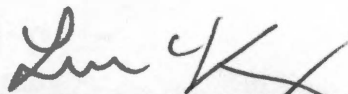


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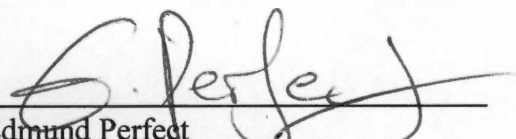


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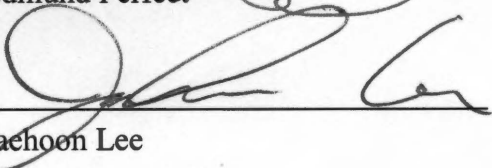
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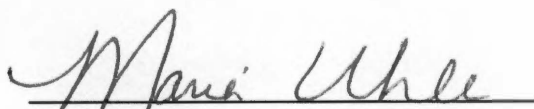
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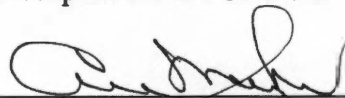


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**UNSATURATED FLOW AND TRANSPORT OF ^{90}Sr ,
 Co(II)EDTA , AND U(VI) IN UNDISTURBED CORES FROM
THE HANFORD FORMATION, HANFORD, WA**

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

Mary Fairfax Nichols Pace
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DEDICATION

I dedicate this dissertation to my entire family who has given me the love and support needed to complete such a daunting task.

ACKNOWLEDGEMENTS

I would like to thank everyone that has helped me complete my Doctor of Philosophy in Geology. Special thanks goes to my co-supervisors - Dr. Phil Jardine and Dr. Larry McKay, my dissertation committee members – Dr. Edmund Perfect and Dr. Jaehoon Lee, as well as my co-workers at Oak Ridge National Laboratory – Melanie Mayes, Tonia Mehlhorn, Tracy Bank, Xiangping Yin, and all of our summer students - who have provided immense help during my research. I would also like to thank Oak Ridge National Laboratory for providing me the laboratory space and resources in which this work was conducted. I would also like to thank the U.S. Department of Energy's Environmental Management Science Program for funding this research.

I would not have been able to accomplish this goal without the love and support of my family. Thank you for all that you have done for me!

ABSTRACT

At the U.S. Department of Energy's Hanford Site in Richland, WA nuclear processing wastes, such as Sr-90, organic chelating agents such as EDTA, Co-60, and U(VI), have been detected in the vadose zone beneath the underground storage tanks. There is concern that waste released to the vadose zone could reach the groundwater and eventually flow into the Columbia River. The goal of this paper is to provide an improved understanding of coupled hydrologic and geochemical mechanisms that influence contaminant transport in the Hanford vadose zone. Disturbed sediment and undisturbed sediment cores were collected from the Environmental Restoration Disposal Facility (ERDF) at the Hanford Site. The disturbed sediment was used in batch sorption experiments as well as saturated repacked column experiments. The undisturbed cores were collected vertically (flow across bedding) and horizontally (flow along bedding) to determine the effect of bedding on fate and transport of contaminants over a range of moisture contents. Multiple non-reactive tracers were used to quantify physical non-equilibrium processes such as preferential flow and media bypass as well as diffusion into immobile water. Miscible displacement experiments were conducted with Sr^{+2} , Co(II)EDTA and U(VI) to quantify the importance of hydrologic processes on the geochemical reactions. Unsaturated undisturbed core experiments indicate the prevalence of unsaturated lateral flow while vertical flow is inhibited due to capillary barriers that develop in the coarse-grain sediment beds resulting in minor perching. During unsaturated lateral flow at low water content, multiple flow paths can develop which may limit the surface sites available for geochemical interactions and therefore "accelerate" transport compared to that predicted from commonly used batch or saturated

packed column experiments. The results indicate that sedimentary bedding controls the flow paths (i.e., the hydrology), which then affects the geochemical processes. These coupled processes appear to significantly affect transport in the Hanford vadose zone and need to be considered in the development of conceptual models of vadose zone transport in arid environments.

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LIST OF ABBREVIATION

PNE = Physical non-equilibrium

BTC = Breakthrough curve

PV = Pore volume ($V_{\text{eluted}} / v_{\text{w(unsat)}}$)

C/C_0 = Relative concentration ($C_{\text{eluted}} / C_{\text{influent}}$)

bp = bubbling pressure

PART I

INTRODUCTION

Transport of chemicals through the vadose zone is a growing concern as waste from various processes is often buried or disposed of on land surface. These chemicals are often derived from agricultural applications, chemical processing plants, and the mining industry. Such chemicals can be categorized as either hazardous, radioactive, or sometimes beneficial chemicals such as plant nutrients. Hazardous and radioactive contaminants are the focus of this dissertation.

Some of the hazardous and radioactive contamination detected in the vadose zone is typically historical or legacy waste from old, abandoned facilities. In the past, waste from a variety of industrial processes has been “disposed of” by simply burying them in the vadose zone in unlined trenches, solid waste burial pits, or in underground storage tanks. Waste from nuclear processing plants (Bolsunovsky, 2004; Freed et al., 2004; Gee et al., 2005; Lenhard et al., 2004) such as Hanford, Oak Ridge National Laboratory, Idaho Engineering and Environmental Laboratory, Savannah River National Laboratory, Paducah Chemical Plant, and others around the world has been disposed of in both unlined trenches and underground storage tanks which have now leaked contaminants into the vadose zone in many places. Chemical processing plants (Malina, 2004), oil refineries and private filling stations, and even metropolitan landfills (El Naqa, 2004; Fityus et al., 1999) are also known to have leaked waste to the subsurface either through the use underground storage tanks (UST) to store fuel or waste ponds (Aichberger et al., 2005; Gaganis et al., 2004; Livingston and Islam, 1999). Mining industries also have waste that tends to accumulate hazardous chemicals and/or compounds which then have the potential to penetrate the soil surface (Lefebvre et al., 2001; Quejido et al., 2005; Romano et al., 2003). Agricultural chemicals also have the potential to penetrate the soil

surface once applied to the field (Coquet et al., 2004; Muszkat et al., 1993; Rosen et al., 2004). These chemicals either get consumed by plants, runoff the field with excess rainwater, and/or eventually penetrate the soil surface. Also, there has been an increased concern about soil contamination from the use of depleted uranium weapons which may lead to subsurface and groundwater contamination (Bikit et al., 2005; DiLella et al., 2004).

These are just a few examples of sources of contamination and how they may reach the subsurface and possibly the underlying groundwater. There are a lot of factors that influence contaminant transport such as the geology of the area, precipitation, vegetation, depth to groundwater, contaminant interactions with various mineral surfaces, chemistry of the waste, etc. It is necessary to understand which of these factors plays a significant role in contaminant transport and exactly how each of these factors impacts transport at the various sites to improve predication of contaminant migration and remediation efforts.

The work presented here focuses on contaminant transport in the vadose zone at the U.S. Department of Energy's Hanford site located just north of Richland, WA which during the cold war era, produced weapons grade plutonium. The site is located in the semi-arid climate of central Washington State and receives ~16 cm of rainfall annually with depth to the groundwater of ~100m across the site. The vadose zone is composed of sediments from the Hanford formation flood deposits, the Cold Creek unit, and the Ringold Formation at the groundwater interface. Processing waste has historically been disposed of in cribs, solid waste burial pits, ponds, and/or underground storage tanks which reside within the Hanford formation which is composed of unconsolidated sand

with small interbedded layers of silt and clay. The most concentrated waste was stored in underground storage tanks. About one-third of the tanks have leaked, resulting in the discharge of more than 4 million liters of hazardous and radioactive waste in the vadose zone. Some of these tanks contain radionuclides such as Sr-90, Co-60, U-238, as well as organic chelating agents such as ethylenediaminetriacetic acid (EDTA) and nitrilotriacetic acid (NTA) with high levels of nitrate and alkalinity (DOE, 1996; Knepp, 2002). Monitoring of the site has detected “accelerated” transport as contamination has been detected further from the original spills than initially predicted by current conceptual models (DOE, 2002b) therefore suggesting the need for an improved understanding of transport in the Hanford vadose zone.

The goal of this project is to provide an improved understanding of coupled hydrologic and geochemical processes governing contaminant transport in the Hanford formation – an unconsolidated sandy unit with interbedded silt and clay lenses. The objectives are to determine the impact of sedimentary bedding and the direction of flow relative to bedding impact unsaturated flow and transport of contaminants such as ^{90}Sr , U(VI) , and Co(II)EDTA .

Part 2 describes and discusses the results from multiple non-reactive tracer displacement experiments conducted in several large undisturbed cores to quantify physical non-equilibrium processes that may occur during unsaturated flow across bedding and parallel to bedding. Differences between unsaturated vertical and horizontal flow are observed and discussed. It is hypothesized that the physical non-equilibrium processes observed will also effect the geochemical reactions during flow across bedding versus flow parallel to bedding.

Part 3 illustrates how sedimentary bedding and direction of unsaturated flow influence strontium transport in Hanford sediments. Specifically, this chapter investigates the prevalence of strontium transport as a divalent cation or as an EDTA⁴⁻ complex as it has been shown that EDTA may enhance the migration of strontium. Results from batch sorption experiments, repacked saturated column experiments, and unsaturated transport through an undisturbed core elucidate the effects of EDTA and unsaturated hydrology on strontium transport. Core disassembly and sequential extractions were done to determine the reactive mineralogies associated with the sorbed strontium during unsaturated transport. This chapter provides a good use of a variety of experimental techniques in order to improve the understanding of coupled hydrogeochemical mechanisms responsible for contaminant transport during unsaturated flow parallel and across bedding in unconsolidated sands such as the Hanford formation.

Part 4 describes the results of U(VI) and Co(II)EDTA unsaturated flow across bedding and flow along bedding in undisturbed sandy cores from the Hanford formation. Four different cores each at different moisture contents were used in this chapter – two vertical and two lateral cores. Results illustrate the effects of hydrology on geochemical reactions and therefore reactive transport.

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PART 2

QUANTIFYING THE EFFECTS OF SMALL-SCALE HETEROGENEITIES ON FLOW AND TRANSPORT IN UNDISTURBED CORES FROM THE HANFORD FORMATION

This part is a lightly revised version of a paper by the same name published in the Vadose Zone Journal in 2003 by M.N. Pace, M.A. Mayes, P.M. Jardine, T.L. Mehlhorn, J.M. Zachara, B.N. Bjornstad. Note that an error was found in the original publication and an errata was published with the corrected data. This errata is located immediately following this Part.

Pace, M.N., M.A. Mayes, P.M. Jardine, T.L. Mehlhorn, J.M. Zachara, and B.N. Bjornstad. 2003. Quantifying the effects of small-scale heterogeneities on flow and transport in undisturbed cores from the Hanford formation. Vadose Zone Journal, 2: 664-676.

ABSTRACT

Accelerated migration of contaminants in the vadose zone has been observed beneath tank farms at the U.S. Department of Energy's Hanford Reservation, Richland, WA. This paper focuses on quantifying hydrologic processes that control the fate and transport of contaminants in the unsaturated sediments beneath the Hanford tank farms. The experimental approach involved the use of field relevant, long-term unsaturated non-reactive transport experiments in undisturbed sediments from the Hanford Formation. Undisturbed sediment cores were collected from a laminated fine-grained sand unit within the Hanford Formation in both the vertical direction (flow cross bedding) and the horizontal direction (flow bedding parallel). Laboratory scale saturated and unsaturated flow experiments were conducted using multiple non-reactive tracers to investigate hydrologic processes controlling the vertical and lateral spread of contaminants. The non-reactive tracers differ in their free-water molecular diffusion coefficients thus providing a quantitative measure of diffusional processes and the presence of immobile water. Asymmetric breakthrough curves and co-elution of tracers were observed during saturated flow in both horizontal and vertical cores indicating advection enhanced solute

dispersion with no accompanying immobile water. Unsaturated tracer transport in the vertical and horizontal cores resulted in earlier breakthrough, asymmetric breakthrough curves, and differential breakthrough of tracers where the elution of PIPES preceded that of PFBA, which preceded that of Br⁻. These results suggest that physical non-equilibrium processes such as preferential finger flow coupled with immobile water may control the unsaturated movement of contaminants in the Hanford Formation.

KEY WORDS: Laminated sediments, preferential flow, immobile water, displacement experiments, PFBA

INTRODUCTION

The U.S. Department of Energy's Hanford Reservation is a nuclear materials processing facility located in the Columbia River Basin in south central Washington. The area receives an average annual rainfall of 16 cm/year. Depth to groundwater averages around 100 m across the site. The vadose zone is composed of sediments from the Hanford Formation, the Cold Creek Unit, and the Ringold Formation at the groundwater interface. Processing waste has historically been disposed of in cribs, solid waste burial pits, ponds, and/or underground storage tanks which reside within the Hanford Formation. The most concentrated wastes were stored in single-shelled tanks in the 200 area of the Hanford Site (Bjornstad, 1990; Agnew et al., 1997). About one-third of the tanks in the 200 Area have leaked resulting in more than 4 million liters of hazardous and radioactive waste in the vadose zone. Relatively mobile radionuclides such as ⁹⁹Tc, ¹²⁹I, U, and ³H have traveled further than predicted by current models and have been detected in the groundwater, which eventually flows to the Columbia River

(Dirkes and Hanf, 1997; Hartman and Dressel, 1997). This suggests the mechanisms of such accelerated contaminant migration remain unclear. It is thought that vertical preferential flow may occur along clastic dikes or uncased well boreholes. Finger flow that results from unstable wetting fronts may also increase the rate of vertical transport in stratified media (Ritsema et al., 1993, 1998; Glass et al., 1988, 1989; Sililo and Tellam, 2000). Variation in hydraulic conductivity caused by differences in grain size may also result in lateral flow and transport along bedding planes (Newman et al., 1998). Further, diffusion into finer grained media may slow the transport of contaminants and may also act as a source of contamination as clean water is transported through the formation. An enhanced conceptual understanding of the influence of physical heterogeneities within the Hanford Formation (e.g. variations in grain size, lithologic stratification, and discontinuities) on contaminant mobility is essential for accurate prediction of flow and transport processes beneath the tank farms.

The effects of physical heterogeneities in undisturbed media on contaminant flow and transport may be quantified by performing miscible displacement experiments using multiple non-reactive tracers that vary in their aqueous rate of diffusion. This technique has previously been used to quantify the effects of physical non-equilibrium processes (PNE) in structured media (Jardine et al., 1998, 1999; Langner et al., 1999; Becker and Shapiro, 2000; Moline et al., 2001; Mayes et al., 2003). PNE results from fast preferential flow coupled with slow diffusion into less mobile water regimes. These phenomena result in separation of tracer breakthrough curves (BTC) due to differential rate of tracer mobility between fast and slow flowing water regimes.

In an effort to better understand how solutes migrate in semi-arid regions, numerous experiments have been conducted in packed columns of silty-sandy media using a single non-reactive tracer (Bond and Wierenga, 1990; Porro and Wierenga, 1993; Padilla et al., 1999; Gamerdinger and Kaplan, 2000). Flow and transport in saturated packed columns typically result in symmetric BTC, while asymmetric BTC are observed under unsaturated conditions. As packed columns become unsaturated, the larger pores are drained, resulting in areas of immobile water (Padilla et al., 1999; Gamerdinger and Kaplan, 2000). Consequently, slow diffusion of tracer into these relatively immobile regions results in more asymmetric BTCs than observed under saturated conditions. The rate of exchange between the mobile and immobile water is typically quantified by modeling BTCs for single non-reactive tracers (Bond and Wierenga, 1990; Porro and Wierenga, 1993; Padilla et al., 1999; Gamerdinger and Kaplan, 2000). Breakthrough asymmetry is not always a good indicator of diffusion controlled mass exchange between different pore water regimes (Becker and Shapiro, 2000), thus single tracer experiments often lack sufficient information for quantifying PNE processes.

A select few studies have successfully combined the use of multiple non-reactive tracers in miscible displacement experiments with undisturbed, stratified silty/sandy media (Mayes et al., 2003) in an effort to quantify PNE processes. Mayes et al. (2003) used the multiple tracer technique to show that undisturbed stratified silty/sandy media of the Ringold Formation has differing responses to unsaturated flow depending on the direction of flow relative to the direction of bedding. When flow was parallel to bedding, no tracer separation was observed, which suggested that diffusional exchange between beds was inhibited during unsaturated conditions. When flow was perpendicular to

bedding, early breakthrough and separation of tracers was observed, which suggested preferential finger flow, formation of perched water and diffusional exchange within zones of perched or immobile water occurred during unsaturated conditions. The anisotropic flow and transport behavior exhibited by the Ringold Formation demonstrated the sensitivity of unsaturated flow to small-scale sedimentary and lithologic features.

The study of Mayes et al. (2003) focused on the flow and transport processes of an intensively stratified portion of the Miocene-Pliocene age Ringold Formation that was deposited in a lacustrine environment, followed by several million years of post-depositional alterations. The portion of the Ringold Formation included in Mayes et al. (2003) was composed of small, much finer-grained laminated silt and sand beds (cm to mm scale) compared to the Hanford Formation. The Pleistocene age Hanford Formation, was formed by the floods of glacial Lake Missoula, and contains deposits such as fine-grained channel fills and coarse-grained flood bars. Such deposits contribute to the wide variation in grain size, which is characteristic of the Hanford formation. The young age of the Hanford formation suggests that less post-depositional alteration of minerals occurred compared to older formations such as the Ringold. Therefore, the diversity in age, sedimentology, and stratigraphy between the two formations demands additional studies to characterize the dominant hydrologic processes in the Hanford Formation. Further, only the use of identical experimental techniques would allow an objective comparison between the Hanford and Ringold Formations.

The goal of this study is to provide an improved understanding of the flow and transport processes that influence the migration of contaminants in the Hanford

Formation in the Hanford Reservation vadose zone. The objectives are to use a multiple tracer strategy in miscible displacement experiments to determine the effects of lithological stratification and discontinuities on flow and transport at various moisture contents within the Hanford Formation. Lateral versus vertical flow will be investigated by comparison of transport through horizontal cores where flow is parallel to bedding and vertical cores where flow is perpendicular to bedding. The presence of preferential flow and matrix diffusion will be determined using multiple non-reactive tracers.

MATERIALS AND METHODS

Collection of Undisturbed Cores

The vadose zone beneath the Hanford Reservation is approximately 100 m deep with the Hanford Formation comprising the upper 70 m. The Hanford Formation is a Pleistocene age deposit formed from multiple floods of glacial Lake Missoula to the east (Bjornstad, 1990; Lindsay, 1995). It is a heterogeneous media of unconsolidated laminated coarse and fine sands that are interbedded with small-scale clay layering (Fig. 1, 2, note all Figures are located at the end of the Part). Often boulder- and gravel-sized rocks are intermixed with the media to create a highly heterogeneous pore size distribution.

Undisturbed cores from the Hanford sediments were collected from the Environmental Restoration Disposal Facility (ERDF) in the 200W Area of the Hanford Reservation (Fig. 1). Freshly exposed escarpments were opened at a depth of ~20 m (Fig. 2) and undisturbed cores were isolated using a hand-sculpting method described by

Jardine et al. (1993) and Reedy et al. (1996). The technique entailed isolating a small pedon, carving the sample to its finished dimensions (~20 cm x 20 cm), and coating with paraffin wax. A relatively high ambient moisture content facilitated collection of the sandy, unconsolidated media. Figure 3 illustrates the collection of undisturbed horizontal (flow parallel to bedding) and vertical (flow perpendicular to bedding) cores from within a fine-grained layer. The cores were placed in a wood crate, entombed in loose sediment, and shipped to ORNL in a vehicle loaded on a flat bed semi-truck. Disturbed material was also collected for characterization of select soil chemical and physical properties (Table 1, note all Tables are located at the end of the Part) and for the determination of the moisture retention function.

Determination of the Moisture Retention Function

The moisture retention function (MRF) was determined for the Hanford Formation material following standard methods (Klute, 1986) on triplicate samples. Brass sleeves, 8.5 cm ID and 6 cm tall, were packed with disturbed media to a bulk density of ~1.5 g/cm³ (Table 2). Samples were saturated from the bottom with 5 mM CaCl₂ using a Mariotte device and then placed into a flow cell for pressures from zero to atmospheric (0 to 1000 cm of water) (Soil Measurement Systems, Tucson, AZ). For pressures greater than atmospheric, small packed rings (5.4 cm ID and 1.1 cm tall) of sediment were placed onto large ceramic plates within the Model 1600 Pressure Extractor (Soil Moisture Co., Santa Barbara, CA). A tension was applied to the samples in the flow cell and allowed to drain. The sample weight was recorded once water loss ceased and

the sample weight remained constant. This was repeated over the range of applied tensions.

Experimental Apparatus

After core shipment, the wax coating was carefully removed from the large undisturbed sediment cores and PVC pipe was placed over the media. The annulus between the sediment and the PVC was then filled with 3M Gray/White epoxy (3M Company, Ann Arbor, MI) and allowed to harden. Airtight endcaps fabricated from acrylic and PVC were attached to the lower end of the PVC encased core as shown in Fig. 4. A multi-channel peristaltic pump (Watson-Marlow Ltd., Cornwall, England) was used to deliver influent to the upper soil boundary where the top of the core was covered with a nylon membrane (-30 cm bubbling pressure) in an effort to evenly distribute the influent. Each drip point from the peristaltic pump created a circular pattern on the nylon membrane with a diameter of ~ 3 cm (larger diameters were observed with higher core moisture contents). There were a total of 11 drip points per pump with a total area of the core equal to ~ 314 cm². The rate of influent delivery for different core saturation levels was estimated from modeled water retention data and generated $K(h)$ functions using the code Retention Curve (van Genuchten et al., 1991). The top of the core was covered with a plexiglass sheet to minimize evaporation. The lower boundary was maintained with either a -30 cm or a -600 cm bubbling pressure (bp) nylon membrane (Soil Measurement Systems, Tucson, AZ) in direct contact with the soil using a perforated aluminum disc held in place by the acrylic/PVC endcap. The -30 and -600 cm bp membranes were used in saturated and unsaturated flow experiments, respectively. Tension at the lower

boundary was controlled by a vacuum chamber (Soil Measurement Systems, Tucson, AZ) that housed an internal fraction collector (Isco Corp., Lincoln, NE). A vacuum gauge (Dwyer Instruments, Michigan City, Indiana) and regulator (Moore Products, Springhouse, PA) were used to regulate the house vacuum source. Soil tension was measured using tensiometers made of one bar standard ceramic cups (diameter 0.635 cm, length 2.858 cm) (Soil Moisture Co., Santa Barbara, CA) placed around the core at various depths approximately 3 cm into the undisturbed cores. The tensiometers were used as a qualitative tool to monitor daily matric potentials. Tensiometer readings typically varied slightly from day to day but were usually stable throughout an experiment. Any significant change in the tensiometer readings indicated a possible change in the moisture content of the core, upon which the core was reweighed and a new moisture content was calculated.

Miscible Displacement Experiments

The undisturbed cores were assembled and weighed prior to experimentation and corrections were made for ambient water content before saturation. The cores were slowly saturated from the lower boundary using a solution of 5 mM CaCl_2 , pH adjusted to 8.2 (the soil pH) using NaOH or KOH, and their saturated weights recorded. Solutions were delivered to the saturated cores using a constant head Mariotte device that maintained a ponded water depth of ~1 cm at the upper boundary of the cores. Saturated miscible displacement experiments were conducted with gravity-induced flow. An estimated saturated pore volume was determined from the Br^- breakthrough curve (BTC) at $C/C_0 = 0.5$ for each core. Actual values would require destruction of the undisturbed

cores, and this was deemed unnecessary considering the future scientific value of the cores.

Upon completion of the saturated experiments, the cores were attached to a vacuum-regulated chamber for unsaturated flow experiments (Fig. 4). The cores were allowed to drain at a desired tension set in the vacuum chamber until water loss ceased and the core weight was again recorded. The carrier solution (5 mM CaCl_2 or 0.1 M NaCl pH = 8.2) was then delivered to the upper boundary of the cores using a multi-channel peristaltic pump (Fig. 4). Samples were collected until the effluent flow rate and the core tensions were stable. The cores were then reweighed. The difference between this weight and the saturated core weight was subtracted from the saturated pore volume and then divided by the total volume of the core to determine the unsaturated moisture content. Flow of the multiple non-reactive tracer solution was then initiated. A flow-interruption experiment was also initiated on one of the cores, where an interruption in influent flow occurred that lasted 11 days. Flow was reinitiated with the carrier (washout) solution until tracer concentration was less than the detection limit. Flow interruption experiments provide a method that also identifies the extent of PNE during solute migration (Reedy et al., 1996). All experimental parameters are listed in Table 4.

The non-reactive tracer influent solution used in saturated miscible displacement experiments consisted of 0.5 mM Br^- as $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$, 0.5 mM pentafluorobenzoic acid (PFBA), 1.0 mM piperazine-1-4-bis(2-ethanesulfonic acid) (PIPES), 4.4 mM CaCl_2 , and 2.4 mM KOH , which resulted in an ionic strength of 0.015 M consistent with the carrier solution of 5 mM CaCl_2 . For unsaturated displacement experiments, the tracer solution was prepared in 0.1 M NaNO_3 or 0.1 M NaCl , as was the carrier solution, to be more

representative of the far-field vadose zone beneath the Hanford tank farms. The pH of the tracer and carrier solution was adjusted to 8.2 with KOH so that the solution pH was equivalent to that of the soil. The difference in ionic strength between the saturated and unsaturated tracer solution will not effect the elution of the anionic non-reactive tracers. Jardine and Taylor (1995), Moline et al. (2001), and Mayes et al. (2003) have used PIPES as a non-reactive tracer. Many investigators have used PFBA as a non-reactive tracer in miscible displacement experiments (Bowman, 1984; Bowman and Gibbens, 1992; Hu and Brusseau, 1994, 1995; Jardine and Taylor, 1995; Langner et al., 1999; Gamerdinger and Kaplan, 2000; McCarthy et al., 2000; Kung et al., 2000; and Mayes et al., 2003). PIPES and PFBA are both large organic molecules (Fig 5) that are deprotonated at the experimental pH values. The chemical structure of each tracer is illustrated in Fig.5; note the circular shape of PFBA and the linear shape of PIPES. The three non-reactive tracers used in this study (Br^- , PFBA, PIPES) differ in molecular size and therefore their free-water diffusion coefficient. Table 3 lists each tracer's free-water diffusion coefficient as well as pK_a values for PIPES and PFBA. The molecular diffusion coefficients for PIPES and PFBA have been calculated according to the Hayduk and Laudie (1974) method (Tucker and Nelken, 1982). This method applies to large spherical molecules diffusing in a continuous solution. The linear shape of PIPES may result in greater error associated with its diffusion coefficient estimate; however, no published estimates for PIPES are available. The PFBA diffusion coefficient calculated by this method differs from published estimates by ~5% (Bowman, 1984; Benson and Bowman, 1994). The Hayduk and Laudie method was used for internal consistency when estimating the PIPES and PFBA diffusion coefficients.

The concentration of Br^- , PFBA, and PIPES was quantified simultaneously using a low-pressure liquid chromatography system with UV detection (190 nm) (Model DX-300 and DX-600 Gradient Pump, Dionex Corp., Sunnyvale, CA). An eluent mix of 1.6 mM HCO_3^- and 1.6 mM CO_3^{2-} was used for elution of Br^- (3.0 min) and PFBA (3.2 min) in an AS-4A column with a flow rate of 2 ml min^{-1} . For the elution of PIPES (6.8 min), the eluent mix was increased at 1.8 min to 4.8 mM HCO_3^- and 4.8 mM CO_3^{2-} . For samples with high Cl^- , the AS-9 column was used with an eluent mix of 9 mM CO_3^{2-} and a flow rate of 1 ml min^{-1} . Detection limits, determined from standard curves, were approximately 0.005 mM for Br^- and PFBA, and 0.02 mM for PIPES. A Total Organic Carbon Analyzer (Model # TOC-5000, Shimadzu, Japan) was also used to determine mass recovery and to confirm the total concentrations of PIPES and PFBA.

Modeling the Displacement Experiments

The steady-state transport of multiple non-reactive tracers through saturated and unsaturated undisturbed cores was mathematically described using two codes based on the convection-dispersion equation (CDE): CXTFIT (Parker and van Genuchten, 1984a) and Stopflow (Reedy et al., 1996). Flux averaged effluent concentrations were used in all modeling, as it is more appropriate for conditions with lower P_e values (Parker and van Genuchten, 1984b; van Genuchten et al., 1986; Jardine et al., 1988; Schulin et al., 1987; Barry and Sposito, 1988). In the absence of physical non-equilibrium processes (i.e. no tracer separation), the CDE model in CXTFIT was used to describe transport. In the presence of perceived PNE (separation of tracers), the mobile-immobile model (MIM) in CXTFIT should be used to describe the experimental data. Input parameters for CXTFIT

were effluent concentrations (C/C_0), length of core ($L(\text{cm})$), time (pore volume), mean water pore velocity ($V(\text{cm hr}^{-1})$) where $V = \text{flow rate} / (\pi r^2 \theta)$, input pulse, and the retardation factor (R). Theoretically, $R = 1$ for conservative non-reactive tracers and this was true for experiments conducted near saturation. A dispersion coefficient ($D(\text{cm}^2 \text{hr}^{-1})$) was determined for each tracer by a single-parameter curve fit while all other parameters remained fixed when using the CDE model. In the MIM model optimized parameters β (dimensionless F , where F is the fraction of mobile water), ω (dimensionless $\alpha (\text{hr}^{-1})$ where α is the first order rate coefficient), and D were determined by fitting the model to the observed data holding all other parameters constant.

Mathematically, flow interruption can be accounted for in the MIM with Stopflow option (Stopflow computer code) by assuming $V = 0$ and $D = D_0 = D_e/\tau$ during conditions where flow has been temporarily stopped (D_e and D_0 are the effective and actual molecular diffusion coefficient, respectively, and τ is a tortuosity factor). Therefore, it is assumed that transport of non-reactive tracers during flow interruption can be described by molecular diffusion within the mobile water regime and the rate of exchange between the mobile and immobile phase (Reedy et al., 1996). For model simulations of experimental data, D was estimated by the CDE in CXTFIT for each non-reactive tracer using only the breakthrough portion of the data. The computer code Stopflow was then used to simulate the experimental data using D estimated by the CDE. Input parameters for Stopflow are the same as for CXTFIT in addition to τ ($\tau = 0.7$, arbitrarily chosen as it was observed to have very little effect of the model results). All physical parameters were held constant and α was varied in order to best simulate the experimental data.

Values of α were chosen that best described the observed concentration perturbations that resulted after the flow interrupt. This criterion was used since mass transfer (α) between pore regimes is essentially the only process occurring during flow interruption (Reedy et al., 1996).

