase due to surface complex formation (Hypothesis 4). All four hypotheses were investigated in a series of targeted kinetic experiments, mostly on the PPU, involving variation in solid:solution ratio, addition of Ca, removal of carbonates, removal of organic matter, and removal of Fe-oxides.

The solid:solution ratio was varied for the PPU sediment to test the influence of surface area upon U sorption (Hypothesis 1). Figure 2.7 shows solid phase U plotted against surface area, resulting in the generation of a nonlinear function for the PPU. Single-point measurements from HL, RL, and the C3177 samples were plotted in the same space, and the equivalent PPU point is circled. Figure 2.7 clearly demonstrates a dependence of U sorption upon surface area, and lends considerable support to Hypothesis 1 which states

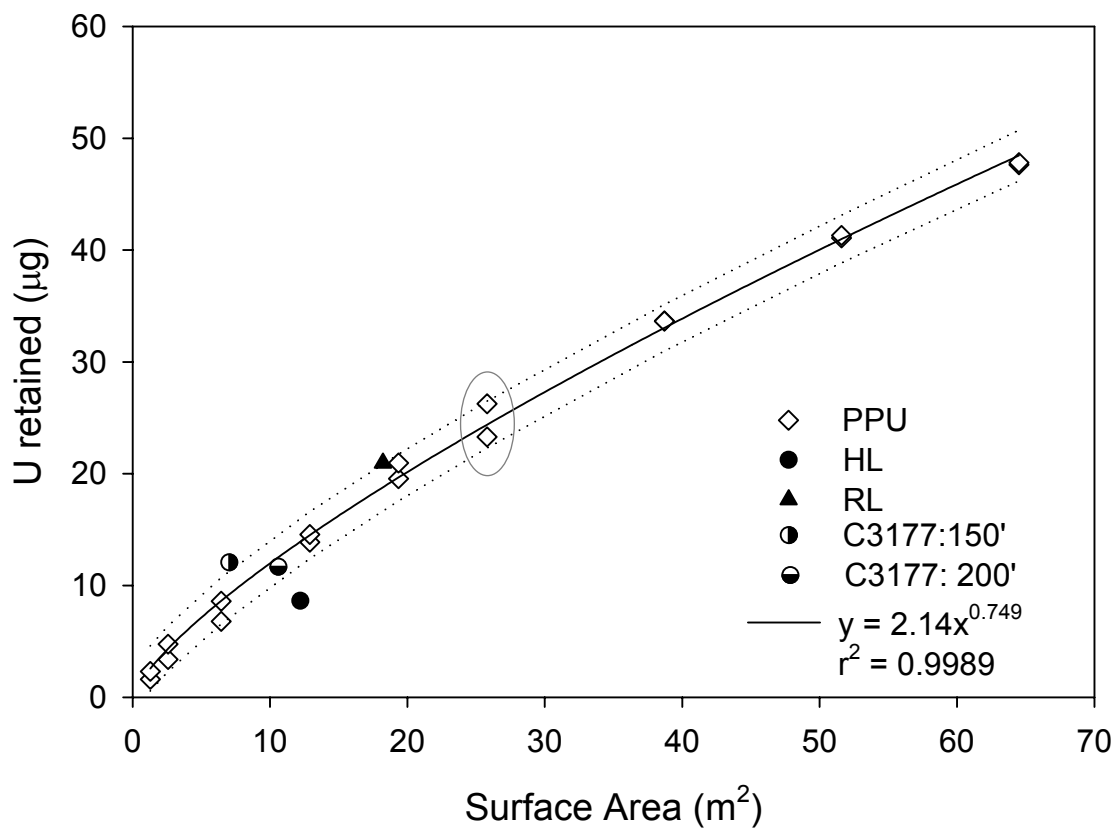


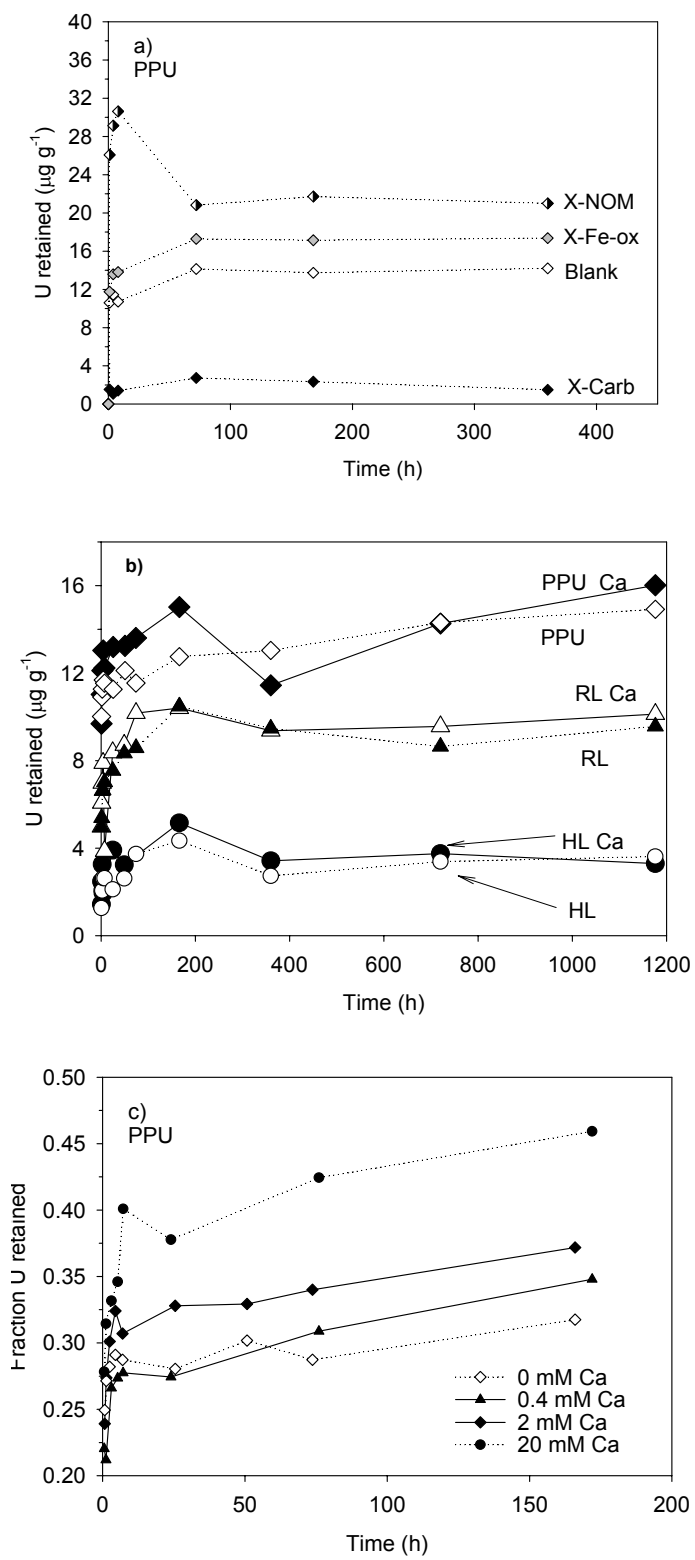
Figure 2.7 Relationship between surface area and U retention. Plio-Pleistocene (PPU) (diamonds) showing nonlinear equation (solid line) and 95% confidence intervals (dashed lines). Points for Hanford laminated (HL), circle; Ringold laminated (RL), triangle; C3177: 150', circle right-filled; and C3177:200', circle bottom-filled, sediments at a single solid:solution ratio (2g:4ml) are also plotted. Equivalent points of the PPU are circled.

that surface area differences contribute to the sorption patterns observed in batch isotherm and transport experiments. However, only one of the Hanford or Ringold samples plots within the 95% confidence intervals of the nonlinear PPU line, suggesting that additional factors might also influence U sorption. In addition, Hypothesis 1 does not address the mechanisms of sorption or the possible sorbents for U.

To determine the effects of Fe-oxides, natural organic matter (NOM) (Hypothesis 2), and carbonates (Hypothesis 3) upon U retention in the PPU, samples were subjected to extraction techniques to remove these components before measuring U-CO₃ sorption (Fig. 2.8a). These results were compared to a control sample which was not subjected to extraction. Uranium retention was observed to be increased above the level of the control sample for samples in which Fe-oxides and NOM were extracted. It is probable that the extraction techniques may have resulted in unintended alteration of remaining sediment, so this exercise should not be considered strictly quantitative. Regardless, the control, the extracted NOM, and the extracted Fe-oxides samples all exhibited significant retention of U, whereas the carbonate-extracted samples exhibited minimal sorption. This experiment suggests that retention of U in the PPU was more associated with carbonates than NOM or Fe-oxides.

Reactivity of the anionic U-CO₃ and the neutral Ca-U-CO₃ complexes was tested using a batch kinetic study on all 3 sediments (Hypothesis 4). Addition of Ca resulted in nearly 100% complexation of U into the Ca-U-CO₃ aqueous complex (Fig. 2.1b), while the

Figure 2.8 Uranium sorption as a function of time on extracted samples. Experimental conditions were $I = 0.1 \text{ M}$, $p\text{CO}_2(\text{g}) = 1 \text{ e-}2$, $8.4 \text{ e-}5 \text{ M U(VI)}$. a) Application of U-CO_3 to Plio-Pleistocene (PPU) sediments in which NOM is extracted (X-NOM), Fe-oxides are extracted (X-Fe-ox), no extractions performed (Blank), and carbonate is extracted (X-Carb). b) Application of anionic U-CO_3 complex (PPU, RL, and HL) and neutral Ca-U-CO_3 complex (PPU Ca, RL Ca, and HL Ca) to sediments. Size of symbols is the standard deviation of 13 influent samples. c) Application of anionic U-CO_3 complex (0 mM Ca), 50% anionic complex and 50% neutral Ca-U-CO_3 complexes (0.45 mM Ca), 96% Ca-U-CO_3 complex (2 mM Ca), > 96% Ca-U-CO_3 complex (20 mM Ca) to Plio-Pleistocene (PPU) sediment.



Similar trends to the U-CO₃ isotherms were observed, in which U immobilization by PPU exceeded that of RL and HL for both uranyl complexes (Fig. 2.8b). Rapid sorption was obtained in ~4 h for all sediments, but immobilization of U continued to increase for 200 h in HL and RL and for at least 1200 h in PPU. For all three sediments, retention was generally observed to increase following the addition of Ca, which suggested that the Ca-U-CO₃ complex was more reactive than the suite of U-CO₃ complexes (Fig. 2.8b) (Hypothesis 4). Such changes, although minor in HL and RL sediments, were outside of the standard deviation of the analyses which are represented by the size of the symbols (Fig. 2.8b). This suggested that the neutrally-charged Ca-U-CO₃ complex was consistently more reactive than the anionic U-CO₃ complex. These findings therefore do not support the hypothesis that the Ca-U-CO₃ complex formed due to calcite dissolution in any of the sediments, because the two curves in Fig. 2.8b are generally different up to 1200 h. If the two curves eventually became equivalent, then it might be inferred that the Ca-U-CO₃ complex formed in solution or on the solid phase. The anionic U-CO₃ complex is probably less reactive than the Ca-U-CO₃ complex due to the effects of competition by dissolved carbonate, present in vadose zone porewaters, for sorption sites. In a system with lower pCO₂, such as groundwater, the anionic U-CO₃ might be equivalently or more reactive than the Ca-U-CO₃ complex. This suggests that additional studies are needed to explore the effects of pCO₂, pH, and other factors upon the reactivity of U as the Ca-U-CO₃ versus the U-CO₃ complex.

The influences of speciation and calcite solubility were tested in a final kinetic experiment on the PPU using three levels of Ca addition. The addition of 0.0004 M Ca

resulted in the complexation of ~50% of U into the anionic U-CO_3 form and ~50% into the neutral Ca-U-CO_3 form, the addition of 0.002 M Ca resulted in the near complete incorporation of U into the neutral Ca-U-CO_3 species, and the addition of 0.02M Ca resulted in oversaturation with respect to calcite. Uranium retention on the PPU was observed to be co-variant with the concentration of added Ca (Fig. 2.8c). Sorption of U onto the PPU, therefore, was observed to increase as the proportion of Ca-U-CO_3 increased, suggesting the neutral complex had a greater affinity for the solid phase in comparison to the U-CO_3 complex. The addition of the highest concentration of Ca, in which calcite was oversaturated, resulted in the greatest loss of U to the PPU, suggesting co-precipitation of calcite and incorporation of U. The results from Fig. 2.8c are most consistent with incorporation of U into precipitating or existing aragonite (Reeder et al., 2000) or calcite (Milton and Brown, 1987; Carroll et al., 1992; Kaplan et al., 1998; Reeder et al., 2001; Kelly et al., 2003), although rutherfordine ($\text{UO}_2(\text{CO}_3)$) (Carroll et al., 1992) and schoepite ($\text{UO}_2 \cdot 2\text{H}_2\text{O}$) (Giammar and Hering, 2001) have also precipitated in systems with similar aqueous chemistry. The similarity between the curves in Fig. 2.8c suggests that precipitation was an important mechanism for uranyl retention in carbonate-rich media, particularly in the presence of dissolved Ca. In general, the PPU samples were not observed to reach equilibrium with respect to U sorption even after 1200h, regardless of speciation (Fig. 2.8b, c). In comparison, the HL and RL samples appeared to reach equilibrium after ~200 h (Fig. 2.8b). Continual uptake of U in a closed system, as for the PPU, is also consistent with precipitation.

The rate and extent of adsorption versus precipitation in the PPU, however, remains uncertain. Adsorption was most closely approximated by the short-term (2 h) transport experiments which exhibited complete mass recovery and minimal tailing. Some precipitation may have occurred in a large intact core with residence time of 240 h, in which 90% of U was recovered (Mayes et al., 2005a). Precipitation, therefore, probably occurred only over the longer time scales, and continued up to 1200 h reaction time. The extent of U retention in the short-term transport experiments was significant, suggesting the adsorptive component, if it exists, should not be ignored. The entire study suggests that solid phase calcite concentration and dissolved carbonate may exert considerable influences upon the mobility of U(VI) in heterogeneous subsurface media. The lack of evidence for precipitation in the overlying Hanford or underlying Ringold sediments further suggests different mechanisms for retention of U in siliciclastic versus carbonate sediments.

1.4 Conclusions

We have found significant differences in the reactivity and mechanisms of uranyl-carbonate complexes towards siliclastic and carbonate sediments co-existing in the Hanford subsurface. Surface area exerted considerable influence in all systems. The siliciclastic Hanford and Ringold sediments exhibited minimal reactivity and adsorption of U-CO₃ was associated with Fe-oxides and 2:1 phyllosilicates. The Plio-Pleistocene carbonate, in contrast, was more reactive and appeared to adsorb to calcite in the short term (< 2 h), and possibly co-precipitate with calcite or aragonite in the long term (up to

1200 h). This suggests that mineralogic heterogeneities, such as enrichment or depletion of Fe-oxides and calcite, may significantly influence the mechanisms of uranyl sorption in the subsurface.

Somewhat greater reactivity of the neutrally-charged Ca-U-CO₃ complex was observed in comparison to the anionic U-CO₃ complex in this chemical system. Differences between the reactivity of the two complexes up to 1200 h suggested that the Ca-U-CO₃ complex did not spontaneously form in any of the sediments. Porewater chemistry representative of vadose zone conditions, i.e., enriched in carbonate, resulted in minimal reactivity due to competition for sorption sites by dissolved carbonate in siliclastic sediments. In contrast, excess dissolved carbonate probably contributed to the propensity for precipitation of uranyl in calcite-rich media. This study has provided an integrated approach and new insights into the speciation and reactivity of uranyl in diverse subsurface sediments.

1.5 Acknowledgements

We would like to acknowledge Roland Hirsh and Mark Gilbertson, who are the program managers for the Environmental Management Science Program (EMSP), for providing support for the ERDF and White Bluffs analyses. EMSP is administered by the US Department of Energy (DOE), Office of Science, Biological and Environmental Research Programs. We would like to acknowledge Fred M. Mann and Frank J. Anderson of the Tank Farm Vadose Zone Group and CH2M Hill Hanford Group, Inc. for providing

support for analyzing samples from the IDF under contract with the US DOE. We acknowledge Scott C. Brooks of ORNL for assistance with geochemical modeling. We gratefully acknowledge the scholarship provided for MAM's Ph.D. work by the Waste Management Research Education Institute (WM-REI) at the University of Tennessee. We would also like to thank Steve Reidel, John Piatt, and R. Jeffrey Serne of Pacific Northwest National Laboratory (PNNL) for their assistance with collection of the IDF sediments, and Bruce N. Bjornstad (PNNL) and John Piatt for assistance with the ERDF and White Bluffs sediments. We would like to thank Yul Roh (formerly of ORNL) for determination of clay mineralogy. We also gratefully acknowledge the efforts and accommodations made by the respective staffs of the IDF and ERDF during sample collections. X-ray absorption spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) operated by the US DOE. Oak Ridge National Laboratory is managed by the University of Tennessee-Battelle, LLC, under contract DE-AC05-00OR22725 with the US DOE.

Chapter 3. The Influence of Heterogeneous Sedimentary Layering on the Saturated Transport of Solutes

1.0 Abstract

Prediction of contaminant transport in unconsolidated, horizontally-layered sediments is complicated by subsurface heterogeneity and directionality of hydraulic properties (anisotropy). The goal of this research was to determine the relationship between heterogeneous sedimentary layering and anisotropy in the flow regime. The objective was to compare transport parameters from saturated intact samples from a variety of sedimentary facies in bedding-parallel (pb) and cross-bedding (xb) orientations. Intact core samples (25 cm x 25 cm) collected from six diverse layered sedimentary units were characterized in terms of heterogeneity of layering and particle size. A variety of quantitative solute transport techniques were applied to the samples. Flow interruption in pb and xb samples with homogenous and heterogeneous layering confirmed that anisotropy was related to heterogeneous layering. Several relationships were generated to determine preference for flow and/or dispersion with respect to sedimentary bedding. The anisotropy of the heterogeneous samples was low and generally between 1-5. The results were generally suggestive of a slight preference for bedding parallel flow and solute transport, and a slight restriction for flow and transport across sedimentary bedding. The quantitative relationships were generally consistent with observed sedimentary characteristics, suggesting physical controls on flow and transport characteristics.

1.1 Introduction

The hydraulics of subsurface sediments is strongly influenced by original sedimentary structures, including thickness and continuity of beds, grain size, and grain size distribution. These factors affect the pore size, pore diameter, and pore connectivity within individual layers. Within groups of layers, flow is affected by the range and variation of hydraulic properties and the connectivity of individual layers. For instance, within a homogenous group of layers, the distribution of hydraulic conductivities or pore-water velocities in the layers is relatively narrow. This scenario is similar to the idealized “piston-flow” model, in which an applied solute evenly displaces a solute occupying a given volume of pores in a soil or sediment.

Within a heterogeneous group of layers, the distribution of velocities may vary substantially. A wide variation in pore-water velocities may cause solute transport to be affected by so-called “preferential” transport processes associated with multiple flow regimes. In preferential transport, portions of saturated media may be partially or completely bypassed. The flow regime becomes isolated to regions of higher conductivity, and therefore regions of lower conductivity may only have limited interaction with the overall flow regime (Pace, 2005). Sometimes such interactions may be dominated by diffusion rather than by advection, even in layered sediments (Pace et al., 2003, 2005; Pace, 2005). This condition is referred to as physical nonequilibrium (PNE) because advective and diffusive processes may be slow to reach equilibrium with

respect to solute concentrations (Jardine et al., 1998, 1993a,b; Reedy et al., 1996; Mayes et al., 2003).

1.1.1. Previous Work

The natural arrangement and heterogeneity of subsurface media are expected to exert primary control on the extent of preferential transport. Mayes et al. (2003) and Pace et al. (2003) investigated solute transport in layered sediments that retained bedding characteristics of natural subsurface media. Intact samples were taken in the horizontal and vertical directions to quantify hydraulic transport parameters both parallel to sedimentary bedding (pb) and across sedimentary bedding (xb). Miscible displacement of nonreactive solutes generally resulted in more asymmetrical breakthrough curves (Fig. 3.1a) and greater dispersion in flow bedding parallel (pb) cores in comparison to cores in which flow was across bedding (xb) (Mayes et al., 2003, 2005a; Pace et al., 2003, 2005; Pace, 2005).

Greater dispersion in pb cores was attributed to a wide distribution of pore-water velocities resulting from differences in grain and pore sizes of adjacent, parallel sedimentary layers, which is illustrated in the conceptual model in Fig. 3.1b. Lower dispersion in the xb cores was attributed to flow across interbedded layers of lower conductivity and dampening of variations in pore-water velocity (Fig. 3.1b). Greater dispersion in the pb versus xb direction was interpreted to indicate a preference for lateral

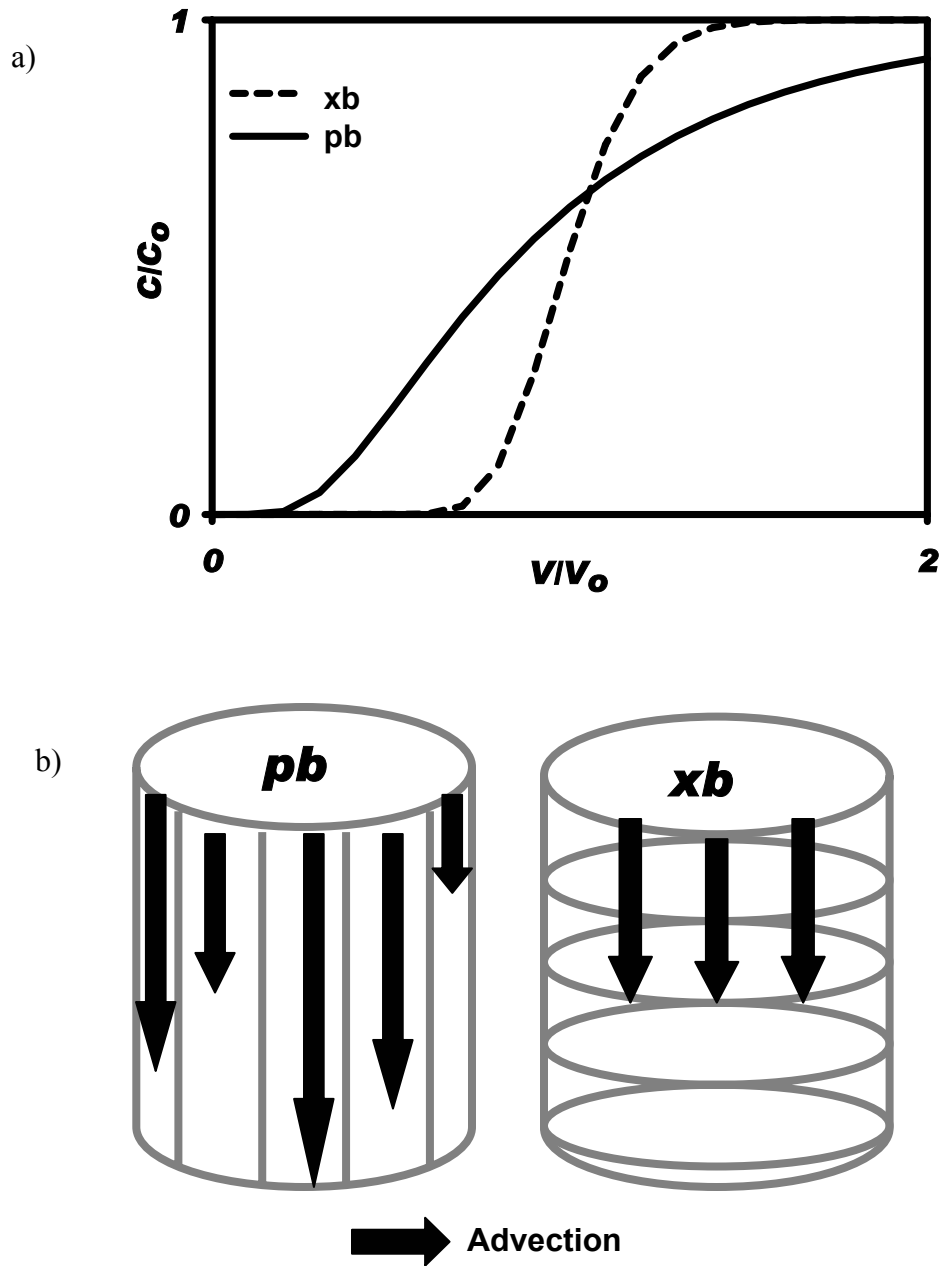


Figure 3.1 Conceptual model of flow and transport in saturated flow bedding parallel (pb) and flow cross bedding (pb) cores. a) Idealized breakthrough curves for solute transport in pb and xb cores, b) Block diagrams of theoretical distributions of pore-water velocities in pb and xb samples.

flow, i.e., anisotropic flow (Mayes et al., 2003, 2005a; Pace et al., 2003, 2005; Pace, 2005). This preference was exacerbated under lower water contents (Pace, 2005) which is consistent with published theoretical predictions (Mualem, 1984; Yeh et al., 1985a,b) and experimental results (Mantoglou and Gelhar, 1987a,b,c; McCord et al., 1991; Stephens and Heerman, 1998; Wildenschild and Jensen, 1999; Khaleel et al., 2002). In this paper I hypothesized that sedimentary heterogeneities, such as interbedded fine-grained layering, are responsible for the observed directionality in the flow regime.