RESULTS AND DISCUSSION

Moisture Retention Function

Moisture retention functions (MRF) (Fig. 6) were determined for the Hanford Formation to quantify the drainage characteristics of the media. The initial saturated water content for all samples was ~ 0.40 and the air entry tension was approximately -30 cm of applied tension which was similar to that observed in Connelly et al. (1992) for fine-grained Hanford Formation media. Water loss was rapid until approximately -200 cm applied tension. The residual moisture content was ~ 0.05 , which also was similar to that of Connelly et al. (1992).

Miscible Displacement Experiments

Saturated flow and transport

Flow and transport through undisturbed cores under saturated conditions was mainly controlled by the direction of flow relative to bedding and the high pore water velocity obtained by gravity-induced flow. Relatively asymmetric breakthrough curves coupled with the synonymous breakthrough of the multiple tracers for both vertical and horizontal cores suggested an advective-dominated flow system (Fig. 7). Due to the method of saturation of the cores, air entrapment should not be disregarded as a possible

cause for preferential flow and asymmetric BTCs. Other possible reasons for the observed asymmetric BTCs are non-Fickian dispersion and heterogeneity of the media. The lack of observed tracer separation indicated that diffusive processes and the presence of immobile water regimes were minimal during saturated conditions possibly due to the high pore water velocities (Mayes et al., 2003). Simultaneous initial tracer breakthrough was observed in both the horizontal and vertical cores. However, at later times (1.2 – 2.5 PV) (Fig 7b) tracer concentrations in the vertical core were greater than the horizontal core due to greater advective-dominated flow parallel to bedding. In the horizontal core, flow is parallel to beds that have wide variations in pore velocity causing greater dispersion in the horizontal core. In the vertical core, flow crosses all beds and can only proceed as fast as the slowest pore water velocity, resulting in greater symmetry in the BTC. The tracer BTCs were adequately fit with the CDE model, the results for Br^- are shown in Fig. 7 and Table 5 (see errata for updated table). The adequacy of the model was consistent with the lack of matrix diffusion processes or immobile water influencing tracer migration. The differences between the horizontal and vertical cores are reflected in the lower Peclet numbers (P_e) and higher mean pore water velocity for the horizontal versus the vertical core (Table 5, see errata for updated table). The difference in observed dispersion in the horizontal and vertical core is a result of the anisotropy of the Hanford Formation and suggests a preference for lateral versus vertical flow.

Unsaturated flow and transport

Br⁻ tracer

Unsaturated flow in both horizontal and vertical cores (Figs. 8a and b, see errata for updated figure) resulted in earlier initial Br⁻ tracer elution compared to saturated conditions but more asymmetric BTCs at 95% and 99% saturation and increasingly symmetric BTCs at 60% and 40% saturation. These results are evidence of preferential finger flow and the development of immobile water due to multi-region flow (Padilla et al., 1999; Gamerding and Kaplan, 2000; Mayes et al., 2003). During unsaturated flow, larger pores are drained, resulting in partial disconnection of the primary porosity from the predominant flow paths. Regions of immobile water can develop allowing for mass exchange between immobile and mobile regions (e.g. preferential flow paths) to occur at water contents near saturation, which is typically governed by diffusive processes (Mayes et al., 2003). However, as water content decreases (60 and 40% saturated experiments) the flow path is isolated to fine-grained layers and less interaction with the immobile water occurs resulting in more symmetric BTCs as evidence by higher P_e values (Table 5, see errata for updated table). Such physical non-equilibrium processes are evidenced by more asymmetric BTCs, early breakthrough of tracers, (Fig. 8, see errata for updated figure) and lower P_e values (Table 5, see errata for updated table) compared to saturated flow. The results are similar to unsaturated experiments in packed semi-arid media (Padilla et al., 1999; Gamerding and Kaplan, 2000) and flow cross bedding cores from the Ringold Formation (Mayes et al., 2003), which show early breakthrough and more asymmetric BTCs relative to saturated conditions. However, these results differ from Ringold flow bedding parallel cores of horizontally-bedded sediments, which exhibited

minimal difference from saturated conditions (i.e. no preferential flow or matrix diffusion) (Mayes et al., 2003). This clearly suggests that different hydrologic processes govern unsaturated transport in the Hanford versus the Ringold Formation. Diffusion into immobile water is restricted in the Ringold flow bedding parallel cores because of the development of capillary barriers in the fine-grained bedding. In contrast, diffusion of tracers into immobile water is observed in the Hanford flow bedding parallel cores because of the presence of two distinct porosities – fine sands and clays (Fig. 2b), which are active at these water contents. These variations in results demonstrate the importance of small-scale differences in sedimentary structures when predicting flow and transport in unsaturated laminated silts and sands.

Multiple tracers

Observed separation of tracers and early breakthrough in the unsaturated horizontal core (flow parallel-bed) and vertical core (flow cross-bed) was also suggestive of physical non-equilibrium processes such as matrix diffusion and preferential finger flow (Fig. 9 and Fig. 10, see errata for updated figures). Differential tracer diffusion into immobile water most likely results in the observed tracer separation during breakthrough and washout. Ideal results should indicate the concentration of PIPES > PFBA > Br⁻ during breakthrough and washout since the D_e for Br⁻ > PFBA > PIPES (Table 3). Larger molecules with lower D_e , such as PIPES, are slower to diffuse into immobile water, thus should breakthrough or washout first. However, as tracers approach equilibrium, crossover of tracer concentration profiles should occur since tracers with larger D_e , such as Br⁻, should reach equilibrium first. This is shown experimentally and numerically by

Jardine et al. (1998, 1999) and Gwo et al. (1998). In the current study, tracer breakthrough and washout patterns were consistent with this scenario, for the most part, with larger separations of the tracer concentration being observed for the vertical core (Fig. 10, see errata for updated figure) versus the horizontal core (Fig. 9, see errata for updated figure). This suggested a greater propensity for immobile water regimes to develop in vertical cores where flow crosscuts sediment beds of varying grain size. The enhanced formation of immobile water in vertical cores is consistent with the development of unstable wetting fronts and immobile, perched water in stratified media, where a positive water head is needed for flow to occur (Mayes et al., 2003). In horizontal cores, flow is much more restrictive since it occurs along bedding minimizing the interaction with immobile water and thus the transfer of mass between beds is minimized as water content decreases.

Although the tracer breakthrough patterns are consistent with the presence of physical non-equilibrium processes, our data deviates from the ideal trends in two ways: (1) PFBA exhibits partial reactive behavior (C/C_0 plateaus near 0.8) and (2) PIPES reaches equilibrium very rapidly, avoiding tracer cross-over, which is suggestive of pore exclusion characteristics. The breakthrough and washout of PIPES compared to the other tracers is consistent with its large size and slow molecular diffusion rate. The early approach to equilibrium, however, suggested that PIPES was less likely to interact with immobile water regimes during transport, which may be related to size exclusion. The plateau region of the PFBA breakthrough curve was significantly removed from equilibrium, which suggested possible reactivity with the solid phase (Fig. 9a, see errata for updated figure). PFBA has successfully been used as a non-reactive tracer in

previous investigations (Hu and Brusseau 1994; Jardine et al., 1998; Langner et al., 1999; Kung et al., 2000; Mayes et al., 2003). However, the results of this study suggest that PFBA was reactive or degraded at longer times, as it never reached $C/C_0 = 1$. Effluent samples were reanalyzed on the IC and confirmed the original IC data. Total organic carbon analysis of effluent samples confirmed that PIPES and PFBA carbon was similar to that measured by IC. Mass balance of PFBA was 82% by both IC and TOC methods (Table 5, see errata for updated table), which strongly suggests that PFBA was either irreversibly sorbed or degraded. Geochemical reactivity is improbable since the system pH is 8.2 and the charge on PFBA and the solid phase will both be negative. Biological reactivity is a possibility since certain bacteria have been isolated that can degrade 4-fluorobenzoate and use it as their sole carbon source (Oltmanns et al., 1989; Jaynes, 1994; Song et al., 2000; Carvalho et al., 2002). Microbiological work was conducted to confirm this hypothesis. A phosphate-buffered minimal medium that consisted of potassium and sodium chloride and trace minerals was inoculated (25X dilution) with effluent from the core. The effluent contained 1.9×10^6 cells/ml as determined with acridine orange direct counts, and the inoculum was incubated in the presence of PFBA (0.6 mM) at 26°C for approximately 60 days. IC analysis indicated that PFBA had decreased 1.6X compared to controls, and that microbial cell numbers had increased. The results suggested that microorganisms possibly indigenous to the column were able to utilize PFBA or at least degradative by-products. Further work is needed to determine the processes involved in PFBA utilization and to identify the responsible microorganism(s) (M. Fields, ORNL, 2003, personal communication). Nevertheless, the observed order of tracer separation during early breakthrough and washout is similar to

studies that have used Br^- and PFBA in highly heterogeneous structured media that consists of a vast array of pore domains (Gwo et al., 1998; Jardine et al., 1998, 1999, 2001; Langner et al., 1999; Kung et al., 2000; Mayes et al., 2003). The observed order of tracer separation is different from that observed in the Ringold Formation (Mayes et al., 2003) where perched water in vertical or cross-bedded cores caused a reversal of the order of tracer separation. Perched water was not observed in the Hanford Formation cores, most likely because it is dominated by fine-sands whereas the Ringold is dominated by silt-sized particles. This supports the notion that the Upper Ringold and Hanford are distinct sedimentary units with different hydrologic transport properties.

In an effort to further substantiate the presence of PNE during solute transport, a flow interrupt was administered on the vertical core (99% saturated) at approximately 2.3 pore volumes (PV) for a duration of ~11 days (Fig. 10, see errata for updated figure). Once flow was reinitiated, a significant concentration perturbation was observed for Br^- and PFBA but not for PIPES. The concentration perturbations for PFBA and Br^- indicated that these tracers were not in equilibrium with the pore water during transport most likely due to rate-limited diffusion into immobile regions (Murali and Aylmore, 1980; Brusseau et al., 1989; Koch and Fluhler, 1993; Reedy et al., 1996; Brusseau et al., 1997; Mayes et al., 2000). The lack of an observed concentration perturbation for PIPES is consistent with the observation that PIPES had reached an apparent equilibrium condition (i.e. $C/C_0 = 1$) prior to Br^- and PFBA. However, PIPES has the smallest diffusion coefficient (Table 3) and should be the last to reach equilibrium with the immobile water. Therefore, the rapid approach to equilibrium and the lack of perturbation in PIPES suggests that this tracer may have been excluded from some

portions of immobile water in the undisturbed cores possibly because of its large, bulky size (Fig. 5).

The MIM model with a flow-interrupt option (computer code Stopflow) was used to simulate the vertical core breakthrough curve using an estimation of 20% immobile water and mass transfer rates between mobile and immobile domains ranging from $4\text{e-}4$ to $4\text{e-}3\text{ h}^{-1}$ for the various tracers (Table 5, see errata for updated table). Note that this was a simulation so no statistics are associated with the model parameters. The transfer coefficient (α) of each tracer should correspond with their diffusion coefficient so that $\text{Br}^- > \text{PFBA} > \text{PIPES}$. However, the transfer coefficients (α) obtained from the MIM (Table 5, see errata for updated table) were an order of magnitude greater for PIPES than for PFBA and Br^- , which is surprising given the slow rate of diffusion for PIPES. It is hypothesized that size exclusion of PIPES may be related to inaccessibility of PIPES to immobile water regimes within clay layers prominent in the Hanford Formation (Fig. 2) resulting in a higher α value than would be expected for PIPES, no observed perturbation in the flow interrupt experiment, and a rapid rise to equilibrium. These conclusions could have implications concerning the transport of bulky organic complexes beneath the tank farms.

Tracer separation, asymmetric and early breakthrough behavior suggests the presence of more than one pore domain within the horizontal core, therefore the MIM model would be appropriate for the data. The MIM model was initially used, but consistently failed and defaulted to the CDE model. This suggests that the MIM model was insensitive to the observed physical non-equilibrium processes, while the CDE model was found to adequately describe the observed tracer breakthrough (Table 5, Fig.

9, see errata for updated table and figure). In order to use the CDE at lower water contents, the retardation of the non-reactive tracers was fitted to values less than 1 to account for the early breakthrough that occurs due to media bypass and preferential flow (Gamerding and Kaplan, 2000). The fitted retardation factor for Br⁻ and PIPES in the 60% saturated horizontal core was 0.57 and in 40% saturated vertical core was 0.47 (Table 5, see errata for updated table). It was assumed that Br⁻ and PIPES should have the same retardation factor and that any difference in the BTC was due to diffusion. Modeling of PFBA was achieved by disregarding the mass loss by microbial degradation. These findings suggest that the MIM model is insensitive to small, but significant amounts of immobile water and demonstrate the importance of using multiple non-reactive tracers to quantify flow and transport in heterogeneous media versus the use of single tracers.

CONCLUSIONS

Our results showed that small differences in the degree of saturation and heterogeneity of subsurface media could have a significant influence on flow and transport of contaminants in the vadose zone beneath the Hanford tank farms. Through the use of a multiple tracer technique and undisturbed core technology, we were able to quantify the influence of preferential flow and the formation of immobile water regimes during solute transport in the Hanford Formation. Enhanced advective dominated flow in the saturated horizontal cores (flow bedding parallel) versus vertical cores (flow cross bedding) indicated that preferential flow along bedding may be preferred over flow across bedding forcing anisotropic lateral flow in the subsurface formation. Anisotropic

flow occurs even at lower water contents as evident by the greater dispersion in the horizontal cores versus the vertical core. Separation of multiple non-reactive tracers that had different rates of diffusion, early breakthrough of tracers, and a change in BTC symmetry from more asymmetric at slightly unsaturated conditions to increasingly symmetric at more unsaturated conditions indicated that preferential flow, media bypass, and the formation of immobile water regimes influenced transport at various water contents. Preferential flow in more conductive layers may result in accelerated transport of contaminants, while immobile water may act as a long-term source / sink for contamination in the vadose zone. Overall, our results indicated the importance of physical non-equilibrium in the Hanford vadose zone, which is due to a significant degree of heterogeneity between adjacent sediment layers in the Hanford Formation. Complex layering of coarse- to fine-grained sand and small-scale clay layers present in the Hanford Formation media can therefore be expected to influence contaminant mobility beneath the tank farms. It is uncertain how the heterogeneity of the Hanford Formation will affect flow and transport under significantly lower water contents. Research is underway to provide an improved conceptual understanding of flow and transport beneath the Hanford tank farms in an effort to aid in the prediction of contaminant movement and remediation of the site.

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Table 1. Select chemical, physical, and mineralogical characteristics of the Hanford Formation used in this study (Roh et al. 2002).

Chemical Properties	
Total Inorganic Carbon	0.22 %
Total Organic Carbon	0.02 %
Poorly Crystalline Iron Oxides	0.51 (g Fe / kg soil)
Total Free Iron Oxides	4.90 (g Fe / kg soil)
Cation Exchange Capacity (CEC)	4.88 (cmol / kg soil)
Particle Size Analysis and Mineralogy	
Sand (> 50 μm)	Quartz > Plagioclase >
95 %	Mica > Kaolinite >
	Chlorite > Calcite
Silt (2-50 μm)	Quartz > Mica >
4 %	Plagioclase > Kaolinite >
	Chlorite > Smectite
Clay (< 2 μm)	Illite > Kaolinite >
1 %	Chlorite/HIV* >
	Smectite > Quartz >
	Plagioclase
Fine Clay (< 0.2 μm)	Illite > Kaolinite >
	Chlorite/HIV* >
	Smectite > Quartz >
	Plagioclase
*hydroxy-interlayered vermiculite	

Table 2. Moisture retention function experimental parameters.

Sample	Bulk density (g cm ⁻³)
HFH1	1.445
HFH2	1.480
HFH3	1.480
HFV1	1.524
HFV2	1.491
HFV3	1.536

[HFV = Hanford Fine material collected near the vertical core, HFH = Hanford Fine material collected near the horizontal core, # = replicates.]

Table 3. Physical characteristics of the non-reactive tracers (Mayes et al., 2003).

Tracer	Diffusion Coefficient (D _e) m ² s ⁻¹	pK _a
Br ⁻	^a 18.7 x 10 ⁻¹⁰	-
PFBA	^b 7.8 x 10 ⁻¹⁰	^c 2.7
PIPES	^b 5.2 x 10 ⁻¹⁰	^d < 3, 6.8

^a Bowman, 1984.

^b Calculated by the Hayduk and Laudie (1974) method (Tucker and Nelken, 1982).

^c McCarthy et al., 2000; Benson et al., 1994.

^d Good et al., 1966.

Table 4. Experimental parameters of undisturbed Hanford Formation saturated and unsaturated miscible displacement experiments (HH = Hanford horizontal core, HV = Hanford vertical core, -sat = 100% saturated conditions, -#% = percent saturation).

Core	Experimental Parameters			
	K _{sat} (cm hr ⁻¹)	Radius (cm)	Pulse (PV)	VC tension (cm)
HH-sat	13.6	11.0	7.3	0
HV-sat	2.77	10.5	2.4	0
HH-95%		11.0	16	-54
HV-99%		10.5	2.6	-60
HH-60%		11.0	29	-160
HV-40%		10.5	1.4	-160

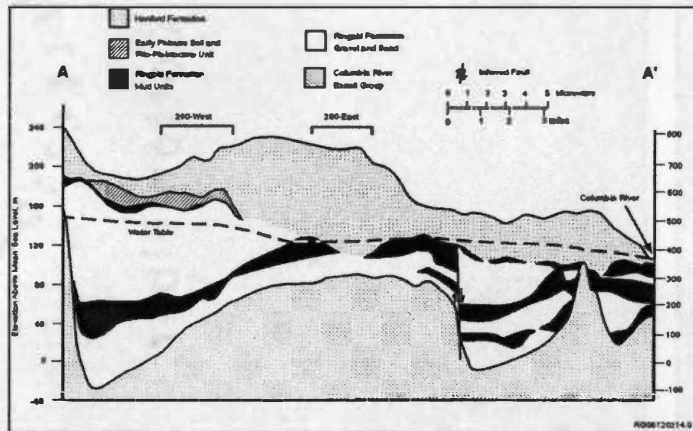
[PV = pore volume, VC = vacuum chamber]

Table 5. Modeling results of undisturbed Hanford Formation saturated and unsaturated breakthrough curve data. Due to similarities, model fits of HH-sat and HV-sat PFBA and PIPES were omitted (see errata for updated table).

	Mass recovery (%)	Model	Model Parameters							
			R	V (cm hr ⁻¹)	L (cm)	P _e	θ	F	α (hr ⁻¹)	r ²
HH-sat Br ⁻	97	CDE	1	41.92	23	17.30 ± 10.62	0.3250	NA	NA	0.9673
HV-sat Br ⁻	98	CDE	1	12.00	21	27.37 ± 9.58	0.4090	NA	NA	0.9782
HH-95% Br ⁻	101	CDE	1	0.0961	23	5.87 ± 7.26	0.3097	NA	NA	0.9409
PFBA	82	CDE	1	0.0961	23	6.10 ± 18.81	0.3097	NA	NA	0.8503
PIPES	99	CDE	1	0.0961	23	11.55 ± 3.56	0.3097	NA	NA	0.9929
HV-99% Br ⁻	100	MIM	1	0.0753	21	6.67 ± 2.79	0.4089	0.80	4.17e-4	NA
PFBA	87	MIM	1	0.0753	21	6.02 ± 3.27	0.4089	0.80	2.08e-4	NA
PIPES	111	MIM	1	0.0753	21	9.58 ± 4.91	0.4089	0.80	4.17e-3	NA
HH-60% Br ⁻	94	CDE	0.5706 ± 0.030	0.1196	23	10.86 ± 1.76	0.1978	NA	NA	0.9836
PIPES	93	CDE	0.5706 ± 0.030	0.1196	23	7.51 ± 2.38	0.1978	NA	NA	0.9890
HV-40% Br ⁻	95	CDE	0.4658 ± 0.014	0.1521	21	13.61 ± 3.32	0.1614	NA	NA	0.9643
PIPES	95	CDE	0.4658 ± 0.014	0.1521	21	17.89 ± 4.52	0.1614	NA	NA	0.9705

[MIM = mobile – immobile model simulation (with Stopflow option), CDE = convective dispersion equation model, R = retardation factor, V = mean pore water velocity, L = length of core, P_e = pecelet number, θ = water content (θ = (PV_{saturated} - ΔSaturated and unsaturated weight) * 1000) / V_t), F = fraction mobile water, α = mass transfer coefficient (hr⁻¹). Confidence intervals are given for fitted parameters.]

(a)



(b)

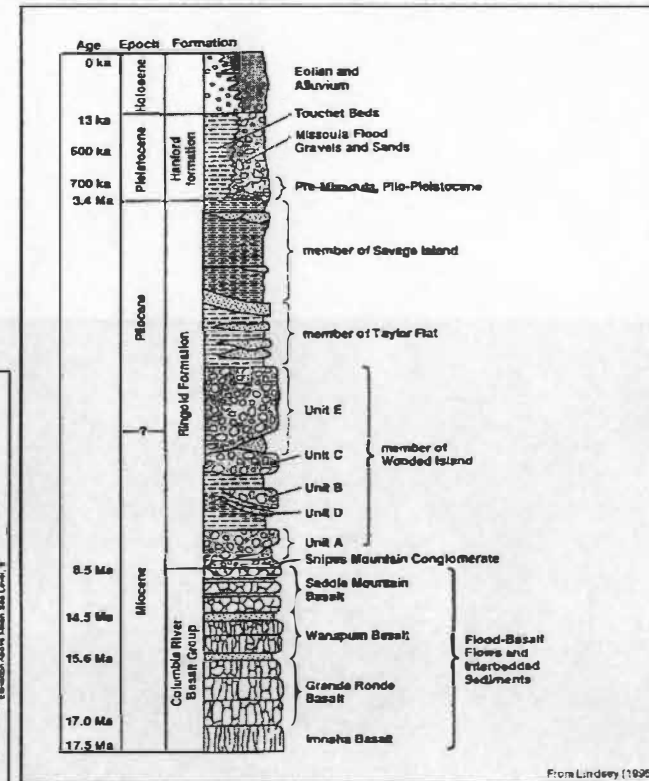


Figure 1. A stratigraphic column of the vadose zone at the 200W Area Environmental Restoration Disposal Facility (ERDF) on the Hanford Reservation. Note that the undisturbed cores used in this study were collected in August 2000 at the 20 m depth.

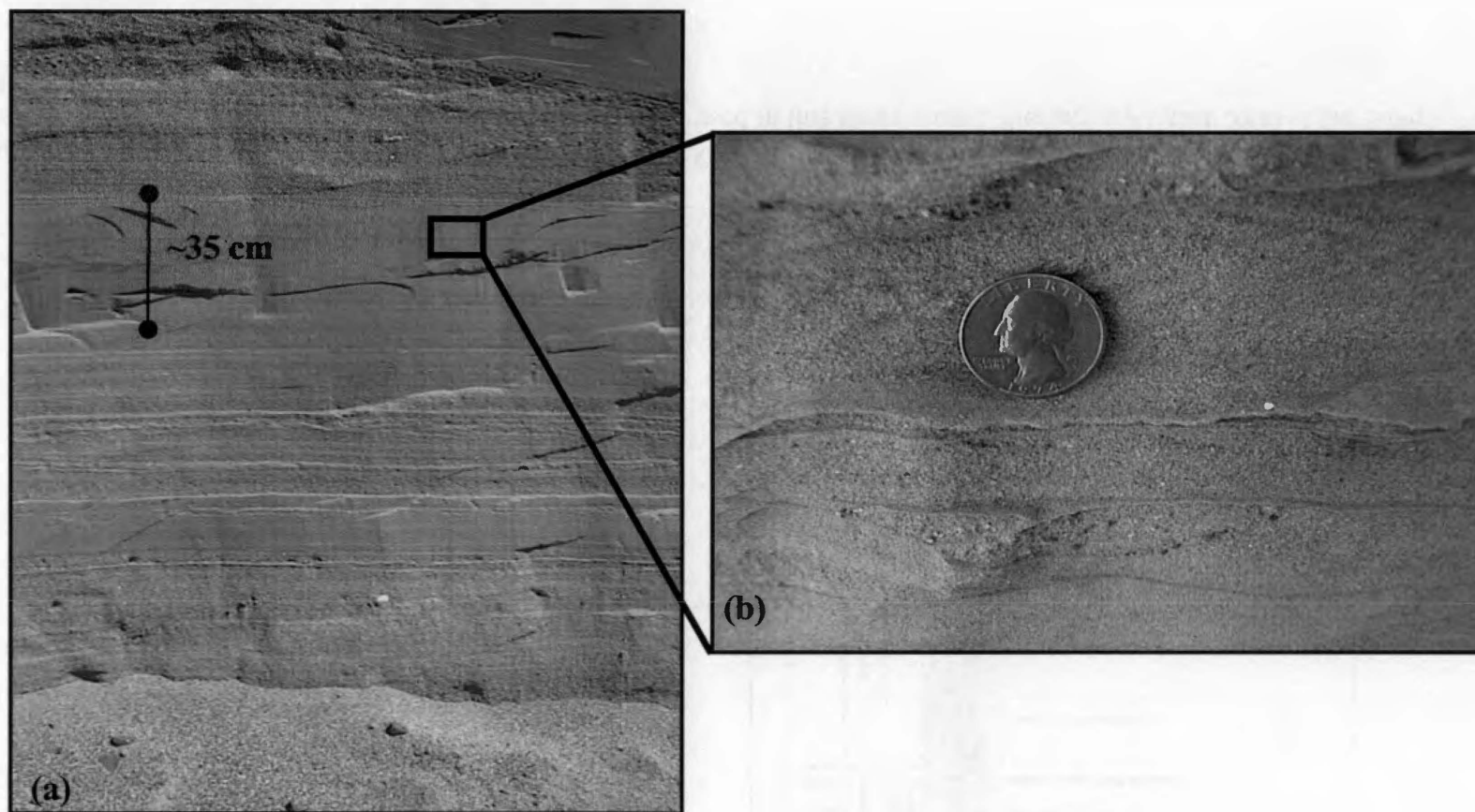


Figure 2. Excavation into the Hanford Formation at the 200-W Area Environmental Restoration Disposal Facility (ERDF) on the Hanford Reservation, 20 m depth. (a) unconsolidated alternating layers of coarse and fine sands. (b) Expanded view of fine-grained layer from which cores were collected. Note small-scale clay layering.

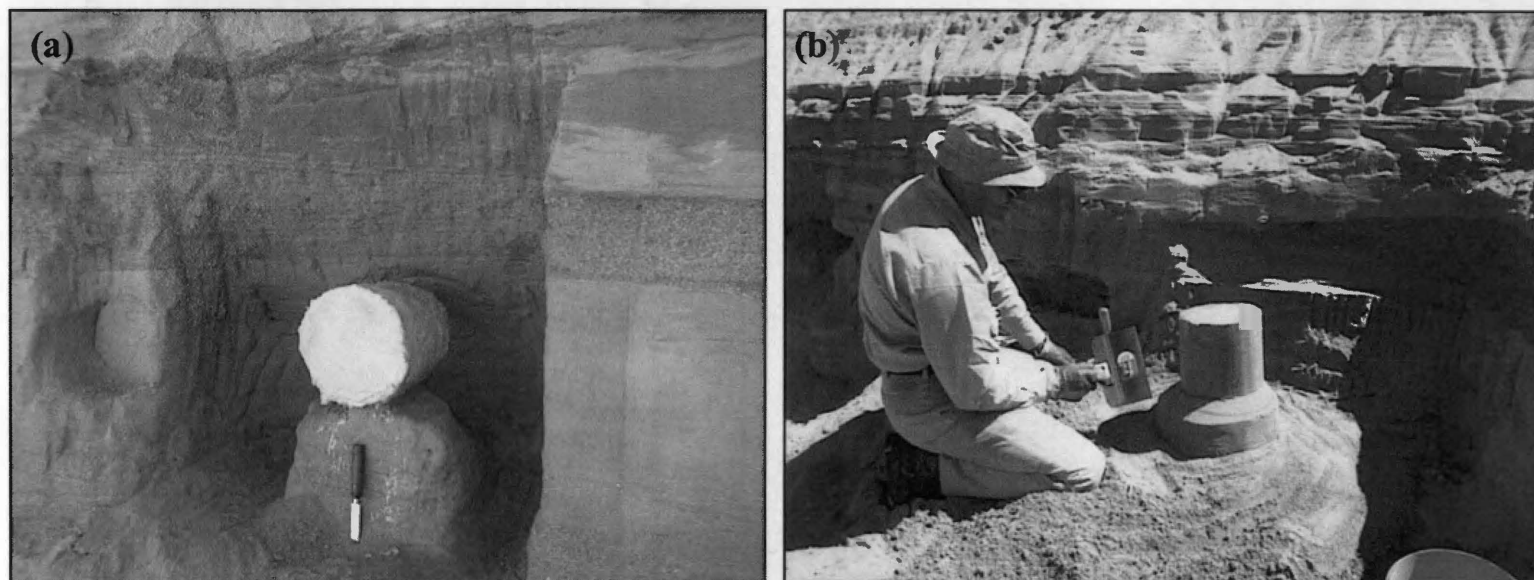


Figure 3. Harvesting of undisturbed cores from the Hanford Formation. (a) Paraffin wax coated horizontal core, and (b) Sculpting of vertical core.

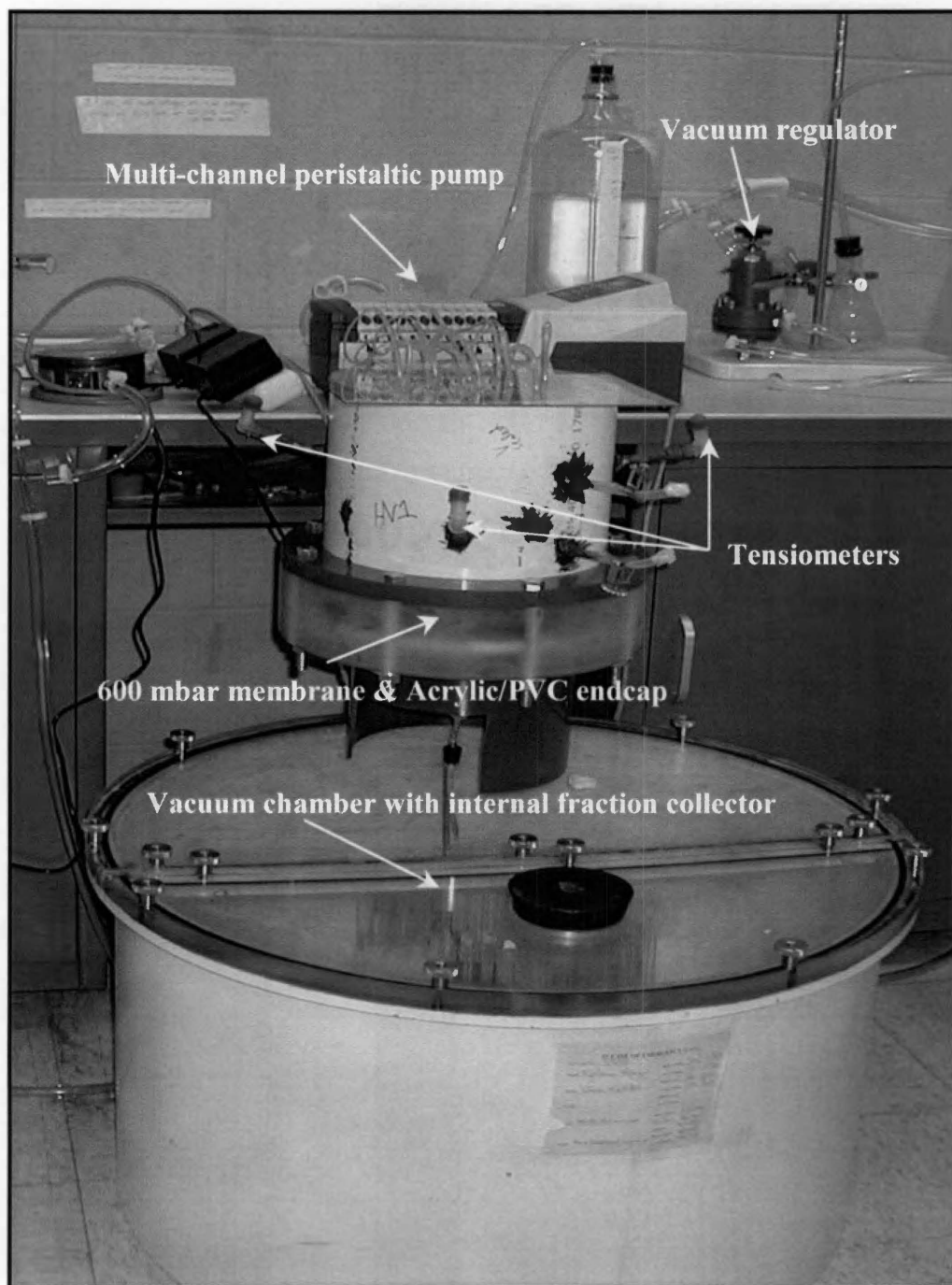


Figure 4. Experimental apparatus for conducting unsaturated flow experiments in undisturbed cores.

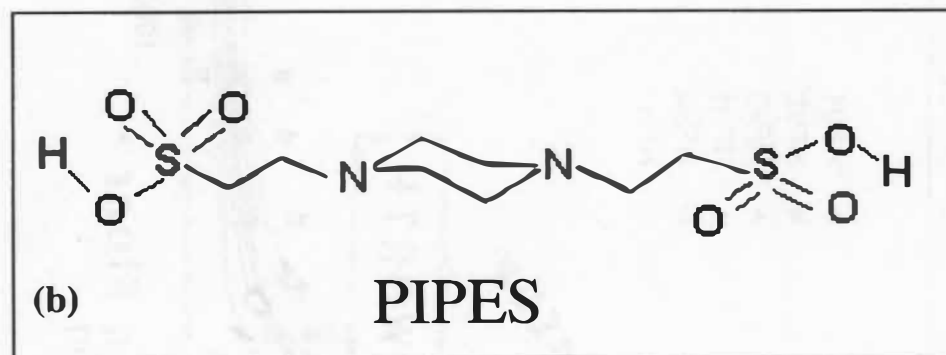
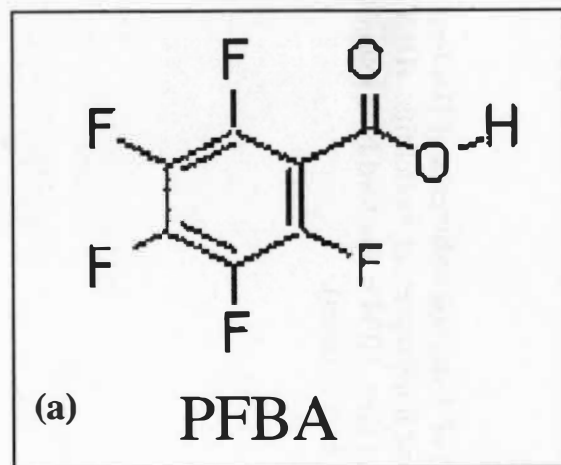


Figure 5. Chemical structure of two large organic molecules that are used as non-reactive tracers. (a) pentafluorobenzoic acid (PFBA) and (b) piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES).

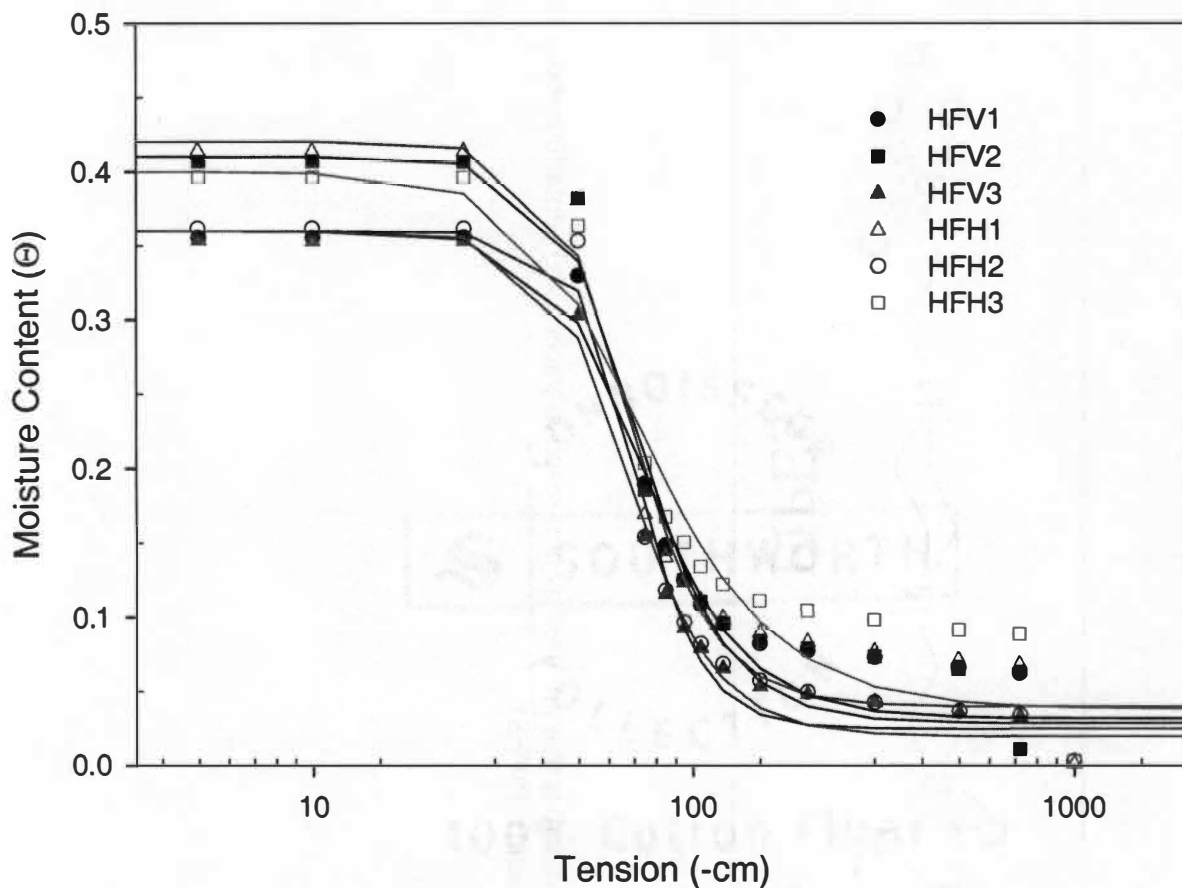


Figure 6. Moisture Retention Functions (MRF) of disturbed sediments of Hanford Formation. Symbols represent observed data and lines represent model fits. (HFV = Hanford Fine material collected near the vertical core, HFH = Hanford Fine material collected near the horizontal core, # = replicate experiments).

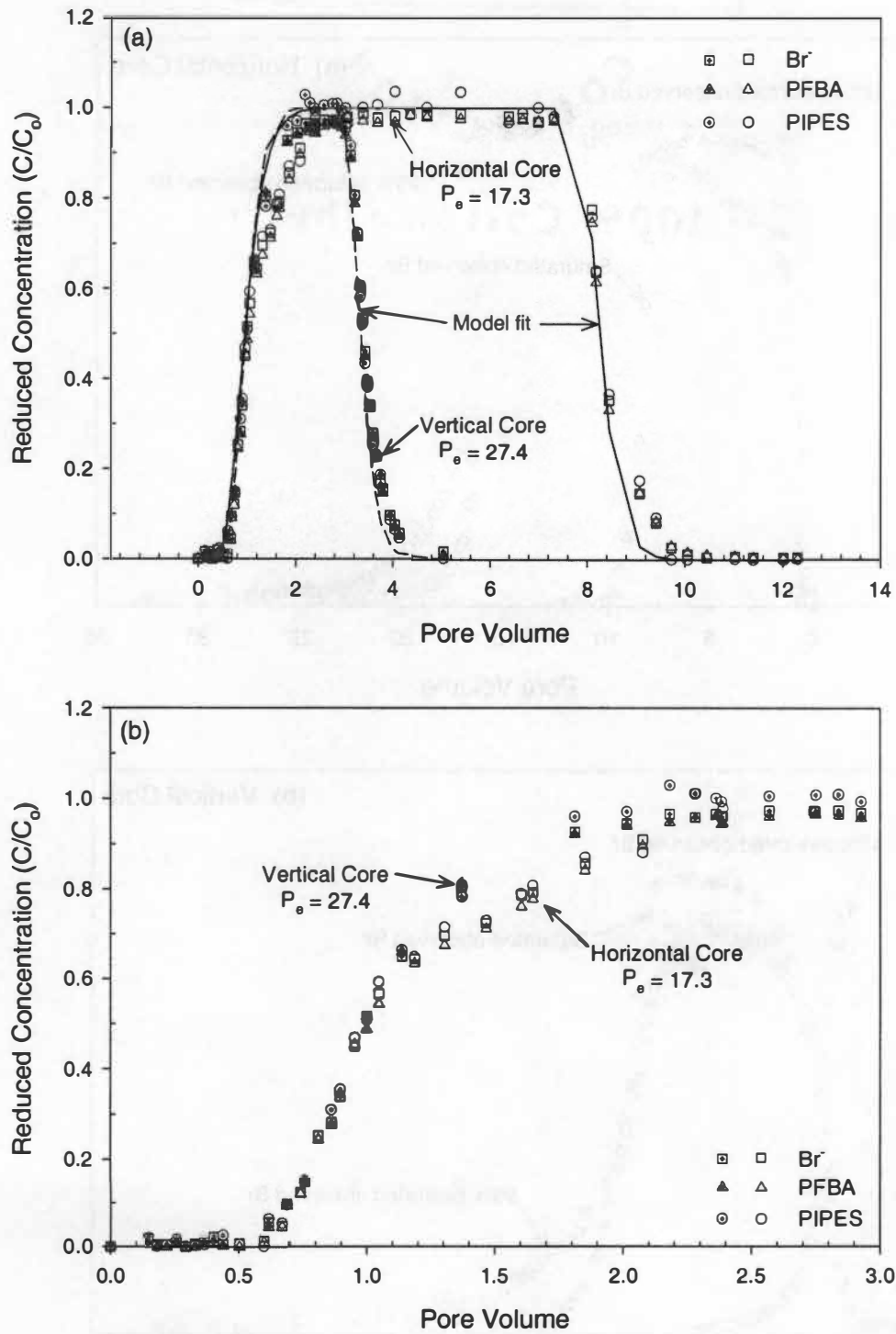


Figure 7. Observed (symbols) and model fitted (lines) tracer effluent concentrations involving the displacement of Br^- , PFBA, and PIPES through saturated cores. Modeled Br^- relative concentrations are shown with model parameters provided in Table 5. Modeled PFBA and PIPES were omitted to improve clarity of figure, since no significant difference in modeled BTCs were observed.

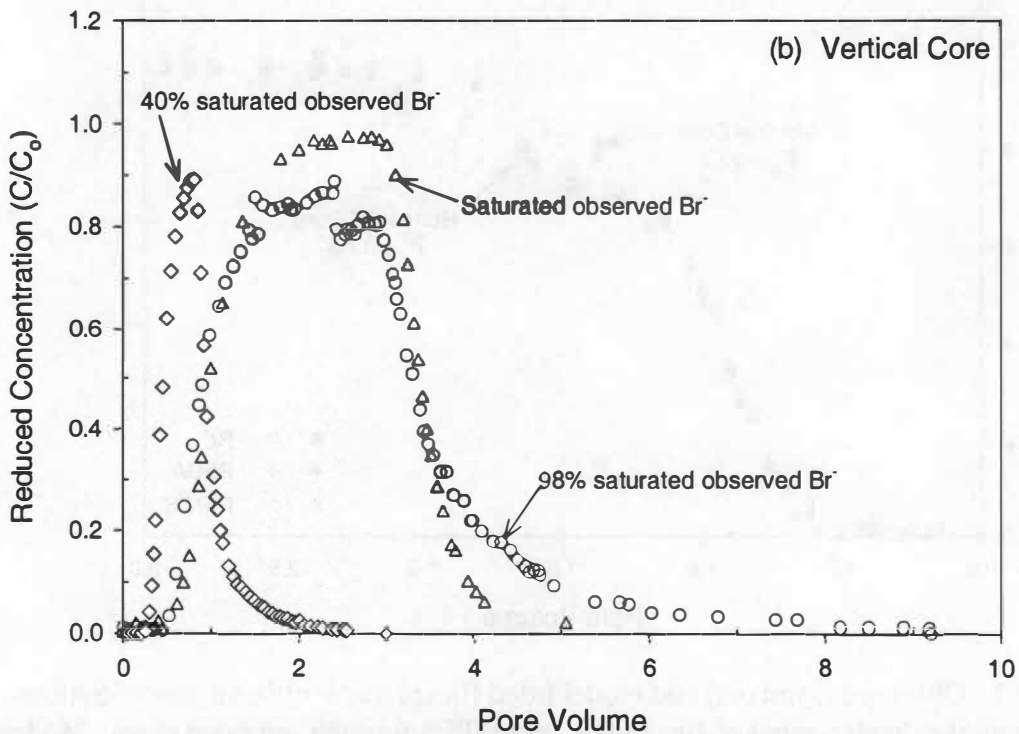
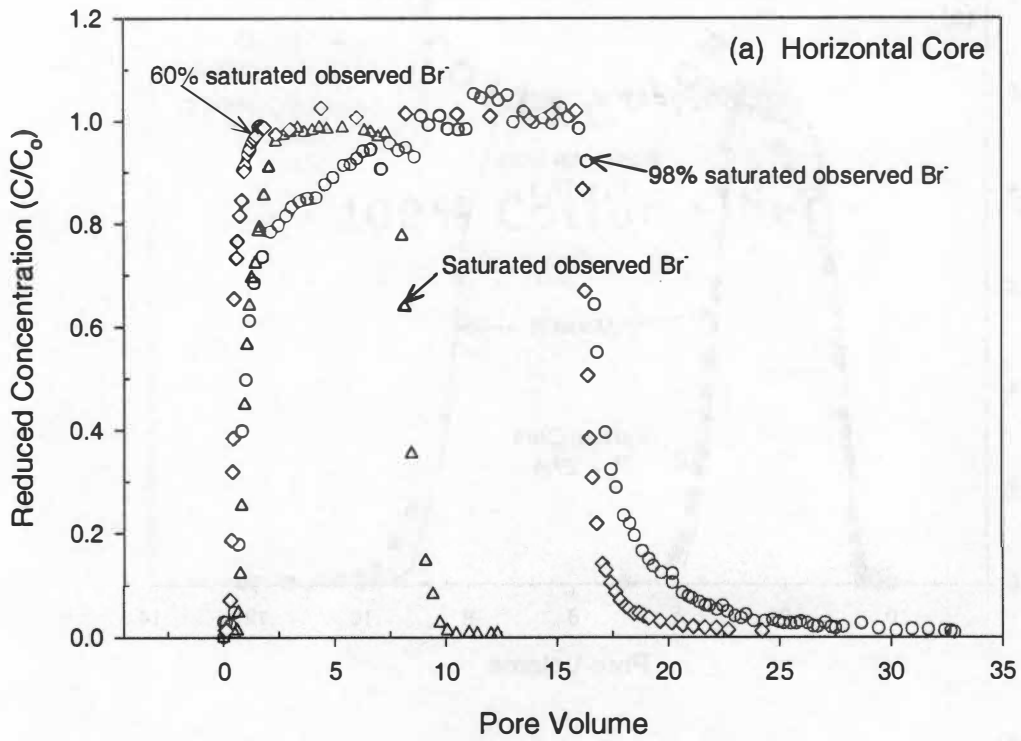


Figure 8. Observed tracer effluent concentrations involving the displacement of Br^- through saturated and unsaturated cores. (a) BTC for the horizontal core under saturated and unsaturated conditions. (b) BTC for the vertical core under saturated and unsaturated conditions (see errata for updated figure).

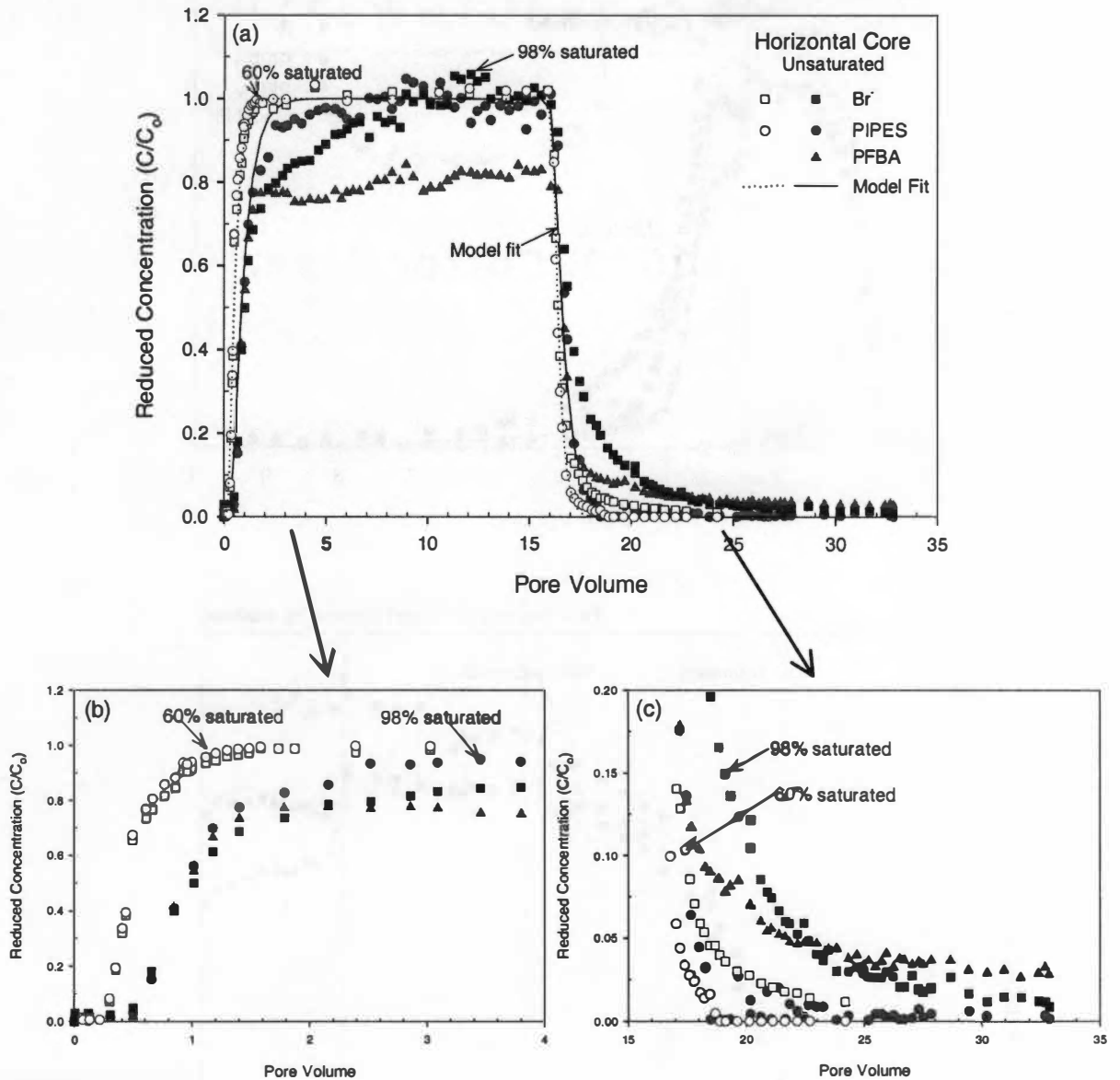


Figure 9. (a) Observed (symbols) and model fitted (lines) tracer effluent concentrations involving the displacement of Br^- , PFBA, and PIPES through the unsaturated horizontal core. Modeled Br^- concentrations are shown with the model parameters provided in Table 5. Modeled PFBA and PIPES concentrations were omitted to improve clarity of figure. (b) Observed initial tracer breakthrough showing separation and crossover of tracers. (c) Observed tracer concentration during washout showing separation and crossover of tracers (see errata for updated figure).

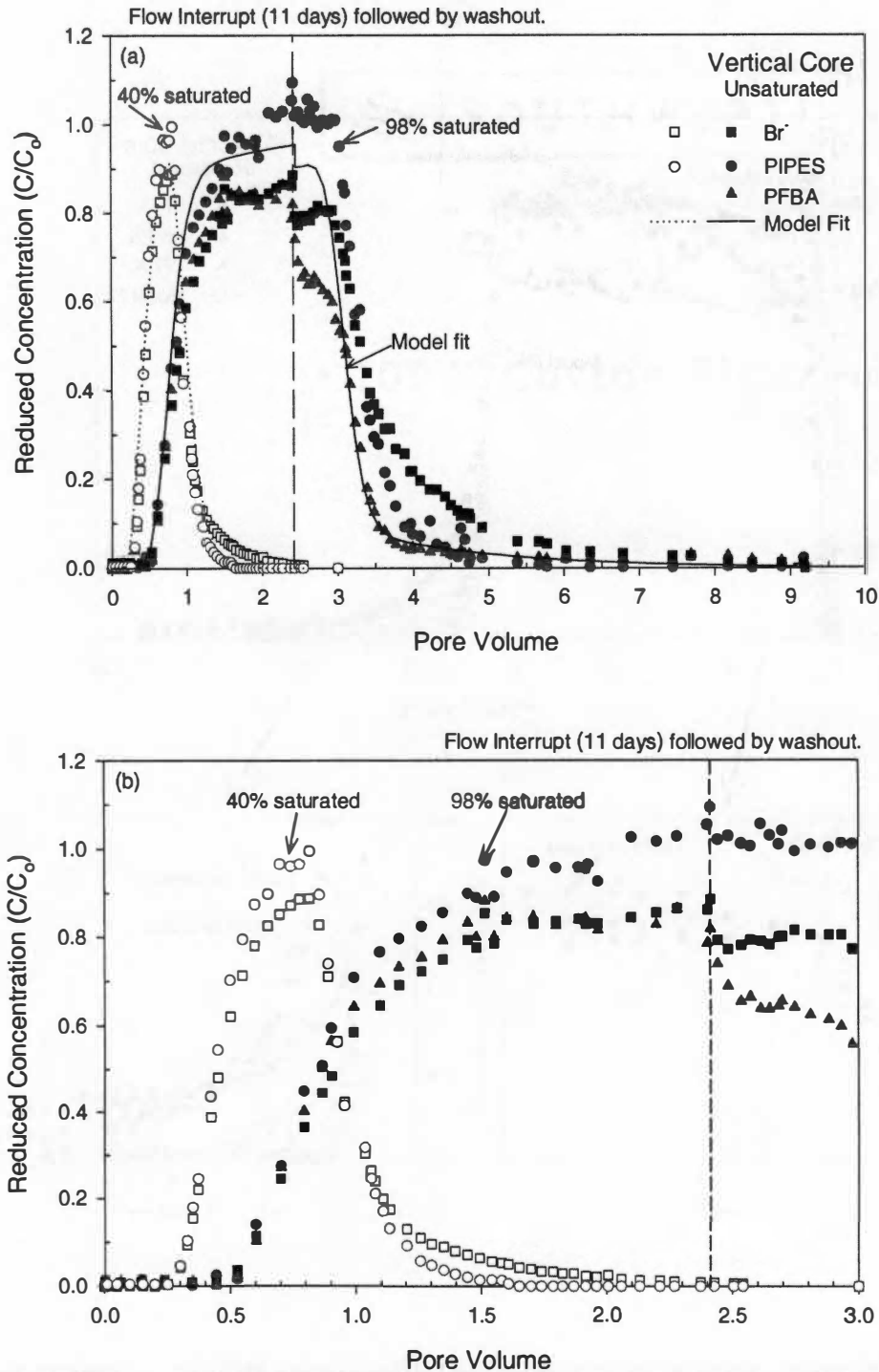


Figure 10. (a) Observed (symbols) and model fitted (lines) tracer effluent concentrations involving the displacement of Br^- , PFBA, and PIPES through the unsaturated vertical core. Modeled Br^- concentrations are shown. Modeled PFBA and PIPES were omitted to improve clarity of figure. (b) Separation of tracers prior to the flow-interrupt in the unsaturated vertical core experiment. Model parameters are provided in Table 5 (see errata for updated figure and table).

ERRATA

Quantifying the Effects of Small-scale Heterogeneities on Flow and Transport in Undisturbed Core from the Hanford Formation.

Pace et al., VZJ, 2:664-676 (2003)

Submitted to Vadose Zone Journal 7/05

A conversion error was found in the calculation for pore volume in several of the unsaturated transport experiment spreadsheets. Figures 8, 9, and 10 have changed only in the PV axis. The relative concentrations remain the same as in the original paper. Modeling results have also changed. These changes are presented in the revised Table 5. The results now show no preferential flow in the unsaturated vertical core, but still significant tracer separation due to matrix diffusion. Preferential flow is still observed in the horizontal core, just not as much as in the original manuscript. The effect of matrix diffusion is the same in both cores as in the original manuscript. The MIM model was used to fit the data from the horizontal core with a retardation factor of 1 for the non-reactive tracers. The CDE was used for the vertical core. The corrected model fit information is in Table 5.

The original conclusions still are valid. The only major difference is that no preferential flow was observed in the vertical core under a range of moisture contents whereas preferential flow and media bypass does occur in the horizontal core. Again, these differences are due to the heterogeneity present in the cores. The observations suggest lateral flow in the Hanford vadose zone.

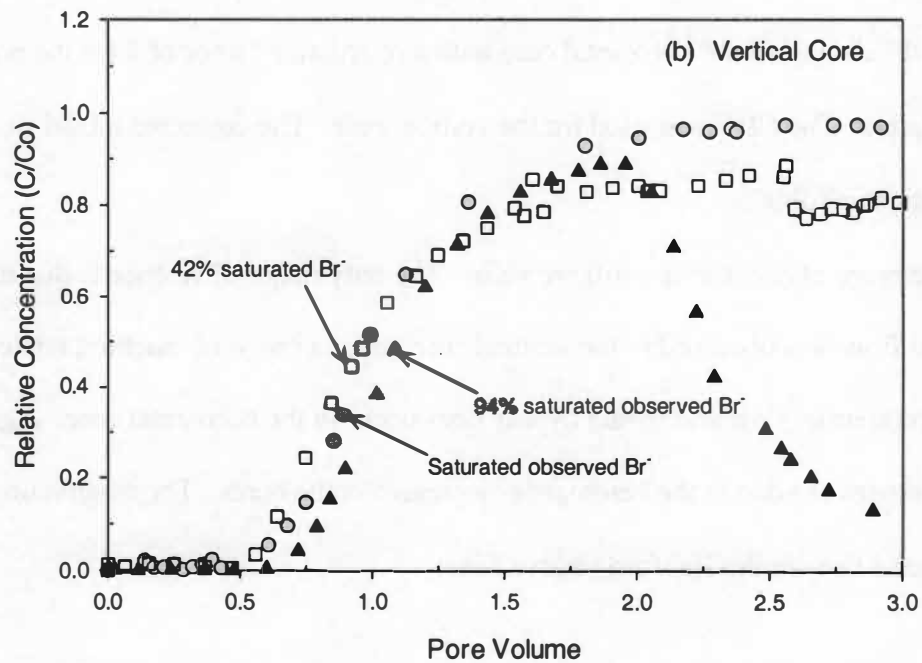
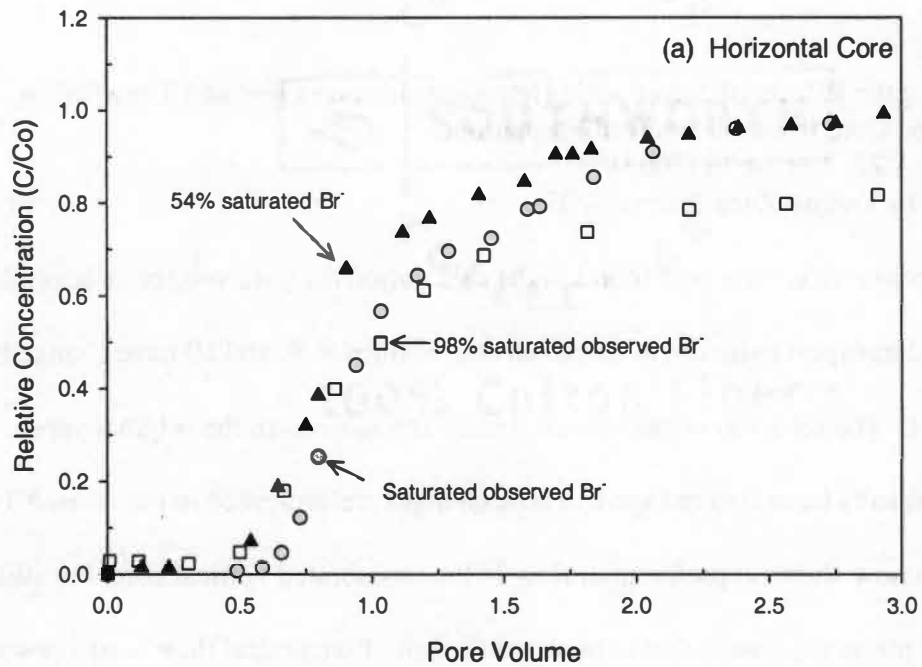


Figure 8. Observed tracer effluent concentrations involving the displacement of Br^- through saturated and unsaturated cores. (a) BTC for the horizontal core under saturated and unsaturated conditions. (b) BTC for the vertical core under saturated and unsaturated conditions.