1.1.2. Goals and Objectives

The goal of this research is to determine the relationship between heterogeneous sedimentary layering and the anisotropy of the flow regime. The objective was to compare bedding-parallel (pb) and cross-bedding (xb) transport parameters in intact samples from a variety of sedimentary facies. A variety of quantitative solute transport techniques were applied in order to determine the anisotropy of the flow regime.

Anisotropy was evaluated by comparing hydraulic conductivity, Peclet numbers, and dispersivity in pb versus xb samples, and was interpreted in terms of sedimentary bedding characteristics such as grain size and the presence or absence of interbedded heterogeneous layers.

1.2 Materials and Methods

1.2.1. Core Collection and Physical Parameters

Sixteen large core samples (25 cm x 25 cm) were taken from six sedimentary units of the Hanford flood deposits and the Ringold Formation on the US Department of Energy Hanford Reservation in southeastern Washington state (Fig. 3.2). Cores were taken in both a vertical orientation in which flow was parallel to sedimentary beds (pb) and a horizontal orientation in which flow crossed beds (xb). A relatively homogenous massive coarse sand unit lacking internal heterogeneous layering (HC) was compared to five sedimentary units having internal fine-grained layers (HI, HL, HD, RL, and RX). The cores were hand-sculpted, coated with paraffin wax, and emplaced in PVC pipe by filling the annulus with epoxy or expandable foam (Jardine et al., 1988, 1993a,b; Reedy et al., 1996; Mayes et al., 2003; Pace et al., 2003). Each sedimentary unit was photographed (Fig. 3.3) and described (Table 3.1). The particle size distribution of the sediments was determined using the bouycous hydrometer method (Gee and Bauder, 1986) (Table 3.1).

Samples of three units of the Hanford deposits, HC, HI, and HD, were taken ~11 m below ground surface near the westernmost wall of the Integrated Disposal Facility (IDF) excavation in the 200 East Waste Management Area (WMA) in November, 2004 (Fig. 3.2). The Hanford Coarse (HC) samples were taken from a massive, grain-supported coarse sand unit in which interbedded heterogeneous layering was minimal (Fig. 3.3a; Table 3.1). For the purposes of this study, HC was considered to be relatively

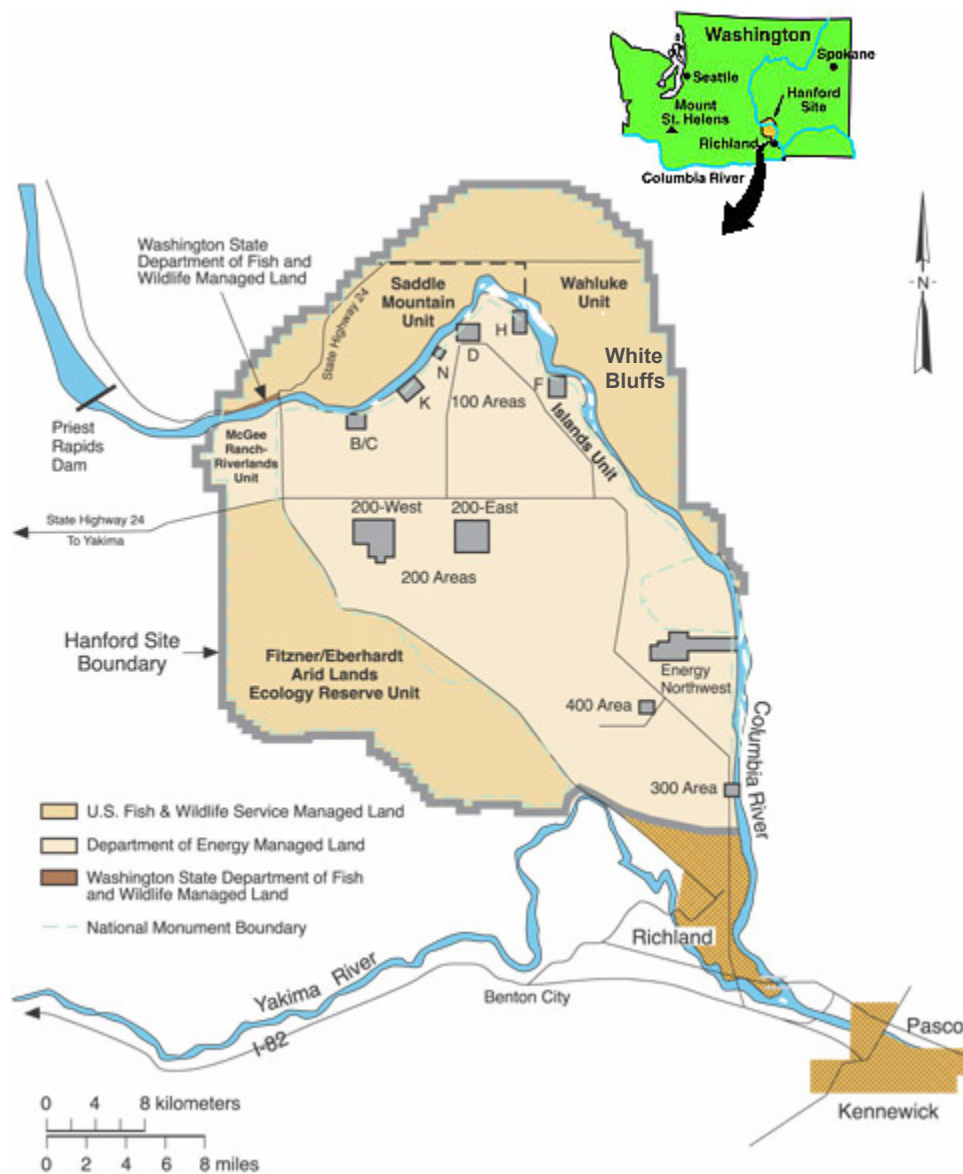


Figure 3.2 Map of Hanford Reservation within Washington state. Sampling locations are at White Bluffs, 200 East Waste Management Area, and 200 West Waste Management Area.

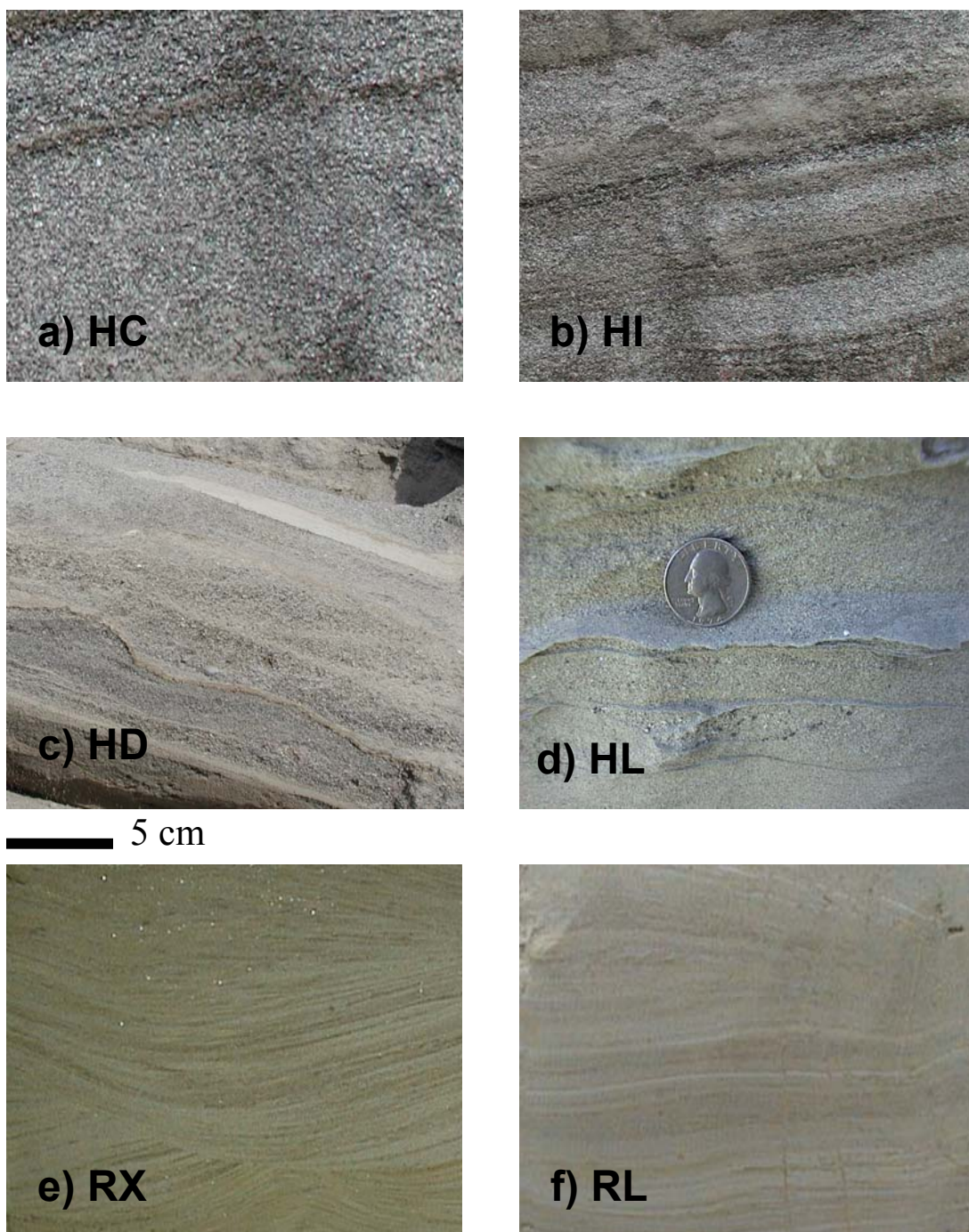


Figure 3.3 Photographs of intact samples from each sedimentary unit. Each sediment is shown at approximately the same scale that is shown within the figure. a) Hanford Coarse (HC), b) Hanford Interbeds (HI), c) Hanford Dike (HD), d) Hanford Laminated (HL), e) Ringold Cross-beds (RX), and f) Ringold Laminated (RL).

Table 3.1 Description and characteristics of sedimentary units.

Name	Formation, Descriptor	Source	Sedimentary Description	*Particle Size Distribution
HC	Hanford, Coarse	IDF	Similar textural layers Flat bedding planes Massive coarse sands	93% sand 4% silt 3% clay
HI	Hanford, Interbeds	IDF	Alternating textural layers Flat bedding planes Coarse sands, coarse sands with silt/clay matrix	89% sand 8% silt 4% clay
HL	Hanford, Laminated	ERDF	Alternating textural layers Flat bedding planes, some ripples Fine-medium sand, clay laminations	95% sand 4% silt 1% clay
HD	Hanford, Clastic Dike	IDF	Alternating textural layers Flat bedding planes, some cross-beds Medium sands, cross-bedded angular basalt sands, silt beds, clay “skins” Partially cemented	84% sand 13% silt 4% clay
RX	Ringold, Cross-beds	White Bluffs	Similar textural layers Cross-bedded and rippled structure Sandy loam, alternating layers of light and dark minerals	57% sand 42% silt 1% clay
RL	Ringold, Laminated	White Bluffs	Similar textural layers Flat bedding planes Silt loam, oxides/clays coat bedding planes	42% sand 56% silt 2% clay

* Bulk soil

homogenous due to the absence of heterogeneous layered interbeds. The Hanford Interbed (HI) samples, in contrast, were composed both of coarse sand layers similar to HC and interbeds of coarse layers that were supported by a fine-grained silt/clay matrix (Fig. 3.3b; Table 3.1). The capillary pressure-saturation function also supports this interpretation (App. A). The HI and HC samples had similar air-entry pressures consistent with a similar component of coarse-grained sand (Fig. A.1). The HC samples exhibited a steeply sloping curve, being composed of massive coarse sands containing few fine-grained materials (Fig. A.1). The HI samples had a shallow slope after the initial air-entry, indicating a more heterogeneous pore size distribution in comparison to the HC. It is likely that the interbeds containing silt matrix-supported sands (Fig. 3.3) more effectively retained water for at least 200 cm in comparison to HC samples (Fig. A.1).

The Hanford Dike (HD) samples were taken from within a clastic dike (Fig. 3.3c; Table 3.1) that was also described in Fig. 4.1.2 of Reidel and Fecht (2005). The dike was identified in the outcrop by several characteristics, first, the feature had a limited expression, second, the vertical orientation of the sediments was distinctly different from those on either side of the feature, and third, the sediments were more cemented, contained complex internal bedding and exhibited clay “skins” between layers (Fecht et al., 1999). Due to its depositional environment, the layering of the HD samples was considerably more diverse than HI or HC.

Samples of the Hanford Laminated (HL) unit were taken from the Environmental Restoration Disposal Facility (ERDF) in the 200 West WMA of the Hanford Plateau in November, 2000 and May, 2003 (Fig. 3.2). The HL samples were fine- to medium-grained sand with some interbedded clay layers and ripples (Table 3.1; Fig. 3.3d). Additional details are available in Pace et al. (2003) in which the samples were referred to as “HH” and “HV.” These sediments were also photographed and described in DOE (2002) (Figure A-38). One pb and one xb core were included in the present study in comparison to Pace et al. (2003, 2005) (Pace, 2005).

Two types of samples of the Miocene-Pliocene age Ringold Formation were collected from the White Bluffs in January, 2000 (Fig. 3.2). The Ringold Cross-beds (RX) is cross-bedded loamy sand which has many curved layers of variant mineralogical compositions (Fig. 3.3e; Table 3.1). The Ringold Laminated (RL) is a silt loam with many horizontally layers having laminations of clays and oxides (Fig. 3.3f; Table 3.1). Details are available in Mayes et al. (2003), in which the RX were referred to as LS/S, and the RL samples were referred to as US. Two additional cores of RL and RX in the pb orientation were included in the present study in comparison to Mayes et al. (2003).

The water content and bulk densities of the IDF cores were calculated gravimetrically (Table 3.2). The core within its PVC assembly was weighed, and the known weight of the PVC and annulus material was subtracted to determine remaining soil and water weight. Samples of wet soil were taken from the ends of each soil column and dried at

Table 3.2 Physical parameters of large intact cores.

Core	L <i>cm</i>	r <i>cm</i>	θ $cm^3\ cm^{-3}$	ρ_b $g\ cm^{-3}$
HC pb	25.0	10.1	0.360	1.697
HC xb	25.0	10.8	0.360	1.697
HI pb	25.0	10.4	0.368	1.674
HI xb	25.0	10.7	0.307	1.836
¹ HL pb1	23.0	11.0	0.325	1.789
HL pb2	23.5	11.0	0.393	1.610
¹ HL xb1	21.0	10.5	0.409	1.566
HL xb2	23.5	11.0	0.425	1.523
HD pb	25.0	10.8	0.411	1.562
HD xb	25.0	10.3	0.269	1.562
² RX pb1	20.0	9.75	0.477	1.387
RX pb2	21.0	9.20	0.526	1.255
² RX xb	22.5	12.5	0.468	1.409
² RL pb1	23.0	12.5	0.417	1.546
RL pb2	23.7	12.7	0.508	1.305
² RL xb	23.7	12.5	0.460	1.432

L = column length, r = column radius, θ = water content,
 ρ_b = bulk density

¹Pace et al., 2003. ²Mayes et al., 2003.

60°C to determine the water content. This water content was used to estimate the pre-existing amount of water in the core and the weight of dry soil. The cores were weighed after saturation to determine the amount of water emplaced within the core, which was added to the antecedent water, resulting in the total estimated weight (volume) of water in the core. A similar method was utilized for the Ringold cores (Mayes et al., 2003), which has been confirmed to be reasonably accurate ($\pm 0.05 \text{ cm}^3 \text{ cm}^{-3}$) for a dissembled core. The volume of water-filled pores (V_o) in the ERDF cores was estimated to be the eluted volume when the Br concentration was equivalent to 50% of the influent concentration during saturated flow (Pace et al., 2003; Pace, 2005). V_o is related to water content θ by the equation $\theta = V_o / V$, where V is the total core volume. This method was confirmed to be reasonably accurate ($\pm 0.03 \text{ cm}^3 \text{ cm}^{-3}$) for a dissembled core. Because the cores are still being used for experimentation, it is not possible to be more accurate at this time.

1.2.2. Miscible Displacement Experiments

General details of our experimental technique for saturated flow can be found in Mayes et al. (2003). All cores were oriented such that flow was downward in the vertical direction. A pond of solution (1-2 cm deep) at the upper boundary was hydraulically connected to a Mariotte (constant head) device to maintain the steady-state flow of solution. Saturated hydraulic conductivity (K_s) was measured by the constant head method during the entire length of the experiments, and the average K_s is shown in Table 3.3. Anisotropy of each sedimentary unit was calculated by the ratio of K_s in pb cores to xb cores (Table 3.3). There is some uncertainty in the single measurement of K_s , which may be influenced by

Table 3.3 Experimental parameters and results from the application of the convective-dispersive equation (CXTFIT) to bromide.

<i>Core</i>	v ($cm\ h^{-1}$)	<i>Pulse</i> (<i>pv</i>)	D $cm^2\ h^{-1}$	P_e	r^2	λ (<i>cm</i>)	K_s ($m\ s^{-1}$)	<i>Anisotropy</i> $K_{s(pb)} / K_{s(xb)}$	<i>Anisotropy</i> $\lambda_{pb} / \lambda_{xb}$
HC pb	82.6	2.56	101+/- 14.0	20.4	0.990	1.23	4.41E-05	0.49	1.44
HC xb	168	2.32	143+/- 41.3	29.5	0.974	0.85	8.97E-05		
HI pb	11.8	2.82	67.4+/- 8.22	4.39	0.992	5.70	6.72E-06	1.17	1.09
HI xb	12.3	2.74	64.1+/- 7.59	4.78	0.992	5.22	5.76E-06		
¹ HL pb1	41.9	7.30	55.7+/- 21.2	17.3	0.967	1.38	1.39E-05	1.44	2.36
³ HL pb2	29.2	2.65	40.2+/- 10.1	17.1	0.978	1.38	1.60E-05		
¹ HL xb1	11.4	2.37	9.60+/- 2.18	26.4	0.980	0.80	5.80E-06		
³ HL xb2	25.3	2.12	9.28+/- 1.74	64.2	0.994	0.37	1.50E-05		
HD pb	0.52	3.42	9.66+/- 1.37	1.34	0.984	18.6	2.87E-07	1.77	18.2
⁵ HD xb	0.40	1.62	0.41+/- 0.03	24.6	0.998	1.02	1.62E-07		
² RX pb1	12.1	3.02	14.9+/- 3.47	16.3	0.975	1.23	6.86E-06	5.62	3.5
⁴ RX pb2	1.27	2.44	2.12+/- 0.41	12.5	0.975	1.68	8.30E-07		
² RX xb	1.95	1.79	0.68+/- 0.18	64.6	0.964	0.35	1.22E-06		
² RL pb1	0.45	3.35	2.03+/- 0.26	5.09	0.990	4.52	2.56E-07	4.88	3.8
⁴ RL pb2	0.05	1.09	0.09+/- 0.02	13.3	0.964	1.78	3.55E-08		
² RL xb	0.08	1.67	0.10+/- 0.03	20.1	0.966	1.18	5.25E-08		

v = average pore-water velocity, pv = pore volumes (relative volume), D = dispersion coefficient, P_e = dimensionless Peclet number = vL/D , Dispersivity (λ) = D/v , K_s = saturated hydraulic conductivity, pb = flow parallel to bedding, xb = flow crosses bedding.

¹Pace et al., 2003. ²Mayes et al., 2003. ³Pace, 2005. ⁴Filter membrane. ⁵Partially-saturated.

sample heterogeneity because each core was unique. However, deterministic solutions are commonplace in transport studies in complex media, and a major objective of this study was to compare results from different sedimentary units. Each sample was subject to the same level of precision.

Either a saturated flow membrane (bubbling pressure, -30 cm) or filter membrane (-600 cm bubbling pressure) were allowed to contact the soil to facilitate the exchange of fluids and prevent the migration of sediment particles into the effluent line at the lower boundary (Soil Measurement Systems, Tucson, AZ). In this study, only three cores (HD xb, RX pb2 and RL pb2) utilized the filter membrane, which resulted in restricted flow rates for each core (Table 3.3). These parameters were not used in the anisotropy calculations (Table 3.3). A single unsaturated flow experiment was performed on the HD xb core, using the methods of Mayes et al. (2003). The methods were identical to the saturated flow experiments, except that a vacuum chamber was utilized at the lower boundary to apply -15 cm of tension, and a multi-channel pump was used at the upper boundary to apply solution at 12 drip points.

Applied background solutions consisted of 5 mM CaCl_2 , 0.1 M NaCl, or 0.1 M KCl. Differences in ionic strength did not appear to systematically influence our results, as evidenced by experiments on duplicate cores. The tracer solution consisted of three multiple nonreactive tracers: 0.5 mM Br (as NaBr, KBr, or CaBr_2), 0.5 mM pentafluorobenzoic acid (PFBA), and 1.0 mM piperazine-1, 4-bis(2-ethanesulfonic acid) (PIPES). The pH of the tracer and background solutions were both adjusted to the native

sediment pH of 8 using 1 N NaOH or KOH, and the ionic strengths of the tracer and background solutions were equivalent (Mayes et al., 2003). The tracers were detected using UV (190 nm) detection using a low-pressure liquid ion chromatography system (Dionex model DX-300 or DX-600, Sunnyvale, CA). Detection limits were approximately 0.005 mM for Br and PFBA, and 0.02 mM for PIPES (Mayes et al., 2003).

Modeling of Br curves was accomplished using CXTFIT Version 2.1 (Toride et al., 1999), which is based upon the convective-dispersive equation (CDE). The lower boundary was interpreted as representing flux-averaged concentrations (van Genuchten and Parker, 1984). The input parameters consisted of the influent pulse, the column length L , and the mean pore-water velocity v (Table 3.3). The output or fitted parameter consisted of the dispersion coefficient D ($L^2 T^{-1}$). D and v are related by the dispersivity (λ) (L) parameter by the equation $\lambda = D/v$. The dimensionless Peclet number (P_e) was equivalent to vL/D . Anisotropy of each sedimentary unit was calculated by the ratios of λ and hydraulic conductivity (K_s) in pb cores to xb cores (Table 3.3).

1.2.3. Flow Interruption Using Multiple Nonreactive Tracers

Two experimental techniques were incorporated into the miscible displacement experiments in order to relate the flow regime and associated physical nonequilibrium (PNE) with sedimentary heterogeneity. In flow interruption, tracer delivery and effluent collection were halted for several days to allow for equilibration between relatively more and less mobile flow regimes. If PNE was significant, a concentration perturbation

would be observed upon resumption of flow (Murali and Aylmore, 1980; Koch and Flühler, 1993; Reedy et al., 1996; Brusseau et al., 1997; Jardine et al., 1998; Mayes et al., 2000). In addition, diffusional separation of the multiple nonreactive tracers would be observed because of the difference in their respective free-water diffusion coefficients (Jardine et al., 1998, 1999; Langner et al., 1999; Mayes et al., 2003; Pace et al., 2003; Mortensen et al., 2004). The time period for application of this method is limited and must be near relative concentrations (C/C_0) of 1 or 0, otherwise the effects of longitudinal dispersion will predominate. Near $C/C_0 = 1$, the perturbation should be negative due to diffusion of tracer into the less mobile pore regime. Near $C/C_0 = 0$, the perturbation should be positive due to diffusion of tracer out of the less mobile pore regime and into the preferential flow regime (Brusseau et al., 1997; Koch and Flühler, 1993; Reedy et al., 1996; Jardine et al., 1998; Mayes et al., 2000).

1.3 Results and Discussion

1.3.1. Anisotropy in Homogenous versus Heterogeneous Sediments

Transport experiments in a relatively homogenous sedimentary unit (HC) and a relatively heterogeneous sedimentary unit (HI) were compared to determine the relationship between heterogeneous layering and anisotropy. The HC sediments were generally identical to HI except for prominent interbedded fine-grained layers in the latter (Fig. 3.3; Table 3.1). Multiple nonreactive tracers having different diffusion coefficients and flow interruption were applied to each unit during miscible displacement. If the HC was truly

homogenous, transport parameters and flow interruption should be similar in xb and pb cores. In contrast, the pb and xb cores in the heterogeneous HI unit should have different transport parameters and should respond differently to flow interruption. HC samples exhibited similar, symmetrically-shaped breakthrough curves (BTC) for both pb and xb cores indicating few velocity variations in the flow regime, regardless of flow direction (Fig. 3.4a). Adequate fits to Br were obtained using the CDE (Fig. 3.4a; Table 3.3). These results were consistent with my hypothesis of minimal anisotropy in the massive coarse HC sand.

A perturbation in tracer concentrations due to flow interruption (FI) was observed for both pb and xb cores, suggesting physical nonequilibrium (PNE) in the flow regime (Fig. 3.4b). There were two observations regarding the FI, 1) that the extent of perturbation was inversely proportional to the tracer diffusion coefficient, and 2) the perturbation was similar for pb and xb cores. Greater perturbations were observed for larger tracers PFBA and PIPES indicating a higher residual concentration of those tracers in the less mobile flow regime compared to Br (Fig. 3.3b). This was consistent with theoretical expectations predicting that the smallest molecule, Br, would have more effectively diffused out of the less mobile pore regime before the interruption. Therefore, perturbations were expected to be greater for the larger, slower molecules PFBA and PIPES. The amount of perturbation was similar for pb and xb cores, suggesting minimal flow and transport anisotropy in the relatively homogenous HC sediment. This appears to be consistent with my hypothesis that sedimentary heterogeneity, or lack thereof, influence directionality in the flow regime in layered sediments.

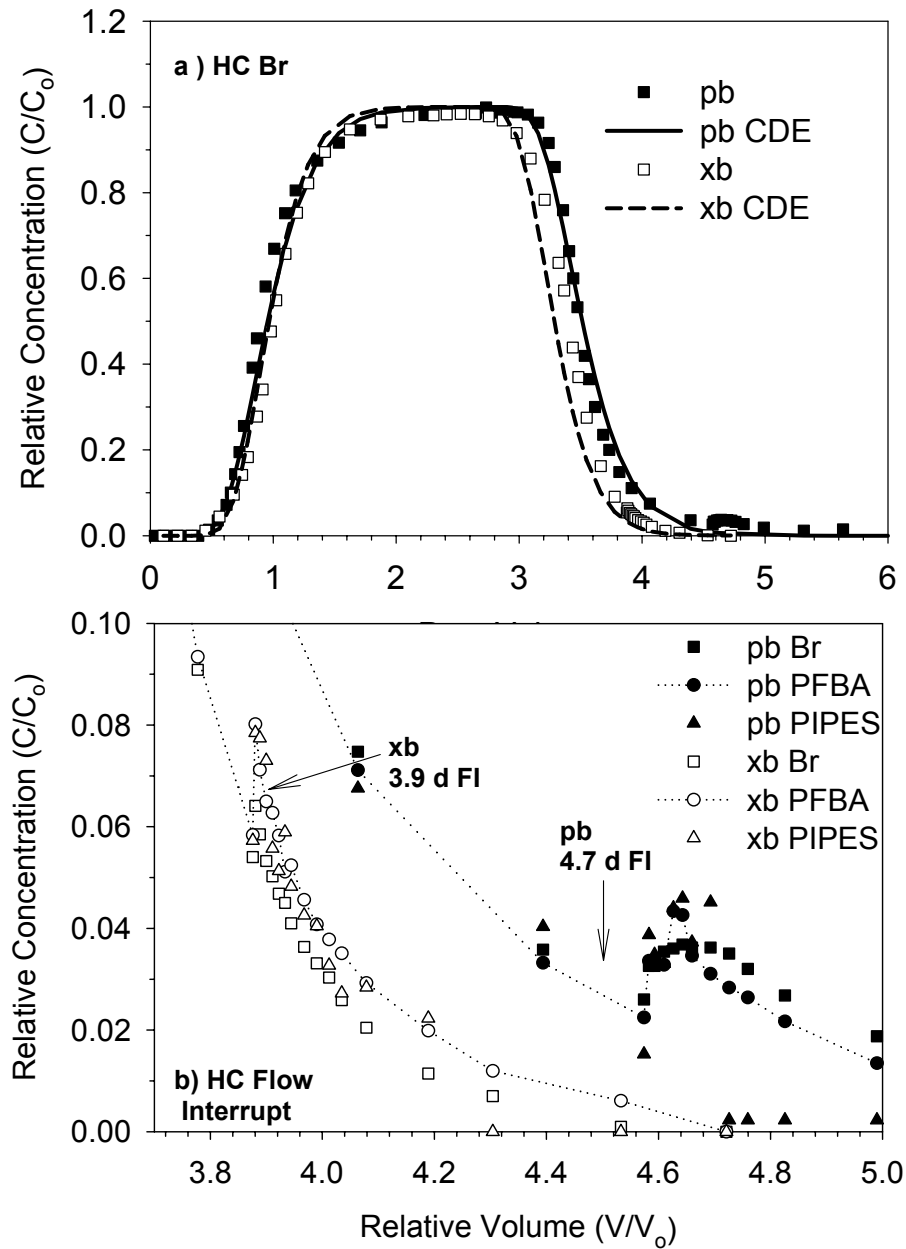


Figure 3.4 Saturated displacement experiment in the HC sediment. a) Observed Br concentrations, with black symbols for pb core and white symbols for xb core. Modeled Br concentrations using the convective-dispersive equation, with solid lines for pb core, and dashed lines for xb core. b) Flow interruption, showing Br (squares), PFBA (circles), and PIPES (triangles), with black symbols for pb core, and white symbols for xb core. A dashed line is added to the PFBA curve to improve clarity.

The more heterogeneous HI pb and xb samples exhibited similar BTCs to each other (Fig. 3.5a), and modeling resulted in similar transport parameters (Table 3.3). Both HI cores exhibited more asymmetric BTCs, greater λ , and lower K_s in comparison to HC (Fig. 3.4a; Table 3.3), which was consistent with my hypothesis. The more heterogeneous HI unit was comprised of two distinct pore regimes, coarse sand and coarse sand having a silt matrix (Fig. 3.3b; Table 3.1). The presence of two pore regimes in the HI presumably led to lower K_s and greater variations in flow velocity (i.e., greater λ) relative to the HC experiments due to relatively rapid breakthrough of tracers from the more mobile pore regime (e.g., coarse sand) and relatively slow breakthrough of tracers from the less mobile pore regimes (e.g., coarse sand with silt matrix). The more coarse-grained and homogenous HC, in contrast, had higher K_s and lower λ .

The physical appearance of the HI sedimentary bedding was heterogeneous and contained internal fine-grained layering (Fig. 3.3b; Table 3.1). The small extent of anisotropy in transport parameters λ and K_s for pb and xb cores was therefore surprising in light of media characteristics. The lack of influence of heterogeneous sedimentary bedding and general absence of anisotropy in transport parameters was inconsistent with my hypothesis.

The flow interruptions in the HI cores, however, demonstrated considerable anisotropy and generally supported my hypothesis. The FI of HI was similar to that of HC in that 1) a concentration perturbation was observed suggesting PNE, and 2) the degree of

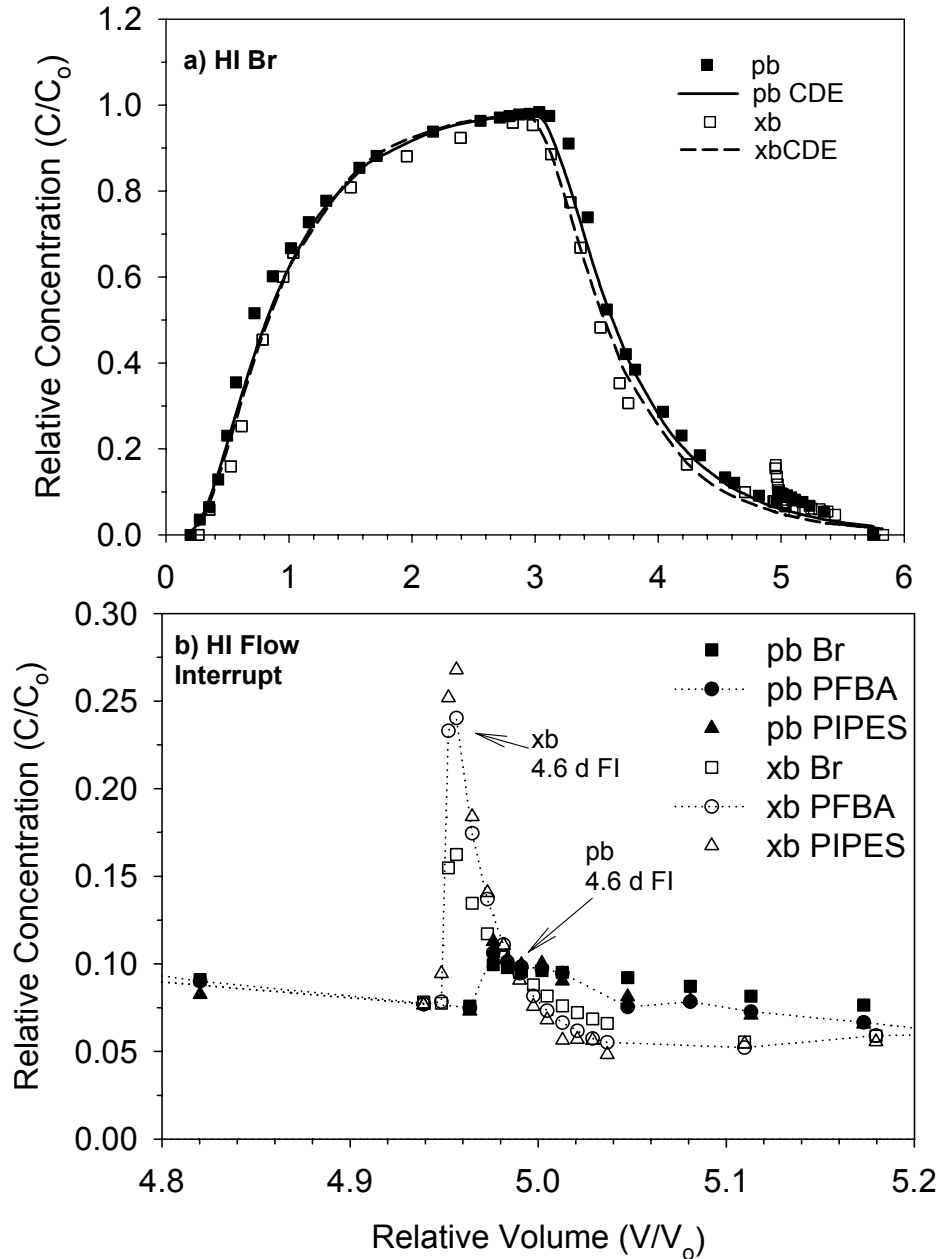


Figure 3.5 Saturated displacement experiment in the HI sediment. a) Observed Br concentrations, with black symbols for pb core and white symbols for xb core. Modeled Br concentrations using the convective-dispersive equation, with solid lines for pb core, and dashed lines for xb core. b) Flow interruption, showing Br (squares), PFBA (circles), and PIPES (triangles), with black symbols for pb core, and white symbols for xb core. A dashed line is added to the PFBA curve to improve clarity.

perturbation was inversely related to diffusion coefficients of the multiple nonreactive tracers. A distinction from the HC, however, was observed in that there was a large difference in the response of the pb versus xb cores (Fig. 3.5b). The change in PIPES concentrations in the xb core was 20% of influent concentration, PFBA was 16%, and Br was 8%. The perturbations of the three tracers were minimal in the pb core (< 5%) (Fig. 3.5b). The FI results suggested that there was considerable anisotropy in the HI unit that was not observed using simple miscible displacement. The pb core likely exhibited a minor perturbation because flow was occurring in both types of bedding (coarse sand, and coarse sand with silt matrix), albeit at different rates. This suggested that the two flow regimes were relatively close to equilibrium and that diffusional exchange was rapid in pb cores. The xb core exhibited a much greater perturbation suggesting significant nonequilibrium between relatively preferential flowpaths and relatively immobile flowpaths. Flow transverse to bedding in the xb core likely developed preferential flowpaths which generally bypassed the less conductive silty interbeds. These results were also similar to unsaturated flow in which xb cores invariably exhibited greater tracer separation than pb cores (Mayes et al., 2003; Pace et al., 2003, 2005; Pace, 2005). This theory also accounts for the greater λ of the HI versus HC units, suggesting the HI unit had multiple pore regimes producing greater velocity variations and slow approach to equilibrium between the two regimes. It also suggested that fine-grained interbeds were effectively bypassed under xb flow.

Finally, these results suggested that flow interruption was a more sensitive indicator of multiple flow regimes than the displacement of multiple nonreactive tracers. The

multiple nonreactive tracer technique worked well for consolidated, fractured sediments under saturated conditions (Reedy et al., 1996; Mayes et al., 2000, 2003). In the current study of saturated transport, however, the tracers did not appreciably separate unless flow interruption was applied (Mayes et al., 2003; Pace et al., 2003). There are at least two possible explanations for this. First, flow velocities were several orders of magnitude greater than the rate of diffusion, which might have prevented significant diffusive separation of tracers. Most of the experiments were complete within a few hours to a day, which might not have been sufficient time to measure diffusional exchange. The flow interruptions, in contrast, occurred over a period of 4-5 days. Second, the mobile and immobile flow regimes in the porous unconsolidated sediments of this study are probably much more similar to each other than mobile/immobile flow regimes in fractured consolidated sediments.

1.3.2. Relationship Between Solute Transport Parameters and Sedimentary Layering

Results from the miscible displacement of Br through all Hanford cores were plotted in Fig. 3.6, and all Ringold cores in Fig. 3.7. Values of D and K_s varied over 4 orders of magnitude for the entire dataset (Table 3.3). The variation was consistent with the particle size distribution, grain size, and sample diversity chosen for this study (Table 3.1). General appearances of BTCs were consistent with the conceptual model (Fig. 3.1), exhibiting greater asymmetry and tailing when flow was pb (Figs. 3.6, 3.7). This was also reflected in greater λ values for pb cores, which were significantly larger than xb

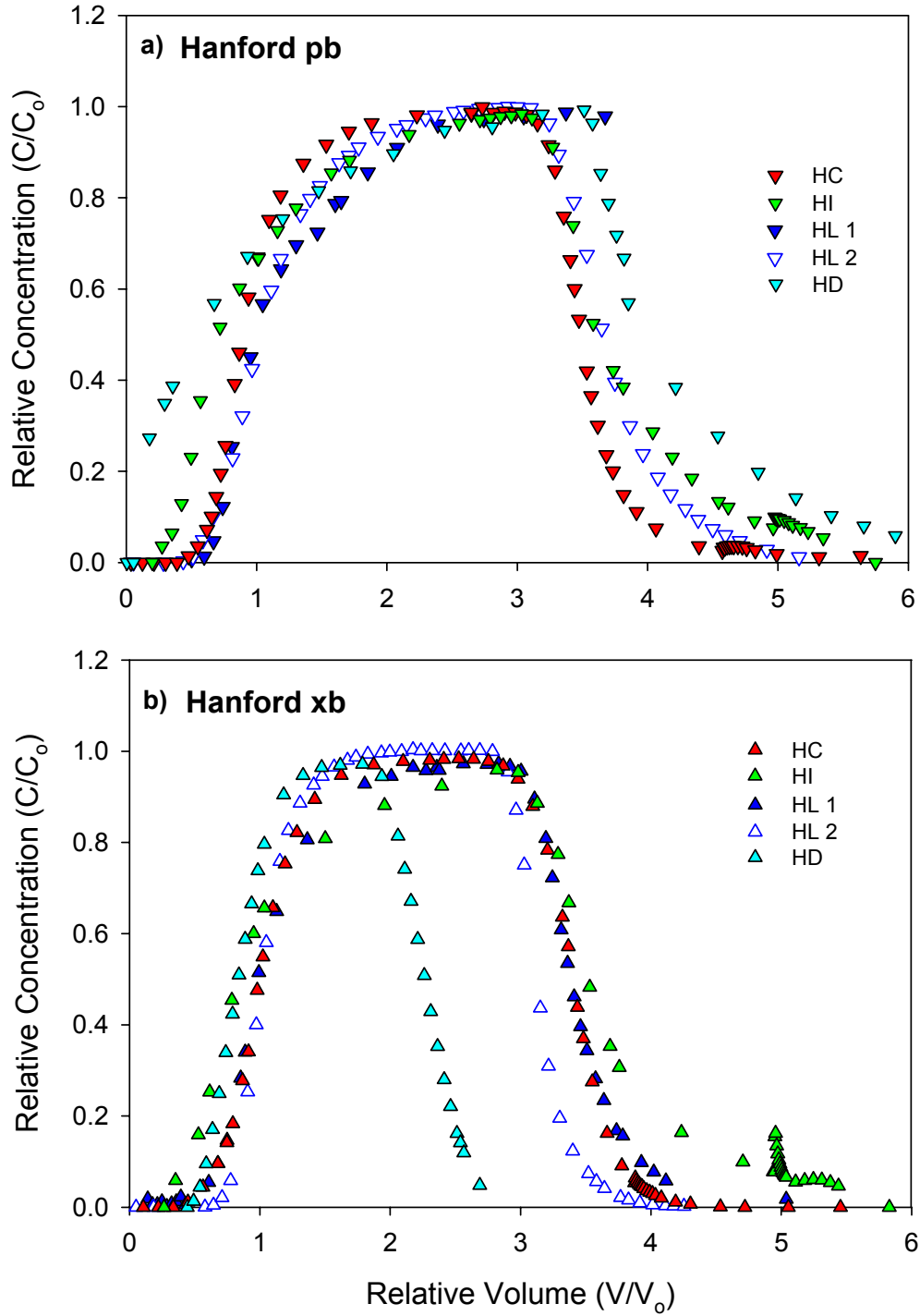


Figure 3.6 Compilation of saturated displacement experiments in Hanford cores. a) Flow bedding parallel (pb) cores. b) Flow crosses bedding (xb) cores.

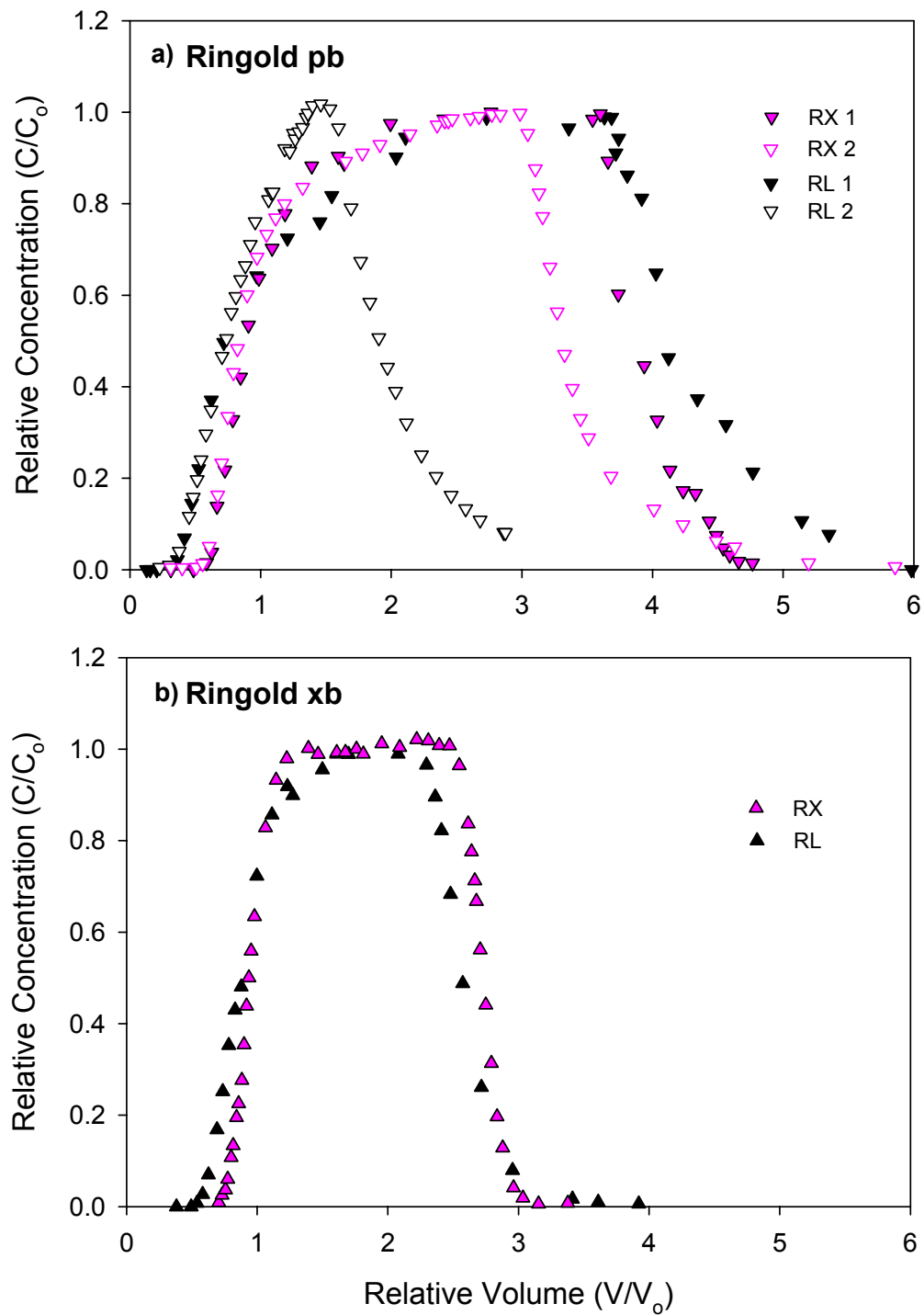


Figure 3.7 Compilation of saturated displacement experiments in Ringold cores. a) Flow bedding parallel (pb) cores. b) Flow crosses bedding (xb) cores.

values, with the exception of HI as discussed above (Table 3.3). This was evidence that our results provided evidence of physical processes, i.e., relation between flow direction and sedimentary properties, rather than of gross heterogeneity between xb and pb samples. Anisotropy of flow velocities was calculated using the equation $K_{s(pb)} / K_{s(xb)}$, and anisotropy of solute transport was calculated using the equation $\lambda_{(pb)} / \lambda_{(xb)}$ (Table 3.3). Anisotropies > 1 indicated preference for bedding-parallel flow. The anisotropy of K_s was > 1 for all samples except HC, suggesting a slight preference for flow pb. Similarly, the anisotropy of λ exceeded unity for all samples. The two anisotropy calculations did not result in an identical relationship between the sedimentary units, suggesting that flow and solute dispersion were not fully coupled. Any other meaning from comparing these two calculations was not readily apparent.