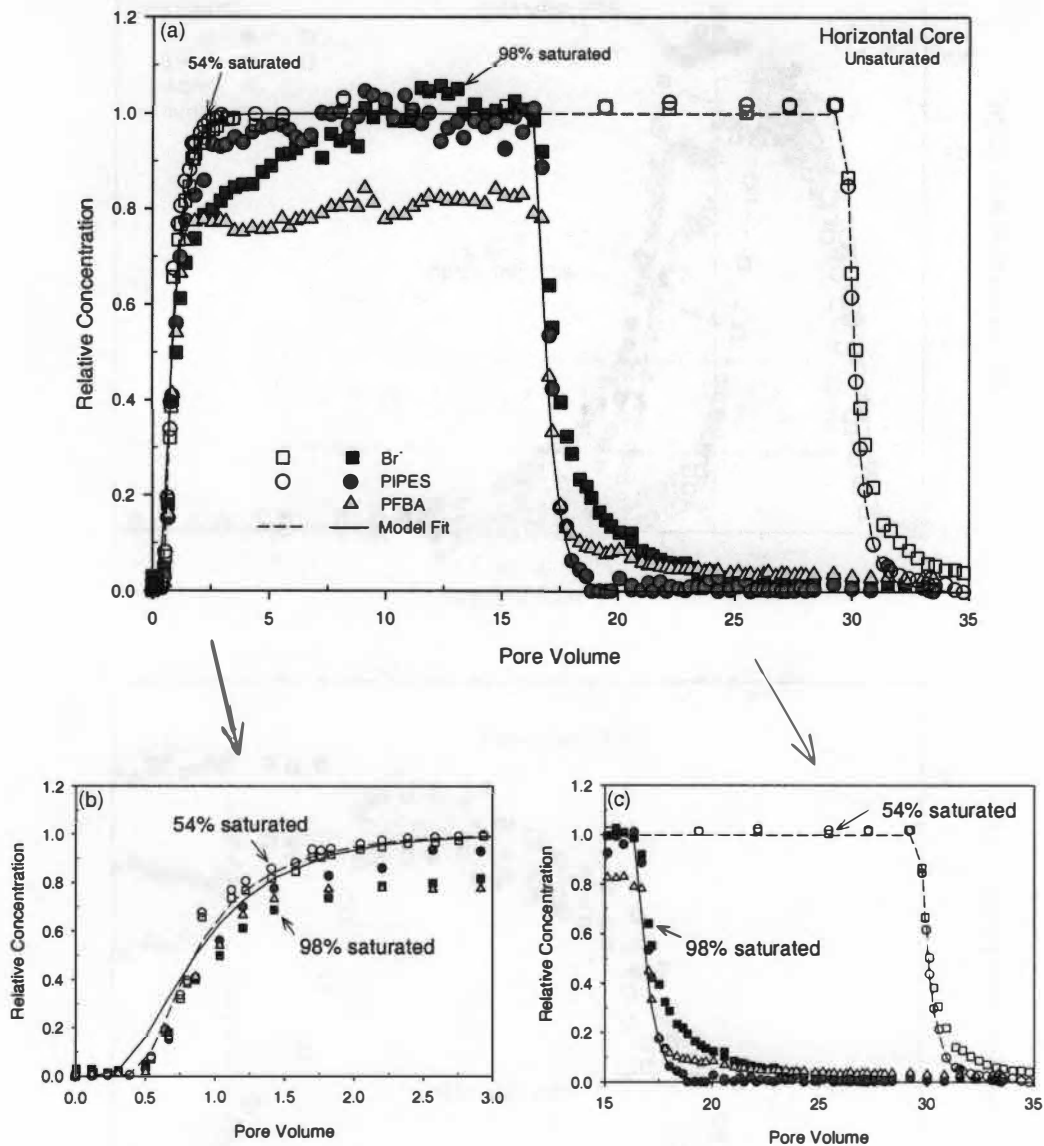


Figure 9. (a) Observed (symbols) and model fitted (lines) tracer effluent concentrations involving the displacement of Br^- , PFBA, and PIPES through the unsaturated horizontal core. Modeled Br^- concentrations are shown with the model parameters provided in Table 5. Modeled PFBA and PIPES concentrations were omitted to improve clarity of figure. (b) Observed initial tracer breakthrough showing separation and crossover of tracers. (c) Observed tracer concentration during washout showing separation and crossover of tracers.

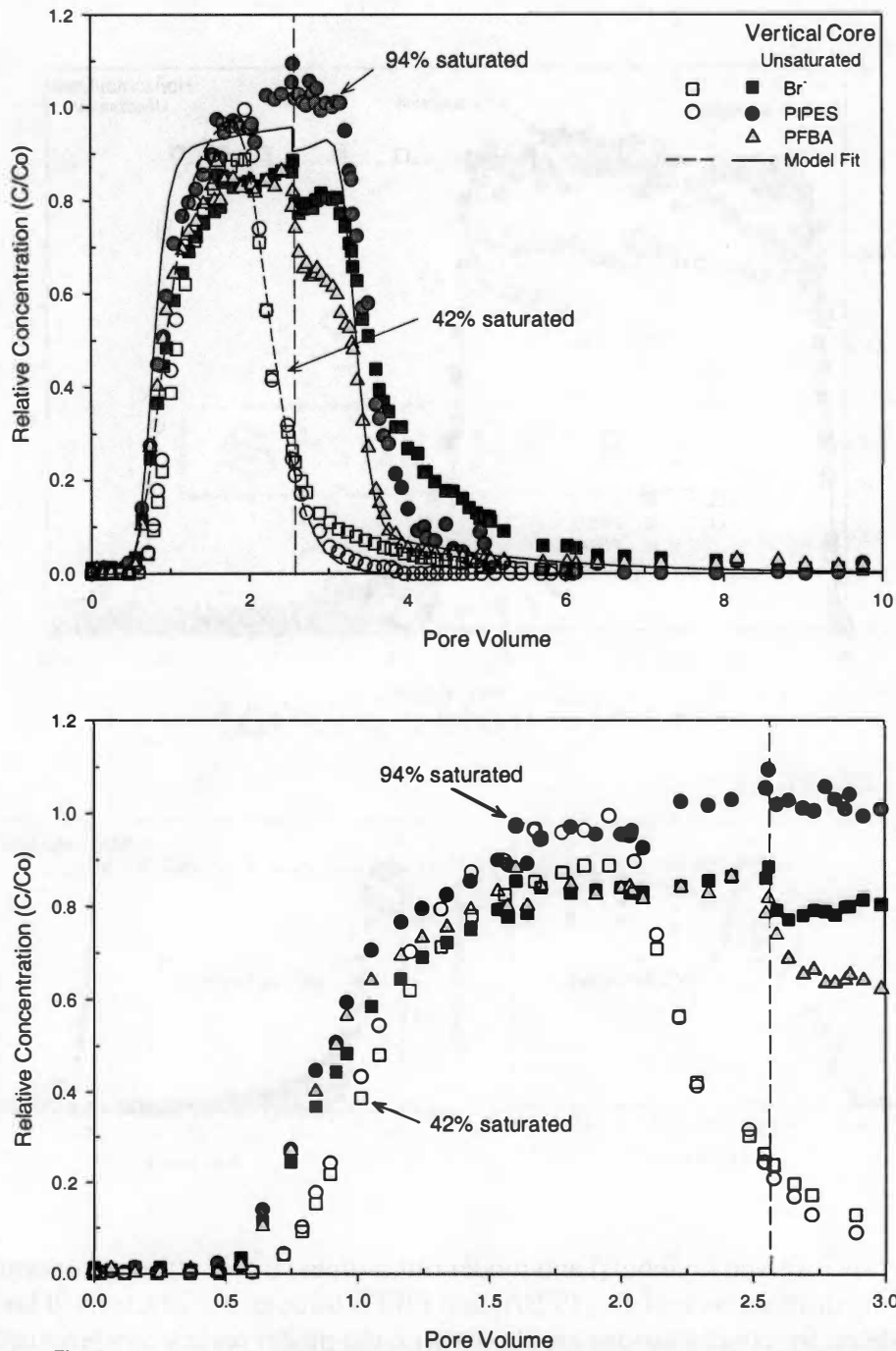


Figure 10. (a) Observed (symbols) and model fitted (lines) tracer effluent concentrations involving the displacement of Br^- , PFBA, and PIPES through the unsaturated vertical core. Modeled Br^- concentrations are shown. Modeled PFBA and PIPES were omitted to improve clarity of figure. (b) Separation of tracers prior to the flow-interrupt in the unsaturated vertical core experiment. Model parameters are provided in Table 5

Table 5. Modeling results of undisturbed Hanford Formation saturated and unsaturated breakthrough curve data. Due to similarities, model fits of PFBA and PIPES during saturated flow were omitted.

Experiment	Tracer	Mass recovery (%)	Model	Model Parameters						
				V (cm hr ⁻¹)	L (cm)	P _e	θ	F	α (hr ⁻¹)	R ²
HH-sat	Br ⁻	98	CDE	41.92	23	16.30 ± 4.26	0.3250	NA	NA	0.9709
HV-sat	Br ⁻	99	CDE	12.00	21	25.10 ± 3.65	0.4090	NA	NA	0.9901
HH-98%	Br ⁻	105	CDE	0.0826	23	5.96 ± 2.11	0.3188	NA	NA	0.9443
	PFBA	87	CDE	0.0826	23	6.53 ± 2.78	0.3188	NA	NA	0.8622
	PIPES	101	CDE	0.0826	23	11.90 ± 2.35	0.3188	NA	NA	0.9924
HV-94%	Br ⁻	107	*MIM	0.0800	21	10.27 ± 3.06	0.3847	0.80	4.17e-4	NA
	PFBA	88	*MIM	0.0800	21	10.40 ± 2.73	0.3847	0.80	2.08e-4	NA
	PIPES	111	*MIM	0.0800	21	14.10 ± 2.19	0.3847	0.80	4.17e-3	NA
HH-54%	Br ⁻	103	MIM	0.1491	23	26.00 ± 15.30	0.1765	0.749 ± 0.231	7.83e-4	0.9883
	PIPES	101	MIM	0.1491	23	25.20 ± 7.66	0.1765	0.793 ± 0.06	4.49e-4	0.9974
HV-42%	Br ⁻	93	CDE	0.1460	21	19.20 ± 33.7	0.1705	NA	NA	0.9240
	PIPES	93	CDE	0.1460	21	27.30 ± 5.08	0.1705	NA	NA	0.9744

[PV = pore volume, VC = vacuum chamber, MIM = mobile – immobile model, CDE = convective dispersion equation model, V = mean pore water velocity, L = length of core, P_e = peclet number, θ = water content, F = fraction mobile water, α = mass transfer coefficient (hr⁻¹).]

*MIM = a simulation using the parameters listed in the table. Therefore, there are no statistics associated with this experiment.

PART 3

UNRAVELING THE FATE AND TRANSPORT OF Sr^{+2} AND SrEDTA^{-2} IN THE HANFORD VADOSE ZONE

ABSTRACT

Transport of strontium-90 has been observed in the vadose zone beneath the Hanford tank farm. The goal of this paper is to provide an improved understanding of the hydrogeochemical processes that contribute to strontium transport in the Hanford vadose zone. It has been suggested that organic chelates such as EDTA may be responsible for the accelerated transport of strontium due to the formation of stable anionic complexes. Laboratory scale batch, saturated packed column experiments, and an unsaturated transport experiment in an undisturbed core were conducted to quantify geochemical and hydrological processes controlling Sr^{+2} and SrEDTA^{-2} sorption to Hanford flood deposits. Duplicate batch and column experiments performed with Sr^{+2} and SrEDTA^{-2} suggested that the SrEDTA^{-2} complex was not stable in the presence of Hanford sediment and rapid dissociation allowed strontium to be transported as a divalent cation. Batch experiments indicated a decrease in sorption with increasing rock:water ratios, whereas saturated packed column experiments indicated equal retardation in columns of different lengths. This difference between the batch and column experiments is primarily due to the difference between equilibrium conditions where dissolution of cations may compete for sorption sites in closed system batch studies versus flowing conditions where dissolved cations are flushed through the system minimizing competition for sorption sites. Unsaturated transport in an undisturbed core resulted in significant Sr^{+2} retardation ($R = 70$). However, this corresponded to a lower K_d value than determined in the saturated packed columns, possibly due to the presence of physical non-equilibrium processes such as media bypass in the undisturbed core. After termination of the unsaturated transport experiment, the undisturbed core was disassembled and samples were collected from

visibly distinct bedding units as a function of depth. The disassembly and sequential extractions performed on the collected samples revealed the mass wetness distribution and reactive mineral phases associated with sorbed strontium in the core. Overall, results indicated that strontium will most likely be transported through the Hanford vadose zone as a divalent cation rather than a complex with EDTA and sorption may be controlled by multiple factors such as physical non-equilibrium processes, grain size, and mass wetness.

KEY WORDS: displacement experiments, undisturbed cores, unsaturated flow, reactive transport, Hanford formation

INTRODUCTION

The U.S. Department of Energy's Hanford Reservation was historically a nuclear material processing facility located in the Columbia River Basin in south central Washington. The area receives an average annual rainfall of 16 cm/year and depth to groundwater averages ~100 m across the site. The vadose zone is composed of sediments from the Hanford formation flood deposits, the Cold Creek Unit, and the Ringold Formation, which occurs at the groundwater interface. Processing waste was historically disposed of in cribs, solid waste burial pits, ponds, and/or underground storage tanks which reside within the Hanford formation. The most concentrated wastes were stored in single-shelled tanks in the 200 Area of the Hanford Site (Agnew et al., 1997; Bjornstad, 1990). About one-third of the tanks in the 200 Area have leaked, resulting in the discharge of more than 4 million liters of hazardous and radioactive waste in the vadose zone. Some of these tanks contain radionuclides such as Sr-90 as well as

organic chelating agents including ethylenediaminetriacetic acid (EDTA) and nitrilotriacetic acid (NTA) (DOE, 1996; Knepp, 2002). Strontium-90 initially traveled further from the source than predicted, although the mechanism for such “accelerated” transport remains unclear (Knepp, 2002). It has been suggested that chelating agents complexed with the radionuclides may have contributed to the observed accelerated transport of Sr-90 (Felmy and Mason, 2003). Sr-90 is an ecological and health concern due to its relatively long half-life (28.8 years) and high energy of β -decay, and because it can substitute for Ca^{+2} in bone tissue (Peterson and Poston, 2000). It is estimated that approximately 2,333,000 Ci Sr-90 may pose a health risk for the next 1000 years at the Hanford Site (Bryce et al., 2002).

Many studies have used batch experiments to describe the general sorption behavior of strontium (Ahmad, 1995; Bunde et al., 1997; Chen and Hayes, 1999; Chorover et al., 2003; Grutter et al., 1994; Hakem et al., 2000; Jeong et al., 1996; Khan et al., 1995; Knepp, 2002; Liu et al., 1995; Porro et al., 2000; Smiciklas et al., 2000; Tsai et al., 2001). Electrostatic exchange is the dominant mechanism by which strontium sorbs to particles; therefore, changes in solution chemistry such as ionic strength and concentrations of competing ions affect strontium sorption. For example, divalent cations such as Ca^{+2} and Mg^{+2} compete with strontium for sorption sites, resulting in a decrease in strontium sorption (Bunde et al., 1997). It has also been shown that strontium can be incorporated into secondary precipitates during the weathering of clay minerals in the presence of simulated Hanford tank waste (Chorover et al., 2003). Sr^{+2} sorption is relatively simple but detailed chemical analysis of solutions must be incorporated into mechanistic models to correctly simulate strontium adsorption/exchange processes in

Hanford soils (Lichtner and Zachara, 2002) and heterogeneity of subsurface sediments cause variations in cation exchange capacities as a function of depth and lithology.

Batch studies specific to the Hanford site have determined that 25% of strontium in the Hanford vadose zone may be co-precipitated in an immobile carbonate phase and 75% may be present as an ion-exchangeable form on silicate minerals (Knepp, 2002). Desorption experiments (Zachara et al., 2002a; Zachara et al., 2002b) conducted on contaminated Hanford soils indicate that the ion exchangeable Sr-90 was rapidly desorbed under appropriate Hanford ionic strengths, while Sr-90 associated with the carbonate phase was not. Based on these results, strontium remaining on the Hanford vadose zone soil as SrCO_3 may be immobile.

The mobility of Sr-90 may be affected by the presence of organic complexing agents such as EDTA and NTA, which were components of the Hanford tank waste (Knepp, 2002). Detailed analysis of soils from the B-BX-BY waste management area measured Sr^{+2} on the soil in the absence of NTA (Serne et al., 2002); suggesting that NTA present in the tank waste may not have complexed with Sr^{+2} . Future releases of organic chelates into the subsurface from tank waste remedial efforts may form complexes with Sr^{+2} sorbed on the sediment, forming a relatively mobile anionic SrEDTA^{-2} or SrNTA complex. The ability of organic chelates such as EDTA to leach Sr^{+2} from the relatively immobile $\text{SrCO}_3(\text{s})$ was described by Felmy et al. (2003) using a pure solid $\text{SrCO}_3(\text{s})$ phase in the absence of Hanford sediment. The ability of EDTA to complex with Sr^{+2} in the presence of native Hanford sediments, however, may be different due to the presence of other soluble cations that form stronger EDTA complexes than does Sr^{+2} .

Packed column studies have been used to determine the reversibility of strontium sorption and the general effects of flow on sorption. Porro et al. (2000) conducted saturated and unsaturated repacked transport experiments as well as batch experiments with crushed basalt collected at the Idaho National Engineering and Environmental Laboratory (INEEL). Batch results indicate that sorption decreased as the solid/liquid ratio increased possibly due to the dissolution of competing cations at higher solid/liquid ratios under equilibrium conditions. However, under flowing conditions the dissolved cations were flushed through the column thereby decreasing the competitive cation effect resulting in an increase in sorption versus batch conditions. Unsaturated transport experiments indicated minimal effects of moisture content on Sr^{+2} transport (Porro et al., 2000). Other saturated transport experiments (Steefel et al., 2002) were conducted in columns packed with sediments from the Hanford formation, which were crushed and treated with sodium acetate solution to remove the carbonate phases and then packed into a column filled with de-ionized water, to test a multi-component cation exchange model derived from batch studies. Strontium transport through the repacked column was successfully simulated using a modified multi-component ion exchange model. However, the sediments were altered from their natural state and may not be representative of the Hanford vadose zone. Little research has been done on flow and transport of strontium in natural, intact media that maintains the sedimentary structure of vadose zone material.

It has been shown that sedimentary structure in the Hanford vadose zone affects unsaturated flow by causing preferential finger flow and media bypass as well as matrix diffusion (Mayes et al., 2003; Mayes et al., 2005; Pace et al., 2003). It is hypothesized

that hydrologic processes occurring under unsaturated conditions will also effect geochemical processes by limiting the amount of reactive media the contaminant contacts and limiting diffusion into immobile regions. Thus, contaminant retardation may decrease due to unsaturated flow processes in natural, layered systems. Further, as water content decreases, the flow regime may become isolated to layers which are mineralogically distinct from bulk sediments, which could either increase or decrease observed contaminant retardation. This hypothesis has not been previously tested under conditions relative to the Hanford subsurface.

This paper seeks to quantify the influence of coupled geochemical and hydrological processes on the fate and transport of strontium and SrEDTA^{-2} transport in the Hanford sediments using saturated batch and repacked column experiments and an unsaturated intact core that retains the natural mineralogy and sedimentary structure of the Hanford vadose zone. Sequential extractions were conducted on sediment samples from the undisturbed core to identify the influence of grain size, mineralogy, and mass wetness on the distribution of Sr^{+2} under unsaturated conditions. Such information will improve our understanding of Sr^{+2} transport and sorption in heterogeneous, unsaturated layered systems common to the western United States and specifically the Hanford Site.

MATERIALS AND METHODS

Characterization of the Sediment

Most of the waste at the Hanford site is located in the Hanford formation, which, comprises the upper ~45 m of the ~100 m thick vadose zone beneath the 200W area tank farms. The formation is a Pleistocene age deposit formed from multiple floods of the

glacial Lake Missoula to the east (Bjornstad, 1990; DOE, 2002; Lindsay, 1995). The core used in this study was collected from a layer which can be described as an unconsolidated, fine sand unit interbedded with small-scale clay laminations (Bjornstad, 1990; DOE, 2002; Pace et al., 2003).

Disturbed and undisturbed sediments from the Hanford formation were collected from freshly exposed escarpments opened at a depth of ~20 m in the Environmental Restoration Disposal Facility (ERDF) in the 200W Area of the Hanford Reservation, which is described in detail by Pace et al. (2003). Extensive chemical and physical characterization was conducted on disturbed sediments (Pace et al., 2003). Undisturbed cores were isolated using a hand-sculpting method, which entailed isolating a small pedon, carving the sample to its finished dimensions (~20 cm x 20 cm), and coating with paraffin wax. Cores were collected horizontally (flow parallel to bedding) and vertically (flow perpendicular to bedding) from a fine-grained layer. A single horizontal core was utilized in this study.

Batch Experiments

Batch experiments were used to determine the equilibrium time and sorption coefficients for strontium under various rock:water ratios with homogenized Hanford sediments. Batch isotherm experiments were carried out in 30 cm³ polyethylene centrifuge tubes at rock:water ratios of 1g:2ml and 1g:1ml. Bulk sediment and the fractionated sand, silt, and clay fractions were all used corrected for the percentage of each fraction contained in the bulk sediment (i.e. 0.95 g of sand was used instead of 1 g). Particle size separation was accomplished following a modified pipet method (Klute, 1986) using 18 MΩ H₂O, in

which sands (95% of bulk sediment), silts (4% of bulk sediment), and clays (1% of bulk sediment) were separated and collected from unaltered bulk sediments. Batch solutions contained 0 – 0.228 mM Sr^{+2} as $\text{Sr}(\text{NO}_3)_2$ or SrEDTA^{-2} in 0.1 M NaCl. The pH was adjusted with 0.1 N NaOH to a final pH of ~8.00 to be in equilibrium with the natural soil pH. Geochemical modeling was conducted with Geochemist Workbench (version 3.1.2, Craig M. Bethke) that confirmed the formation of a stable SrEDTA^{-2} complex at pH 8. Blanks were run that contained strontium solution and no soil to account for loss of Sr^{+2} to the tube which was found to be negligible. Samples were run in duplicate. Centrifuge tubes were placed on a shaker for ~84 hrs to ensure equilibrium. Upon completion of the experiments, the tubes were placed in a centrifuge for 15 min at ~2300 RPM. The supernatant was decanted into glass tubes for Sr^{+2} analyses. The pH was measured in the remaining clear solution above the soil in the centrifuge tubes.

Miscible Displacement Experiments

Saturated packed columns

Miscible displacement experiments were conducted to determine the effect of flow versus batch techniques and the effects of different column lengths (sediment mass) on strontium sorption. Experiments were conducted with Sr^{+2} and SrEDTA^{-2} in glass columns 1 cm in diameter packed with saturated bulk media to lengths of 4.5 cm and 2 cm (Fig. 3a). The media was wet packed then slowly flushed for several days to ensure removal of entrapped air. The solution used for the column experiments contained 0.5 mM Br^- and 0.228 mM Sr^{+2} as $\text{Sr}(\text{NO}_3)_2$ or SrEDTA^{-2} in 0.1 M NaNO_3 or NaCl, adjusted to pH 8 with NaOH. A non-pulsing medical pump was used to deliver solution to the

bottom of the column at an average flux (volume of water per unit timer per unit area) of 2 cm h^{-1} for the 4.5 cm columns and approximately 1 cm h^{-1} in the 2 cm columns. All column experiments were designed to have similar residence times ($R_t = 1\text{-}2 \text{ h}$). Experimental parameters are listed in Table 1 (note all Tables are located at the end of the Part). Evaporation during the experiments was monitored with specific samples prepared to measure daily evaporation rates and was found to be minimal.

Undisturbed core

An unsaturated flow and transport experiment was conducted in an undisturbed horizontal core (flow parallel to bedding) to quantitatively investigate the coupled hydrologic and geochemical mechanisms controlling Sr^{+2} transport in the Hanford vadose zone. The experimental apparatus used in the unsaturated flow experiment is described in detail by Pace et al. (2003) (Fig. 3b). The core was initially slowly saturated from the bottom and then attached to a vacuum-regulated chamber for unsaturated flow experiments. The core was allowed to drain at a desired tension set in the vacuum chamber until water loss from the core ceased. The core weight was recorded. A solution of 0.1 M NaCl, pH 8.0 was then delivered to the upper boundary of the core at twelve contact points using a multi-channel peristaltic pump. Effluent samples were collected until the flow rate and the core tensions, monitored by small tensiometers along the distance of the core, were stable. The core was then reweighed. The unsaturated moisture content was determined by the difference between the unsaturated weight and the saturated core weight minus the saturated pore volume and divided by the total

volume of the core. Flow of the tracer solution was then initiated. All experimental parameters are listed in Table 1.

The tracer solution contained 0.5 mM Br^- as NaBr, 1.0 mM piperazine-1-4-bis(2-ethanesulfonic acid) (PIPES), and 0.228 mM Sr^{+2} as $\text{Sr}(\text{NO}_3)_2$ prepared in 0.1 M NaCl, as was the washout solution, to be representative of the far-field vadose zone beneath the Hanford tank farms. The pH of the tracer and washout solution was adjusted to 8 with NaOH so that the solution pH was equivalent to that of the soil. The two non-reactive tracers used in this study (Br^- , PIPES) differ in molecular size and therefore their free-water diffusion coefficient (Pace et al., 2003). Separation of tracer concentration profiles should be observed if any physical non-equilibrium processes (PNE) such as preferential flow and matrix diffusion occur (Jardine et al., 1998; Jardine et al., 1999; Langner et al., 1999; Mayes et al., 2003; Pace et al., 2003).

Core Disassembly

The unsaturated reactive transport experiment was terminated early (38% of injected Sr^{+2} mass remained in the core) at 122 PV (relative volume) and the core was disassembled. Sediment samples were collected at every 2-cm depth interval along the length of the core and at each visibly different bedding unit across the face of the core. The samples were then dried in an oven at 40°C to determine the gravimetric water content (mass wetness) as a function of depth and grain size determined visually during core dissection. The samples were dried at 40°C in order to preserve the mineral structures as sequential extractions of each mineral phase were to be conducted. It was determined that this lower drying temperature represents a 1% difference in the mass

wetness calculation commonly performed at 105°C. The strontium sorbed to the soluble and carbonate fractions were extracted from 4 samples at each depth that represented the 2 driest and 2 wettest samples from that depth within the entire core. In order to determine the relationship between remaining strontium sorbed, mineral reactivity, and mass wetness, sequential extractions were performed on samples from a single layer collected at 13.5cm core depth. The soluble fraction was initially extracted from the sediments using 5 mM MgCl_2 , pH adjusted to 7 with 0.1M NaOH (Kunze and Dixon, 1986). The dissolution of carbonates was next performed using 0.5 M sodium-acetate, buffered to pH 5 with acetic acid (Kunze and Dixon, 1986). Oxides finally were extracted from the sediments using a 1 L solution of 78.4g/L sodium citrate, 9.33 g/L sodium bicarbonate, and 22.2 g/L sodium dithionite (Kunze and Dixon, 1986). A total digestion of the samples was performed at Activation Laboratory, Ancaster, Ontario, Canada following procedure 1F in which 0.25 g of sample is digested with four acids beginning with hydrofluoric, followed by a mixture of nitric and perchloric acids, then heated using a precise programmable heating unit ramping and holding the temperature for several cycles which takes the sample to dryness. The sample is then dissolved using hydrochloric acid. The samples are then analyzed using a Perkin-Elmer Optima 3000 Inductively coupled plasma (ICP) emission spectroscopy.

Analytical Techniques

Analysis was performed using an ion chromatograph (IC, Dionex600)), inductively coupled plasma mass spectrometry (ICPMS, ELAN-6100, Perkin-Elmer), atomic adsorption – emission spectroscopy (AA-ES, AAnalyste 800, Perkin-Elmer), and

an ion chromatograph coupled to an inductively coupled plasma mass spectrometry (IC-ICPMS (Dionex IC coupled to a PerkinElmer ELAN DRCplus ICP-MS instrument, conducted by Hakan Gurleyuk, Applied Speciation, LLC.). The concentrations of Br^- and PIPES were quantified simultaneously using a low-pressure liquid chromatography system with UV detection (190 nm) (Pace et al., 2003). Strontium analysis was conducted by atomic adsorption or inductively coupled plasma mass spectrometry. A Total Organic Carbon Analyzer (Model # TOC-5000, Shimadzu, Japan) was used to determine the concentration of EDTA. An IC-ICPMS was used to quantitatively measure SrEDTA^{2-} and other Me-EDTA complexes that may have formed in the initial and final batch solutions. The EDTA complexes were separated on an AG16 anion exchange guard column using NH_4NO_3 as the mobile phase. The eluant was adjusted to 8 to match the pH of the samples. The ICPMS portion of the IC-ICPMS was operated in the DRC mode with NH_3 as the reaction gas to eliminate polyatomic interferences.

Modeling the Displacement Experiments

The steady-state transport of non-reactive tracers through the packed columns and unsaturated undisturbed core was mathematically described using CXTFIT version 2.1 (Toride et al., 1999), a code based on the convection-dispersion equation (CDE). In the absence of physical non-equilibrium processes (PNE), the CDE model in CXTFIT was used to describe transport. In the presence of perceived PNE (i.e. media bypass or separation of non-reactive tracer concentration profiles), the mobile-immobile model (MIM) in CXTFIT was used to describe the experimental data. Input parameters for CXTFIT were effluent concentrations (C/C_0), length of core (L (cm)), time (pore

volume), mean water pore velocity (V (cm hr⁻¹)) where V = flow rate / ($\pi r^2 \theta$), input pulse (relative volume), and the retardation factor (R). Theoretically, $R = 1$ for conservative non-reactive tracers. In the CDE model, a dispersion coefficient (D (cm² hr⁻¹)) was determined for each non-reactive tracer by a single-parameter curve fit while all other parameters remained fixed. In the MIM model optimized parameters β (dimensionless f , where f is the fraction of mobile water) (eq. 1), ω (dimensionless α (hr⁻¹) where α is the first order rate coefficient, eq. 2), and D were determined by fitting the model to the observed data holding all other parameters constant (Toride et al., 1999).

$$f = \frac{\beta(\theta_m + \rho_b K_d) - \theta_m}{\rho_b K_d} \quad (1)$$

$$\alpha = \frac{\omega v}{(1 - \beta)RL} \quad (2)$$

Strontium retardation factors (R) in the packed column were determined by fitting R and D to the experimental data in the CDE holding all other parameters constant. To fit the strontium breakthrough curve in the presence of PNE such as preferential flow, the MIM was used to determine Sr⁺² R , ω , and β holding D constant to that determined in the model fit of the non-reactive tracer, Br⁻, data. Strontium K_d values for the packed column and undisturbed core experiments were calculated from the model fitted R value (eq. 3).

$$K_d = \frac{(R - 1)\theta}{\rho_b} \quad (3)$$

RESULTS AND DISCUSSION

Batch Experiments

Linear isotherms were used to describe the batch experimental data conducted with the bulk Hanford sediment as well as the sand (95% of bulk), silt (4% of bulk), and clay (1% of bulk) fractions. Bulk sediment K_d values (3 – 4.3 ml/g) were within the range of K_d values obtained by Steefel et al., 2002; Zachara et al., 2002b. Strontium sorption was significantly affected by the rock:water ratio in the bulk and sand fractions (Fig. 1, note all Figures are located at the end of the Part). More strontium was sorbed at the 1:2 rock:water ratio compared to the 1:1 rock:water ratio which was unexpected since a higher rock:water ratio allows for a greater concentration of sorption sites (i.e. more soil) and therefore potentially greater sorption. The observed results were most likely due to the dissolution of cations from the soil that then compete for sorption sites with strontium in these closed batch systems. Porro et al. (2002) also observed similar behavior with crushed basalt from the Idaho National Engineering and Environmental Laboratory (INEEL).