Anisotropy values of 1.5 were typical for many saturated sediments and were thought to increase to 40 or greater under unsaturated conditions (Mualem, 1984; McCord et al., 1991; Glass et al., 2003; Pruess, 2004). The anisotropy of saturated Hanford sediments can be up to 10 and may increase by an order of magnitude under unsaturated conditions (Khaleel et al., 2000). It is uncertain why the anisotropy values shown here are generally much lower, although scale of experiments, experimental technique, and error in measurements are all viable explanations. More measurements on duplicate samples would certainly improve the precision of K_s , λ and calculated anisotropy values. Regardless, the general consistency of our results provides support for our approach of

sampling from multiple sedimentary units and examining the entire dataset for overall trends.

Bedding-parallel (pb) cores were expected to reflect variations in pore-water velocities and presumably, solute dispersion. The relationship between v and D was plotted for all pb cores (Fig. 3.8a) and all xb cores (Fig. 3.8b). The relationship was generally linear for the pb samples, resulting in a P value of 0.002 (where $P < 0.05$ is significant) (Fig. 3.8a). In contrast, the relationship between v and D for the xb cores appeared to be bi-modal (Fig. 3.8b). An apparent linear relationship was rejected because the HC sample accounted for 98% of the variance in the regression (Fig. 3.8b). We tested the relationship of the remaining sediments and again found the relationship was not significant ($r^2 = 0.35$) (Fig. 3.8b). This suggested a difference in the $v - D$ relationship (λ) in pb versus xb cores. The relationship appeared to exist only for flow parallel to bedding, and was very close to a λ value of one for the entire dataset.

These observations were physically related to the sedimentary texture and structure of the samples. The bimodality of xb cores resulted from two theoretical populations of sedimentary facies (Fig. 3.8b). The HC core represented one which is mostly devoid of internal fine-grained interbeds. This was observed visually (Fig. 3.3a), in symmetrically-shaped BTCs (Fig. 3.4), in minimal response to FI for both pb and xb cores (Fig. 3.4b), and in anisotropy values < 1 (Table 3.3). The remainder of the samples, in contrast, were either fine-grained and/or had significant internal fine-grained interbeds (Fig. 3.3; Table

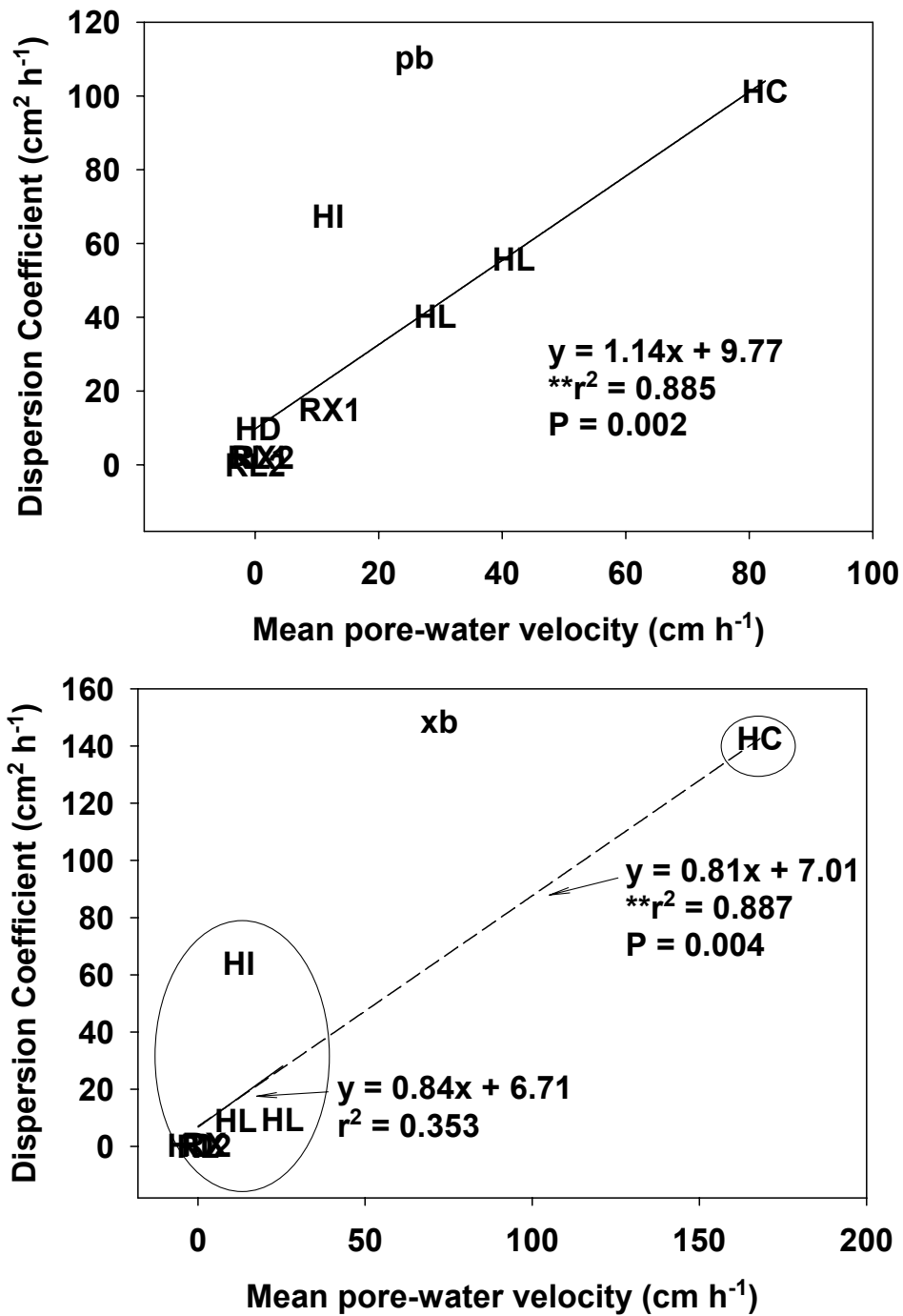


Figure 3.8 Plots of average pore-water velocity (v) versus dispersion coefficient (D). a) Flow bedding parallel (pb) cores, and b) Flow cross bedding (xb) cores. The slope of the lines represent the average dispersivity (λ) (cm) for all cores of a particular orientation. $P < 0.05$ implies the relationship was significant.

3.1). This suggested that internal fine-grained beds may have restricted the dispersion of solutes in the vertical direction only in heterogeneous sediments. Microscopic factors such as the shape and horizontal orientation of clay-sized minerals and the overall horizontal orientation of macroscopic bedding features could have promoted these conditions. These observations were consistent with my hypothesis suggesting that internal heterogeneous layering caused anisotropy in the flow regime.

Mathematically, the relationship in Fig. 3.8a could represent an artifact of scaling effects in the $v - D$ relationship. The CDE assumes that dispersion can be represented by an expression analogous to Fick's second law of diffusion. This assumption states that velocity variations will decrease asymptotically as the characteristic mixing length, the so-called Taylor limit, is approached (Anderson, 1984). Until then, velocity variations have not adequately sampled the entire flow field, and the resultant dispersion coefficient changes with spatial and/or temporal scales (Gelhar et al., 1992). As pointed out by Khaleel et al. (2002), the key to reaching the Taylor limit was adequate mixing, which occurred readily in xb cores, where the dampening effect of interbedded fines ensured that interaction between preferential and non-preferential flow regimes occurred. In pb cores, however, flow may be isolated to distinct sedimentary layers parallel to the direction of flow, thus preventing adequate mixing and meeting the Fickian assumption.

Matheron and de Marsily (1980) concluded that the Fickian regime (or Taylor limit) will not be reached when the velocity field is strictly parallel to layering, as in these experiments. They have also pointed out that the Fickian regime may never be reached

under certain conditions, and further were doubtful of the length and time scales of most field-scale experiments (e.g., Gelhar et al., 1992). Matheron and de Marsily (1980) and Gelhar et al. (1979) have each modified the CDE to accommodate the pre-Fickian regime, while Padilla et al. (1999) and Khaleel et al. (2002) have suggested that the mobile-immobile model (MIM) might be appropriate. The MIM, however, consistently defaulted to the CDE for these saturated experiments (Pace et al., 2003; Mayes et al., 2003). Further, the linear relationship in Fig. 3.8a can be predicted using a hypothetical range of pore-water velocities and dispersivity equal to unity. This suggested that the observed proportionality was consistent with the governing equations of the CDE, implying that the CDE was correctly applied in this study. The absence of a relationship in Fig. 3.8b, however, was surprising and suggested that solute dispersion might have been limited due to flow across bedding. This may suggest a physical reality of xb cores (interbedded fines) and/or the need for additional experiments to define a relationship, if it exists. While it should not be assumed that the values of D and v in Fig. 3.8 will be constant for larger spatial scales (Gelhar et al., 1992), the λ relationship (or apparent lack thereof) might be generally applicable for pb and/or xb flow directions. This question should be resolved with additional experiments over larger spatial and longer temporal scales. In addition, changes in the relationship as a function of saturation should be investigated.

Because D and v were expected to be linearly related based upon the formulation of the CDE, the relationships, or lack thereof, shown in Fig. 3.8 were not conclusive. Three additional methods were tested to compare flow and transport parameters in xb versus pb

cores. The λ and Peclet numbers (P_e) were compared in pb versus xb cores (Fig. 3.9a,b), and the anisotropy of K_s was compared with the anisotropy of λ (Fig. 3.9c). For all 3 comparisons, a slope of 1 would signify isotropic conditions, a slope > 1 would signify preference for pb, and a slope of < 1 would signify preference for xb. Most of the results were generally similar to those suggested by Fig. 3.8, but overall the evidence was not very conclusive. The dispersivity method (Fig. 3.9a) might have suggested a preference for xb flow (slope = 0.78). The relationship was not robust, however, because the outlier HD sample was excluded from the regression, and the remaining data tended to cluster around 1. The Peclet number method (Fig. 3.9b) yielded a slope of 2.18 and an r^2 of 0.82, suggesting a preference for solute dispersion parallel to bedding. The data exhibited sufficient scatter and no outliers, suggesting the regression was generally valid. The anisotropy ratios (Fig. 3.9c) exhibited a slope of 1.78 and r^2 of 0.95, which might have suggested a preference for pb flow. However the HD data was an outlier and the distribution of the remainder of the samples was somewhat bi-modal. Of four total treatments of the data, three treatments were generally supportive of a slight preference for flow parallel to bedding and a slight restriction during flow across bedding. The remaining one treatment was inconclusive. The lack of total agreement between the treatments and the small number of datapoints, however, suggested that these conclusions were tentative.

To determine if the observed dispersivities were reasonable, they were compared with published values. Gelhar (1986) and Gelhar et al. (1992) compiled dispersivity values from the literature and generated an empirical relationship with the scale of observation,

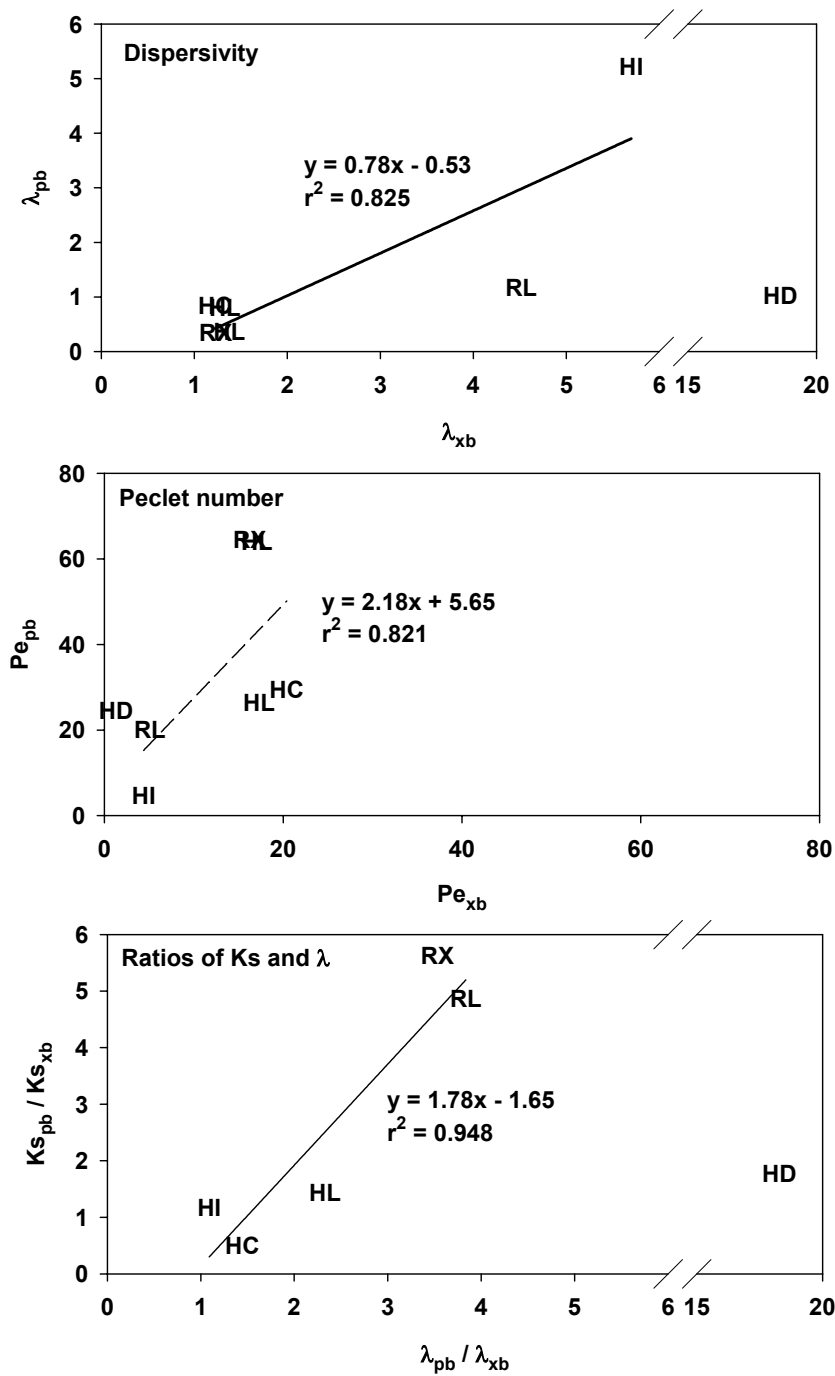


Figure 3.9 Comparison of pb and xb parameters. a) Dispersivity (λ), b) Peclet number (Pe), and c) Ratio of hydraulic conductivity (Ks_{pb}/Ks_{xb}) versus ratio of dispersivity ($\lambda_{pb}/\lambda_{xb}$). Note HD was not included in regressions in (a) and (c).

where dispersivity was equivalent to 0.1 times the scale of observation. Figure 3.10 compares the Gelhar (1986) relationship with the pb and xb core data of this study. The data from the current study vary over 2 orders of magnitude and fall above the line to varying degrees, which suggested that the dispersivities were somewhat higher than would be expected. The pb and xb data overlapped, but the pb data were noticeably more removed from the line than the xb data. This analysis suggested that our data was generally reasonable, and further suggested that pb dispersivities were somewhat greater than xb dispersivities. These results were consistent with my previous interpretations of somewhat greater dispersion parallel to bedding, and somewhat less dispersion perpendicular to bedding.

1.4 Conclusions

The results of this investigation suggested the influences of heterogeneous sedimentary facies upon saturated hydrology of intact layered sediments were pervasive. Slightly greater velocity variations and solute dispersivity were observed when flow was parallel to sedimentary bedding. Velocity variations and solute dispersivity appeared to be somewhat dampened in xb cores, based upon symmetrical BTCs and lower values of K_s and λ , which was most likely due to the presence of interbedded fine layers. These results suggested that internal heterogeneous layers influenced solute transport and the anisotropy of transport parameters. The anisotropy of the samples utilized in this study, however, was quite low, ranging from 1-5, which was not consistent with other studies using Hanford sediments. Flow interruption demonstrated that interbedded fines were the

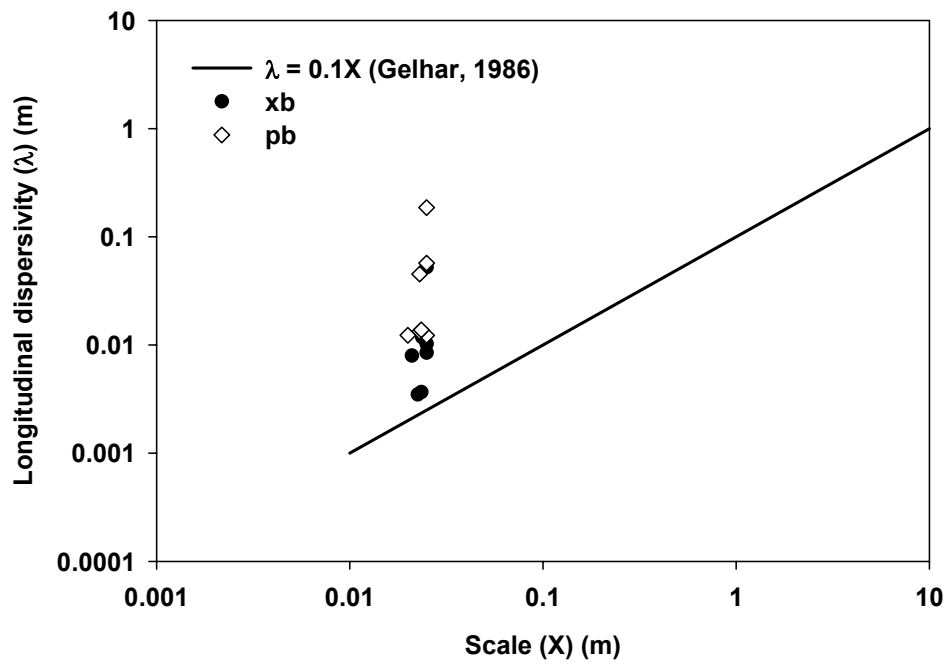


Figure 3.10 Longitudinal dispersivity as a function of length scale. Flow bedding parallel cores (pb) and flow crosses bedding cores (xb) are compared with the empirical relationship from Gelhar (1986).

most likely source of relatively immobile water in layered sediments. Flow interruption appeared to discern multiple flow regimes better than the transport of multiple nonreactive tracers. Our experimental results are generally consistent with observed, laterally-oriented subsurface contaminant distributions at several western semi-arid sites in the US.

1.5 Acknowledgements

We would like to acknowledge Frederick M. Mann and Frank J. Anderson of the Tank Farm Vadose Zone Group and CH2M Hill Hanford Group, Inc. for providing support for analyzing samples from the IDF under contract with the US DOE. We also acknowledge Environmental Management Science Program (EMSP) and program managers Roland Hirsh and Mark Gilbertson, for providing support for the ERDF and White Bluffs samples. EMSP is administered by the US DOE, Office of Science, Biological and Environmental Research Programs. We gratefully acknowledge the fellowship provided for MAM's Ph.D. by the Waste Management Research and Education Institute (WMREI) at the University of Tennessee. We would like to thank Steve Reidel, John Piatt, and R. Jeffrey Serne of Pacific Northwest National Laboratory (PNNL) for their assistance with the IDF coring process, and John Piatt and Bruce N. Bjornstad (PNNL) for ERDF and White Bluffs coring trips. We also gratefully acknowledge the efforts and accommodations made by the respective staffs of the IDF and ERDF during core

collection trips. Oak Ridge National Laboratory is managed by the University of Tennessee-Battelle, LLC, under contract DE-AC05-00OR22725 with the US DOE.

Chapter 4. Solute Transport in Partially-Saturated, Layered Fine Sediments

1.0 Abstract

Sedimentary heterogeneities may influence unsaturated flow in layered, partially-saturated porous media by causing several “preferential” hydraulic processes, e.g., finger flow, funnel flow, or anisotropic lateral flow. The goal of this study was to reconcile these general conceptual models of preferential flow with observed solute transport in intact samples of cross-bedded sandy, loamy sediments (0.25 m x 0.25 m). Samples were taken in flow bedding-parallel (pb) and flow cross-bedding (xb) orientations.

Nonreactive tracers Br and PIPES were applied under transient and steady-state unsaturated water contents. Comparison with saturated flow experiments suggested that preferential flow consistently occurred under unsaturated conditions, and became more pronounced at lower water contents. This was related to perching in natural sedimentary layering and concomitant increase in volumetric water content in the cores. A “reversed” order of nonreactive tracer elution indicated that the formation of perched water zones created a reservoir from which the nonreactive tracers diffused. The reversed tracer separation may be an indicator of a flow regime that becomes restricted when crossing sedimentary beds of limited hydraulic conductivity. The general conceptual models of unsaturated flow in porous media provided limited insight into the multiple and complex mechanisms of solute transport in natural, fine-grained layered sediments.

1.1 Introduction

In natural media, the distribution of pore sizes is not random but is generally influenced by geologic heterogeneities such as sedimentological variations in grain size or mineralogy, the presence of bedding planes, fractures associated with structural deformation, and/or the influence of weathering processes. Such physical heterogeneities disproportionately influence the hydrologic transport of contaminants or other solutes of interest in the subsurface by isolating the flow regime to certain preferential pathways while restricting it from others. The location and significance of heterogeneous features may not be readily observable or predictable over appropriate spatial or temporal scales. Consequently, heterogeneity and associated flow patterns typically increase the level of uncertainty for predictions of subsurface solute mobility.

1.1.1. Conceptual Models of Unsaturated Preferential Transport

Preferential flow in unconsolidated, unsaturated media is currently characterized using at least three different general conceptual models, finger flow, funnel flow, and anisotropic lateral flow. Finger flow occurs as isolated “fingers” rapidly moving in response to gravity through initially dry, unconsolidated media (Hill and Parlange, 1972; Glass et al., 1988, 1989; DiCarlo et al., 1999; Sililo and Tellam, 2000; Wang et al., 1998, 2003). Field observations of unstable finger flow are typically associated with water repellent media or layering (Ritsema et al., 1993, 1998; Wang et al., 2003), but many investigations have been conducted in the laboratory using dry repacked sediments.

Several criteria have been used to predict likelihood of the occurrence of finger flow, such as slow infiltration, air compression, texture, and fine over coarse layering (Wang et al., 1998).

Funnel flow is a special case of finger flow in which lens-shaped features in heterogeneous media act to laterally divert infiltrating solutions, resulting in isolated fingers or flowpaths that can travel to greater depths (Kung, 1990a,b; Walter et al., 2000; Heilig et al., 2003). The lens-shaped features need only be of limited spatial extent and of sufficiently different hydraulic conductivity from the surrounding media to induce funnel flow. This mechanism tends to divert flow through or around the heterogeneous feature, resulting in a funneling or focusing of the flow pathways towards the edge. Fine-grained lenses embedded within coarse sediments may either attract flow into the lens or divert flow to the edge of the lens, depending on the antecedent moisture conditions. Similarly, coarse lenses embedded in fine materials may either attract flow into or divert flow around the lens. Regardless, a funnel-shaped preferential pathway might be formed in any of these scenarios.

Anisotropic lateral flow is a consequence of variations in the water content and unsaturated hydraulic conductivities of heterogeneous layered sediments. Coarse-grained layers become less conductive at low water contents, becoming partial or complete capillary (air) barriers. Barriers tend to prevent stable infiltration and promote lateral migration within surrounding sedimentary beds (Matheron and de Marsily, 1980; Mualem, 1984; Yeh et al., 1985a,b; Khaleel et al., 2002). Under some instances, the

importance of anisotropic flow has been shown to increase with decreasing water content (Padilla et al., 1999), particularly when flow is parallel to bedding (Khaleel et al., 2002; Pace et al., 2003, 2005; Pace, 2005). The process has also been implicated in small-scale miscible displacement experiments in which increasingly anisotropic breakthrough curves were observed with decreasing water contents (Padilla et al., 1999). The phenomenon is often marked by observed scale dependence of transport parameters as enhanced dispersion is typically associated with increasing scales of observation (Yeh et al., 1985a,b; Gelhar et al., 1992).