Experiments performed on the different size fractions indicated that sorption was much greater in the silt and clay size fractions than the sand fraction and bulk sediment. Sorption to the clay and silt size fractions did not seem to be affected by the rock:water ratio in comparison to the bulk sediment and sand fractions (Fig. 1). This may be attributed to the large number of sorption sites (i.e. ion exchange sites) on the clay and silt fractions. This suggests that under unsaturated conditions where transport occurs through smaller pores (i.e. smaller particle sizes), should be greater relative to saturated conditions where the entire bulk soil is active.

Sorption isotherms (Fig. 1) indicated that there are only minor differences between Sr^{+2} and SrEDTA^{-2} sorption in all size fractions including the bulk fraction. This suggests that the SrEDTA^{-2} complex maybe dissociating upon contact with the Hanford sediment and this was confirmed by IC-ICPMS analysis (Fig. 2). IC-ICPMS analysis of batch solutions indicated that the SrEDTA^{-2} complex was not stable in the presence of the Hanford sediment and that MgEDTA^{-2} was the resulting stable complex with an unidentified Ca-complex and minor amounts of MnEDTA and PbEDTA . Strontium, on the other hand, was released as a divalent cation or existed as an unidentified strontium complex (Fig. 2).

Miscible Displacement Experiments

Saturated packed columns

All packed column experiments involving complexed and uncomplexed Sr resulted in the delayed breakthrough of Sr^{+2} relative to the non-reactive tracer Br^- which suggests that strontium was very reactive with the media (Fig. 4). Column K_d values, calculated from the model fitted R values, were an order of magnitude greater than batch K_d values (Fig. 1 and Table 2) due to the increase in sediment mass and suggests that removal of reaction products in flow-through systems versus the competition of dissolved species in closed system batch conditions, resulted in increased sorption. No significant differences in Sr^{+2} K_d values were observed with different column lengths (Table 2), suggesting that retardation was independent of sediment mass given that the experiments had similar residence times.

Aqueous EDTA concentrations indicated that EDTA eluted from the columns at approximately the same time as the non-reactive tracer, Br^- (Fig. 4) and this was observed in all experiments. Thus, SrEDTA^{-2} ($\log K = 10.43$) (from the GWB database, Thermo.com.V8.R6.full – modified by Scott Brooks, ORNL) must be dissociating during transport resulting in the formation of more stable cation complexes available in the soil such as MgEDTA^{-2} ($\log K = 10.51$), CaEDTA^{-2} ($\log K = 12.37$), Fe(III)EDTA^- ($\log K = 27.7$), and AlEDTA^- ($\log K = 18.97$) (all values for 0 M IS at 25°C obtained from the GWB database, Thermo.com.V8.R6.full – modified by Scott Brooks, ORNL). This is consistent with the results of Jardine et al. (1993) and Jardine and Taylor (1995) which demonstrated that SrEDTA^{-2} was not stable in the presence of acidic, Al^{+3} and Fe^{+3} rich ORNL sediments. Fe(III)EDTA^- and AlEDTA^- are not likely to form at near neutral pH (Girvin et al., 1993; Mayes et al., 2005; Nowack and Sigg, 1997; Szecsody et al., 1994; Zachara et al., 1995). IC-ICPMS was used to analyze the samples, but unfortunately there was not enough sample volume available to obtain reliable results. However, analysis of our batch experiments did suggest the formation of MgEDTA^{-2} , MnEDTA^- , and PbEDTA complexes which are also more stable than SrEDTA^{-2} (Fig. 2). These cations may be released into solution during the ion exchange process with Sr^{+2} . The results presented here strongly suggest that EDTA does not contribute to the accelerated transport of Sr^{+2} in Hanford sediments for the conditions studied. Strontium is not expected to be transported as an EDTA complex, but rather a divalent cation or an unknown reactive complex (Fig. 2). Therefore, an unsaturated strontium transport experiment in an undisturbed core from the Hanford formation was conducted with Sr^{+2} rather than SrEDTA^{-2} .

The results from the packed columns were modeled with the CDE model in CXTFIT version 2.1. The K_d values ranged from 9.93 - 14.31 for the Sr^{+2} columns and 16.11 - 21.80 for the SrEDTA^{-2} experiments (Table 2). The two 2-cm column experiments were more difficult to model due to the small length to diameter ratio in which the CDE theory begins to fail. The model was not able to perfectly fit the first arrival of strontium. In some cases, the model resulted in slightly earlier first arrival of Sr^{+2} breakthrough compared to observed BTCs. This is most significant in the Sr^{+2} - 4.5 cm which is consistent with its lower fitted K_d value. Therefore, it is concluded that the K_d values from the different column lengths are in general fairly similar. The slightly larger K_d values observed from the SrEDTA^{-2} experiments may have resulted from the release EDTA^{-4} during SrEDTA^{-2} dissociation which then may complex with other dissolved cations such as Mg^{+2} creating more sorption sites on the sediment for Sr^{+2} therefore increasing retardation through the column.

Undisturbed cores

A multiple non-reactive tracer technique was used to quantify the hydrologic transport mechanisms present in the Hanford undisturbed core. Pace et al. (2003) described, in detail, the hydrologic results of the non-reactive tracer saturated and unsaturated flow experiments conducted in undisturbed core. In summary, unsaturated flow resulted in early tracer breakthrough relative to saturated conditions and with slight tracer separation (Fig. 5 a,b). These results are suggestive of physical non-equilibrium resulting from preferential finger flow and media bypass with a slight development of immobile water during flow parallel to bedding (Gamerding and Kaplan, 2000; Mayes

et al., 2003; Padilla et al., 1999). These results are similar to unsaturated experiments in repacked sandy sediments (Gamerding and Kaplan, 2000; Padilla et al., 1999) and in both horizontal and vertical cross-bedded cores from the Ringold Formation at Hanford (Mayes et al., 2003), in that all experiments indicate early breakthrough and more asymmetric BTCs relative to saturated conditions. During unsaturated flow, larger pores are drained, resulting in partial disconnection of the primary porosity from the predominant flow paths. Regions of immobile water can develop allowing for mass exchange between immobile and mobile regions to occur at water contents near saturation, which is typically governed by diffusive processes. As moisture content decreases further, the flow paths are isolated to fine grained layers and less interaction with the immobile water occurs, resulting in more symmetric BTCs compared to saturated conditions (Fig. 5b). Gravity driven flow along the coarser beds due to the vertical orientation of the core may also result in preferential flow and media bypass. In fact, the fraction of mobile water in the Hanford flow bedding parallel core was calculated to be 79% with very low rate of exchange (α) between the two phases (Table 2).

The observed strontium breakthrough curve was significantly retarded compared to the non-reactive tracers despite preferential flow and media by-pass (Fig. 5a). Modeling of the Sr^{+2} data resulted in a K_d value of 6.7 ml/g with a fraction of equilibrium sites of 48% and an exchange coefficient of $4.4\text{e}^{-4}\text{h}^{-1}$ (Table 2). The K_d calculated from the fitted R value for the unsaturated undisturbed core was less than the saturated packed column K_d values despite longer residence times (Table 2) which was unexpected as unsaturated flow generally occurs through small pore spaces occupied by small particles

such as clay and silt, and batch experiments indicated that these particles had a greater sorption capacity for strontium than the bulk sediment (Fig. 1). This geochemical observation coupled with observed physical non-equilibrium processes, such as preferential flow in which flow is sequestered into conductive sediment beds, minimizes the interaction with immobile water and possibly reactive exchange surface sites and may result in “accelerated” transport. This phenomenon was not observed in packed columns of crushed basalt conducted under various moisture contents (Porro et al., 2000). The difference in behavior is most likely due to the nature of the different media as well as disturbed versus undisturbed samples. It appears that by using undisturbed samples, which preserves the heterogeneity of the media, the “accelerated” transport of strontium due to preferential flow and media bypass was observed.

The unsaturated core experiment was terminated to determine mass wetness and to perform sequential extractions on visibly distinct beds as a function of depth. Figure 6a shows the distribution of mass wetness in the core. Mass wetness at the top of the core was relatively uniform and became more heterogeneous with depth as the various sediment beds began to influence the distribution of moisture. Note also the correlation of “coarse” and “fine” layers with mass wetness which confirms the objective of the disassembly method (Fig. 6a). The amount of extractable strontium increased with depth due to a higher concentration of strontium remaining in the bottom of the core due to the intentional premature termination of the washout phase of the transport experiment (Fig. 6a).

The results from the sequential extractions on samples collected at one depth (13.5 cm) suggest that 60 – 100 % of the 0.03 mg/g of sorbed strontium was recovered in

the carbonate and soluble fractions (Fig. 6b, Table 3) with strontium being approximately equally distributed between these two phases. The extraction procedure was tested with test duplicates and results show very good reproducibility (Fig. 6b). Approximately 15-18% of the 0.03 mg/g sorbed strontium was recovered in the oxide fraction of the sediments. All together, ~100% of the 0.03 mg/g sorbed strontium was recovered in the soluble, carbonate, and oxide fraction except for four samples in which the recovery ranged from 70 – 95 % (Fig. 6b). These results are similar to Knepp (2002) which suggested that only 25% of strontium was associated with the carbonate phase. It is also significant in that Zachara et al. (2002a, b) concluded that strontium associated with carbonate was immobile.

A strong negative correlation was observed between sorbed strontium and the drier / coarser grained sediments (Fig. 6b). This suggests a relationship between grain size, water content, and strontium sorption, and validates the use of intact cores in transport experimentation. During the washout phase of transport, our extraction experiments indicate that more strontium may be recovered from samples with lower mass wetness possibly due to the lesser amount of water passing by the coarser grains delaying Sr^{+2} desorption, the inter-porosity of the coarse basalt fragments (Tokunaga et al., 2003), and/or the formation of precipitates. The greater amount of extracted strontium recovered from the lower mass wetness samples may also be due to gravity driven flow during the unsaturated transport experiment due to the vertical orientation of the core.

Total digestions were initially performed to determine the amount of remaining sorbed strontium on the soil. Results of the total digestions show similar concentrations

of Sr^{+2} in the residual material from the sequential extraction procedure, untreated (no extraction) sediment from the undisturbed core, and bulk disturbed material separate from the core. These results suggest that there is a large amount of strontium indigenous to the soil (~0.38 mg/g) that is most likely associated with the basalt fragments in the soil. It was determined that the indigenous strontium was not available during the sequential extractions due to the large volume of solution that had been flushed through the core prior to experimentation and ICPMS analysis confirmed low concentrations of strontium prior to initiating the tracer experiment. Therefore, the total amount of strontium available for extraction on these samples was estimated from mass balance calculations and determined to be 0.03 mg/g.

The results suggest that strontium transport in the Hanford vadose zone may be controlled by multiple factors such as preferential flow and differential sorption to size fractions / mass wetness, and that strontium sorbed may act as a long term source from the coarse-grained sediments. Despite the similarities between the unsaturated undisturbed core K_d value and batch K_d values, batch experiments are not appropriate for measuring strontium unsaturated transport in flowing systems. Flowing systems and closed systems, such as in batch experiments, respond differently to various experimental conditions, such as amount of sediment mass. Results presented here suggest that strontium transport parameters are best measured with natural, intact sediments and that while batch results were similar to those of Steefle et al. (2002) which used altered sediment, the intact core results measure the influence of sedimentary structure on strontium transport and the interaction of strontium with distinct mineral phases of varying reactivity. Saturated and unsaturated packed columns fail to account for the

influence of sediment structure on contaminant transport as suggested by the observed data presented here and by Porro et al. (2002). Processes such as preferential flow and media bypass that occur during unsaturated flow along bedding may affect transport of reactive contaminants, such as strontium, yielding earlier than expected first arrivals of contaminants.

CONCLUSIONS

Strontium transport in vadose zones of semi-arid environments, such as the Hanford vadose zone, is affected by multiple processes. Batch and saturated re-packed column experiments conducted with SrEDTA^{-2} indicate that the metal-organocomplex dissociates upon contact with the soil due to the formation of stronger complexes such as MgEDTA^{-2} , MnEDTA^{-} , and PbEDTA . Therefore, strontium is most likely transported as a reactive divalent cation or some undetermined reactive strontium-complex, perhaps aqueous strontium carbonate. Batch K_d values, which are representative of a closed system, may not be appropriate for the prediction of Sr^{+2} transport due to the dissolution of competing cations which inhibit strontium sorption. Batch experiments conducted with the various size fractions indicate that Sr^{+2} sorption is greatest in the clay fraction, followed by the silt and sand fraction, respectively while the bulk sediment K_d is dominated by the more abundant sand fraction. From this, it may be hypothesized that under unsaturated conditions, Sr^{+2} sorption may increase as flow is sequestered into smaller pore regimes. However, the Sr^{+2} K_d in the unsaturated core is slightly less than the saturated packed column K_d values which was unexpected since batch experiments showed the fine fraction material had a higher K_d than the coarser material. Termination

of the washout phase of the undisturbed core experiment and disassembly of the core indicated a more heterogeneous mass wetness distribution with depth through the core. Extractable strontium was observed to increase with depth through the core as the core was terminated during the washout phase of the experiment resulting in more strontium remaining at the bottom of the core. Sequential extractions from samples collected at one depth of the core indicate a higher concentration of strontium remaining in the soluble and carbonate fractions of the coarse-grained particles (drier fractions). Therefore, more complex coupled hydrologic and geochemical processes must be occurring such as the formation of precipitates, sorption in the inter-porosity of the basalt fragments, preferential flow and media bypass as well as diffusion into immobile water, and / or gravity driven flow through the coarse (dry) fractions due to the orientation of the core.

All of the experiments presented in this paper suggest that preferential sorption to the fine grain material under unsaturated conditions may not be the only factor influencing strontium transport. Physical non-equilibrium processes such as preferential flow and media by-pass may result in “accelerated” transport of Sr^{+2} while differential sorption to mineral phases and grain-sizes may create a “sink” for strontium. Strontium transport through vadose zone sediments such as unconsolidated layered silts and sands common to the western U.S. may be complicated by these various processes and cannot be easily predicted with batch or saturated packed column experiments. and therefore complicate the transport processes in

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Table 1. Experimental parameters for re-packed column experiments and undisturbed core experiments.

Experiment	Metal	Length (cm)	Radius (cm)	Tracer Pulse (PV)	Residence Time (h)	ρ_b (gcm ⁻³)	θ (cm ³ cm ⁻³)
Saturated packed columns							
	Sr ⁺²	2.0	0.5	13.81	2.3	1.86	0.3636
	Sr ⁺²	4.5	0.5	125.36	2.1	1.71	0.3820
	SrEDTA ⁻²	2.0	0.5	24.32	1.7	1.87	0.2972
	SrEDTA ⁻²	4.5	0.5	11.93	0.8	1.88	0.3368
Undisturbed core	Sr ⁺²	23	11.0	29.25	154.2	1.79	[†] 0.1765

[†]unsaturated experiment.

[Tracer pulse in relative volume ($V_{\text{pulse}} / V_{\text{w(unsat core)}}$)]

Table 2. Modeling parameters for re-packed column and undisturbed core experiments.

Experiment	Tracer	Mass Recovery (%)	Model	V (cm/h)	P_e	f	α (h^{-1})	R	r^2	K_d (ml/g)
Saturated Packed columns	2 cm Sr^{+2}	112	CDE	0.86	0.11 ± 0.08	NA	NA	1.00	0.465	
		133	CDE	0.86	11.6 ± 1.6	NA	NA	74.35 ± 2.87	0.925	14.31 ± 0.59
	4.5 cm Sr^{+2}	99	CDE	2.10	83.6 ± 22.7	NA	NA	1.00	0.993	
		99	CDE	2.10	23.0 ± 8.4	NA	NA	45.50 ± 2.89	0.946	9.93 ± 0.64
	2 cm $SrEDTA^{-2}$	118	CDE	1.17	12.9 ± 7.8	NA	NA	1.00	0.676	
		113	CDE	1.17	15.7 ± 1.0	NA	NA	102.6 ± 1.5	0.968	16.11 ± 0.22
	4.5 cm $SrEDTA^{-2}$	109	CDE	5.62	16.6 ± 7.9	NA	NA	1.00	0.925	
		96	CDE	5.62	8.41 ± 0.12	NA	NA	122.6 ± 0.6	0.999	21.80 ± 0.09
	Undisturbed core [†]	103	MIM	0.15	26.0 ± 15.3	0.749 ± 0.231	$7.83e-4 \pm 1.27e-3$	1	0.988	
		101	MIM	0.15	25.2 ± 7.7	0.793 ± 0.063	$4.49e-4 \pm 2.91e-4$	1	0.997	
		62	MIM	0.15	26.0	0.482 ± 0.017	$4.40e-4 \pm 5.03e-3$	68.93 ± 0.97	0.969	6.70 ± 0.10

[†]unsaturated experiment.

[V = pore water velocity, P_e = Peclet number, f = fraction of mobile water, α = rate of exchange between mobile and immobile water, R = retardation factor, Parameters with no 95% confidence intervals are fixed. Note the poor fit of the Br^- data for the 2cm columns, dimensions in which the CDE begins to fail.]

Table 3. Sequential extraction results

Sample	Description	Soluble (mg/g)	Carbonate (mg/g)	Oxide (mg/g)
Hf-6k	sand	0.0214	0.0160	0.0056
Hf-6j	silt	0.0128	0.0152	0.0042
Hf-6d	sand	0.0084	0.0142	0.0059
Hf-6g	clay	0.0160	0.0147	0.0057
Hf-6i	clay	0.0083	0.0123	0.0055
Hf-6a	sand	0.0135	0.0155	0.0053
Hf-6c	clay	0.0054	0.0122	0.0021
Hf-6f	silt	0.0112	0.0154	0.0045
Hf-6h	sand	0.0113	0.0196	0.0034
Hf-6e	clay	0.0065	0.0173	0.0050

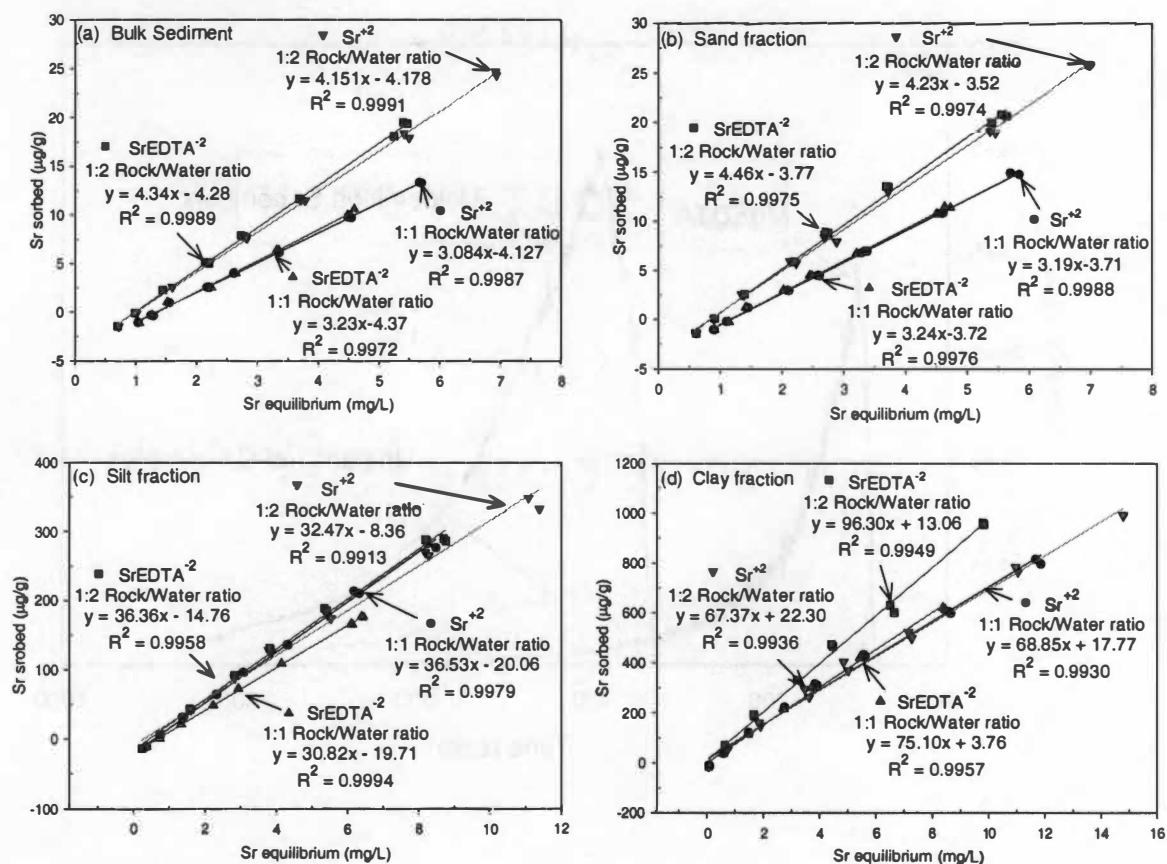


Figure 1. Results from Sr^{+2} and SrEDTA^{-2} batch sorption experiments conducted at two different rock:water ratios (1:2 or 1:1) with bulk Hanford sediment and the various size fractions (95% sand, 4% silt, and 1% clay). The K_d values are represented as the slope in the equation of the line that fits each data set.

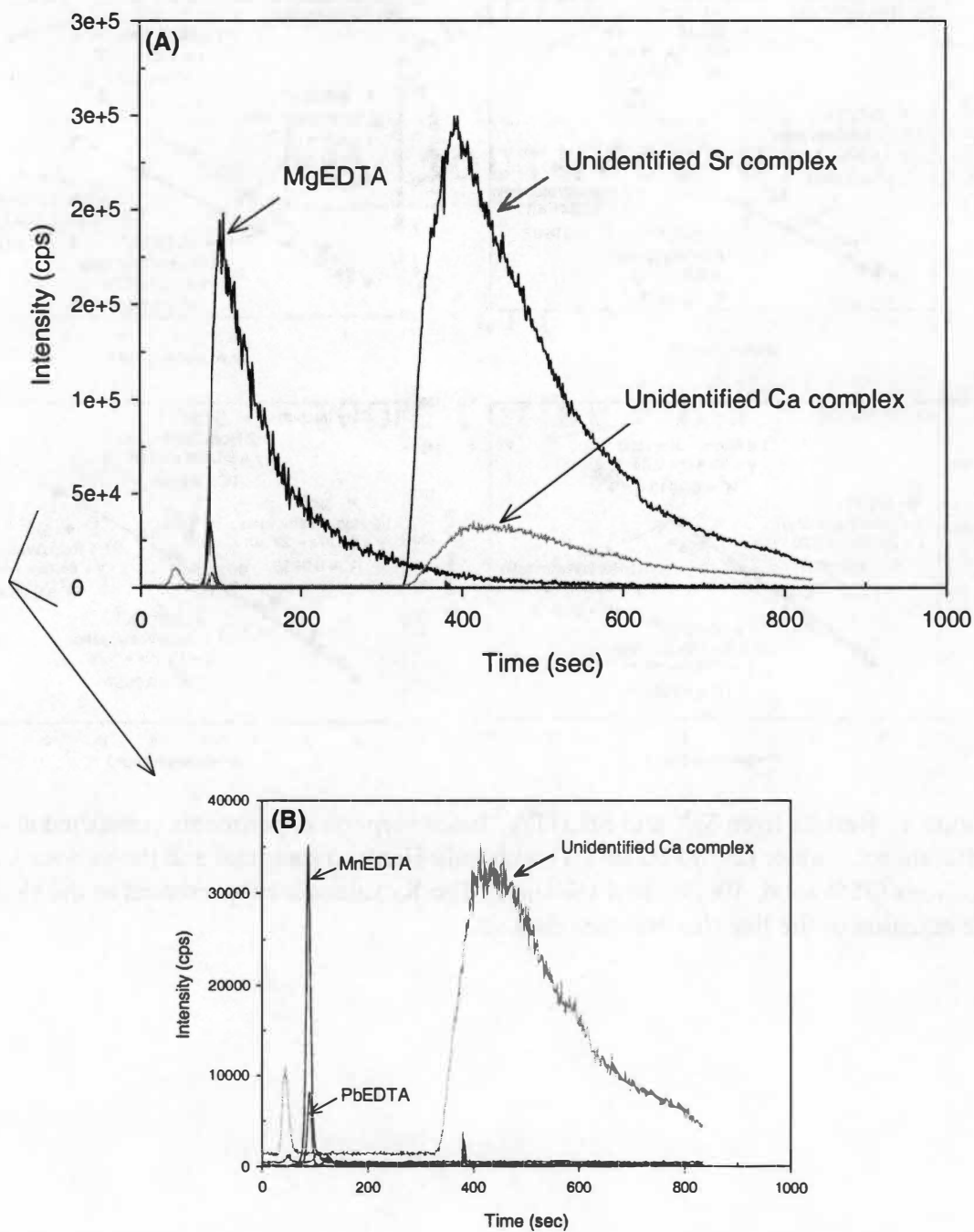


Figure 2. Results from IC-ICPMS analysis. (a) and (b) are results from analysis of batch experiment solutions confirming the absence of SrEDTA^{-2} in the equilibrium solution and the formation of an unknown Sr-complex. Note the different intensity scale.

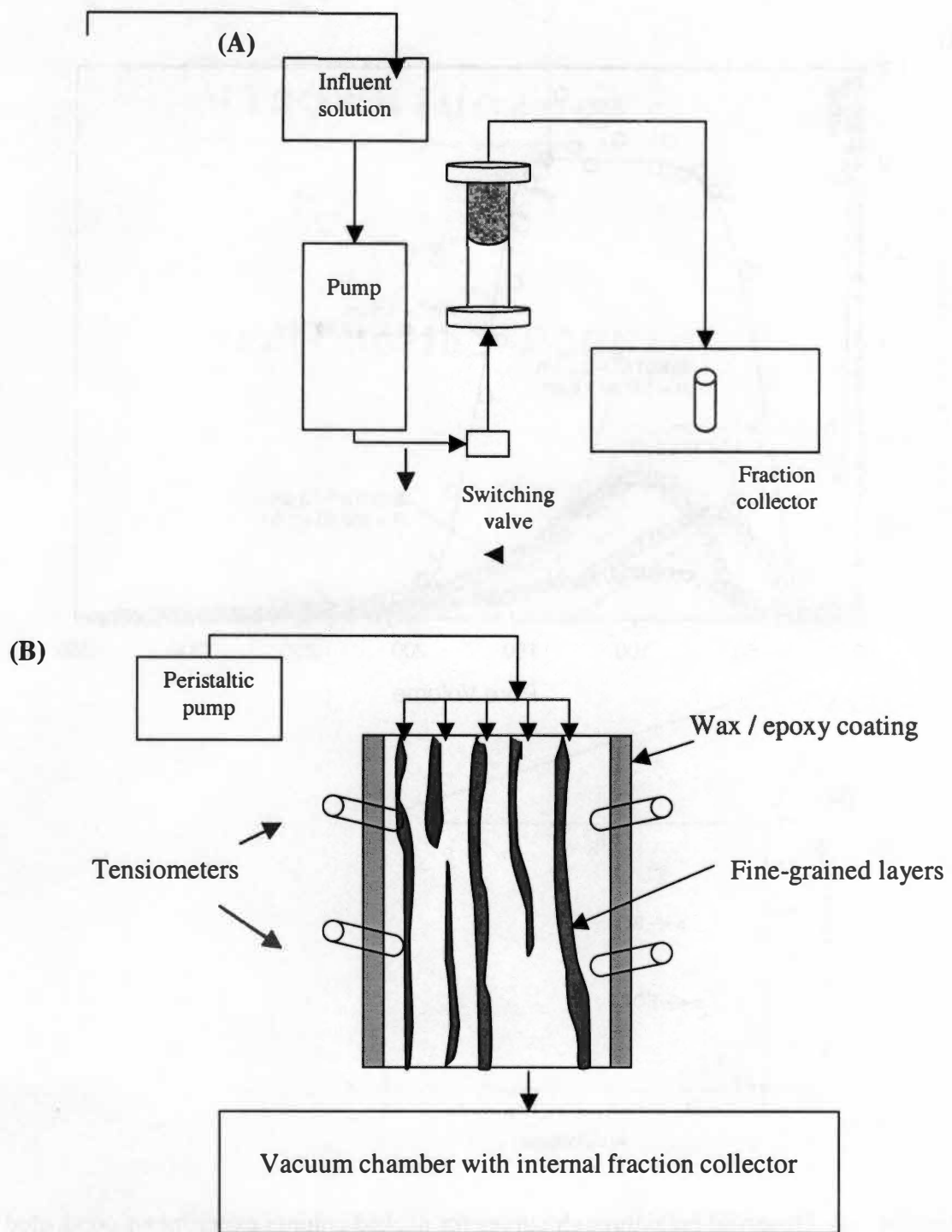


Figure 3. Diagrams of the experimental setup for (A) the saturated packed columns and (B) the unsaturated undisturbed core experiments.

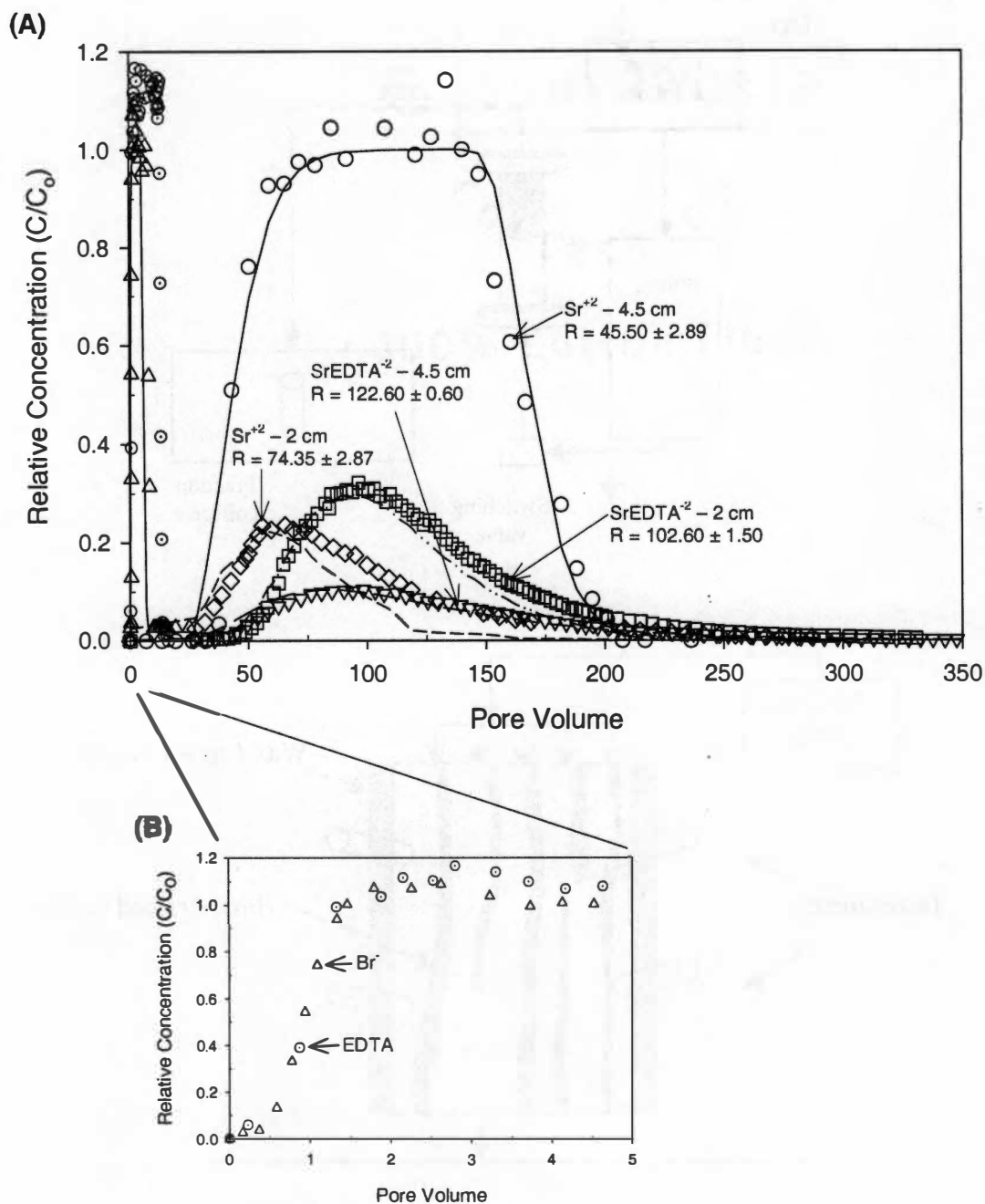


Figure 4. (a) Observed breakthrough curves for packed column experiments conducted with Sr^{+2} and SrEDTA^{-2} , note the SrEDTA^{-2} curve represents dissociated Sr^{+2} . Solid lines represent the model fits, while the symbols represent observed data. (b) Example of coelution of Br^- and EDTA which was observed in all four saturated packed column experiments.

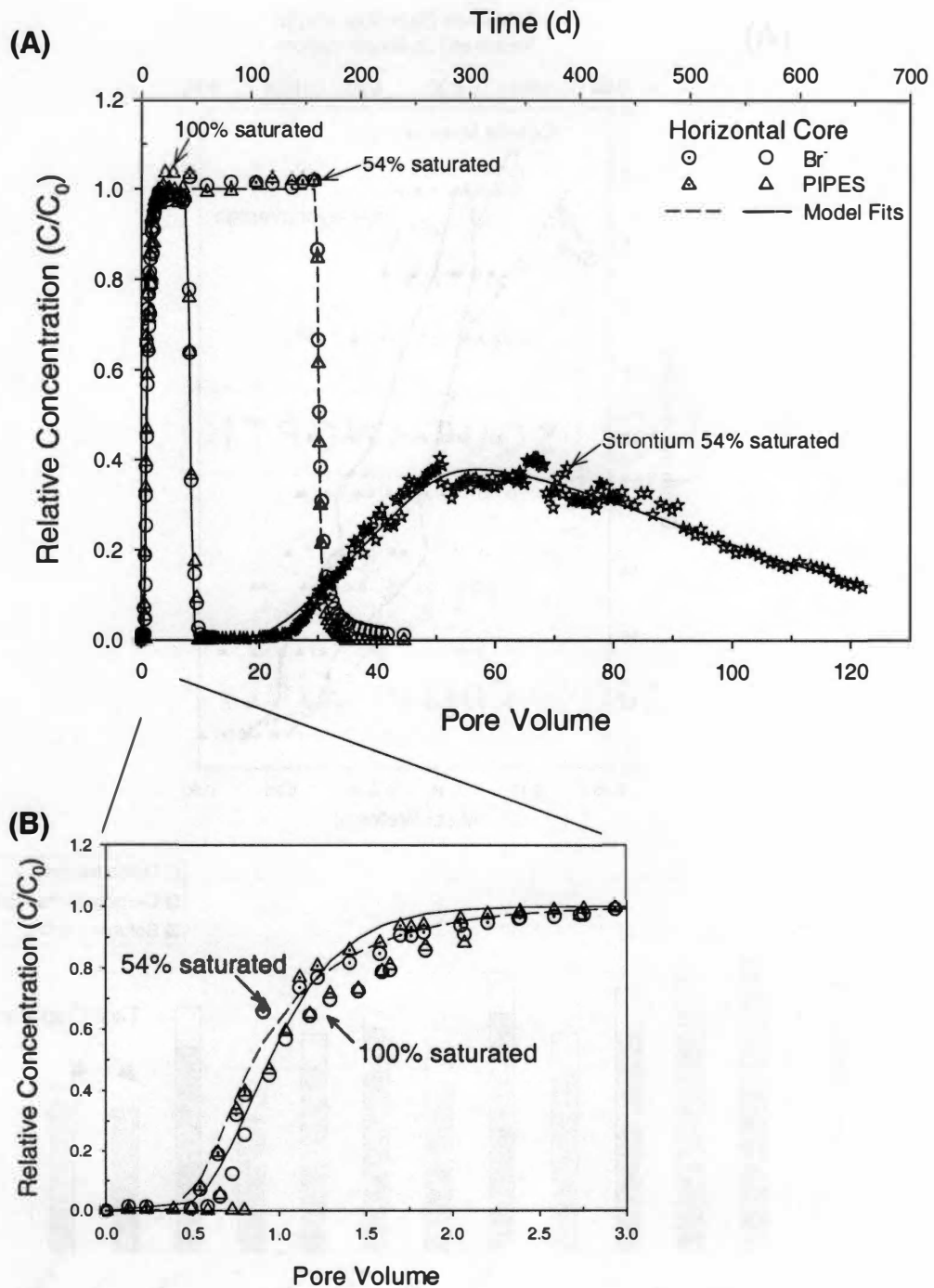


Figure 5. (a) Observed breakthrough curve of Sr^{+2} at unsaturated conditions in the undisturbed core. Solid lines represent the model fit while symbols represent the observed data (reproduced from Mayes et al. (2005) with permission). (b) Observed breakthrough curves for multiple non-reactive tracers under saturated and unsaturated conditions in the undisturbed core illustrating physical non-equilibrium processes (reproduced from Pace et al. (2003) with permission).

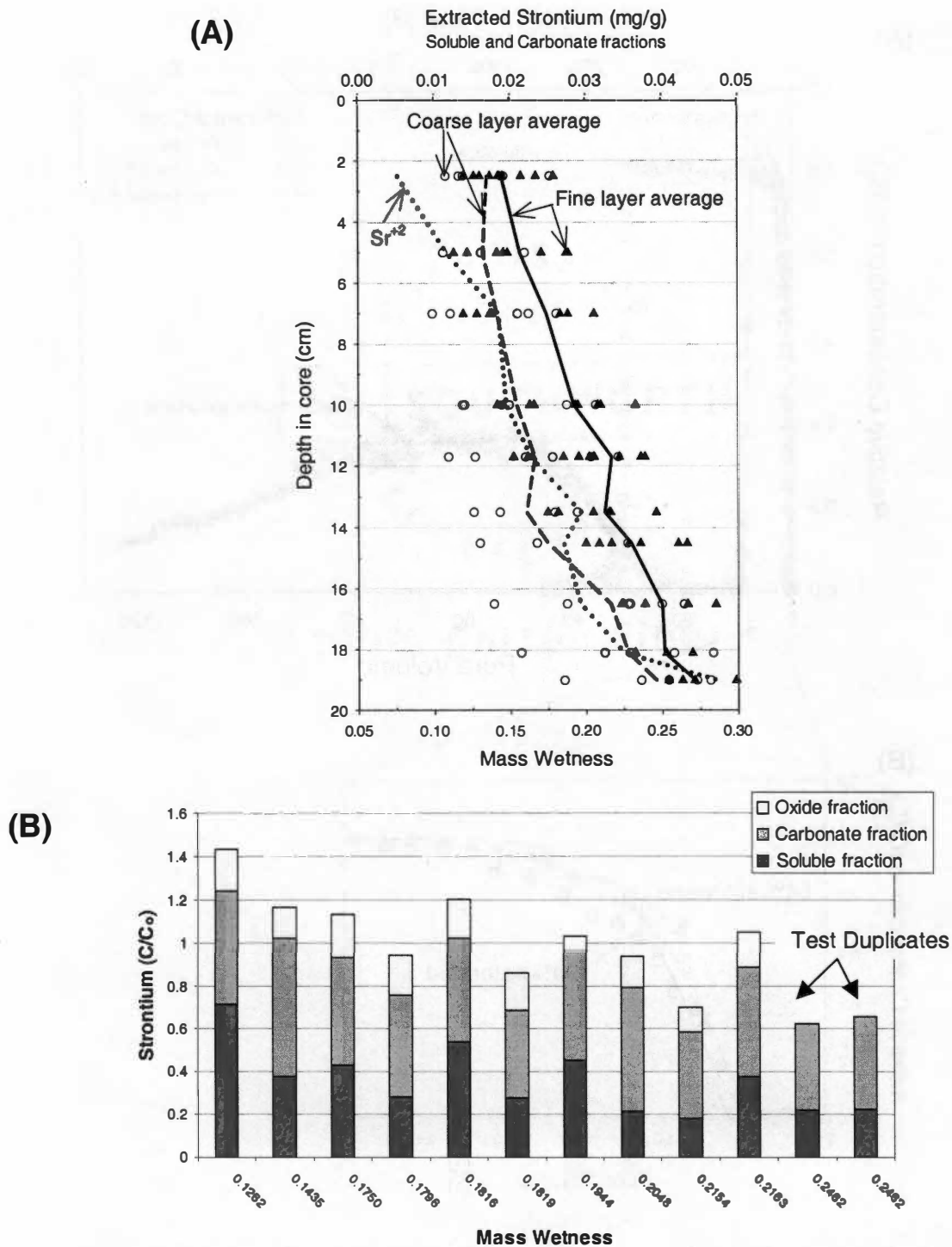


Figure 6. (a) Moisture distribution and extracted strontium as a function of depth in the intact horizontal core and (b) mineralogical association of sorbed Sr^{+2} as determined by sequential extractions on sediments collected at 13.5 cm depth represented as a fraction of sorbed strontium in the core (0.03 mg/g) at the time of termination of the experiment.

PART 4

U(VI) AND CO(II) EDTA TRANSPORT THROUGH UNSATURATED UNDISTURBED CORES FROM THE HANFORD FORMATION, RICHLAND, WA

ABSTRACT

At the U.S. Department of Energy's Hanford Site in Richland, WA nuclear processing waste containing contaminants such as Co(II)EDTA and U(VI), were released in the vadose zone from leaking underground storage tanks and have been detected in the vadose zone. There is concern that waste released to the vadose zone could ultimately reach the groundwater and eventually flow into the Columbia River. The goal of this manuscript is to quantitatively investigate reactive transport of Co(II)EDTA and U(VI) in undisturbed Hanford sediments during unsaturated flow along bedding and across bedding. Laboratory scale undisturbed sediment cores were collected from the Environmental Restoration Disposal Facility (ERDF) at Hanford. The cores were collected vertically (flow across bedding) and horizontally (flow along bedding) to determine the influence of bedding and flow anisotropy on transport of reactive contaminants over a range of moisture contents. Multiple non-reactive tracers, which differ in their diffusion coefficients, were used to quantify physical non-equilibrium processes such as preferential flow and media bypass as well as diffusion into immobile water. Miscible displacement experiments were conducted with Co(II)EDTA and U(VI) in an effort to quantify the importance of these hydrologic processes on reactive transport. Results indicated the preference of unsaturated flow along bedding while flow across bedding was inhibited due to perched water in fine-grained layers as capillary barriers developed in the underlying coarse-grain sediment beds. During unsaturated flow along bedding, multiple flow paths, most likely along layers of different pore size, developed as suggested by the bimodal characteristics of the tracer breakthrough curves. Differential reactivity of U(VI) and Co(II)EDTA was observed in flow along bedding

versus flow across bedding as suggested by early first arrival of the reactive tracers which was ~ 0.33 pore volumes (V_{eluted}/V_w) during flow along bedding, compared to ~ 0.8 pore volumes during flow across bedding. The results indicated that sedimentary bedding controlled the hydrology which then affected the geochemical processes at different moisture contents. These coupled processes may significantly affect contaminant transport in sediments from semi-arid environments such as Hanford.

KEY WORDS: displacement experiments, reactive tracers, Hanford Site, hydrogeochemical processes.

INTRODUCTION

The U.S. Department of Energy Hanford Site, located in the semi-arid climate of south central Washington State, was used to produce weapons-grade plutonium during the cold war era. Approximately 200 million liters of waste from this process and from related activities was stored in 177 underground storage tanks in the 200W / 200E areas (Agnew et al., 1997; Bjornstad, 1990). Of the total storage tanks, 149 of them are single-shell tanks of which 67 have leaked high-level radioactive and hazardous waste into the deep vadose zone. The waste in the tanks is composed of a complex mixture of high-level radioactive contaminants such as U(VI), organic chelates including EDTA⁻⁴, and other hazardous elements such as Co-60. Monitoring of the site has indicated that contaminants have traveled much further from the original spill sites than initially predicted by current conceptual models (Dirkes and Hanf, 1997; DOE, 2002; Hartman and Dressel, 1997), suggesting the likelihood of preferential flow and the need for an improved understanding of transport processes in the Hanford vadose zone.

The goal of this paper is to quantitatively investigate Co(II)EDTA and U(VI) transport in undisturbed sediment cores from the Hanford site during unsaturated flow along bedding and across bedding. The objectives are to provide an improved conceptual and predictive capability of flow and reactive transport processes in sediments from semi-arid regimes. We also seek to assist Hanford site performance / risk assessment and decision-making processes for Tank Farm restoration.

Typical batch sorption experiments indicate that U(VI) interaction with the sediment is influenced by dissolved carbonate, pH, and iron oxide content on the solid phase (Bargar et al., 1999; Barnett et al., 2002; Bostick et al., 2002; Duff et al., 2002; Echevarria et al., 2001; Liger et al., 1999; Payne et al., 1994). Surface complexation models using two-sorption-sites (a strong oxide site and a weak oxide site) have been developed (Barnett et al., 2002; Barnett et al., 2000) using high iron and manganese Ringold sediments from the White Bluffs area and shows the importance of Fe- and Mn-oxides as well as carbonate on uranium sorption. Packed column experiments (Gamerding et al., 2001) conducted at various moisture contents indicated less U(VI) sorption under dynamic (flowing) conditions versus equilibrium conditions, and less U(VI) sorption at lower moisture contents due to possible kinetic effects during transport at high flow velocities.

There is also a tremendous amount of literature on Co(II)EDTA reactions (Brooks et al., 1996; Jardine and Taylor, 1995a; Jardine and Taylor, 1995b; Kent et al., 2002; Mayes et al., 2000; Mayes et al., 2005; Nowack, 2002; Nowack and Sigg, 1997; Zachara et al., 1995a; Zachara et al., 1995b). Recent investigations of Co(II)EDTA interactions with Hanford sediment indicate that Mn-oxide content may be used to predict the

oxidation rate using known geochemical parameters (Mayes et al., 2005) and that the heterogeneous nature of the original sedimentary depositional environments / characteristics and mineral alterations influence the reactivity of the sediment complicating reactive transport through the Hanford vadose zone. Kinetic sorption experiments indicate fast oxidation followed by a slower oxidation process with a total of ~12% oxidation of Co(II)EDTA to Co(III)EDTA and very minor sorption of Co and EDTA in Hanford formation sediments and suggests that the rate of oxidation may be different under transport conditions.

Previous work has suggested the preference for flow along bedding versus across bedding in the Hanford vadose zone (Pace et al., 2003). It is hypothesized that this flow anisotropy will also impact geochemical interactions that influence reactive transport. Physical non-equilibrium processes may result in either rapid transport of reactive tracers due to the preferential flow and media bypass or significant retardation of the reactive tracers due to interactions with the immobile water. In order to investigate the effects of these processes on reactive transport, four large undisturbed cores were used in this study – two cores collected vertically to investigate flow across bedding, and two cores collected horizontally to investigate flow along bedding. Miscible displacement experiments using multiple non-reactive tracers as well as reactive tracers were conducted in these cores to quantitatively investigate the coupled geochemical and hydrological processes during unsaturated flow along bedding and across bedding.

Previous Work

In Pace et al. (2003), multiple non-reactive tracers, Br^- , PFBA, and PIPES, were used to quantify hydrologic processes during unsaturated flow in four undisturbed cores from the Hanford formation. The tracers have different diffusion coefficients and therefore if any diffusion limited processes are present in these cores, there should be a separation in the tracer concentration profiles. One of the cores used in Pace et al. (2003) is also presented in this reactive transport study (HV1). Within Pace et al. (2003) tracer data for the horizontal core, 60% saturated, and the vertical core, 40% saturated, should be ignored since it has recently been found that the published pore volumes for these experiments are erroneous. This error was corrected and will be published as an errata. Regardless of this error, Pace et al. (2003) showed that flow across bedding resulted in significant tracer separation and an absence of early breakthrough of tracers which was suggestive of the development of immobile water and minimal preferential flow. Unsaturated flow along bedding, however, resulted in early tracer breakthrough with minimal separation of tracers compared to saturated and flow across bedding suggesting significant preferential flow and media bypass with minor development of immobile water. Therefore, it was concluded that during unsaturated flow in unconsolidated sandy media such as the Hanford formation, flow along bedding is preferred over flow across bedding. These results are consistent with Mayes et al. (2003a) who observed similar transport processes in Ringold sediments that are also present under the Hanford tank farms.

A second study was conducted that investigated ^{90}Sr fate and transport using batch sorption experiments, saturated packed column experiments and a horizontal

undisturbed core (HH1) where flow was along bedding. Careful core disassembly, which was conducted as a function of grain size, and subsequent sequential extractions on collected sediment were conducted to determine which mineral phases were associated with sorbed Sr^{+2} . Results from these experiments showed a clear linkage between hydrologic flow processes and geochemical reactivity. This core is not discussed in this paper.

The work presented in the following manuscript differs from previous manuscripts in that U(VI) and Co(II)EDTA reactive transport are examined during unsaturated flow both along bedding and across bedding. The fate and transport of these contaminants are of particular concern at Department of Energy (DOE) facilities such as Hanford because they are anions and tend to travel conservatively through the vadose zone. Knowledge on the influence of hydrology on geochemical reactivity in realistic intact sediments is lacking in the literature and thus the rationale of this manuscript.

MATERIALS AND METHODS

Core Collection

The Hanford formation comprises the upper ~45 m of the 100 m thick vadose zone beneath the 200W area tank farms. The formation is a Pleistocene age deposit formed from multiple floods of the glacial Lake Missoula to the east (Bjornstad, 1990; Lindsay, 1995b). The undisturbed cores were collected from freshly exposed escarpments opened at a depth of ~20 m in the Environmental Restoration Disposal Facility (ERDF) in the 200W Area of the Hanford Reservation. Undisturbed cores were isolated using a hand-sculpting method, which entailed isolating a small pedon, carving

the sample to its finished dimensions (~20 cm x 20 cm), and coating with paraffin wax. The cores were sealed in wax and sealed to PVC with epoxy. The cores used in this study were collected from a layer which can be described as an unconsolidated, coarse and fine sand unit interbedded with small-scale clay laminations (see Pace et al., 2003 for photographs). Cores were collected from the same depositional unit with their long axis horizontal (parallel to bedding) or vertical (across bedding). Four cores were used in this study – two horizontal (HH2 and HH3) and two vertical (HV1 and HV2). Note that the non-reactive tracer data and corrected data for core HV1 are also published in Pace et al., (2003).

Miscible Displacement Experiments

The cores were then brought to the lab and setup vertically (long axis perpendicular to the laboratory floor) for saturated and unsaturated flow experiments. The experimental apparatus for saturated and unsaturated flow experiments is described in detail within Pace et al. (2003) (Fig. 1a, b, note all Figures are located at the end of the Part). For saturated flow experiments, the cores are allowed to saturate from the bottom until solution pooled on the top of the core. Saturated flow was gravity driven and effluent solution is collected in a fraction collector. Upon completion of a saturated flow experiment, the cores were attached to a vacuum-regulated chamber in preparation for the unsaturated flow experiments. The cores were allowed to drain at a desired tension set in the vacuum chamber until water loss was negligible. The weight of each core was recorded. A background solution (0.8 M NaCl, 20 mM NaHCO₃, 1% CO₂(g)) was then delivered to the top of the cores using a multi-channel peristaltic pump. Samples were

collected until the effluent flow rate and the tension in the cores were stable. The cores were then reweighed. The unsaturated moisture content (θ_{unsat}) was determined by the difference between the unsaturated weight measured throughout the experiment (W_{unsat}) and the saturated core weight (W_{sat}) minus the saturated pore volume ($V_{w(\text{sat})}$), divided by the total volume of the core (V_{total}) as expressed in equation 1.

$$\theta_{\text{unsat}} = \frac{V_{w(\text{sat})}(\text{cm}^3) - [(W_{\text{sat}}(\text{kg}) - W_{\text{unsat}}(\text{kg})) * (1000\text{g} / \text{kg}) * (1\text{cm}^3 / \text{g})]}{V_{\text{total}}(\text{cm}^3)} \quad (1)$$

Flow of the reactive tracer solution was then initiated.

The reactive tracer solution consisted of two non-reactive tracers, Br^- and PIPES, and two reactive tracers, U(VI) and Co(II)EDTA, in 0.8 M NaCl, 20 mM NaHCO_3 in equilibrium with 1% $\text{CO}_2(\text{g})$, and pH 8 to be in equilibrium with the sediment. The solution was prepared by first adding 0.8 M NaCl, 2 mM NaBr, and 5 mM PIPES. The pH was adjusted to 8 using 1 M NaOH, which is the pH of the indigenous soil, and 2 mM CoCl_2 was subsequently added. 2 mM $\text{Na}_2\text{H}_2\text{EDTA}$ was slowly added to ensure complete complexation of the Co(II) with the EDTA. The pH was constantly monitored and maintained at pH 8 with 1 M NaOH. Once all of the EDTA was added, 20 mM NaHCO_3 was then added and immediately purged with 1% $\text{CO}_2(\text{g})$ for at least 1 hr. 0.084 mM $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added next. The solution was again purged with 1% $\text{CO}_2(\text{g})$ and capped to maintain the $\text{CO}_2(\text{g})$ head space. 1% $\text{CO}_2(\text{g})$ and 20 mM NaHCO_3 were necessary to ensure the formation of a stable U-carbonate complex and maintain the concentration of U(VI) throughout the experiments. The background solution, used to

reach steady flow rates during the initial setup of unsaturated flow and following the pulse of tracer solution during the descending limb of the breakthrough curves, was prepared with 0.8 M NaCl, 20 mM NaHCO₃ and bubbled with 1% CO₂(g) for at least 1 hr and then capped. The resulting pH of the background solution was pH 8 which is in equilibrium with the sediment.

All solutions were modeled with Geochemist Workbench to ensure that the ionic strength and solution species were appropriate. U(VI) and total Co were analyzed on a Perkin Elmer Elan 6100 Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). An ion chromatograph (IC) was used to analyze Co(II)EDTA, Co(III)EDTA, Br⁻, and PIPES using an AS9 separation column with an eluent mix of 9 mM sodium carbonate and detected by UV-VIS at 190 nm and 254 nm (Mayes et al., 2003b).

The two non-reactive tracers (Br⁻ and PIPES) differ in molecular size and therefore their free-water diffusion coefficient (Mayes et al., 2003a; Pace et al., 2003). Separation of tracer concentration profiles will be observed if any physical non-equilibrium processes (PNE) such as preferential flow and matrix diffusion occur (Jardine et al., 1999; Langner et al., 1999a; Mayes et al., 2003a; Pace et al., 2003).

Mass balance of the tracers was obtained by calculating the area under the curve for the input and the output (Table 2). Note that there was a 10-20% difference in the ICPMS and IC analysis of the Co influent which skews the mass balance numbers. The amount of uncomplexed Co was calculated as the difference between total Co as analyzed on the ICPMS and the sum of Co(II)EDTA and Co(III)EDTA concentrations as analyzed by the IC. All physical and experimental parameters for the cores are listed in Table 1 (note all Tables are located at the end of the Part).

Modeling

The steady-state transport of non-reactive tracers through the unsaturated undisturbed cores can be mathematically described using CXTFIT version 2.1 (Toride et al., 1999), a code based on the convection-dispersion equation (CDE). This code was used to model the experimental results in order to quantify dispersion, retardation coefficients, the fraction of mobile water, and the rate of exchange between the mobile and immobile water for each experiment. In the absence of physical non-equilibrium processes (PNE) (no observed separation or early breakthrough of non-reactive tracers), the CDE model in CXTFIT was used to describe transport. In the presence of perceived PNE (indicated by observed separation or early breakthrough of non-reactive tracers), the mobile-immobile model (MIM, or two region model) in CXTFIT was used to describe the experimental data. Input parameters for CXTFIT were effluent concentrations (C/C_0), length of core ($L(\text{cm})$), time (pore volume), mean pore water velocity ($V(\text{cm hr}^{-1})$) where $V = \text{flow rate} / (\pi r^2 \theta)$, input pulse, and the retardation factor (R). Theoretically, $R = 1$ for conservative non-reactive tracers. A dispersion coefficient ($D(\text{cm}^2 \text{hr}^{-1})$) was determined for each non-reactive tracer either using the CDE, a single parameter fit holding all other parameters constant, or the MIM model, a multiple parameter fit where the optimized parameters dimensionless β (mathematically related to f , where f is the fraction of mobile water), dimensionless ω (mathematically related to $\alpha (\text{hr}^{-1})$ where α is the first order rate coefficient), and D were determined by fitting the model to the observed data and holding $R = 1$.

Two different strategies were used in modeling the reactive tracers. In the absence of PNE (no observed separation or early breakthrough of non-reactive tracers), the CDE was used to determine cobalt retardation coefficients (R) by fitting the observed cobalt data while the dispersion coefficient (D) was fixed to equal that obtained in the Br⁻ fit. In the presence of perceived PNE (observed separation or early breakthrough of non-reactive tracers), the CDE model was used to determine an effective retardation coefficient for both the cobalt data as well as the Br⁻ data which resulted in R<1 for both cobalt and Br⁻ due to the observed PNE. The actual cobalt retardation coefficient was calculated by dividing the cobalt effective retardation coefficient by the Br⁻ effective retardation coefficient ($R_{Co-real} = R_{Co-effective} / R_{Br-effective}$). This method is referred to as the CDE Reff method. In order to determine the U(VI) retardation, the MIM two- site model was used in all cases as it is known that U(VI) follows a two-site sorption model (Barnett et al., 2002; Barnett et al., 2000; Dzombak and Morel, 1990; Payne et al., 1994; Waite et al., 1994). For U(VI) model fits, a dispersion coefficient fixed to that obtained with the Br⁻ model fit while all other parameters (R, β , and ω) were fit to the observed data. A K_d value was calculated from the model fitted R value for U(VI) and Co according to the following equation.

$$K_d = \frac{(R-1)\theta}{\rho_b} \quad (2)$$

The fraction of mobile water within the core or the fraction of equilibrium sorption sites was calculated according to equation (2) (Toride et al., 1999)

$$f = \frac{\beta(\theta_m + \rho_b K_d) - \theta_m}{\rho_b K_d} \quad (3)$$

where β is obtained from the MIM fit of the U(VI) data, θ_m is obtained from the MIM fit of the non-reactive tracer data, and K_d is calculated from the U(VI) R as determined in the MIM fit (Toride et al., 1999). The rate of exchange between the mobile and immobile regions was calculated using equation (3) (Toride et al., 1999)

$$\alpha = \frac{\omega\nu}{(1 - \beta)RL} \quad (4)$$

where ω , β , and R are obtained from the MIM fit of the U(VI) data.

RESULTS AND DISCUSSION

Hydrology and Transport of Non-Reactive Solutes

Flow across bedding

The two flow across bedding experiments (HV1 and HV2) differ in that the flow rate of HV2 was much slower than in HV1 in hopes to reach drier conditions in HV2. However, this did not occur. In fact, the slow flow rate in HV2 resulted in a significantly lengthy experiment relative to HV1 which allowed the moisture content to increase over time most likely due to pore water perching within fine-grained layers. This may have occurred in HV1 to a limited extent, however the experiment was completed in a much shorter time-frame relative to HV2. HV1 was treated as a steady-state experiment with $\theta_{\text{unsat}} = 0.171 \pm 0.009$. In HV2, the observation of erratic effluent flow and increasing core weight throughout the experiment resulted in transient flow where θ_{unsat} varied from 0.184 at the beginning of the experiment to $\theta_{\text{unsat}} = 0.454$ at the end of the experiment. It

can be concluded that unsaturated flow across bedding was partially inhibited due to the capillary barriers that develop in coarse-grained layers, that underlie fine-grained layers and leads to minor perching along the latter and wetting of the core. The erratic flow rate observed in HV2 is attributed to perched water heads exceeding the capillary barriers and the subsequent rapid movement of pore water from fine-grained layers through coarse-grained layers.

Typically, the tracer concentration profiles are plotted versus a relative volume, pore volume (PV), which is defined as the volume eluted divided by the total volume of water in the core ($PV = V_{\text{eluted}} / V_{w(\text{unsat})}$). The tracer concentration profiles for the transient flow experiment (HV2) cannot be plotted with respect to pore volume as typically done because $V_{w(\text{unsat})}$ changes over time. Therefore, the transient flow experiment (HV2) was plotted with respect to time (h) (Fig. 2a) as was the non-reactive tracer data for HV1 for comparison. Initially HV2 was ~40% relative saturation, which was drier than HV1, but due to significant perching, and the long duration of the experiment, the water content increased to near 90% relative saturation. The flow velocity ($V = \text{flow rate} / (\pi r^2 \theta)$) through HV2 was 0.035 cm/h compared to 0.146 cm/h in HV1 which is ~4x greater. In order to compare these two experiments, the elution time must be corrected for the flow velocity. The elution of non-reactive tracers begins at ~500 h in HV2 and ~110 h in HV1 but flow in HV1 is 4x faster than in HV2. These first arrival times can be corrected for the differences in flow velocity by multiplying the time of initial tracer breakthrough in HV1 (110 h) times 4 which equals 440 h which is comparable to the tracer elution time in HV2. These results suggest that preferential flow was most likely minimal as indicted by the absence of early breakthrough of tracers

relative to saturated conditions (not shown); however, immobile water may be prevalent as observed by tracer separation in the two breakthrough curves.