1.1.2. Conceptual Models of Flow in Layered Sediments

Our previous work concluded that finger flow influenced the hydrology of fine-grained, layered, intact sediments (Mayes et al., 2003). Large core samples of horizontally-bedded lacustrine silts (RL) and cross-bedded sandy loams (RX) were taken in both directions, one in which flow was parallel to bedding (pb) and the other in which flow crossed bedding (xb) (Mayes et al., 2003). Miscible displacement experiments using multiple nonreactive tracers (Br, PFBA, and PIPES) were conducted under saturated and unsaturated conditions. A generalized conceptual model for observed flow and solute transport under partially-saturated conditions is shown in Fig. 4.1. Figure 2.1 shows the conceptual model for flow under saturated conditions. In partially-saturated RL xb cores and in RX samples, water content increased, tracers became separated, and media bypass occurred. This was attributed to perching and unstable finger generation associated with

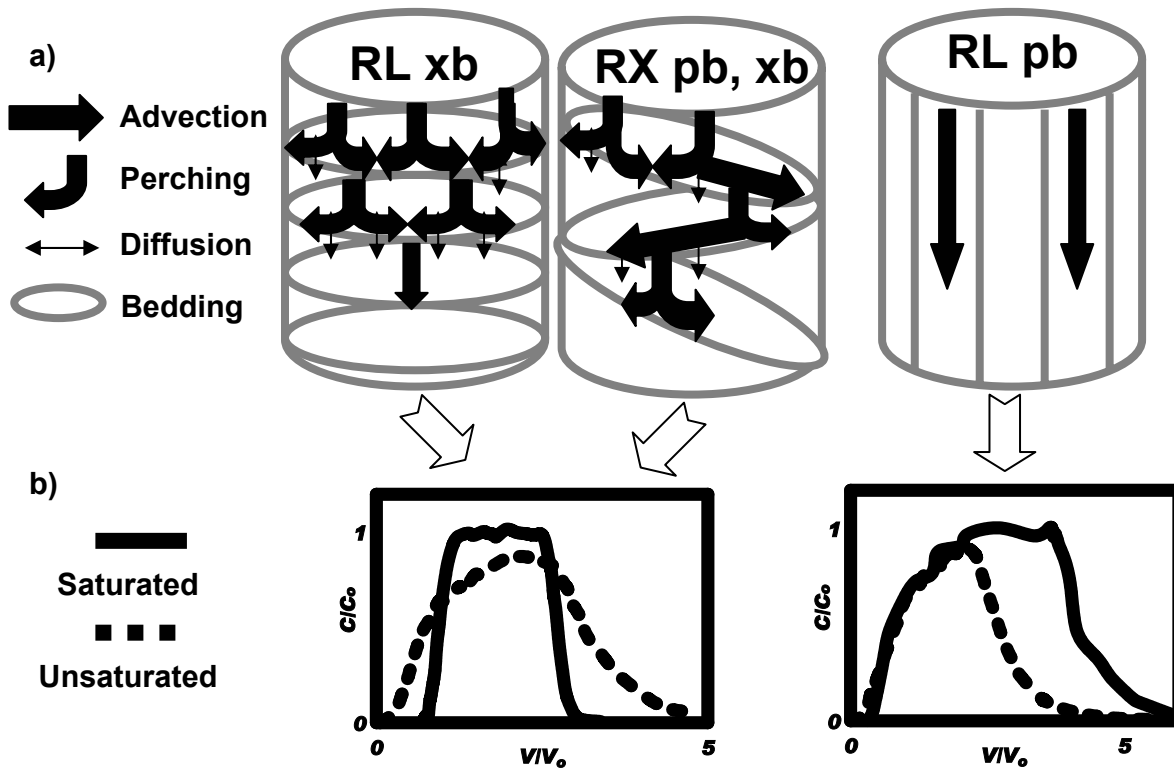


Figure 4.1 Conceptual model of flow and transport in lacustrine silts (RL) and cross-bedded sandy loam (RX). Partially-saturated conditions in pb (flow parallel to bedding) and xb (flow crosses bedding) cores are shown in the block diagrams (see Fig. 2.1 for saturated conditions). The model is based on the results of Mayes et al. (2003). a) Block diagrams represent partially-saturated sediment cores showing conceptualized flow patterns (advection, perching, and diffusion) with respect to orientation of sedimentary bedding. b) Graphs represent generalized data for saturated (solid lines) and unsaturated (dashed lines) flow in terms of relative concentration (C/C_0) and relative volume (V/V_0).

flow crossing sediments of different conductivities (Fig. 4.1a) (Mayes et al., 2003).

Partially-saturated RL pb cores, in contrast, maintained steady-state water content, had no tracer separation, and exhibited minimal evidence of media bypass. These observations were attributed to formation of capillary barriers in select sedimentary bedding which promoted bedding-parallel transport rather than preferential transport (Fig. 4.1a) (Mayes et al., 2003; Pace et al., 2003, 2005; Pace, 2005).

The RL pb results were not suggestive of preferential flow because similar breakthrough curves (BTC) were obtained for saturated and unsaturated conditions (Fig. 4.1b). This suggested that the proportion of hydraulically-active media was similar regardless of water content (Mayes et al., 2003). The RX (pb and xb) and RL xb results, in contrast, were suggestive of preferential flow because unsaturated BTCs exhibited the classical asymmetric shape indicative of media bypass associated with multiple flow regimes (Fig. 4.1b) (Seyfried and Rao, 1987; Jardine et al., 1988, 1993a,b; Gamerdinger and Kaplan, 2000; Gamerdinger et al., 2001a,b). Preferential flow only occurred when flow crossed bedding (Fig. 4.1a), and it was associated with observation of increasing water content, i.e., transient flow conditions.

Though the experiments met many of the criteria used to predict the occurrence of finger flow, it is generally not predicted at higher water contents (50 – 90%) such as in these experiments (Bauters et al., 2000). Mayes et al. (2003) suggested that adjacent sedimentary beds might have significant differences in unsaturated hydraulic conductivities that could result in fingering into the sub-layers and the observed

preferential flow (Fig. 4.1). Wang et al. (1998) suggested that finger width grows by capillarity in fine-grained sediments, resulting in rapid equilibration between wetted and non-wetted sediments and an absence of gravity-driven fingers (DiCarlo et al., 1999). Capillary theory predicts a pause in the wetting front at the interface between layered fine-over-coarse sediments, resulting in infiltration into the sub-layer only after saturation of the entire fine top-layer (Hillel and Baker, 1988). This was consistent with observed perching in RL and RX sediments, but inconsistent with observed preferential flow. We hypothesize that finger flow might not explain preferential transport associated with perching in natural, partially-saturated sedimentary beds, but that some combination of general conceptual models of unsaturated flow will explain the observations in Fig. 4.1.

1.1.3. Goals and Objectives

The goal of this study was to test the validity of the conceptual model in Fig. 4.1 which predicts that preferential flow was associated with perching and crossing sedimentary bedding under partially-saturated conditions. The cross-bedded RX unit, in which flow crossed sedimentary beds in both vertical and horizontal cores, was used. The first objective was to validate the relationship between preferential flow and water content by performing additional experiments under various water contents. The second objective was to determine the mechanism(s) of perching and preferential flow in fine-grained natural sediments.

1.2 Materials and Methods

1.2.1. Miscible Displacement Experiments

The cross-bedded and rippled fine sandy loam, RX, was more affected by preferential flow than the lacustrine silt RL in previous experimental studies (Mayes et al., 2003). RX was therefore targeted for five miscible displacement experiments using one xb and two pb (pb1, pb2) cores (Table 4.1). Experiments were performed near saturation and at significantly unsaturated conditions. Because low water contents were associated with increasing water content (Mayes et al., 2003), the latter experiments were performed under transient moisture conditions. Steady-state (S) and transient (T) conditions were compared in the following experiments, pb1T and pb2T versus pbS, and xbT versus xbS. The presence of multiple pore regimes was tested using multiple nonreactive tracers and by applying the equilibrium convective-dispersive equation and the mobile-immobile model.

The RX cores were collected from the White Bluffs area of the Department of Energy's Hanford Reservation, noting that RX was referred to as "LS/S" in Mayes et al. (2003). Particle size distribution was 57% sand, 42% silt, and 1% clay. BTCs from saturated flow in pb1 (pb1SAT), pb2 (pb2SAT) and xb (xbSAT) are included for reference (Mayes et al., 2003; Chapter 3). The initial portion of the xbT experiment (0-1.2 pore volumes) was presented and the initial portion of the pb1T experiment was discussed in Mayes et al. (2003, 2005). The remaining experiments were new. For all experiments, water content was measured gravimetrically, and matric potential was measured by

Table 4.1 Description of experiments.

¹ Core	² Exp	Water content	Pulse (d)	Experiment (d)
pb1	pb1S	Steady-state	9.13	59
	pb1T	Transient	210	763
pb2	pb2T	Transient	17.2	153
xb	xbS	Steady-state	13.7	83
	³ xbT	Transient	376	691

¹pb = flow bedding parallel; xb = flow bedding perpendicular; 1,2 = duplicate cores

²T = transient water content, S = steady-state water content

³ Mayes et al., 2003

tensiometers (Mayes et al., 2003; Pace et al., 2003). Experimental and physical parameters are presented in Table 4.2.

The experiments were conducted at the natural sediment pH of 8, and the bulk ionic strength of all solutions was balanced at 0.1 M or 0.01 M using NaCl or CaCl₂. Applying different ionic strengths did not appear to influence the transport of applied tracers. A background solution of 0.1M NaCl or 0.005 M CaCl₂ was used to saturate the cores from the lower boundary. After saturation, cores were flushed. The cores were subsequently de-saturated by applying tension through a vacuum chamber at the lower boundary (Mayes et al., 2003). The background solution was applied to the cores and was allowed to reach steady-state conditions only in “S” experiments (Table 4.1). A pulse of tracer solution containing multiple nonreactive tracers Br, PFBA (pentafluorobenzoic acid), and PIPES (piperazine-1, 4-bis(2-ethanesulfonic acid)) was applied to the cores (Mayes et al., 2003) (Table 2). After the tracer pulse, the background solution was re-supplied to the core to facilitate elution of the tracers. The mass and volume recoveries of the applied tracers are in Table 4.3.

In the long-term pb1T and xbT experiments, volume recovery was incomplete (Table 4.3), most likely due to evaporation from the partially-open upper boundary. This resulted in eluted tracer concentrations exceeding influent tracer concentrations by up to 20% in the pb1T experiment. The volume of eluted solution was also reduced compared to the volume of applied solution, which gave the appearance of tracer elution at an earlier point on the relative volume axis (x-axis of BTCs). The mass balances of the

Table 4.2 Physical parameters of cores and experiments.

Exp	r <i>cm</i>	L <i>cm</i>	θ_{avg} $\text{cm}^3 \text{cm}^{-3}$	θ_{range} $\text{cm}^3 \text{cm}^{-3}$	v cm h^{-1}	Pulse <i>L</i>
pb1T	9.75	20.0	0.51	0.29-0.56	0.0061	6.20
xbT	12.5	22.5	0.48	0.42-0.48	0.0075	13.6
pb2T	9.20	21.0	0.53	0.27-0.56	0.0223	1.40
pb1S	9.75	20.0	0.51	0.51-0.51	0.0447	1.52
xbS	12.5	22.5	0.48	0.48-0.48	0.0353	2.73

r = radius, L = length, θ = water content, v = mean pore-water velocity

Table 4.3 Mass recoveries of applied tracers.

Exp	¹ Volume Recovery	² Br	² PIPES
pb1T	72.4	91.1	88.0
xbT	85.3	84.5	84.9
pb2T	99.0	102	99.1
pb1S	104	96	89.6
xbS	98.4	92	87.2

¹ % L L⁻¹

² % mol mol⁻¹

tracers (Table 4.3) were not influenced by these processes. Evaporation from effluent tubes and influent solutions was measured and could not account for the observed solution loss, suggesting evaporation from the core was the primary cause of the incomplete volume recoveries in Table 4.3. Because the tracer concentrations and the volume of column effluent exhibited strong artifacts of evaporation, the BTCs were affected and could not be directly compared with experiments having complete recoveries and no such artifacts. Therefore, the tracer concentrations and the effluent volumes were subjected to a correction factor based upon the mass recovery in Table 4.3. The BTCs of the pb1T and xbT experiments shown in this study have been corrected for evaporation.

1.2.2. Transport Modeling

The two steady-state experiments (pb1S) and (xbS) cores were modeled using CXTFIT (Toride et al., 1999). The three transient flow experiments were not modeled because a single deterministic solution was inappropriate. The 1-region convective-dispersive model (CDE) and the 2-region mobile-immobile model (MIM) were applied to determine if observed solute transport could be quantified in terms of one or two flow regimes. Separation of tracers indicated the presence of multiple pore regimes, suggesting the use of the MIM. The retardation factor (R) of the nonreactive tracers was always assumed to be 1. Three parameters were fitted with the MIM, dispersivity λ (L), the fraction of mobile water F , and the rate of mass transfer between the mobile and immobile pore regimes, α (T^{-1}). Only λ was fitted for the CDE.

Input parameters consisted of column length (L), the input pulse (L^3), relative tracer concentration (C/C_o), relative effluent volume (V/V_o), and the pore-water velocity v ($L T^{-1}$) (Tables 4.1, 4.2). Pore-water velocity was derived from the equation $v = J_w \theta$, where J_w is the volumetric water flux density ($L T^{-1}$) and θ is the volumetric water content ($L^3 L^{-3}$) (Toride et al., 1999). More detailed discussion specific to these types of experiments is available in Mayes et al. (2003).

1.3 Results and Discussion

1.3.1. *Miscible Displacement Experiments*

Experiments performed in the xb core exhibited key features predicted by the conceptual model (Fig. 4.1), including preferential flow as suggested by greater BTC asymmetry in comparison to saturated flow (Fig. 4.2a) and multiple flow regimes as evidenced by tracer separation (Fig. 4.2b). Media bypass was greater in the xbT versus xbS experiments, confirming its relationship with lower water contents and transient conditions (Fig. 4.2). It was surprising to observe bypass in the xbS experiment because the core was nearly saturated. Therefore, the degree of preferential flow in the RX was related to unsaturated conditions. This is generally consistent with steady-state experiments in disturbed sediments which exhibited enhanced media bypass under conditions of progressive desaturation (Padilla et al., 1999; Gamerding and Kaplan, 2000; Gamerding et al., 2001a,b; Khaleel et al., 2002). In addition, tracer separation

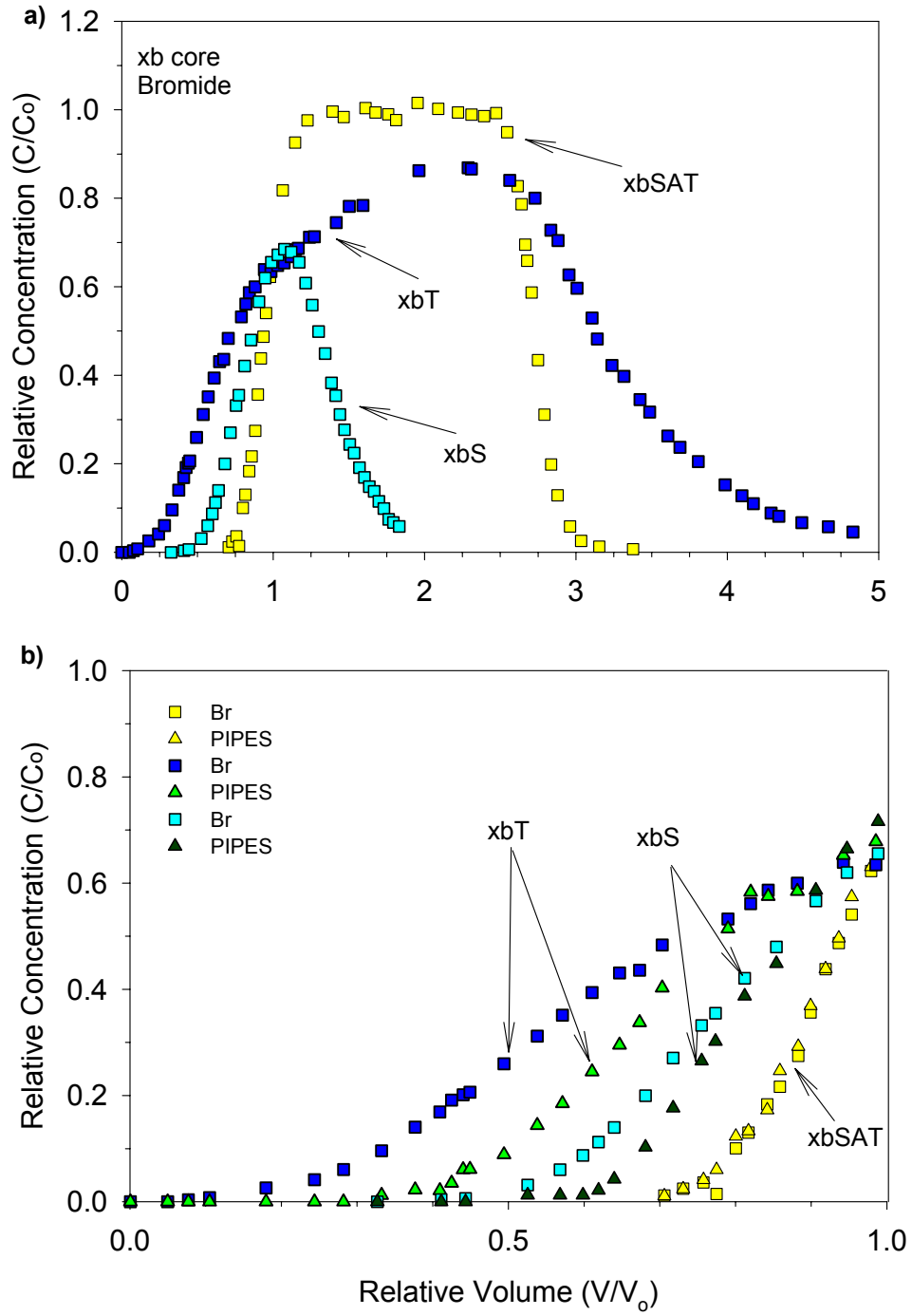


Figure 4.2 Observed relative tracer effluent concentrations involving the displacement of Br (squares) and PIPES (triangles) through the xb core. a) Br for experiments xbSAT, xbS, and xbT. b) Br and PIPES for 0 – 1 relative volume range for same experiments as in (a).

was greater in the xbT versus xbS experiments, suggesting a relation with either water content or transient conditions (Fig. 4.2a,b). The order of tracer separation was reversed from that typically observed in fractured and in sandy media containing multiple flow regimes (Jardine et al., 1998, 1999; Langner et al., 1999; Mayes et al., 2003; Pace et al., 2003, 2005; Pace, 2005; Mortensen et al., 2004). Three unsaturated experiments in pb cores 1 and 2 were generally similar to the xb results. Saturated experiments pb1SAT (Mayes et al., 2003) and pb2SAT (Chapter 3), two unsaturated transient experiments pb1T and pb2T, and a steady-state experiment pb1S are shown in Fig. 4.3. Fig. 4.3a shows that the Br BTCs of the two saturated experiments pb1SAT and pb2SAT were nearly identical, suggesting that the cores were adequate duplicates. The transient unsaturated experiments in the same cores, pb1T and pb2T, were also nearly identical. This is probably because the initial water contents of the experiments were similar (Table 4.2). As in the xb experiments, a pattern of increasing BTC asymmetry with decreasing water content was suggestive of enhanced preferential flow under drier conditions (Fig. 4.3a). “Reversed” tracer separation was observed only in the unsaturated experiments, again suggesting the presence of multiple flow regimes or other processes specific to unsaturated conditions in fine-grained sediments (Fig. 4.3b).

1.3.2. Transient Conditions and Preferential Flow

The relationship between transient water content and media bypass is the most important characteristic of flow in the RX. Increasing moisture content during the experiments

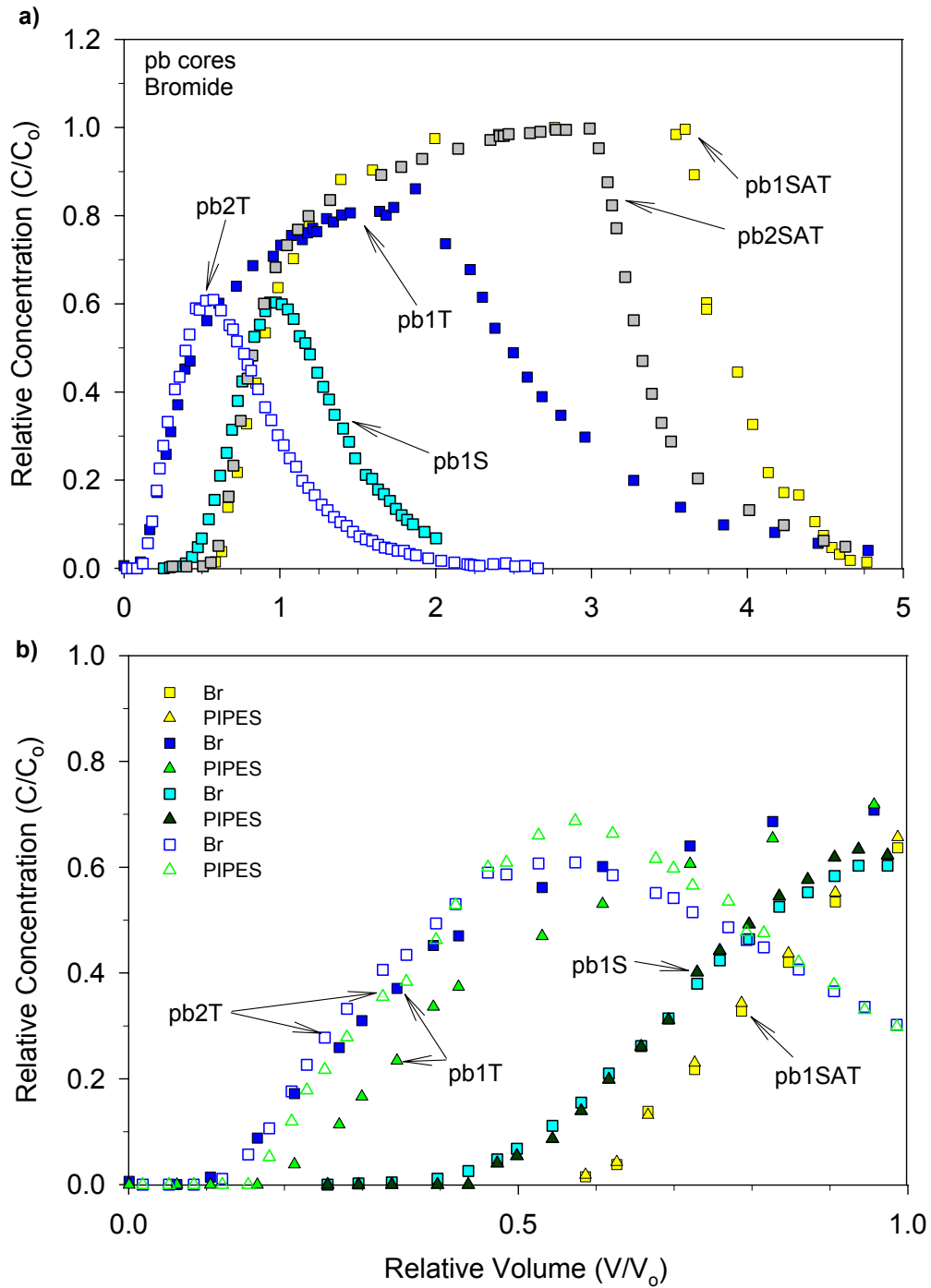
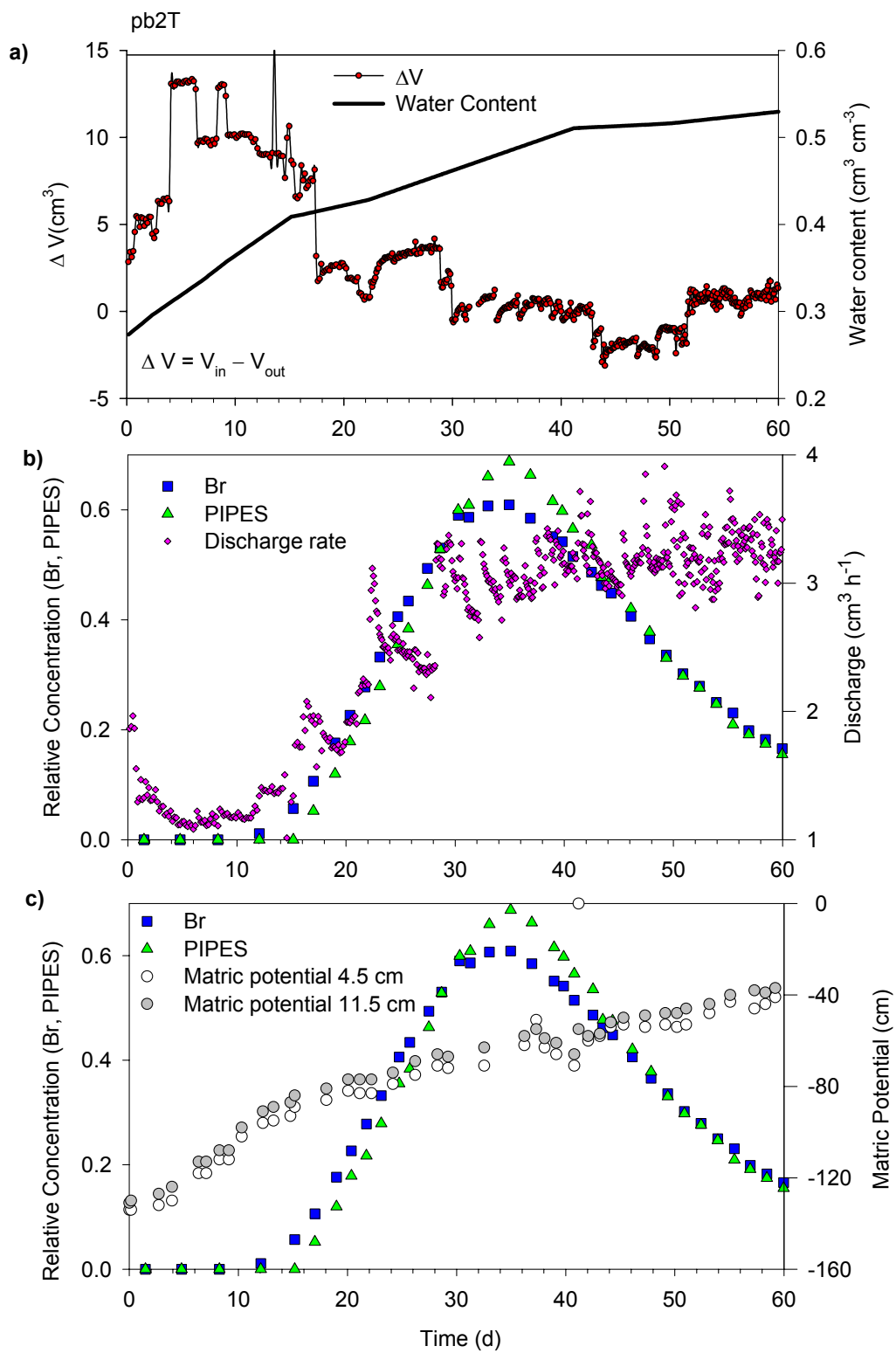


Figure 4.3 Observed relative tracer effluent concentrations involving the displacement of Br (squares) and PIPES (triangles) through pb core 1 and 2. a) Br for experiments pb1SAT, pb1S, pb1T, pb2SAT, and pb2T. b) Br and PIPES for 0 – 1 relative volume range for same experiments as in (a).

suggested that the unsaturated hydraulic conductivity of the media was exceeded. During the initial portions of the pb2T experiment, which was typical of the transient experiments, the volume of solution applied (V_{in}) exceeded the volume of solution eluted (V_{out}) (Fig. 4.4a). The concurrent increase in water content (Fig. 4.4a) and matric potential (Fig. 4.4c) suggested the sediment retained the excess solution. The discharge rate was generally stable for the first 12 d, but subsequent pulses in the discharge rate suggested the formation and periodic elution of perched water (Fig. 4.4b). Discharge rate increased thereafter as more pores became connected and began to participate in flow. The breakthrough of tracers was concurrent with the beginning of perching (Fig. 4.4b), which was probably the arrival of the tracer wetting front. Arrival of tracers therefore occurred well before the core became saturated. This was inconsistent with the capillary theory of Hillel and Baker (1988) and observations of finger flow in Wang et al. (1998), both of which suggested that fine-grained layers must become fully saturated before water may enter underlying layers. These experiments suggested that the finger flow theory (Mayes et al., 2003) was probably not appropriate for flow in layered systems composed exclusively of fine materials. Finally, the concurrent arrival of tracers and the wetting front suggested that the tracers were truly nonreactive and were not subject to chemical processes such as anion exclusion (James and Rubin, 1986; Porro and Wierenga, 1993).

Co-migration of tracers with the wetting front was not supportive of the theory of preferential flow suggested by asymmetrical BTCs in Figs 4.2 and 4.3, or the conceptual model in Fig. 4.1. Each of these figures used a relative volume, or “pore volume,” axis

Figure 4.4 Change in experimental parameters as a function of time over the 0-60 d portion of the pb2T experiment. a) Left axis applies to the mass balance of applied volume (red circles), where V_{in} is the volume of applied solution and V_{out} is the volume of eluted solution. Right axis applies to the water content (solid black line). b) Left axis applies to the relative concentration of nonreactive tracers Br and PIPES. Right axis applies to the discharge rate (pink diamonds). c) Left axis applies to the relative concentration of nonreactive tracers bromide Br (blue squares) and PIPES (green triangles). Right axis applies to the matric potential at depths 4.5 cm (white circles) and 11.5 cm (gray circles).



for the x direction. The relative volume axis is widely used because it allows experiments performed in media of different sizes, water contents, flow rates, or temporal scales to be plotted on the same graph. As pointed out by Pace (2005), in transient experiments the relative volume axis was suspect because the volume of wetted pores (V_o) was not constant. The relative volume axis, however, was the primary criteria for comparing results with saturated conditions and determining if preferential flow occurred (e.g., Fig. 4.1). Figures 4.2 and 4.3, therefore, also used the average V_o observed in the experiments. If V_o was unreasonably large, it might have shifted tracer BTCs to the left, leaving the appearance of preferential flow (e.g., Pace et al., 2005).

To determine if the appearance of media bypass in Figs. 4.2 and 4.3 was an artifact of the choice of V_o , a data manipulation experiment was conducted with pb2T (Fig. 4.5). The Br data were plotted using a relative volume of $V/V_{o \text{ min}}$, where V was the cumulative eluted volume and $V_{o \text{ min}}$ was the minimum V_o observed in the experiment; i.e., when the tracer injection began. The data were also plotted using a relative volume of $V/V_{o \text{ avg}}$, where $V_{o \text{ avg}}$ was the average V_o over the entire experiment (Figs. 4.2, 4.3). While this approach was not strictly quantitative, both V_o resulted in a more asymmetric BTC than the pbSAT experiment, suggesting some portion of the media was bypassed under unsaturated conditions (e.g., Fig. 4.1).

These methods, however, do not consider the solution emplaced into the cores during the experiments (V_{soil}). Perched water was included into V and V_o using the equation $(V + V_{\text{soil}})/(V_o + V_{\text{soil}})$ (Fig. 4.5). In this case, there was no appearance of preferential flow

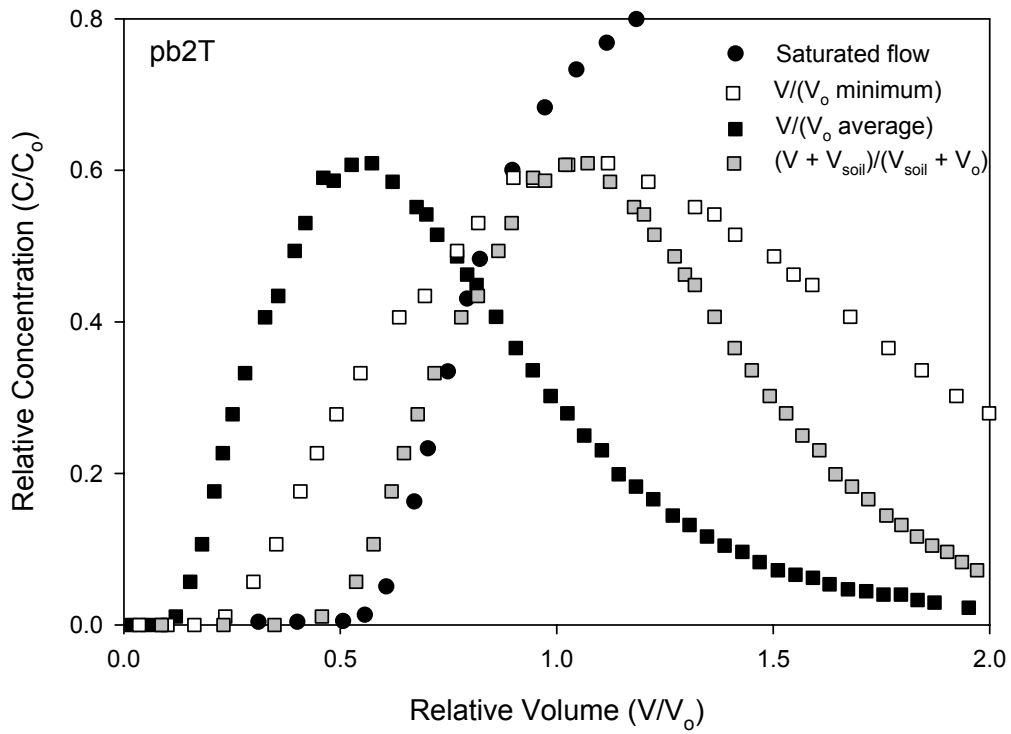


Figure 4.5 Appearance of bromide breakthrough curves with different relative volume (V/V_0) calculations. Saturated flow experiment pb2Sat (black circles) is shown for reference. pb2T data plotted using minimum volume of wetted pores ($V/V_{0 \text{ min}}$) (open squares), pb2T data plotted using average volume of wetted pores ($V/V_{0 \text{ avg}}$) (black squares), and pb2T data plotted considering the addition of solution volume to soil (V_{soil}) and the change in V_0 during transient conditions ($(V + V_{\text{soil}})/(V_{\text{soil}} + V_0)$) (gray squares).

because the unsaturated BTC overlies the saturated BTC, in which all the media theoretically participated in flow (pb core in Fig. 4.1a). V_{soil} , however, was not eluted from the system. The effective sequestration of solution volume into the dry soil gave the appearance of preferential transport, which is the characteristic feature of preferential flow in the RX. Solution was most likely drawn into the pores by capillarity. Vertical migration was concurrent with this process, lending to the appearance of preferential flow. It is also possible that the solutions and tracers were pulled through sedimentary layering in response to the applied vacuum (force) at the lower boundary. Although the two aforementioned hypotheses may contribute to the appearance of preferential flow, the sedimentology of the RX may provide the underlying explanation. Perching of solutions at the curved interface of the RX unit (Chapter 3, Figure 3.3) could produce a limited pathway to hydraulically connect overlying wet sediments with underlying dry sediments.

1.3.3. Causes of Tracer Separation

“Reversed” tracer separation was observed in all experiments in the RX sediments, in the transient RL xb core, and in a transient experiment in Pace (2005). “Reversed” refers to the order of tracer elution, in which the smallest, more rapidly-diffusing ion (Br) elutes in higher concentrations than the larger and more slowly-diffusing ion (PIPES) (Figs. 4.2, 4.3). “Normal” tracer separation was characteristic of mobile-immobile interactions in soils with macroporosity (Langner et al., 1999; Mortensen et al., 2004), in fractured saprolite (Jardine et al., 1998; Mayes et al., 2003), in fractured limestone (Sanford et al.,

1996; Jardine et al., 1999), and in unconsolidated Hanford sediments (Pace et al., 2003, 2005; Pace, 2005). In a mobile-immobile system, Br diffuses into relatively immobile water at a faster rate than PIPES and therefore elutes in lower concentrations during initial breakthrough.

The reversed pattern in RX and other transient experiments, therefore, was probably suggestive of different hydraulic processes. Mayes et al. (2003) noted the similarity of the reversed separation with the washout curves in mobile-immobile systems, and suggested the separation resulted from the initial formation of perched water and subsequent diffusion into preferential flowpaths. The findings on perching and preferential flow discussed above, which suggested that the tracer solution became effectively sequestered during uptake by the soil volume, were very consistent with that hypothesis. Tracers eluting from the RX looked like a typical washout curve, because they had already interacted with the sediments during perching. Steady-state experiments also exhibited “reversed” separation, and it is likely that the reversal is also due to perching during transport through nearly saturated layers of low conductivity.

1.3.4. Transport Modeling of Steady-state Experiments

Transport modeling was used to determine if flow occurred through one flow regime or two in the steady-state experiments. Tracer displacement was best quantified using the MIM, resulting in good fits to the data (Fig. 4.6; Table 4.4). The CDE fits, in contrast, were not able to reproduce the sharp tracer peaks (Fig. 4.6), resulting in significantly

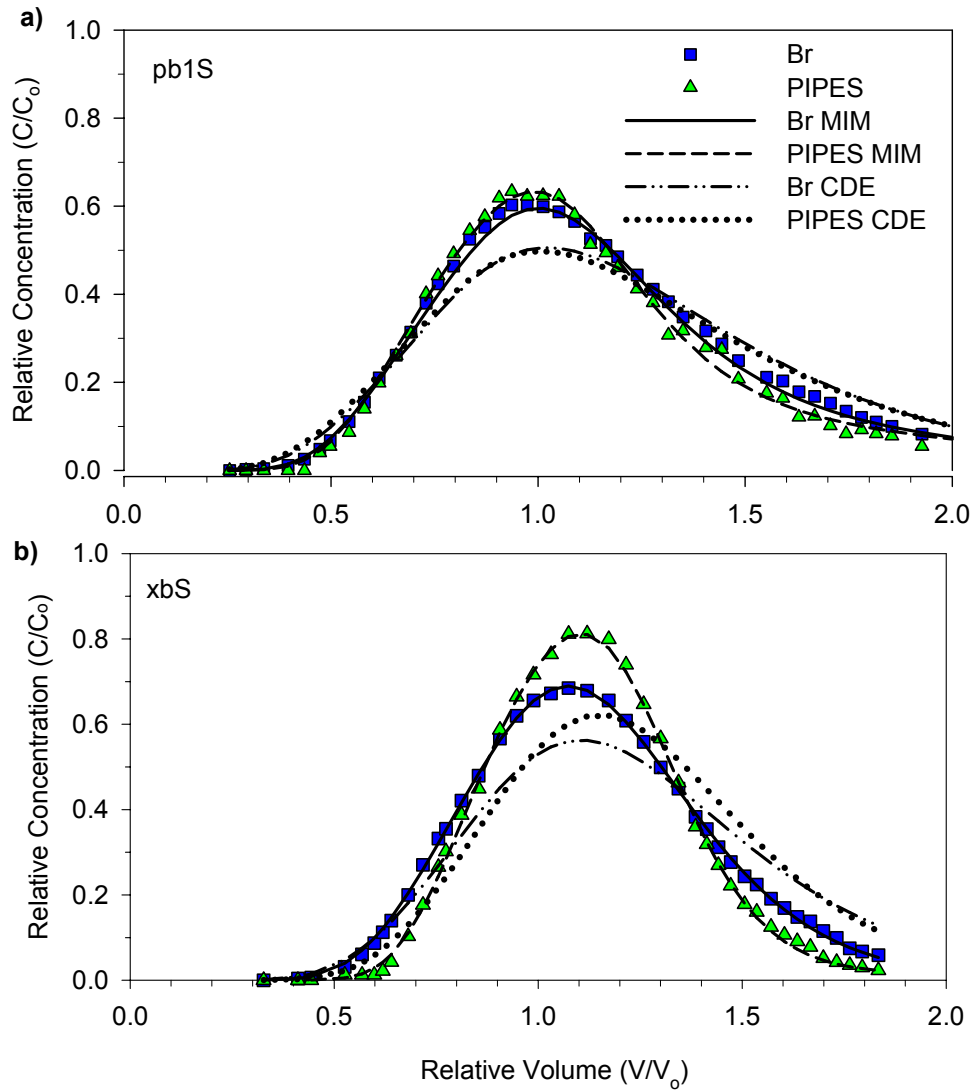


Figure 4.6 Observed (points) and modeled (lines) for relative tracer effluent concentrations involving the displacement of Br (squares) and PIPES (triangles). Modeled Br (solid lines) and modeled PIPES (dashed lines) using the MIM and CDE (Br, dash-dot-dot lines; PIPES, dotted lines). a) pb1S experiment. b) xbS experiment.

Table 4.4 Results of the application of CXTFIT (Toride et al., 1999) to steady-state reactive experiments.

Exp	Tracer	¹ Model	λ (cm)	F	α (h ⁻¹)	r ²
pb1S	Br	MIM	1.023 +/- 0.159	0.796 +/- 0.029	4.37 e-4 +/- 1.45 e-4	0.995
	Br	CDE	2.298 +/- 0.302			0.934
	PIPES	MIM	0.773 +/- 0.136	0.752 +/- 0.023	4.78 e-4 +/- 1.20 e-4	0.993
	PIPES	CDE	2.468 +/- 0.470			0.879
xbS	Br	MIM	0.940 +/- 0.028	0.895 +/- 0.003	1.02 e-5 +/- 6.55 e-6	0.999
	Br	CDE	1.459 +/- 0.282			0.806
	PIPES	MIM	0.425 +/- 0.028	0.871 +/- 0.004	6.07 e-5 +/- 1.69 e-5	0.998
	PIPES	CDE	1.048 +/- 0.343			0.891

¹MIM = mobile-immobile model, CDE = convective-dispersive equation

λ = dispersivity; F = fraction of mobile water; α = mass transfer coefficient.

lower r^2 values (Table 4.4). The CDE fits also produced greater dispersivity values, suggesting the MIM was needed to quantify the diffusive exchange with the relatively immobile flow regimes. It is notable that the CDE was used to model results from saturated RX cores (Chapter 2; Mayes et al., 2003), while the MIM was necessary for the slightly unsaturated experiments presented here. This was consistent with earlier results (Figs. 4.2 , 4.3) suggesting that the development of multiple flow regimes was exclusively related to unsaturated flow (Mayes et al., 2003, 2005a; Pace et al., 2003, 2005, Pace, 2005).

Tracers from the pb1S experiment exhibited greater tailing and lower maximum concentrations in comparison to the xbS, possibly suggesting some anisotropy in the flow regime (Fig. 4.6). This was consistent with greater fitted dispersivities for pbS versus xbS experiments (Table 4.4). The fraction of mobile water F was smaller in pbS, suggesting slightly more media bypass in pbS versus xbS experiments (Table 4.4). The F values were slightly different for Br and PIPES in both experiments, but these differences were very minor ($< 4\%$) and can probably be safely ignored. The rate of mass transfer between relatively mobile and relatively immobile flow regimes was an order of magnitude greater in the pb1S versus xbS experiment, suggesting that the smaller proportion of immobile pore regimes in xb cores was less accessible than those in pb cores. This probably explains the greater tracer separation observed in xb versus pb cores (Figs. 4.2 , 4.3). This combination of observations suggested that flow in the RX was slightly anisotropic, but much greater anisotropy was observed in flat-lying sediments (Chapter 3; Pace et al., 2003, 2005; Pace, 2005).

1.3.5. Comparison to Conceptual Hydrological Models

Unsaturated experiments in the RX had three common factors, including increasing water content, reversed tracer separation, and asymmetric BTCs (Figs. 4.2, 4.3). Figure 4.4 strongly suggested that the increase in water content was related to local-scale and bulk perching. Tracer elution was concurrent with the wetting front, which was not indicative of preferential transport processes. Uptake of solution volume during the perching process, however, gave the appearance of preferential flow (Fig. 4.5). Reversed separation of tracers was related to the initial mechanism of perching, and subsequent diffusional separation during migration of solutes out of perched water. The process leading to reversed separation was similar to that governing washout curves in mobile-immobile systems. The MIM model was appropriate for steady-state unsaturated flow experiments in the RX, which supports the other observations of multiple flow regimes. Some anisotropy was observed in the cross-bedded RX sediments, but it was minor and flow through the sediments was mostly isotropic. My findings suggest a mechanism for sequestration of contaminants in regions of relatively immobile water within fine-grained subsurface materials.

The general models of preferential flow in porous unsaturated sediments appeared to provide only limited insight into actual mechanisms of flow through natural RX sediments, which appears to have aspects of capillarity and funnel flow. Observation of media bypass attributed to finger flow in Mayes et al. (2003, 2005) now appears to be

inconsistent with our observations. The close association between the wetting front and tracer elution (Fig. 4.4), was consistent with capillary action in which the wetting front and the tracers were pulled into drier sediments. Solute migration, however, was not completely inhibited and elution of tracers occurred well before the sediments became fully saturated. This appeared to be inconsistent with the capillary theory of Hillel and Baker (1972) which suggested that fine-grained layers must become fully saturated before solution would enter underlying sediments. The curved bedding planes of the cross-bedded sediments in both pb and xb cores (Mayes et al., 2003, 2005; Chapter 2), however, could induce a type of funnel flow. Perching of solutions at the curved interface could produce a limited pathway to hydraulically connect overlying wet sediments with underlying dry sediments. This theory would allow solution to enter underlying layers before the overlying layers become fully saturated. These experiments demonstrated the major characteristics of flow in layered sediments of limited unsaturated hydraulic conductivity, which were the sequestration of perched water and the associated appearance of preferential flow. Solute transport studies such as these are highly quantitative, but can be difficult to interpret in terms of unique hydraulic mechanisms, particularly in natural sediments.

1.4 Conclusions

No single generalized conceptual model, such as capillarity, finger flow, funnel flow, or anisotropic lateral flow, adequately described the results shown here. Cross-bedded sedimentary structures promoted the development of localized zones of perched water.

The curved bedding planes most likely increased the local hydraulic head and permitted solution to enter into underlying partially-saturated layers. This mechanism was similar to preferential funnel flow with the influence of capillarity. The arrivals of the wetting front and nonreactive tracers were concurrent, but the elution of the tracers occurred well before the core became saturated. It is uncertain if preferential flow occurred, because the increasing water contents during the experiments decreased the volume of the effluent solutions and contributed to the appearance of preferential flow. Overall flow appeared to be inhibited, suggesting that the fine-grained and cross-bedded sediments will be a barrier to contaminant migration in the subsurface and might divert flow in the lateral direction.

1.5 Acknowledgements

We gratefully acknowledge the Environmental Management Science Program (EMSP) and program managers Roland Hirsh and Mark Gilbertson for supporting this work. EMSP is administered by the US DOE, Office of Science, Biological and Environmental Research Programs. We appreciate the fellowship provided for MAM's Ph.D. by the Waste Management Research and Education Institute (WMREI) at the University of Tennessee. We would like to thank B.N. Bjornstad and J. Piatt of Pacific Northwest National Laboratory (PNNL) for their assistance with core collection. Oak Ridge National Laboratory is managed by the University of Tennessee-Battelle, LLC, under contract DE-AC05-00OR22725 with the US DOE.