Significant tracer separation is observed in HV2 (Fig. 2a) and is slightly greater than that observed in HV1 (Fig. 2a) which suggests that the development of immobile water is more pronounced during transient flow across bedding due to perching and diffusion of tracers within that perched zone. Typically, the largest non-reactive tracer, PIPES, elutes at higher concentrations early during the breakthrough while Br^- , the smallest tracer, diffuses into the immobile regions faster than PIPES and results in lower concentrations during the early portion of the breakthrough curve. However, during flow across bedding (HV1 and HV2) there was a reversal of the order of tracer separation. The tracer separation is more pronounced in the transient experiment (HV2) (Fig. 2a) due to the perching during the relatively lengthy flow experiment. The observed order of tracer separation in both HV1 and HV2 is consistent with transient experiments in the Ringold material (Mayes et al., 2003a) which is composed of very small fine grained layers and in general is more homogeneous than the Hanford sediments. Modeling results for HV1 are in Table 2. HV2 could not be modeled due to the transient nature of the experiment. Model fitted pecllet numbers (P_e) were ~19-27 suggesting advective dominated flow, however, some immobile water must be forming as suggested by tracer separation. The MIM model was not sensitive enough to detect this amount of immobile water, therefore, the CDE model was used to fit the observed tracer data in the HV1 core.

Flow along bedding

Consistent with the results of Pace et al., 2003, early tracer breakthrough relative to saturated conditions and minimal tracer separation observed in both HH2 and HH3 suggested preferential flow and media bypass with minor development of immobile water (Fig. 2b). The first arrival of the tracers in HH3 is significantly earlier than in HH2 most likely due to the lower moisture content in HH3 relative to HH2 (Gamerding et al., 2001; Szenknect et al., 2003). Therefore, it can be concluded that moisture content plays a significant role during flow along bedding.

Typically during unsaturated flow along bedding, larger pores are drained, resulting in partial disconnection of the primary porosity from the predominant flow paths. Because of this, regions of immobile water can develop within the coarse layers that have very little interaction with the mobile water within the fine layers due to diffusional barriers. Thus, as the moisture content decreases flow paths become isolated to fine grained layers and minimal interaction with the immobile water occurs, resulting in more symmetric BTCs compared to saturated conditions and possible bimodal behavior of tracers indicative of distinct multiple flowpaths. However, due to the orientation of the cores during unsaturated transport, gravity driven flow through the coarse layers with fine-grained layers acting as immobile regions cannot be disregarded. All unsaturated flow experimental parameters and modeling results for the various cores used in this study are shown in Table 2. Model fitted P_e values, which are lower than in the flow across bedding cores, again suggest advective dominated flow but with slightly more dispersion where the fraction of mobile water (f) was ~70-78% of the unsaturated water content.

Coupled Hydrology and Transport of Reactive Solutes

Flow across bedding

Results indicate significant retardation and reactivity of U(VI) and Co(II)EDTA during unsaturated vertical transport as evidenced by delayed breakthrough curves compared to non-reactive tracer breakthrough and oxidation of Co(II)EDTA to Co(III)EDTA (Table 2, Fig 2a, b). The delayed breakthrough of U(VI) and Co(III)EDTA is indicative of reactive processes such as sorption due to the formation of uranium-carbonate surface complexes (Barnett et al., 2002; Bostick et al., 2002), oxidation / reduction processes involving Co(II)EDTA, and the formation of metal-EDTA complexes (Brooks et al., 1996; Jardine and Taylor, 1995a; Kent et al., 1991; Mayes et al., 2000; Szecsody et al., 1998; Zachara et al., 1995b). U(VI) is much more retarded relative to Co(II)EDTA during unsaturated flow across bedding (Fig. 3a, b) as evidenced by the greater delay in U(VI) breakthrough as compared to Co(III&II)EDTA. This is because most of the Co(II)EDTA was oxidized to Co(III)EDTA, most likely due to Fe- and Mn-oxides present in the sediments (Jardine and Taylor, 1995c; Mayes et al., 2000; Zachara et al., 1995b) and Co(III)EDTA is only slightly reactive with the solid phase (Jardine et al., 1993a; Jardine and Taylor, 1995b). The amount of oxidation, which is approximately equal in each core, could not have been predicted by batch experiments (Mayes et al., 2005b) as only 15% of the Co(II)EDTA was oxidized to Co(III)EDTA in the latter experiments. This is most likely the result of lower solid to solution ratios in batch experiments compared to displacement experiments, the latter being more indicative of conditions in the field.

A small amount of un-complexed Co was detected in both experiments which suggests the dissociation of Co(II)EDTA to other metal-EDTA complexes possibly due to Fe^{3+} in the sediment forming FeEDTA^- complexes (Jardine and Taylor, 1995a; Jardine and Taylor, 1995c; Zachara et al., 1995b; Zachara et al., 1995c). Previous research on Co(II)EDTA transport suggests that at near neutral pH, Mn-oxides play a significant role in the oxidation of Co(II)EDTA to Co(III)EDTA (Jardine et al., 1993a; Jardine et al., 1993b; Mayes et al., 2000; Zachara et al., 1995b). It has also been shown that Fe-oxides can cause disassociation of the Co(II)EDTA complex by forming a strong FeEDTA complex (Jardine and Taylor, 1995c; Zachara et al., 1995c). Fe-oxides are known to promote oxidation by direct surface-mediated reactions but this generally occurs at lower pH (Brooks et al., 1996; Mayes et al., 2000; Szecsody et al., 1998) and the experiments presented here were conducted near neutral pH. Therefore, Fe-oxides most likely only contributed to the disassociation of Co(II)EDTA and not oxidation in the Hanford sediments. ICPMS analysis detected aqueous Fe and Mn in only one of the flow across bed experiments (Fig. 4). The amount of Mn and Fe detected is not enough to account for all of the uncomplexed Co and, therefore, other dissociation mechanisms must be occurring. The detection of minor amounts of Fe and Mn may suggest that these metals may potentially play a significant role in the oxidation and or dissociation of Co(II)EDTA during unsaturated vertical transport. This observation agrees with the results of Mayes et al (2005) in which statistical analysis of batch experimental results indicated that Mn-oxides are important for Co(II)EDTA sorption and oxidation. Non-stoichiometric quantities of effluent Mn are to be expected, since Mn^{+2} is strongly resorbed and reoxidized by Mn-oxides (Jardine and Taylor, 1995b).

The shape of the breakthrough curves for all tracers differ in the transient (HV2) versus the steady-state (HV1) experiments (Fig. 3a, b). The initial breakthrough is steeper in the transient experiment compared to the steady-state experiment. This may be a result of the perching and hence diffusion of tracers into immobile water. More tailing is also observed in the transient experiment versus the steady-state experiment. In fact, all tracers, especially the reactive tracers, have significant tailing during the washout which is most likely due to the perching which allows the tracers to diffuse or react with surfaces in the immobile water. Note also that U(VI) appears to have a change in slope during the washout in HV2 which may be due to the diffusion into the immobile water and the transient nature of the experiment. This suggests that during transient vertical flow, regions of immobile water may act as long-term sinks and/or sources of contamination.

Only the HV1 experiment was modeled with CXTFIT as parameters for HV2 changed throughout the experiment. The MIM-two region model failed to capture the PNE processes responsible for the observed tracer separation and defaulted to the CDE. Therefore, the CDE model was used as no early breakthrough of tracers was observed. The Co-EDTA breakthrough curve is only slightly delayed compared to the non-reactive tracers in HV1 with a model fitted retardation coefficient of 1.26 suggesting minimal sorption by the solid phase. The MIM-two site model was used to describe U(VI) transport as U(VI) typically sorbed via a two-site sorption process (Barnett et al., 2002; Barnett et al., 2000; Dzombak and Morel, 1990; Payne et al., 1994; Waite et al., 1994). Model fitted f values suggested that the sorption sites were composed of ~25% rapid equilibrium sites and 75% slow kinetic based sites with an exchange coefficient of $1.31e-$

3 h^{-1} . A retardation coefficient of 4.37 was obtained for U(VI) which is significantly larger than the retardation coefficient for Co-EDTA species which is consistent with the observed tracer data and with the results of Gamerding et al., (2001).

In general, during unsaturated flow across bedding immobile water develops due to short term perching within the fine-grained layers which leads to significant reactivity of contaminant with the sediments. Preferential flow is minimal during flow across bedding and thus should not contribute significantly to “accelerated” vertical transport. However, contaminants may get sequestered into the immobile water which may then act as a long-term source within the vadose zone.

Flow along bedding

All tracers, non-reactive and reactive, elute earlier during flow along bedding relative to flow across bedding which indicated the possible presence of preferential flow and media bypass (Fig. 5a, b). Note that the first arrival of U(VI) and Co-species during flow along bedding in HH2 occurs at ~ 0.4 PV and in HH3 at ~ 0.25 PV (Fig. 5a, b). These first arrival times are earlier than in flow across bedding which occurs at ~ 0.8 PV (Fig. 3a, b). This difference is most likely due to the difference in unsaturated hydrology (i.e. flow across bedding versus flow along bedding) under the influence of gravity which may contribute to the observed preferential flow and media bypass during flow along bedding (Fig. 5a, b) and supports our hypothesis that hydrology effects reactive transport. Also, significantly less oxidation of Co(II)EDTA to Co(III)EDTA occurred during unsaturated flow along bedding (Table 2, Fig. 5a, b) compared to flow across bedding and is mostly likely related to the media bypass and preferential flow that was absent

during flow across bedding. The lack of complete oxidation to Co(III)EDTA coupled with the lack of uncomplexed Co (i.e. all Co occurs as Co(III)EDTA or Co(II)EDTA) may result from sequestered flow along fine-grained layers which lack sufficient Mn-oxides and Fe-oxides to cause dissociation and oxidation (Mayes et al., 2005b).

However, oxide extraction on the silt and sand size fractions indicate that there is actually more Fe and Mn in the silt fraction (15.37 $\mu\text{g/g}$ Fe, 0.36 $\mu\text{g/g}$ Mn) than in the sand fraction (5.43 $\mu\text{g/g}$ Fe, 0.16 $\mu\text{g/g}$ Mn). Therefore, another mechanism, which we were unable to decipher, must be responsible for the lack of oxidation. Analysis by ICPMS was unable to detect aqueous Fe or Mn in the effluent samples which was expected since there was an absence of uncomplexed Co in the effluent and any aqueous Fe and Mn may either precipitate in the core at pH 8 (Fe) or re-absorb (Mn).

Bimodal transport was also observed during lower moisture contents (Fig. 5b) as indicated by a change in slope along the breakthrough curves. This was more evident in the reactive tracers as retardation of these tracers tends to accentuate the apparent change in slope along the BTC. This was not as apparent in the “wetter” horizontal core (HH2) (Fig. 5a) because the core was not dry enough for the flow paths to be sequestered into distinct paths and created a more homogeneous moisture distribution in the core. Such experiments indicate the importance of moisture content on lateral flow and transport. Bimodal transport could potentially complicate prediction and monitoring of contaminant migration in semi-arid environments such as the Hanford site where the vadose zone is composed of unconsolidated layered silts and sands with both size fractions having a variety of particle sizes.

Modeling results (Table 2) indicate that the K_d values for the Co-species are approximately the same as in HV1, showing minimal retardation of Co-EDTA by the solid phase. The U(VI) K_d values are significantly lower than that determined in HV1. Note that the fraction of mobile water decreases as the moisture content of the core decreases. The fraction of mobile water suggests that only certain sediment beds in HH2 and HH3 are conductive and contribute to the retardation of U(VI) and Co(II)EDTA. Model fitted f values again suggest that U(VI) sorption was associated with 10 to 35% rapid equilibrium sites and 65 to 90% slower kinetically controlled sites with first-order exchange coefficients ranging from 1 to $4 \times 10^{-3} \text{ h}^{-1}$.

The environmental implication of Co(II)/(III)EDTA and U(VI) reactivity with the solid phase are pronounced. Oxidation of Co(II)EDTA to Co(III)EDTA is significant since the oxidation product, Co(III)EDTA, is extremely stable, with a stability constant of $K = 10^{40}$ (for comparison Co(II)EDTA has a stability constant $K = 10^{16}$). This extraordinary strong metal-organic complex enhances the persistence and transport of Co-EDTA in subsurface environments. If, in fact, the oxidant, MnO_2 , serves as a catalyst during Co(II)EDTA oxidation, this suggest that the subsurface mineral regenerates its oxidative potential and can continue to produce the very stable Co(III)EDTA species. The regeneration process depends on the availability of dissolved O_2 in groundwater which is necessary to oxidize Mn^{+2} to MnO_2 (Jardine and Taylor, 1995b). Likewise, retardation of U- CO_3 species to the Hanford solid phase is significant since vertical (flow across bedding) and lateral (flow along bedding) migration of U(VI) toward groundwater will be slightly impeded and significantly affected by flow anisotropy. Very low sorption values obtained in this study are comparable to that of Serne et al. (2002) in which

bimodal transport behavior was also observed possibly due to precipitation. Generally, U(VI) sorbs to the solid phase as an anionic carbonate complex and therefore is considered nearly non-reactive (Barnett et al., 2002; Barnett et al., 2000; Bostick et al., 2002; Duff et al., 2002; Echevarria et al., 2001). This current study suggests otherwise.

The results presented here confirm the hypothesis that anisotropic unsaturated flow significantly influences reactive contaminant transport. Experiments indicate early breakthrough of tracers as moisture content decreases during flow along bedding. This was also observed in unsaturated flow through repacked media at high flow velocities and low moisture content (Gamerding et al., 2001; Szenknect et al., 2003). However, anisotropic flow can only be observed in undisturbed cores that preserve the structure of the bedding. Our results indicate different physical non-equilibrium processes such as diffusion into immobile water during flow across bedding and media bypass during flow along bedding all of which influences reactive transport. It can be concluded that hydrology, which varies with respect to direction of flow, has a significant influence on geochemical interactions with reactive mineral surfaces. This type of information may be used to improve the conceptual model of unsaturated transport in the Hanford vadose zone as well as other similar environments where the vadose zone is composed of unconsolidated layered sands.

CONCLUSIONS

The geochemical behavior observed during flow across and along bedding is most likely due to anisotropic hydrological processes occurring at the various moisture contents in the undisturbed cores. As discussed previously, during transport across

bedding there is less preferential flow and media bypass but greater diffusion into pockets of immobile water as evidenced by separation of non-reactive tracer concentration profiles. These hydrologic processes allow reactive tracers plenty of surface sites for sorption and geochemical interactions. The prevalence of preferential flow and media bypass with minimal diffusion into immobile water during flow along bedding and may result in “accelerated” transport as suggested by the early first arrival of tracers. Bimodal behavior became prevalent at lower moisture contents during lateral flow as suggested by the breakthrough curves (Fig. 5b). As media is bypassed during lateral flow, the mineral surfaces that interact with contaminants such as U(VI) and Co(II)EDTA may differ compared to the surfaces during vertical flow where flow crosses all sedimentary beds thereby affecting geochemical reactions such as sorption and oxidation. Some of the observed anisotropic flow along bedding may be caused by gravity driven flow through the coarse layers due to the orientation of the cores during unsaturated transport experiments and needs to be taken into account. Perhaps, in the field, flow along bedding may not be as significant, but results do suggest that the sedimentary structure (i.e. whether flow is across or along bedding) may significantly influence contaminant transport in unconsolidated layered systems such as the Hanford vadose zone. Therefore, quantification of such coupled hydrological and geochemical interactions when flow is along bedding and across bedding is necessary to improve the understanding of contaminant transport in arid environments such as Hanford, WA.

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Table 1. Experimental parameters for undisturbed core experiments.

Experiment	V (cmh ⁻¹)	L (cm)	Radius (cm)	Pulse (L)	ρ_b (gcm ⁻³)	θ (cm ³ cm ⁻³)	% Sat	VC Tension (-cm)
HV1	0.146	21.0	10.5	1.78	1.57	0.17	42	-160
HV2	0.035	23.5	11.0	1.47	1.67	0.18-0.45	40-99	-180
HH2	0.057	23.5	11.0	1.54	1.61	0.34	87	-190
HH3	0.044	23.5	11.0	1.40	1.61	0.15	39	-180

Table 2. Modeling parameters for unsaturated undisturbed Hanford cores.

Core	Tracer	Mass Recovery (%)	Model	Fixed Parameter	P_e	f	α (h^{-1})	K_d (ml/g)	R	r^2
HV1	Br-	93	CDE	R	19.2 ± 4.65	NA	NA	NA	1	0.924
	PIPES	93	CDE	R	27.3 ± 5.08	NA	NA	NA	1	0.974
	U	82	Two-site	D	19.2	0.252 ± 0.110	$1.31e-3 \pm 7.75e-5$	0.366 ± 0.076	4.37 ± 0.70	0.982
	Co(III)	91	CDE	D	19.2	NA	NA	0.028 ± 0.003	1.26 ± 0.03	0.977
	Co(II)	1.3								
	CoT	97	CDE	D	19.2	NA	NA	0.029 ± 0.003	1.27 ± 0.03	0.978
HV2	Transient Experiment – unable to model									
HH2	Br-	124	Two region	R, ω	15.4 ± 2.27	0.783 ± 0.027	~0	NA	1	0.952
	PIPES	119	Two region	R, ω	16.8 ± 2.20	0.765 ± 0.022	~0	NA	1	0.966
	U	93	Two site	D	15.4	0.368 ± 0.127	$1.34e-3 \pm 2.75e-4$	0.218 ± 0.039	2.03 ± 0.18	0.980
	Co(III)	73	CDE-Reff	D	15.4	NA	NA	0.026 ± 0.004	1.12 ± 0.02	0.722
	Co(II)	18								
	CoT	119*	CDE-Reff	D	15.4	NA	NA	0.027 ± 0.002	1.13 ± 0.01	0.961
HH3	Br-	110	Two region	R, ω	10.8 ± 1.22	0.690 ± 0.015	~0	NA	1	0.990
	PIPES	107	Two region	R, ω	10.7 ± 1.41	0.666 ± 0.017	~0	NA	1	0.986
	U	81	Two site	D	10.8	0.109 ± 0.120	$4.15e-3 \pm 1.89e-3$	0.178 ± 0.010	2.86 ± 0.10	0.886
	Co(III)	88	CDE-Reff	D	10.8	NA	NA	0.030 ± 0.002	1.31 ± 0.016	0.944
	Co(II)	1								
	CoT	110*	CDE-Reff	D	10.8	NA	NA	0.029 ± 0.002	1.31 ± 0.016	0.981

[CDE-Reff = CDE model used to model Co(III) and Co(t) to determine an effective R which was then used along with the effective R from Br⁻ CDE fit to calculate the real R as listed in the table above. CXTFIT MIM can either be used as a two-region model or a two-site model. V = pore water velocity, P_e = Peclet number, f = fraction of mobile water, α = rate of exchange between mobile and immobile water, R = retardation factor]

*There was a 10-20% difference in ICPMS and IC analysis of the influent concentrations which skews the mass balance calculations of total cobalt measurements.

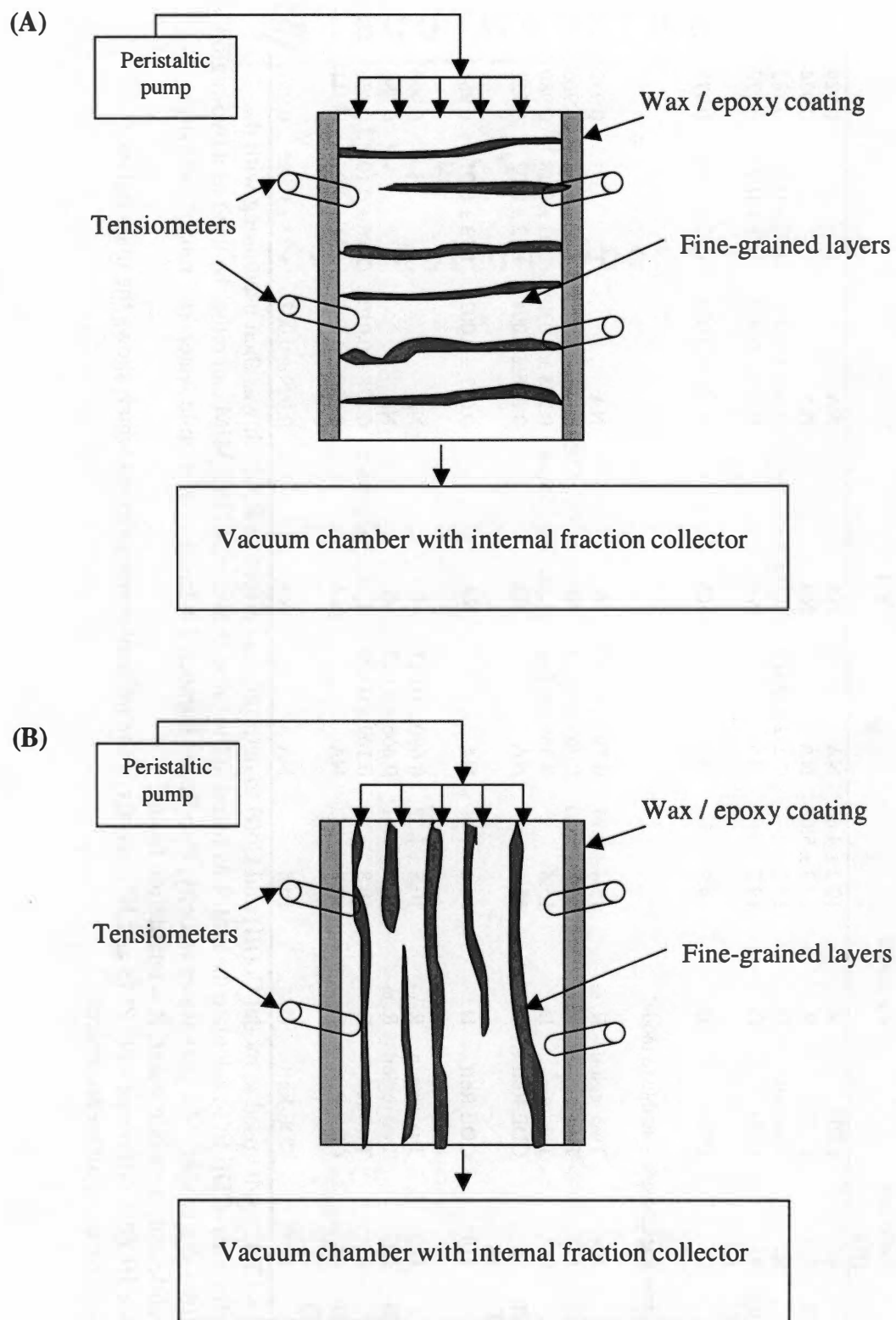


Figure 1. Schematic diagrams of (A) unsaturated flow across bedding and (B) unsaturated flow along bedding experiments.

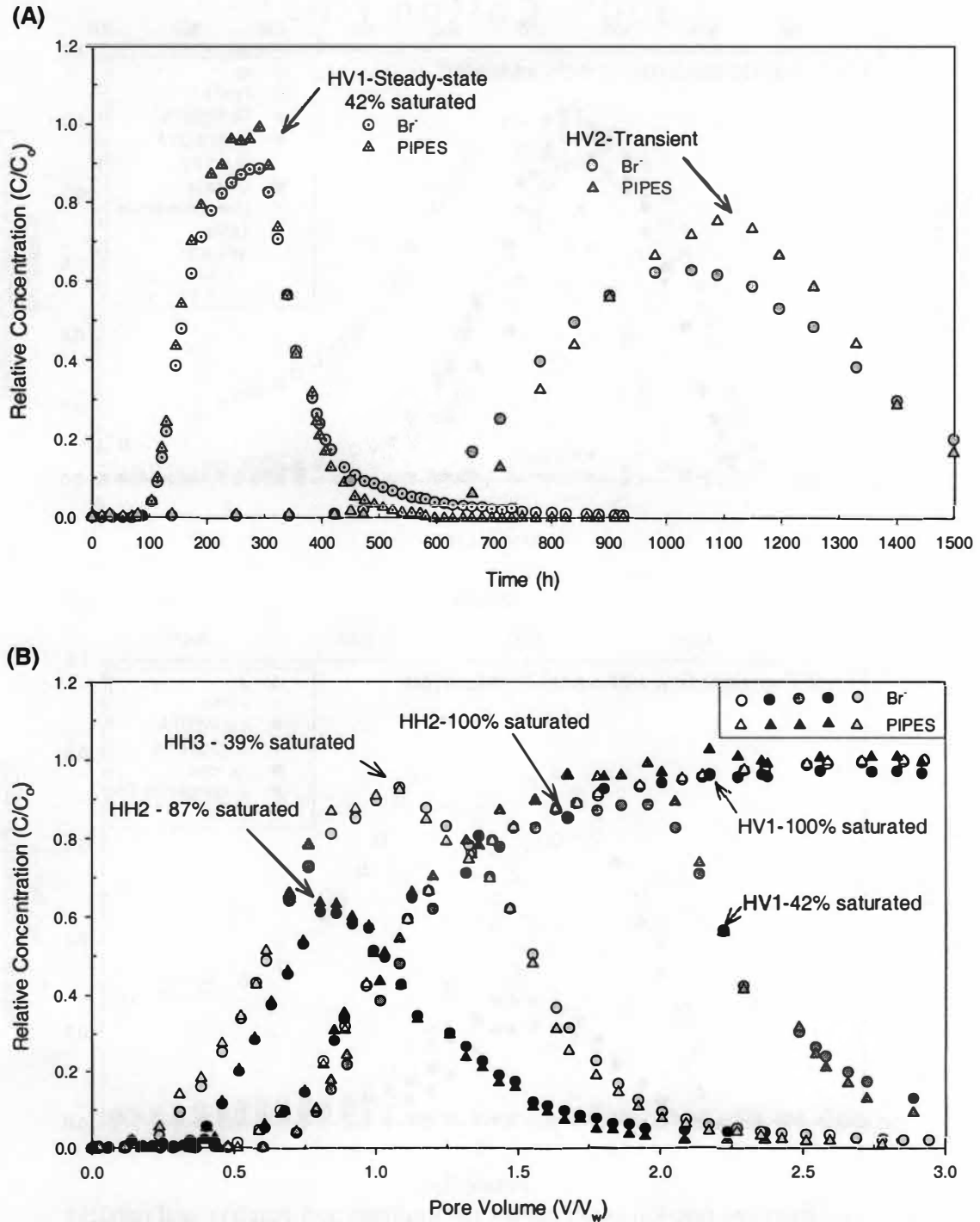


Figure 2. (a) Observed breakthrough curves for multiple non-reactive tracers under unsaturated conditions in undisturbed cores collected vertically (HV#) plotted with respect to time. Model fits were omitted for clarity. (b) Observed breakthrough curves for the two horizontal undisturbed cores (HH#) plotted with respect to relative volume (pore volume = $V_{eluted} / V_{w(unsat)}$).

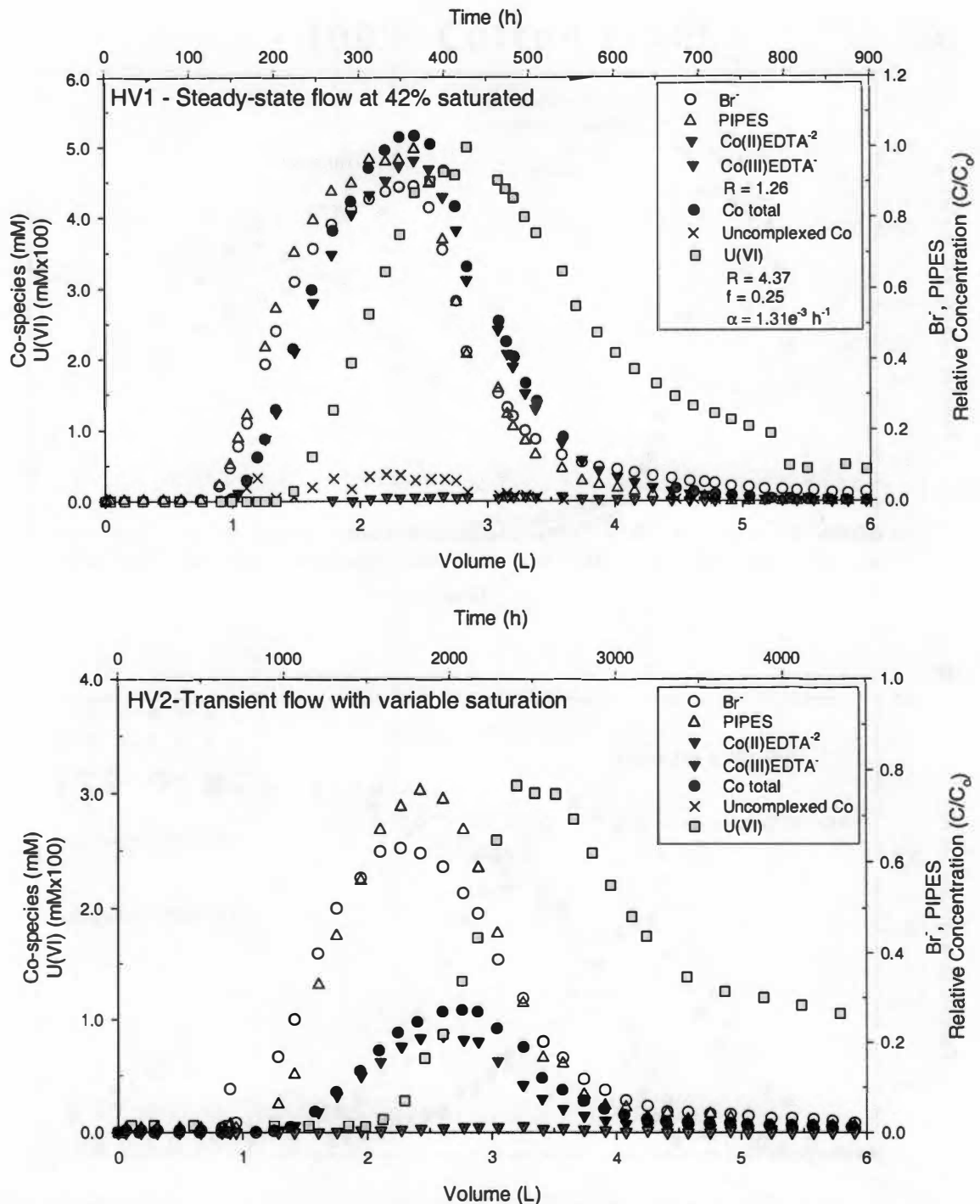


Figure 3. (a) Observed breakthrough curves for multiple non-reactive and reactive tracers under unsaturated conditions in one of the undisturbed vertical cores (HV1) representing one moisture content. Model fits were omitted for clarity. (b) Observed breakthrough curves for multiple non-reactive and reactive tracers under unsaturated conditions in HV2 representing a transient flow case. Again, model fits were omitted for clarity.