Chapter 5. Conclusions and Implications

The goal of this research was to determine the relationship between sedimentary geology and solute transport. I hypothesized that the transport of reactive and nonreactive solutes could be qualitatively predicted using observable sedimentary depositional characteristics. I tested this hypothesis using approaches designed to delineate both geochemical and hydrological aspects of subsurface sedimentology. The geochemical aspect was tested by comparing the reactivity of uranium(VI) in carbonate and siliciclastic sedimentary mineralogies. The hydrological aspect was tested using a variety of quantitative solute transport experiments in intact layered sediment samples from different facies. In addition, solute transport under partially-saturated conditions was investigated in a single sedimentary facies to determine the influence of water content upon transport parameters.

There were several new and unique aspects to my approach, which was probably the first of its kind. First, I used natural heterogeneous sediments to determine the reactivity of U(VI). Surprisingly, most published studies still focus on the reactivity of pure mineral phases. Such studies provide insight into the actual rates and mechanisms of contaminant interactions, and new sophisticated analytical techniques such as x-ray absorption spectroscopy can determine the molecular-scale mechanisms of contaminant reactivity. However, field-scale contaminant interactions occur in a heterogeneous mineralogical environment, where multiple geochemical mechanisms may be occurring at different rates and in different proportions. My research in Chapter 2, for example, found that that

uranium(VI) reactivity was consistently greater in carbonate versus siliciclastic sediments. A variety of experimental tests suggested that the mechanism of U(VI) reactivity was reversible sorption to Fe-oxides in siliciclastic sediments, and precipitation in carbonate sediments. In addition, short- and long-term reactivity rates appeared to be dependent upon sedimentary mineralogy. This suggested that heterogeneities in calcite content might influence contaminant reactivity in the subsurface, and should be considered in regional-scale contaminant migration models. In the terrestrial sediments at Hanford, for instance, paleosols and clastic dikes tend to have higher calcite content, while glacial flood deposits and fluvial deposits tend to have less. The location of both is known with some certainty in the Hanford subsurface, therefore we could incorporate this kind of constraint in site-wide transport models.

A second unique aspect of this research involved the systematic use of intact sedimentary samples from different sedimentary facies to quantify solute transport parameters (Chapter 3). Samples from a homogenous coarse sand, two heterogeneous sands, and two fine-grained silty sands were collected parallel and perpendicular to bedding. Comparison of bedding-parallel and bedding-perpendicular solute transport parameters (e.g., dispersivity) and hydraulic parameters (e.g., hydraulic conductivity) suggested that flow and/or solute dispersion were slightly anisotropic, i.e., were influenced by the direction of flow with respect to sedimentary bedding (Chapter 3). Directionality of hydraulic and/or transport parameters was probably related to the natural depositional arrangement of fine-grained minerals present in heterogeneous layer(s), such as clay and silt. In the Hanford subsurface lateral transport may greatly exceed vertical transport, and

anisotropy ranges from 10 under saturated conditions to >50 under unsaturated conditions (Khaleel et al., 2000). Anisotropy of the sediments in this study, however, was very low (1-5) and our results should therefore be interpreted cautiously. It is possible that subsurface anisotropy results from larger-scale features than were preserved in the relatively small (0.25 m) samples used in this study. Regardless, the differences between bedding parallel and bedding-perpendicular transport parameters from this study could be incorporated into models of contaminant transport in layered sediments to help predict the tendency for subsurface flow to take either vertical or horizontal pathways in the subsurface.

In Chapter 4, I investigated hydrological processes occurring in single sedimentary unit of cross-bedded loamy sand. Flow under unsaturated conditions was partially restricted when it crossed sedimentary bedding, resulting in local-scale and bulk perching. Chapter 3 demonstrated that the saturated conductivity of the fine-grained RX was $\sim 10^{-6} \text{ m s}^{-1}$, and unsaturated conditions should cause the conductivity to decrease by several orders of magnitude. Perching was related to crossing sedimentary beds and occurred in all samples in the cross-bedded RX. Perching was not exclusively related to grain size, because experiments in a similar fine-grained media in which flow was strictly parallel to bedding did not exhibit perching (Mayes et al., 2003). Finally, separation of multiple nonreactive tracers signified the development of a relatively immobile flow regime, which was supported by the successful application of the mobile-immobile model (Toride et al., 1999). The extent to which bypass of the developing immobile regime occurred, however, was uncertain due to the change in moisture content associated with perching.

The results do suggest that flow through fine-grained facies was inhibited under partially-saturated conditions, which implies that flow might be laterally diverted in real subsurface sediments. A “reversed” separation of multiple nonreactive tracers appeared to be diagnostic of this type of flow regime. No single existing conceptual model of unsaturated flow in layered sediments was able to completely describe the observations. This suggested that multiple conceptual models or a new model should be considered to understand and predict subsurface contaminant migration in natural sediments.

While this approach was labor-intensive, my research group has generated unique quantitative data that improves the understanding of layer-scale interactions in natural, layered sediments. Heterogeneous sedimentary facies significantly influenced the hydrology and geochemistry of contaminants in the subsurface, as predicted by my hypothesis. Once the boundary conditions are properly established, a modeler could use geochemical (i.e., Chapter 2 and Mayes et al. (2005b)) and hydrological data (Chapters 3-4; Mayes et al., 2003, 2005a; Pace et al., 2003, 2005; Pace, 2005) to construct artificial layered systems and predict observed transport parameters for groups of heterogeneous sedimentary layers (see also Future Work). A database of transport parameters from sediments having natural sedimentary structure and mineralogy will be useful to predict subsurface contaminant transport in heterogeneous materials, once appropriate “up-scaling” techniques have been developed.

Chapter 6. Future Work

1.0 The Influence of Heterogeneous Sedimentary Layering Upon Unsaturated Transport of Nonreactive and Reactive Solutes through Layered Heterogeneous Sediments

Research is currently ongoing to determine nonreactive and reactive transport parameters of the three sedimentary units from the IDF site under partially-saturated conditions (described in Chapter 3). This research is funded by one of the major site contractors at the DOE's Hanford Reservation, CH2M Hill Hanford Group, Inc. I led a successful effort in 2004 to do this work, which was subsequently renewed in fiscal year 2006. After the experiments are completed, the approach of Chapter 3 will be revisited. Data from the six different sedimentary units described in Chapter 3 will be compiled and analyzed for patterns in the unsaturated hydraulic and geochemical transport parameters. The new IDF studies will be combined with the current work that determined nonreactive and reactive transport parameters of the RX samples of the Ringold Formation (Chapter 4 and Appendix B) and recent work on the HL sediments (Pace, 2005). Appendix B represents a beginning of this process by comparing the reactive transport parameters of the RX with those of the HL samples of Hanford flood deposits from the ERDF site (Pace, 2005). One to two papers may be generated from this work.

1.1 Quantitative Analysis of Intact Core Sedimentology

It would be extremely useful to dissect several of the cores described in this study in order to quantitatively relate observed hydrology to sedimentology, following the methods of the Sr study of Pace (2005). Determining the connections between water content and grain size as a function of sedimentary layering would provide a much improved quantitative basis for interpreting hydrology in terms of sedimentology than the solute transport experiments presented here. As demonstrated in Chapter 4 and in Appendix B, transport experiments do not necessarily result in a unique solution in terms of relevant mechanisms. This method may be attempted in the near future with selected samples such as a homogenous HC core and heterogeneous HI and HL cores. Cristina Carbajo, a senior at Tennessee Technological University and promising hydrogeologist, will be returning for a second summer internship with my group in 2006. This idea will most likely constitute the most important work of her internship.

1.2 Modeling and Up-scaling of Core Experiments

I recently led a group of scientists including Dr. Phil Jardine of Oak Ridge National Laboratory, Dr. Edmund Perfect of The University of Tennessee, Dr. Jin-Ping Gwo of the University of Maryland at Baltimore County, and Dr. Scott Fendorf of Stanford University in a successful proposal to the Department of Energy's Environmental Remediation Sciences Program to expand the research in this dissertation and that of Pace (2005) to both larger and smaller experimental scales in the next 3 years. Detailed

hydrological and geochemical transport models will be applied to existing data at the core scale used in these studies, and in future experiments at both larger and smaller scales.

The resultant transport parameters will be analyzed for scale-dependent patterns. A variety of modeling approaches will be applied to determine appropriate scaling methods to apply transport parameters to progressively larger spatial and longer temporal scales such as are typically observed in the field.

The work in this dissertation, the dissertation of Pace (2005), the aforementioned future work, and previous published and unpublished studies (Pace et al., 2003, 2005; Mayes et al., 2003, 2005b) will form the basis for many decisions about the upcoming work.

These studies can be considered the foundation for our future work, and lessons learned will be applied to our future experiments.

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Appendices

Appendix A Capillary Pressure-Saturation of Sediments

1.0 Goals and Objectives

Because pore-size distribution and retention of fluids under tension are related, the goal of Appendix A was to determine the capillary-pressure saturation curves for five of the six sedimentary units from Chapter 3. Core samples were not collected from HD due to time constraints during field sampling. Chapter 3 related sedimentary facies to sediment hydrology using a variety of quantitative solute transport techniques. The objective of Appendix A was to describe the moisture retention function in terms of sedimentary facies, i.e., grain size and pore size distribution.

1.1 Materials and Methods

The capillary-pressure saturation curve, or moisture retention function, was determined for each media following standard methods as suggested by Klute (1986). Small intact cores (~ 4 cm x 6 cm) were collected from all sedimentary units except HD (Table 3.1). The small cores were emplaced into a flow cell (Soil Measurement Systems, Tucson, AZ), saturated, and drained by applying pressure in small increments (10-50 cm) from 0 to a total of 1000 cm. The RX and RL cores were presented in Mayes et al. (2003), which describes the experimental methodology. The undisturbed HL cores in the present study have not been published, although moisture retention in disturbed HL samples was presented in Pace et al. (2003).

1.2 Results and Discussion

The sediments were subjected increasing pressure, which resulted in the loss of water from the pore regime (Fig. A.1). The sediments were photographed (Fig. 3.3) and described in Table 3.1 in terms of layering characteristics and particle size distribution . The slopes of the curves reflect the heterogeneity of pore sizes, in which shallow slopes tend to occur in heterogeneous or more fine-grained samples, while steep slopes are typically observed in more homogeneous or coarse-grained samples (Hillel, 1998). The RL samples were very fine-grained as evidenced by high air-entry pressures (Fig. A.1). The shallow slope indicated some heterogeneity within the pore (grain) size distribution. The RX samples, similarly, were quite fine-grained and had a high air-entry pressure (Fig. A.1), but the steeper slope suggested less heterogeneity in pore sizes. The HL samples had a reasonably high air-entry pressure (Fig. A.1) for a media containing 95% sand, indicating the HL was composed of finer-grained sands. The rather steep slope suggested a relatively homogenous grain size distribution (Fig. A.1). The HI and HC samples had similar air-entry pressures (Fig. A.1) consistent with a similar component of coarse-grained sand (Fig. 3.3a,b). The HC samples exhibited a steeply sloping curve, being composed of massive coarse sands containing few fine-grained materials (Fig. 3.3a). The HI samples had a shallow slope after the initial air-entry, indicating a more heterogeneous pore size distribution in comparison to the HC. It is likely that the interbeds containing silt matrix-supported sands (Table 3.1; Fig. 3.3b) more effectively retained water for at least 200 cm in comparison to HC samples (Fig. A.1). Observed

moisture retention is related to sedimentary characteristics, and is relevant to saturated flow experiments in Chapter 3.

It was difficult to determine if there were significant differences between flow bedding parallel (pb) and flow crosses bedding (xb) cores. Three units were sampled in both directions (HL, RL, and RX), while the remaining cores (HI and HC) were only sampled in the xb direction. The HI and HC cores exhibited significant variations in volumetric water content and moisture retention curves, suggesting that gross heterogeneity between the cores was significant. Consequently I did not feel confident attributing differences in moisture retention between pb and xb samples to flow direction. It appeared that the RL and RX pb cores might retain more water than the xb cores, but these effects were minor as discussed by Mayes et al. (2003). Some further analysis of the HL cores, however, might provide some insight into this matter. Figure A.1 shows the average of two pb cores and the average of four xb cores. These should be analyzed more carefully in the future to determine the answer to this question.

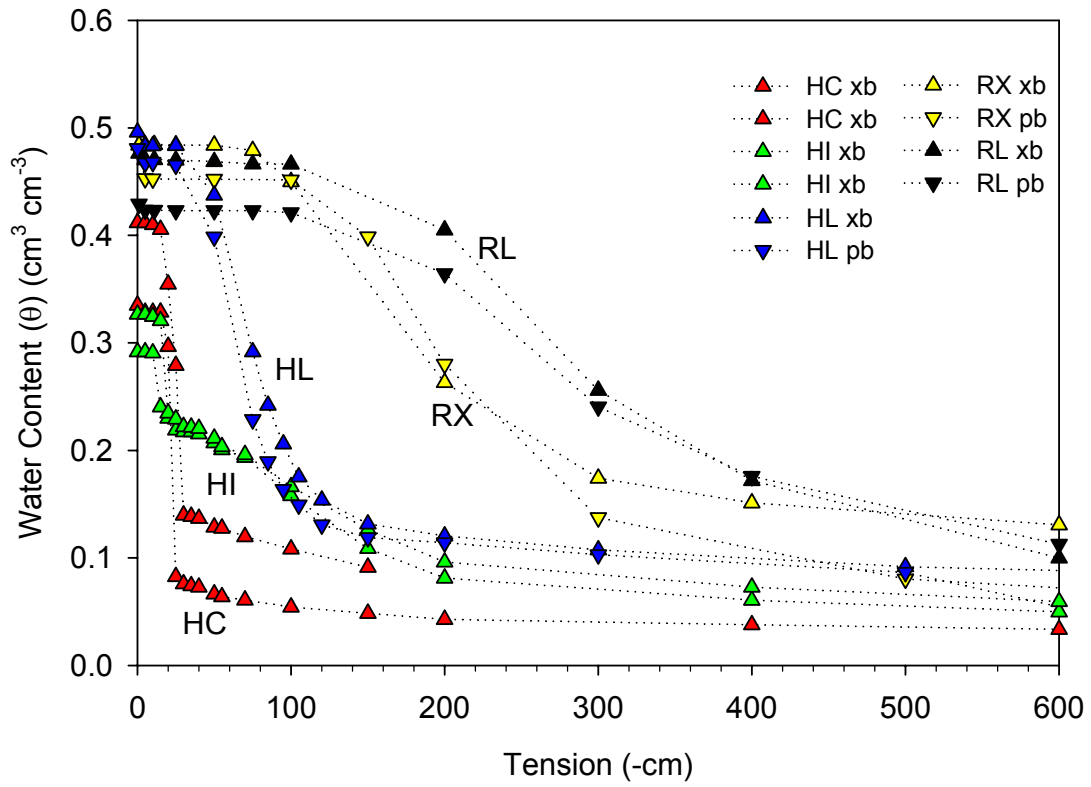


Figure A.1 Capillary-pressure saturation (drainage) curves showing water content as a function of tension. “pb” implies flow bedding parallel in undisturbed cores (inverted triangles), and “xb” implies flow crosses bedding in undisturbed cores (triangles). Note that HL symbols are an average of 2 samples (pb), and 4 samples (xb).

Table A.1. Physical parameters of moisture retention cores.

Core	L <i>cm</i>	r <i>cm</i>	θ_{sat} $\text{cm}^3 \text{cm}^{-3}$	ρ_b g cm^{-3}
HC xb1	6	4.35	0.335	1.61
HC xb2	6	3.73	0.396	1.51
HI xb1	6	3.88	0.283	1.66
HI xb2	6	3.64	0.296	1.72
¹ HL pb	6	3.60	0.481	1.45
¹ HL xb	6	4.00	0.449	1.31
² RX pb	6	4.13	0.480	1.31
² RX xb	6	4.13	0.480	1.33
² RL pb	6	4.13	0.430	1.38
² RL xb	6	4.13	0.480	1.35

¹Average of 2 samples (h), and 4 samples (v).

²Mayes et al. (2003).

Appendix B The Effect of Transient Flow upon Reactive Transport through Layered Natural Sediments

1.0 Introduction

The goal of Appendix B was to determine mechanisms leading to coupled hydrological and geochemical effects upon the reactive transport of U(VI) and CoEDTA in intact porous sediments. I hypothesized that transient flow conditions might lead to coupled effects in heterogeneous sediments, based upon previous results in the Hanford flood deposits (Pace, 2005). The objective was to compare new reactive experiments under transient flow conditions in the Ringold Cross-beds (RX) with a similar transient experiment in the Hanford Laminated sediments (HL) (Pace, 2005).

1.1 Materials and Methods

1.1.1. Description of Samples and of Experiments

Information about the sedimentology of the RX and HL sediments is in Chapter 3. Miscible displacement experiments were conducted following the experimental methodology described in Chapter 4 and in Mayes et al. (2003). Multiple nonreactive tracers, U(VI), and Co(II)EDTA were applied to partially-saturated intact cores from the RX sedimentary unit. Cores were collected in flow bedding parallel (PB) and flow cross bedding (XB) orientations, and steady-state (S) and transient (T) conditions were applied

in the following experiments, PB1S, PB2T, and XBS (Chapter 4). These were compared with steady-state and transient experiments in the HL (HL XBS and HL XBT) (Pace, 2005). Pace (2005) provides details of reactive transport and chemical analysis of U(VI) and Co(II)EDTA. Uranium(VI) was introduced into the columns as one or more anionic carbonate complexes (Chapter 2). The influent concentration of U(VI) was 8.4×10^{-5} M and was in equilibrium with a 1% CO₂ headspace (Pace, 2005; Chapter 2).

Co(II)EDTA²⁻ is a redox-active anionic complex which may become transformed to Co(III)EDTA⁻ (Mayes et al., 2005b). Influent concentration of Co(II)EDTA was 2×10^{-3} M.

1.1.2. Transport Modeling

The two steady-state reactive experiments were modeled using CXTFIT (Toride et al., 1999). Three sets of equations were used for the steady-state experiments, the equilibrium convective-dispersive model (CDE), the 2-region mobile-immobile model (MIM), and the two-site chemical nonequilibrium model (2-site). Input parameters consisted of column length (L), the input pulse (L^3), relative tracer concentration (C/C_0), relative effluent volume (V/V_0), and the pore-water velocity v ($L T^{-1}$) (Tables 4.1 and 4.2). Pore-water velocity was derived from the equation:

$$(1) \quad v = \frac{Q}{\pi r^2 \theta}$$

where Q is the discharge rate ($L^3 T^{-1}$), r is the column radius (L), and θ is the water content ($L^3 L^{-3}$). This modeling strategy is widely used, therefore discussion of the governing equations will be limited here. More detailed discussion specific to these types of experiments is available in Mayes et al. (2003).

Separation of multiple nonreactive tracers was used to determine the choice of CDE versus MIM for Br and PIPES. Tracer separation indicated the presence of multiple pore regimes, dictating the use of the MIM. The retardation factor (R) of the MNRTs was always assumed to be 1. Three parameters were obtained from the application of the MIM, the dispersion coefficient D ($L^2 T^{-1}$), the fraction of mobile water F , and the rate of mass transfer between the mobile and immobile pore regimes, α (T^{-1}). If the MIM was used for the MNRT, it was assumed that the 2-site model should be used for the reactive tracers Co and U(VI). The 2-site model would thus represent the combined effects of physical and chemical nonequilibrium, e.g., the effects of multiple flow regimes upon chemical processes, and chemical processes that were kinetically rate-limited. I assumed that reactive tracers would follow the same hydrologic flowpaths as the nonreactive tracers, therefore we used D from the MNRT and solved the model for R , F , and α . The relationship between R and the distribution coefficient (k_d) ($M L^{-3}$) that described the linear adsorption of a reactive contaminant is:

$$(2) \quad R = 1 + \frac{k_d \rho_b}{\theta}$$

where ρ_b is the dry bulk density ($\text{L}^3 \text{M}^{-1}$). If this strategy was unsuccessful, then D was allowed to also be fitted to the reactive tracer curve. Finally, if the 2-site model was unsuccessful, the CDE was applied to the data. The dispersion coefficient D obtained by application of the MIM to the MNRT was not expected to be valid for any application of the CDE, because the MIM assumes two pore regimes, while the CDE assumes one. Consequently the CDE was fitted to the curve by estimating both parameters D and R .

1.2 Results

The effects of transient flow upon the transport of U(VI) and Co(II)EDTA was investigated by simultaneously injecting MNRTs Br and PIPES along with reactive tracers U(VI) and Co(II)EDTA into all three RX cores. BP1S and XBS core experiments were conducted under steady-state conditions, while the BP2T experiment was transient (Table B.1). The results of the MNRTs are plotted in Fig. B.1, the Co system in Fig. B.2, and U(VI) in Fig. B.3. Volume and mass recoveries are available in Table B.1. Three modeling strategies were applied to the steady-state experiments using CXTFIT (Table B.2) (Toride et al., 1999).

MNRT displacement was quantified using the MIM, resulting in good fits to the data (Fig. B.1b,c). It is notable that the CDE was used to model results from saturated RX cores (Chapter 3; Mayes et al., 2003), while the MIM was necessary for the slightly unsaturated experiments presented here, as described in Chapter 4. This suggested that

Table B.1 Mass recoveries of applied tracers.

Exp	¹ Volume Recovery	² Br	² PIPES	² U(VI)	² Co	² Co(II)EDTA	² Co(III)EDTA	^{2,3} Co ²⁺
BP2T	99.0	102	99.1	88.9	92.6	1.50	81.8	9.30
BP1S	104	96	89.6	79.6	96.4	0.70	82.0	13.7
XBS	98.4	92	87.2	80.4	90.1	11.5	71.7	6.9
⁴ HLXBS	93.4	93	93	82	97	1.3	91	4.7
⁴ HLXBT	87.6	82	81	67	68	2	43	23

¹ units in % L L⁻¹; ² units in % mol mol⁻¹; ³Co²⁺ = Co – Co(II)EDTA – Co(III)EDTA; ⁴HL = Hanford Laminated (Pace, 2005).

Table B.2 Results of the application of the CXTFIT to steady-state reactive experiments.

Exp	Tracer	¹ Model	D (cm ² h ⁻¹)	R	F	α (h ⁻¹)	r ²
BP1S	Br	MIM	0.045 +/- 0.007	1.0	0.796 +/- 0.029	4.37 e-4 +/- 1.45 e-4	0.995
	PIPES	MIM	0.034 +/- 0.006	1.0	0.752 +/- 0.023	4.78 e-4 +/- 1.20 e-4	0.993
	Co	CDE	0.080 +/- 0.012	0.921 +/- 0.011			0.959
	U(VI)	CDE	0.140 +/- 0.027	1.782 +/- 0.179			0.846
XB S	Br	MIM	0.033 +/- 0.001	1.0	0.895 +/- 0.003	1.02 e-5 +/- 6.55 e-6	0.999
	PIPES	MIM	0.015 +/- 0.001	1.0	0.871 +/- 0.004	6.07 e-5 +/- 1.69 e-5	0.998
	Co	CDE	0.020 +/- 0.001	0.962 +/- 0.002			0.993
	U(VI)	CDE	0.030 +/- 0.004	1.41 +/- 0.011			0.895
	U(VI)	2-Site	0.007 +/- 0.002	1.640 +/- 0.014	0.737 +/- 0.075	0.003 +/- 5.20 e-4	0.988

¹MIM = mobile-immobile model; CDE = convective-dispersive model, 2-site = two-site chemical nonequilibrium model. D = dispersion coefficient, R = retardation coefficient, F = fraction of mobile water, α = mass transfer coefficient.

Figure B.6.1 Observed (points) and modeled (lines) for nonreactive relative tracer effluent concentrations. The displacement of Br (squares), PIPES (triangles), modeled Br (solid lines), and modeled PIPES (dashed lines) using the MIM. a) PB2T experiment, no modeling. b) PB1S experiment. c) XBS experiment.

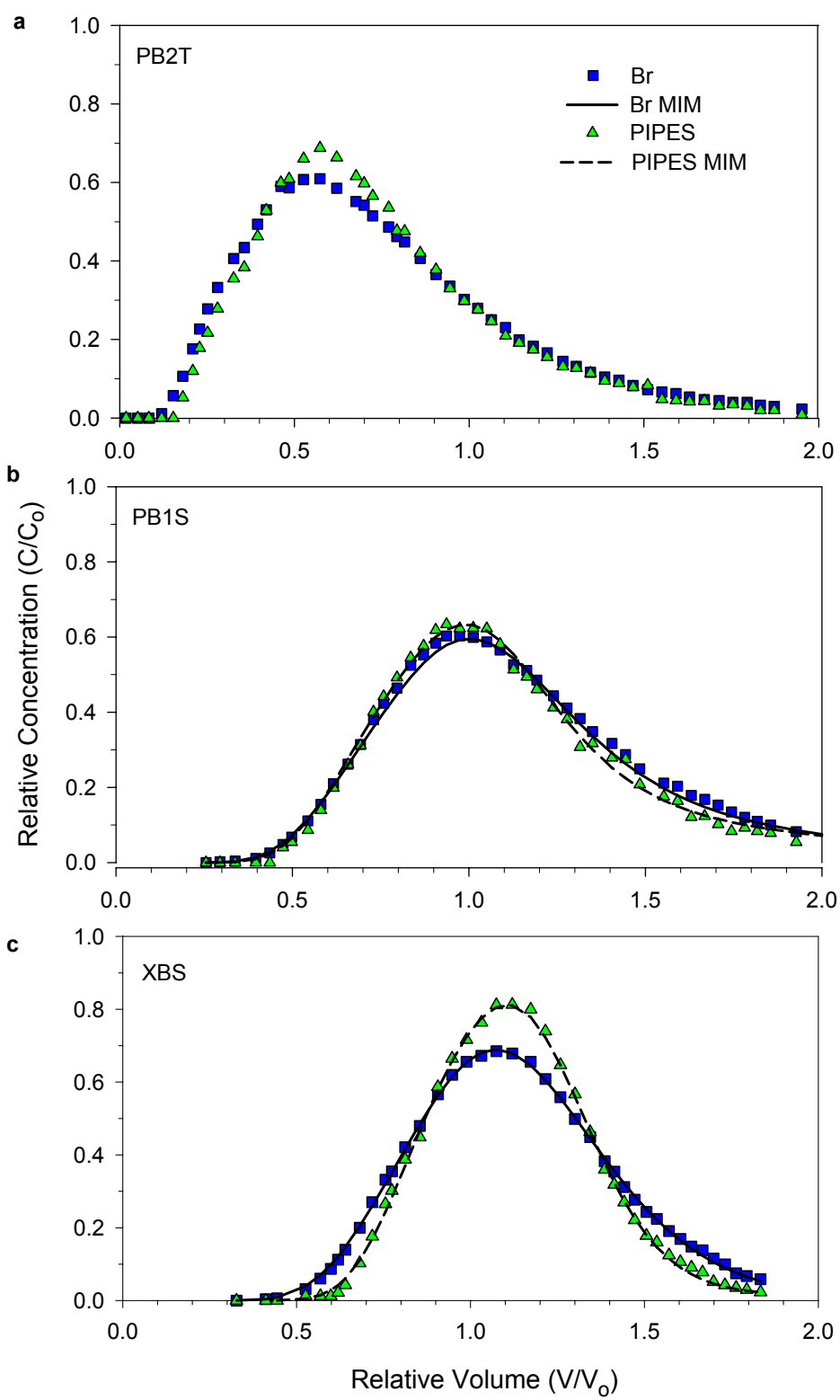


Figure B.1.2 Observed (points) and modeled (lines) for Co-EDTA relative tracer effluent concentrations. The application of Br (squares) and CoT (black diamonds) as Co(II)EDTA (pink diamonds), and the production of Co(III)EDTA (purple diamonds), and modeled Co_T (solid lines) using the CDE. a) PB2T experiment, no modeling. b) PB1S experiment. c) XBS experiment.

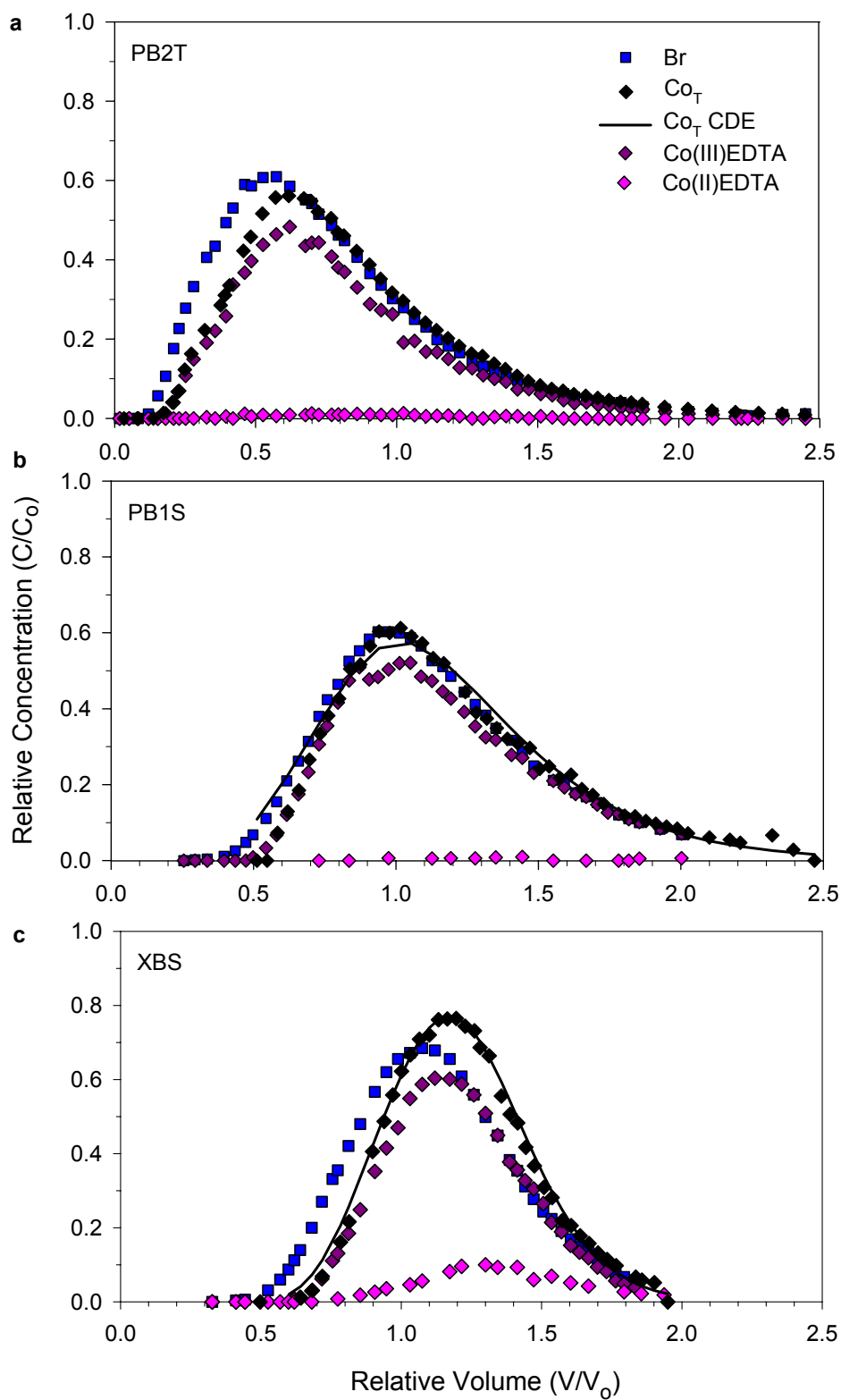
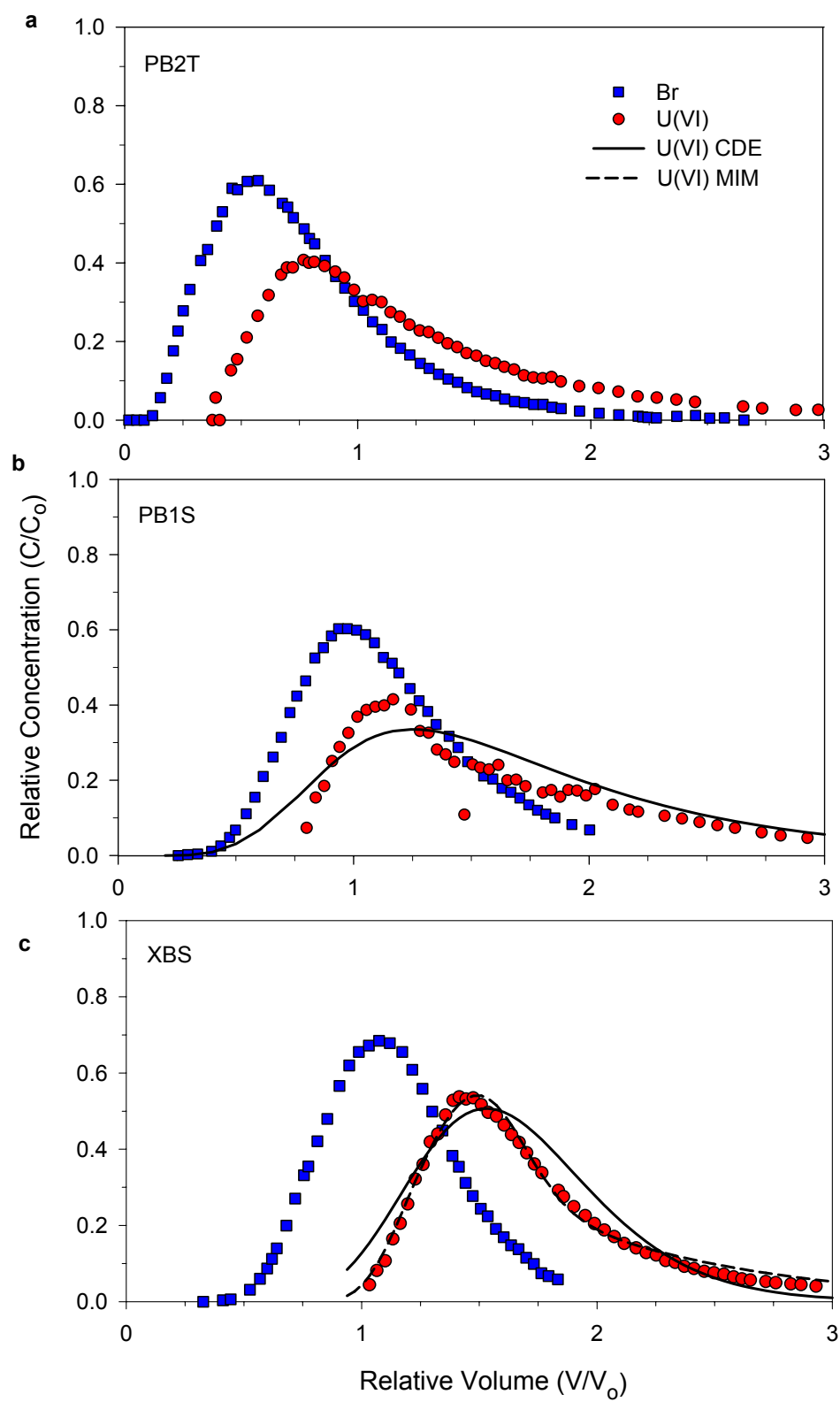


Figure B.1.3 Observed (points) and modeled (lines) for (U(VI) relative tracer effluent concentrations. The displacement of Br (squares) and U(VI) (circles), modeled U(VI) (solid lines) using the CDE, and modeled U(VI) (dashed lines) using the MIM. a) PB2T experiment, no modeling. b) PB1S experiment. c) XBS experiment.



the development of multiple flow regimes was exclusively related to unsaturated flow (Mayes et al., 2003, 2005a; Pace et al., 2003, 2005; Pace, 2005).

Anisotropy, or directionality with respect to flow, was observed in RX, despite the fact that the cross-bedded sands and silts of the RX unit were not exactly parallel or perpendicular to flow (Mayes et al., 2003, 2005a). MNRT from the PB1S and PB2T experiments exhibited greater tailing and lower maximum concentrations in comparison to the XBS (Fig. B.1). The fraction of mobile water was smaller and dispersion was greater in PB1S versus XBS, suggesting more media bypass in the PB core (Table B.2). The rate of mass transfer between relatively mobile and relatively immobile flow regimes was an order of magnitude greater in the PB1S versus XBS experiment, suggesting that the smaller proportion of immobile pore regimes in XB cores was less accessible than those in PB cores. This combination of observations suggested that flow parallel to bedding was somewhat anisotropic under unsaturated conditions. However, this degree of anisotropy is minor in comparison to that observed in flat-lying sediments (Chapter 3; Mayes et al., 2003; Pace et al., 2003, 2005; Pace, 2005).

The speciation of Co was dominated by oxidation of influent Co(II)EDTA to Co(III)EDTA (Fig. B.2). This redox reaction has been well-characterized (Jardine and Taylor, 1995a,b; Zachara et al., 1995; Jardine et al., 1993a,b; Mayes et al., 2000; Mayes et al., 2005b) and has been specifically shown using X-Ray Absorption Spectroscopy (XAS) to be facilitated by surface-mediated reduction of Mn(IV)oxides (Fendorf et al., 1999) and to a limited extent by Fe(III)oxides (Brooks et al., 1996). The environmental

implications of the reaction are profound, due to the stability of the Co(III)EDTA complex ($\log K \cong 40$) (Jardine and Taylor, 1995a). The transformation reaction was complete for both PB cores, resulting in <2% of influent Co(II)EDTA being eluted (Table B.1). The reaction was incomplete for the XBS experiment as evidenced by the pulse of Co(II)EDTA (Fig. B.2), which accounted for 12% of the applied Co mass (Table B.1). Transformation to Co(III)EDTA accounted for ~80% of applied Co in the BP experiments, and ~70% in the XBS experiment. This suggested that reactivity was somewhat decreased when flow was perpendicular to bedding.

The transport of Co, regardless of speciation, was minimally retarded in comparison to Br, suggesting the surface-mediated redox reaction was rapid (Fig. B.2). The 2-site model could not successfully simulate the transport of Co. The CDE was used to quantify the retardation (R) of Co, resulting in R slightly less than unity (Table B.2). While the fits were adequate for both experiments (Fig. B.2), the CDE conceptual model was inappropriate for these experiments.

Using 20 sediments from the Hanford region, Mayes et al. (2005b) observed that the extent of oxidation to Co(III)EDTA in a static batch system could be generally predicted by knowing the amount of Mn oxides in the sediment. The reaction was very rapid in the first 24 – 48 hours, proceeded at slower rates for at least 30 d, and tended to proceed until the supply of Co(II)EDTA and/or Mn-oxides became exhausted. The static batch system with RX sediments resulted in 52% Co(II)EDTA, 25% Co(III)EDTA, 19% dissociation of the Co-EDTA complex, and < 3% sorption after 30 d (Mayes et al., 2005b). The

nearly complete transformation to Co(III)EDTA in the column systems (Table B.1) was probably a result of unlimited supply of solid phase oxides in the large cores. Incomplete oxidation in the XBS core might indicate that the Mn oxides were not readily accessible, as also suggested by the lower α (Table B.2). Dissociation of 5-15% of the Co-EDTA complex was suggested by the mass balance in the current experiments (Table B.1), which was significantly less than would be predicted by batch experiments. It is likely that the high supply of Mn-oxides in the column system promoted the more rapid oxidation reaction over the slower dissociation reaction (Mayes et al., 2000, 2005b). Similar to batch experiments, none of the transport experiments resulted in extensive immobilization of total Co (as Co_T) as evidenced by similar recoveries of Co_T and MNRTs (Table B.1).

The transport of U(VI) appeared to follow the same trends as observed for MNRT and Co (Fig. B.3). Somewhat more preferential flow was observed in the PB2T experiment, followed by PB1S and XBS. For all experiments, the mass recoveries of U(VI) were 10% less than the recoveries of the MNRT and Co, therefore it is likely that some irreversible immobilization of U(VI) occurred (Table B.1). The chemical form of the applied U(VI) was a suite of related anionic U- CO_3 complexes (Chapter 2). XAS on RX and HL sediments treated with U(VI) indicated that adsorption was primarily onto Fe-oxides and was reversible, while the RL sediments tended to reversibly adsorb U(VI) onto edge sites of clay minerals (Chapter 2). Precipitation was only implicated in sediments with high calcite content over longer time intervals (Chapter 2). The calcite content in the RX (approximately 2%) was insignificant in closed-system batch

experiments (Chapter 2), but amounted to several hundred grams of calcite in each intact core. This could suggest that even low concentrations of natural sedimentary calcite might immobilize significant U(VI).

The transport of U(VI) was well-quantified with the 2-site chemical nonequilibrium model in the XBS experiment (Table B.2, Fig. B.3c). The dispersion coefficient from the MNRT was not appropriate for U(VI), and was an order of magnitude greater than that obtained for U(VI). This observation is probably consistent with expectations for reactive components in which adsorption tends to inhibit dispersion. The fraction of equilibrium sites was 74%, 10% less than the fraction of mobile sites for the MNRT. This was consistent with the expected influence of the hydrologic flow regime upon the chemical sorption of U(VI), and suggested that both physical and chemical nonequilibrium influenced the transport of U(VI). The 2-site model, however, was not successful for the PB1S experiment using any combination of input and output parameters. The CDE was therefore used to fit the U(VI) data (Fig. B.3b). It is apparent that the CDE was not appropriate and required unrealistically increasing D to obtain the fit (Table B.2). The CDE was also applied to the XBS experiment solely for comparison purposes (Fig. B.3c). The CDE fits suggest that R was greatest in the BP1S experiment (Table B.2), but visual examination of Fig. B.3 does not support those results. Regardless, the k_d for both experiments was the same order of magnitude as k_d obtained from closed system equilibrium batch experiments (Chapter 2). Similar to the Co results in which transformation to Co(III)EDTA was nearly complete, the U(VI) results suggested the system was close to equilibrium with respect to geochemical reactions.

1.3 Discussion

Similar hydrological processes, perching, transient flow, and media bypass, appeared to influence flow in the RX (Chapter 4) and select samples from the HL (Pace, 2005) sedimentary units. Increasing water content and reversed tracer separation were observed in the RX and in a single XB core in the HL unit (HLXBT) (Chapter 4; Pace, 2005). As discussed in Chapter 4, reversed tracer separation was characteristic of local-scale perching and transient conditions. Increasing moisture in the HLXBT was attributed to the lengthy nature of the experiment (Pace, 2005), but re-examination of the data showed that other steady-state experiments were of similar lengths, and that changes in moisture occurred rapidly (within 30 d). Therefore we now suggest that the observed behavior in the HLXBT experiment was related to flow crossing one or more sedimentary layers of low conductivity, and that the mechanisms of flow and transport were similar to those observed in the RX (described in Chapter 4). That such behavior was not observed for all HL XB cores is probably due to gross heterogeneity in the HL unit.

Although this interpretation suggested that similar hydrological processes (perching, transient flow, and media bypass) influenced flow in both HL and RX units, a dramatic difference was observed in the resultant coupled hydrology and geochemistry of the two units. Overall, reactivity in the RX unit was similar regardless of steady-state or transient conditions (Table B.1; Figs. C.2, C.3). In contrast, transient conditions greatly affected the sorption and transformation of contaminants in HL (Pace, 2005). Mass recoveries of

reactive and nonreactive tracers were considerably lower in the HLXBT (transient) versus HLXBS (steady-state) experiments (Table B.1). In addition, dissociation of the Co-EDTA complex was much greater (23%) in the HLXBT versus HLXBS (5%) experiments (Table B.1). These results suggested the influence of transient versus steady-state conditions may be profound under certain conditions.

We hypothesize that the different response to transient flow in RX versus HL was related to the sedimentology of the two units. In the RX cores, there were tens to possibly hundreds of individual sedimentary layers that existed within several distinct sedimentary units (Mayes et al., 2003; Fig. 3.3e). The beds appeared to be relatively homogenous in terms of thickness, hydrology, and mineralogy (Chapter 3). In the HL cores, the number of beds was probably on the order of tens (Pace et al., 2003). The HL unit was, however, comprised of two distinct sedimentary units, Sh(f), which is described as a horizontally-laminated silty fine to medium sand, and Sr, a rippled fine sand with clay lenses (DOE, 2002b). Pace et al. (2003) observed a few prominent clay stringers within the HL cores (Fig. 3.3c). Transient conditions in HLXBT versus HLXBS may be related to one or more prominent clay stringers or fine-grained interbeds present only in the former. A single layer with high clay content embedded within a sand unit would be expected to dramatically influence the hydrology and could possibly induce observed perching, associated transient conditions, and “reversed” tracer separation. This could theoretically be due to a combination of the low conductivity of the clay layer, and the development of a capillary barrier in an underlying coarser-grained layer.

A fine-grained or clay-rich layer might have also biased the geochemistry towards the observed greater irreversible sorption of U(VI), Co_T and greater dissociation of Co-EDTA (Table B.1). Dissociation of Co(II) EDTA ($\log K \cong 18$) is dominantly associated with Fe oxides and the formation of the strong Fe(III)EDTA complex ($\log K \cong 28$) (Szecsody et al., 1994, 1998a,b; Nowack and Sigg, 1997; Mayes et al., 2000). Pace (2005) demonstrated that the silt-sized component was relatively rich in Fe-oxides. Clays in the HL contained Fe, such as chlorite, hydroxyl-interlayered vermiculite, and smectite (Pace et al., 2003), and proximal Fe-containing weathering products or even clay minerals might have potentially dissociated the Co(II)EDTA complex. The dissociation reaction is a kinetically-limited, four-step reaction involving the formation and subsequent dissociation of the ternary surface complex $\text{Co} \equiv \text{EDTA} \equiv \text{Fe-oxide}$ (Nowack and Sigg, 1997; Mayes et al., 2000). Observed irreversible sorption of Co_T in the HL (Table B.1) may be related to the slow kinetics of this reaction. Fe-oxides were also identified as primary sorbents of U(VI) using XAS in the HL (Chapter 2). Edge sites of clay minerals were the dominant sorbents of U(VI) sites in the RL, and the clay mineralogy of RL, RX, and HL was very similar (Chapter 2). This suggested that the observed reactivity of both Co-EDTA and U(VI) might have been influenced by the presence of iron-containing clay minerals and/or weathering products present in a fine-grained layer or layers.

1.4 Preliminary Conclusions and Future Work

The interpretations presented in this appendix are preliminary. The sedimentological heterogeneity theory discussed here appears to account for the differential hydrologic response in RX and HL. The theory can account for the dissociation of Co-EDTA observed in the HLXBT, but it does not fully account for the lack of oxidation from Co(II)EDTA to Co(III)EDTA observed in the HLXBT. In batch experiments (Mayes et al., 2005b), in RX cores (Fig. B.2), and in other HL cores (Pace, 2005), Mn- and Fe-oxides were plentiful and the oxidation reaction was dominant. Therefore, the theory presented here implies that the proposed fine-grained layer in the HLXBT was also lacking in Mn-oxides. Currently there is no evidence to support this hypothesis.

One possible avenue to test this theory would involve dissection of the HLXBT core following the methods of the Sr study of Pace (2005). If such a layer were found, it should be analyzed for the presence of distinct mineral assemblages, water content, and Fe- and Mn-oxide content. These analyses should be compared with other sedimentary layers to determine the validity of this theory.

Vita

Melanie A. Mayes was born in Lebanon, Missouri, where she attended local public schools until her graduation. She received several scholarships to study at the University of Missouri in Columbia. Her initial interest in journalism faded, and she chose a new career path in Geological Sciences. After receiving her B.S. degree in 1995, she interned at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. After completing her internship, she began graduate school at the Geology Department at The University of Tennessee in Knoxville. Her 1999 Master of Science degree was based upon her work with contaminant transport in fractured saprolites. After receiving the M.S. degree, she was hired as a Research Associate through Oak Ridge Institute for Science and Education, and began to work in layered sediments from semi-arid environments. A year later, she began part-time class work at The University of Tennessee towards her Doctorate in Geology. In 2002, she was hired into a Research Scientist position at ORNL.