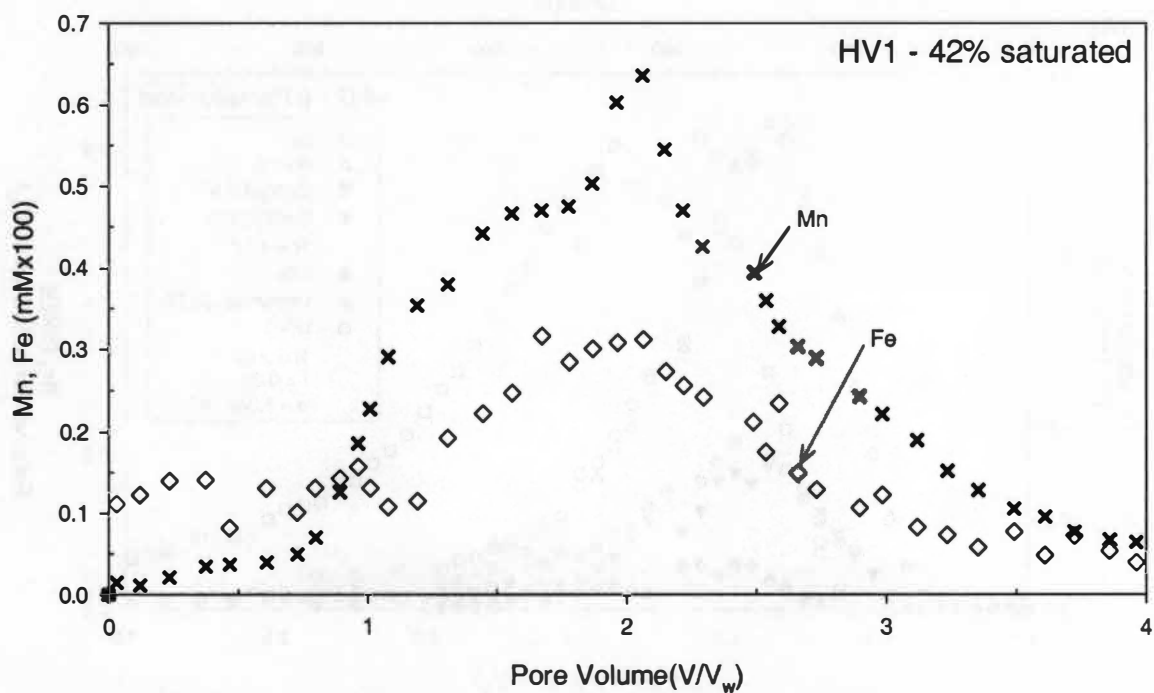


Figure 4. Concentration profiles of Mn and Fe as eluted from HV1 during reactive transport during unsaturated flow.

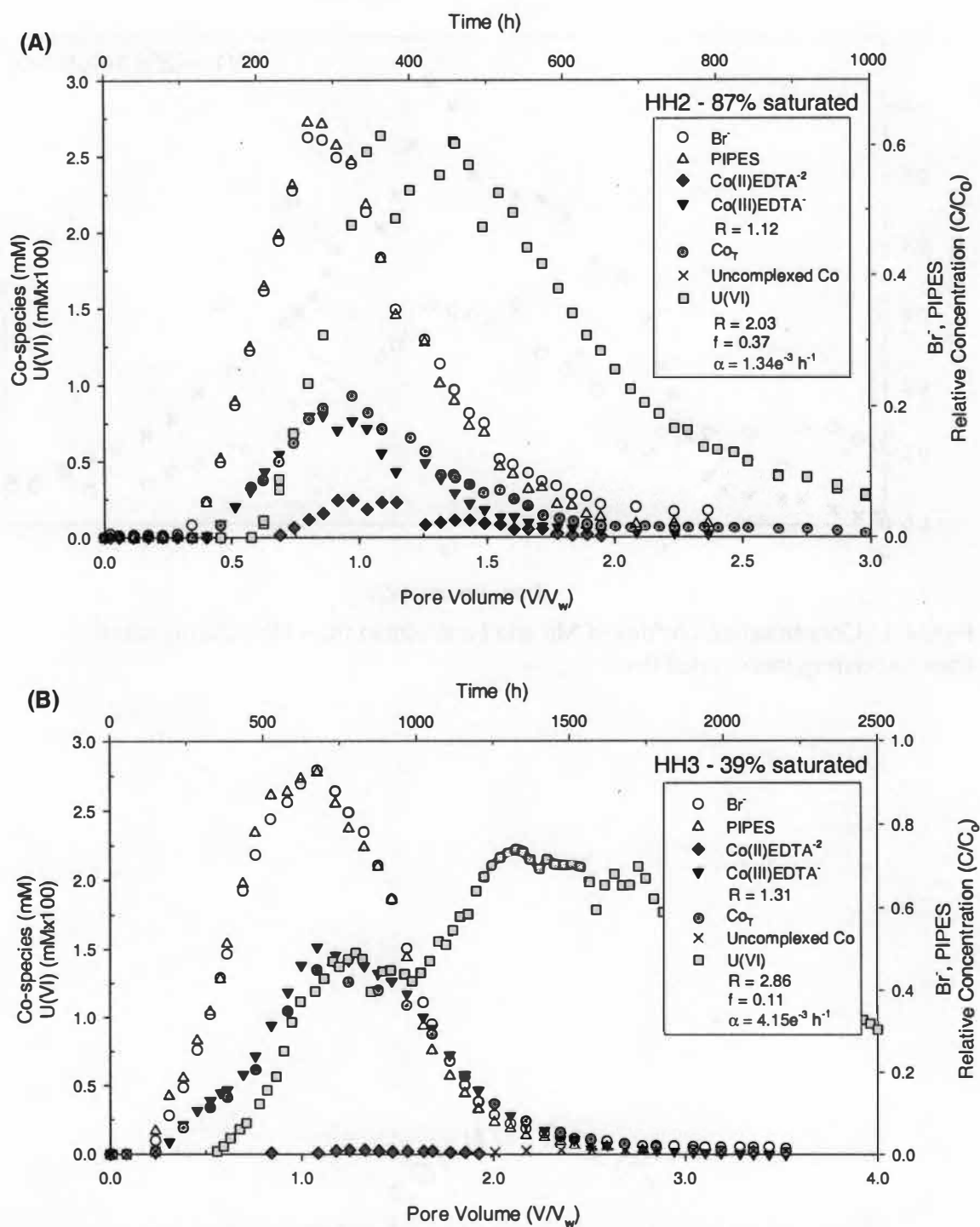


Figure 5. (a) Observed breakthrough curves for multiple non-reactive and reactive tracers under unsaturated conditions in one of the undisturbed cores collected horizontally (HH2) representing one moisture content. Model fits were omitted for clarity. (b) Observed breakthrough curves for multiple non-reactive and reactive tracers under unsaturated conditions in HH3 representing a second moisture content. Again, model fits were omitted for clarity.

PART 5

CONCLUSIONS AND FUTURE RESEARCH

The goal of this project was to quantify coupled hydrologic and geochemical processes during unsaturated flow along and across bedding. My hypothesis was that sedimentary bedding plays an important role on unsaturated hydrology which then impacts reactive transport. The results confirm this hypothesis. In fact, the results indicate the prevalence for lateral flow along sedimentary bedding layers over vertical flow in semi-arid vadose zones composed of unconsolidated sands. During vertical flow, water perches in the fine-grained sedimentary layers overlying coarse grained-layers thereby resulting in areas of immobile water that develop in these fine-grained layers until enough water pressure develops upon which there is a sudden release of the perched water to the coarse layer below. The presence of immobile water allows contaminants to diffuse into these areas possibly yielding more reactive surface sites for the contaminants compared to the limited reactive surface sites during preferential flow along bedding due to media bypass. Therefore, immobile water may act as a long-term sink or source of contamination. During unsaturated flow along bedding bimodal transport becomes apparent as moisture content decreases where multiple flowpaths develop. This observation may be accentuated by gravity driven flow due to the orientation of the cores during experimentation. Such behavior may complicate the modeling and prediction of contaminant transport and should be included in the conceptual model of vadose zone transport. The main conclusion of this work is that the direction of flow with respect to sedimentary bedding significantly effects geochemical reactions during unsaturated transport and is best approximated using undisturbed media instead of batch or saturated packed columns. These coupled processes need to be considered and implemented into site-wide models.

This work demonstrates the value of unsaturated flow and transport experiments in undisturbed media that preserves the structure of the vadose zone material. Specifically, the results indicate the importance of preferential flow / media bypass and vadose zone heterogeneity on geochemical reactions responsible for contaminant retardation. The observation of preferential flow during flow along bedding may suggest that lateral flow is prevalent over vertical transport in the Hanford vadose zone which is also confirmed by field observations at Hanford (Serne et al., 2002). Bimodal transport of non-reactive and reactive tracers was observed due to preferential flow during vertical flow along bedding at low water contents and may significantly impact predictions of contaminant transport. Processes such as precipitation may result in bimodal transport (Serne et al., 2002). However, in the case presented here, physical non-equilibrium processes such as preferential flow and media bypass are most likely to cause the observed bimodal transport as even the non-reactive tracers indicated bimodal transport as evidenced by the shape of the breakthrough curves. The observed experimental data does not indicate rapid vertical transport. In the field, rapid downward migration of contaminants generally occurs along clastic dikes and/or well bore holes (Hartman and Dressel, 1997; Serne et al., 2002). Therefore, future experiments should focus on the heterogeneous features in the Hanford vadose zone such as clastic dikes.

However, this was one of the first studies of this type to be conducted with the Hanford formation and much has been learned so that better experiments can be conducted in the future. The data presented here provides insight into the fate and transport of ^{90}Sr , U(VI) , and Co(II)EDTA in unconsolidated layered sands, such as the Hanford vadose zone, and indicates the importance of geology, not only sedimentary

bedding but also mineralogy, on unsaturated transport of contaminants. Slight differences in geology (i.e. structure) and mineralogy may significantly affect contaminant transport. Most of the hazardous and nuclear waste in the U.S. will most likely be stored in semi-arid to arid environments due to deep vadose zones and deep groundwater. Therefore, it is important to understand how unsaturated flow anisotropy effects reactive transport in order to prevent the migration of wastes that might leak from these waste repositories.

It is apparent that there are some issues concerning the experimental design. All of the undisturbed cores were setup so that flow occurred vertically either across bedding or along bedding. This design imposed gravitational forces on flow along bedding which may have resulted in some artificial preferential flow that would not occur in the field. Therefore, future experiments should be conducted with flow along bedding cores orientated horizontally to better simulate field conditions. It would be ideal if a block of the vadose zone material could be setup in the laboratory with sampling ports on the bottom and side to investigate simultaneous flow along and across bedding. This type of experimental design poses significant challenges, thus the lack of such published data..

It would be beneficial to conduct saturated experiments with reactive tracers in the undisturbed cores. This would allow a more sound development of the relationship between moisture content and reactive transport as a function of direction of flow relative to sedimentary bedding layers and a comparison with commonly used saturated packed column experiments. However, this would require the collection of more undisturbed cores as only one core can be used for each reactive tracer and more time as reactive experiments often last a long time, especially with more reactive tracers, due to the

reactive nature of the tracers. The focus of this work was to quantify the influence of sedimentary bedding on unsaturated transport of contaminants applicable to the Hanford vadose zone.

There were a few experimental problems during this research. For example, the transient experiments, which occurred during flow across bedding, pose problems specifically in modeling of the breakthrough curves. Transient conditions arose due to the long period necessary to reach complete mass recovery of the reactive tracers and the use of a large undisturbed core in which flow crossed sedimentary bedding allowing for perching of water in the fine grained layers until the water pressure was sufficient to release the water into the underlying coarse layer. There appears to be a lower limit on the moisture content that could be reached with our experimental setup during flow across bedding due to the structure and composition of the media. Slower flow rates were used to try to get to drier conditions which worked for the flow parallel to bedding, but failed for flow across bedding.

Mechanical problems also occurred with the fraction collectors as the high concentration salt solution often corroded the fraction collector resulting in its failure. When this occurred, the fraction collector was replaced and the experiment continued. The volume of effluent solution that was lost was then estimated. Also, microbial growth occasionally developed in the effluent lines which tended to plug the effluent flow. Therefore, we monitored and changed the effluent line when needed which did not harm the experiment. NaCl was used as the matrix in all experimental solution instead of NO_3 because nitrate reducing microbes thrived in that environment and degraded one of the non-reactive tracers. However, NO_3 would have been more applicable to the Hanford

waste problem. Often, we had difficulty maintaining the moisture content in the cores as the environmental factors in the laboratory changed. In order to prevent this from occurring in the future, an environmental chamber would be necessary.

There are obviously many ways in which to improve the experimental design and setup. The most significant areas for improvement are the use of an environmental chamber, field appropriate orientation of cores, and the development of a computer model that could appropriately model unsaturated flow in natural heterogeneous systems. Also, it would be helpful to visually observe the unsaturated flow and transport experiments. Scaling effects also need to be addressed. This is the focus of the next USDOE EMSP proposal call in which a proposal based on this work and others was submitted. It would also be interesting to see how these results compare to those of centrifuge techniques. Ultimately, the combined effects of geochemical reactions, solution chemistry, and microbial activity during unsaturated flow need to be investigated and incorporated into computer models.

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APPENDICES

APPENDIX A – An example of batch experimental datasheets

Strontium Batch Experiment - Sr+2 Bulk 1:1 rock:water ratio										
MNP										
sample	start date/time	end date/time	equi. hrs	solution	sed mass (g)	sol vol (ml)	Sr(I) (ppm)	Sr(eq) (ppm)	pH(I)	pH(f)
1	7/12/2004 14:15	7/15/2004 13:45	71:30:00	1 blank	0.0000	10.00	0.0000	0.0026	8.06	6.06
2	7/12/2004 14:15	7/15/2004 13:45	71:30:00	1 dup1	9.9997	10.00	0.0026	1.0526	8.06	7.87
3	7/12/2004 14:15	7/15/2004 13:45	71:30:00	1 dup2	9.9992	10.00	0.0026	1.0473	8.06	7.88
4	7/12/2004 14:15	7/15/2004 13:45	71:30:00	2 blank	0.0000	10.00	1.0000	0.9622	8.06	5.79
5	7/12/2004 14:15	7/15/2004 13:45	71:30:00	2 dup1	10.0002	10.00	0.9622	1.3016	8.06	7.89
6	7/12/2004 14:15	7/15/2004 13:45	71:30:00	2 dup2	9.9998	10.00	0.9622	1.2584	8.06	7.90
7	7/12/2004 14:15	7/15/2004 13:45	71:30:00	3 blank	0.0000	10.00	3.0000	2.5500	8.04	6.22
8	7/12/2004 14:15	7/15/2004 13:45	71:30:00	3 dup1	10.0004	10.00	2.5500	1.5627	8.04	7.88
9	7/12/2004 14:15	7/15/2004 13:45	71:30:00	3 dup2	10.0002	10.00	2.5500	1.5475	8.04	7.87
10	7/12/2004 14:15	7/15/2004 13:45	71:30:00	4 blank	0.0000	10.00	5.0000	4.7690	8.09	5.67
11	7/12/2004 14:15	7/15/2004 13:45	71:30:00	4 dup1	9.9996	10.00	4.7690	2.1751	8.09	7.86
12	7/12/2004 14:15	7/15/2004 13:45	71:30:00	4 dup2	9.9996	10.00	4.7690	2.2135	8.09	7.89
13	7/12/2004 14:15	7/15/2004 15:15	73:00:00	5 blank	0.0000	10.00	7.0000	6.6588	8.06	6.04
14	7/12/2004 14:15	7/15/2004 15:15	73:00:00	5 dup1	10.0006	10.00	6.6588	2.6116	8.06	7.87
15	7/12/2004 14:15	7/15/2004 15:15	73:00:00	5 dup2	10.0006	10.00	6.6588	2.6172	8.06	7.91
16	7/12/2004 14:15	7/15/2004 15:15	73:00:00	6 blank	0.0000	10.00	10.0000	9.5280	8.08	6.16
17	7/12/2004 14:15	7/15/2004 15:15	73:00:00	6 dup1	10.0003	10.00	9.5280	3.3504	8.08	7.90
18	7/12/2004 14:15	7/15/2004 15:15	73:00:00	6 dup2	10.0006	10.00	9.5280	3.3596	8.08	7.91
19	7/12/2004 14:15	7/15/2004 15:15	73:00:00	7 blank	0.0000	10.00	15.0000	14.2820	8.02	6.16
20	7/12/2004 14:15	7/15/2004 15:15	73:00:00	7 dup1	10.0004	10.00	14.2820	4.4817	8.02	7.91
21	7/12/2004 14:15	7/15/2004 15:15	73:00:00	7 dup2	10.0003	10.00	14.2820	4.5381	8.02	7.91
22	7/12/2004 14:15	7/15/2004 15:15	73:00:00	8 blank	0.0000	10.00	20.0000	19.0196	8.10	6.27
23	7/12/2004 14:15	7/15/2004 15:15	73:00:00	8 dup1	10.0008	10.00	19.0196	5.6880	8.10	7.92
24	7/12/2004 14:15	7/15/2004 15:15	73:00:00	8 dup2	10.0006	10.00	19.0196	5.6554	8.10	7.96

mass/vol (g/ml)	vol/mass (ml/g)	Δ Sr (l-f)	Δ pH (f-l)	Sr sorbed (μ g/g)	Sr Kd (ml/g)	Kd ave (ml/g)
0.0000		-0.00257	-2	na	na	
1.0000	1.0000	-1.05	-0.19	-1.0500	-0.9976	
0.9999	1.0001	-1.04471	-0.18	-1.0448	-0.9976	-0.9976
0.0000		0.03785	-2.27	na	na	
1.0000	1.0000	-0.33944	-0.17	-0.3394	-0.2608	
1.0000	1.0000	-0.2962	-0.16	-0.2962	-0.2354	-0.2481
0.0000		0.44997	-1.82	na	na	
1.0000	1.0000	0.98736	-0.16	0.9873	0.6318	
1.0000	1.0000	1.00251	-0.17	1.0025	0.6478	0.6398
0.0000		0.23105	-2.42	na	na	
1.0000	1.0000	2.59385	-0.23	2.5940	1.1926	
1.0000	1.0000	2.55545	-0.2	2.5556	1.1545	1.1735
0.0000		0.34118	-2.02	na	na	
1.0001	0.9999	4.04726	-0.19	4.0470	1.5497	
1.0001	0.9999	4.04166	-0.15	4.0414	1.5442	1.5469
0.0000		0.472	-1.92	na	na	
1.0000	1.0000	6.1776	-0.18	6.1774	1.8438	
1.0001	0.9999	6.1684	-0.17	6.1680	1.8359	1.8399
0.0000		0.71805	-1.86	na	na	
1.0000	1.0000	9.80025	-0.11	9.7999	2.1866	
1.0000	1.0000	9.74385	-0.11	9.7436	2.1471	2.1668
0.0000		0.9804	-1.83	na	na	
1.0001	0.9999	13.3316	-0.18	13.3305	2.3436	
1.0001	0.9999	13.3642	-0.14	13.3634	2.3629	2.3533

EXPLANATION

Experiment title = Strontium Batch Experiment – Sr^{+2} Bulk 1:1 Rock:water ratio

Conducted by = MNP

Sample = centrifuge tube number

Start date/time = the date and time in which the centrifuge tubes were placed on the shaker.

End date/time = the date and time in which the centrifuge tubes were removed from the shaker.

Equi. Hrs = the amount of time the centrifuge tubes were on the shaker.

Solution = a description of the solution in each centrifuge tube.

Sed. Mass = the amount of sediment in each centrifuge tube.

Sol. Vol. = the volume of solution in each centrifuge tube.

$\text{Sr}(i)$ = the initial concentration of strontium in each centrifuge tube prior to mixing on the shaker. For the blank samples, this value was equal to concentration that the solution was made to be. For the other samples, this value was equal to the concentration of strontium in the blank samples after mixing with the soil on the shaker, therefore, accounting for sorption of strontium to the tube wall.

$\text{Sr}(eq)$ = the concentration in the solution after mixing with the soil on the shaker.

$\text{pH}(i)$ = the initial solution pH prior to mixing with the soil.

$\text{pH}(f)$ = the final solution pH after mixing with the soil.

Mass/vol = the sediment mass to solution volume ratio in each centrifuge tube.

Vol/mass = the solution volume to sediment mass ratio in each centrifuge tube.

$\Delta \text{Sr}(i-f)$ = the difference between the initial strontium concentration in solution and the final strontium concentration in solution after mixing with the sediment.

$\Delta \text{pH}(f-i)$ = the difference between the final (after mixing with the soil) and initial solution pH values.

$\text{Sr sorbed} = [\text{Sr}(i) (\mu\text{g/ml}) - \text{Sr}(f) (\mu\text{g/ml})] * [\text{Solution vol. (ml)} / \text{Sediment mass (g)}]$

$\text{Sr } K_d = [\text{Sr}(i) (\mu\text{g/ml}) - \text{Sr}(f) (\mu\text{g/ml})] * [\text{Solution vol. (ml)} / \text{Sediment mass (g)}] / [\text{Sr}(eq) (\mu\text{g/ml})]$

$K_{d\text{ave}}$ = the average of the two duplicate samples for each solution.

APPENDIX B – An example of saturated packed column experimental datasheets

Hanford Fm - 4.5 cm column - SrEDTA-2										
0.1M NaCl, 0.228 mM SrEDTA, 2.0 mM Br										
Start Date:	6/29/2004									
pH	8									
Bulk Volume	3.540375					Volume pulse:		influent flux	1.403921	
Solid Mass	6.6519					14.2264 ml		effluent flux	0.587111	
Pore Volume	1.1923					PV pulse:		average	0.995516	ml/h
bulk density	1.878868764	— optimized				11.93189633				Corr for Volume of po
correction	0.4629									CUM VOL
notes	date	time	FC (min)	sample #	dry weight	wet weight	volume	mL / hour	0 PV	
			30	1	3.1712	3.3684	0.1972	0.3944	-0.2657	0.0827
			30	2	3.2503	3.5015	0.2512	0.5024	-0.0145	-0.1175
			30	3	3.2046	3.4561	0.2515	0.503	0.237	0.0933
			30	4	3.4458	3.7508	0.3050	0.61	0.542	0.3267
			30	5	3.1957	3.4493	0.2536	0.5072	0.7956	0.5609
			30	6	3.2007	3.4545	0.2538	0.5076	1.0494	0.7737
			30	7	3.2822	3.5346	0.2524	0.5048	1.3018	0.9860
			30	8	3.1900	3.4985	0.3085	0.617	1.6103	1.2212
			30	9	3.1950	3.4498	0.2548	0.5096	1.8651	1.4574
			30	10	3.4458	3.4458	0.0000		1.8651	1.5643
			30	11	3.4433	3.6997	0.2564	0.5128	2.1215	1.6718
			30	12	3.2798	3.5902	0.3104	0.6208	2.4319	1.9095
			30	13	3.1989	3.4563	0.2574	0.5148	2.6893	2.1476
			30	14	3.1943	3.5055	0.3112	0.6224	3.0005	2.3861
			30	15	3.4490	3.7070	0.2580	0.516	3.2585	2.6248
			30	16	3.2462	3.2462	0.0000		3.2585	2.7330
			30	17	3.2003	3.4599	0.2596	0.5192	3.5181	2.8418

	30	18	3.2027	3.5165	0.3138	0.6276	3.8319	3.0823
	30	19	3.2498	3.5099	0.2601	0.5202	4.092	3.3229
	30	20	3.2871	3.5480	0.2609	0.5218	4.3529	3.5414
	30	21	3.2638	3.5787	0.3149	0.6298	4.6678	3.7829
	30	22	3.1905	3.4516	0.2611	0.5222	4.9289	4.0244
	30	23	3.2500	3.4946	0.2446	0.4892	5.1735	4.2365
	30	24	3.2668	3.5285	0.2617	0.5234	5.4352	4.4488
	30	25	3.4481	3.7101	0.2620	0.524	5.6972	4.6685
	30	26	3.2634	3.5793	0.3159	0.6318	6.0131	4.9108
	30	27	3.2095	3.4724	0.2629	0.5258	6.276	5.1535
	30	28	3.2690	3.5323	0.2633	0.5266	6.5393	5.3742
	30	29	3.2608	3.5760	0.3152	0.6304	6.8545	5.6168
	30	30	3.2686	3.5328	0.2642	0.5284	7.1187	5.8598
	30	31	3.2070	3.5257	0.3187	0.6374	7.4374	6.1042
	30	32	3.2671	3.5302	0.2631	0.5262	7.7005	6.3482
	30	33	3.3042	3.5696	0.2654	0.5308	7.9659	6.5698
	30	34	3.2013	3.2013	0.0000		7.9659	6.6811
	30	35	3.4629	3.7836	0.3207	0.6414	8.2866	6.8156
	30	36	3.2623	3.5291	0.2668	0.5336	8.5534	7.0620
	30	37	3.4442	3.7654	0.3212	0.6424	8.8746	7.3086
	30	38	3.2497	3.5175	0.2678	0.5356	9.1424	7.5556
	30	39	3.2491	3.5172	0.2681	0.5362	9.4105	7.7803
	30	40	3.2237	3.2237	0.0000		9.4105	7.8927
	30	41	3.2638	3.5289	0.2651	0.5302	9.6756	8.0039
	30	42	3.2798	3.5990	0.3192	0.6384	9.9948	8.2489
	30	43	3.2640	3.5294	0.2654	0.5308	10.2602	8.4941
	30	44	3.2681	3.5866	0.3185	0.637	10.5787	8.7389
	30	45	3.2004	3.4675	0.2671	0.5342	10.8458	8.9845
	30	46	3.2828	3.5496	0.2668	0.5336	11.1126	9.2084

		30	47	3.1707	3.4718	0.3011	0.6022	11.4137	9.4466
		30	48	3.2479	3.4937	0.2458	0.4916	11.6595	9.6759
		30	49	3.4612	3.7626	0.3014	0.6028	11.9609	9.9054
		30	50	3.1663	3.4143	0.2480	0.496	12.2089	10.1358
		30	51	3.2053	3.4541	0.2488	0.4976	12.4577	10.3441
		30	52	3.2014	3.2014	0.0000		12.4577	10.4485
		30	53	3.2013	3.5055	0.3042	0.6084	12.7619	10.5760
		30	54	3.2134	3.4636	0.2502	0.5004	13.0121	10.8085
		30	55	3.1886	3.4929	0.3043	0.6086	13.3164	11.0411
		30	56	3.1899	3.4390	0.2491	0.4982	13.5655	11.2731
		30	57	3.1739	3.1739	0.0000		13.5655	11.3776
		30	58	3.1703	3.1703	0.0000		13.5655	11.3776
stop influent		30	59	3.1690	3.3670	0.1980	0.396	13.7635	11.4606
		30	60	3.1672	3.3652	0.1980	0.396	13.9615	11.6267
		30	61	3.2499	3.4486	0.1987	0.3974	14.1602	11.7930
		30	62	3.1899	3.3886	0.1987	0.3974	14.3589	11.9597
		30	63	3.2636	3.4620	0.1984	0.3968	14.5573	12.1262
		30	64	3.2809	3.5341	0.2532	0.5064	14.8105	12.3156
		30	65	3.1891	3.3903	0.2012	0.4024	15.0117	12.5062
		30	66	3.1898	3.3911	0.2013	0.4026	15.213	12.6750
		30	67	3.4573	3.6582	0.2009	0.4018	15.4139	12.8436
		30	68	3.2018	3.4577	0.2559	0.5118	15.6698	13.0352
		30	69	3.1895	3.4459	0.2564	0.5128	15.9262	13.2500
		30	70	3.2624	3.2624	0.0000		15.9262	13.3575
		30	71	3.2143	3.4188	0.2045	0.409	16.1307	13.4433
		30	72	3.1895	3.4474	0.2579	0.5158	16.3886	13.6372
		30	73	3.2809	3.4853	0.2044	0.4088	16.593	13.8311
		30	74	3.2062	3.4650	0.2588	0.5176	16.8518	14.0253
		30	75	3.3046	3.5638	0.2592	0.5184	17.111	14.2426
		30	76	3.2689	3.5281	0.2592	0.5184	17.3702	14.4600
		30	77	3.2008	3.4073	0.2065	0.413	17.5767	14.6552

		30	621	3.2497	4.0879	0.8382	1.6764	427.6559	358.3300
		30	622	3.2109	3.2109	0.0000		427.6559	358.6815
		30	623	3.2002	4.0995	0.8993	1.7986	428.5552	359.0586
		30	624	3.2741	4.1203	0.8462	1.6924	429.4014	359.7906
		30	625	3.4445	4.3458	0.9013	1.8026	430.3027	360.5234
		30	626	3.2110	4.0611	0.8501	1.7002	431.1528	361.2579
		30	627	3.2638	4.1625	0.8987	1.7974	432.0515	361.9912
		30	628	3.4450	3.4450	0.0000		432.0515	362.3681
		30	629	3.3006	4.1540	0.8534	1.7068	432.9049	362.7260
		30	630	3.4458	4.3526	0.9068	1.8136	433.8117	363.4641
		30	631	3.4461	4.3012	0.8551	1.7102	434.6668	364.2030
		30	632	3.2057	4.1160	0.9103	1.8206	435.5771	364.9433
		30	633	3.2227	4.0811	0.8584	1.7168	436.4355	365.6851
		30	634	3.2642	3.2642	0.0000		436.4355	366.0450
		30	635	3.2486	4.1392	0.8906	1.7812	437.3261	366.4185
		30	636	3.3011	4.1395	0.8384	1.6768	438.1645	367.1436
		30	637	3.4446	4.2806	0.8360	1.672	439.0005	367.8458
		30	638	3.2123	4.1043	0.8920	1.784	439.8925	368.5704
		30	639	3.1993	4.0414	0.8421	1.6842	440.7346	369.2976
		30	640	3.1662	3.1662	0.0000		440.7346	369.6508
		30	641	3.2010	4.0444	0.8434	1.6868	441.578	370.0044
		30	642	3.2053	4.1032	0.8979	1.7958	442.4759	370.7347
		30	643	3.2651	4.1066	0.8415	1.683	443.3174	371.4641
		30	644	3.1906	4.0917	0.9011	1.8022	444.2185	372.1949
		30	645	3.2096	4.1082	0.8986	1.7972	445.1171	372.9496
		30	646	3.2847	4.1342	0.8495	1.699	445.9666	373.6827
		30	647	3.1709	4.0764	0.9055	1.811	446.8721	374.4186
		30	648	3.1908	4.0436	0.8528	1.7056	447.7249	375.1560
		30	649	3.2120	4.1198	0.9078	1.8156	448.6327	375.8943
		30	650	3.2120	4.0670	0.8550	1.71	449.4877	376.6336
		30	651	3.2496	4.1599	0.9103	1.8206	450.398	377.3739

EXPLANATION

The first couple of rows contain descriptive information for this experiment.

The Pore volume is calculated on another datasheet (see Appendix C).

The correction represents the volume correction necessary to correct for the volume in the tubing pre- and post-column.

The volume pulse is the total volume collected when the pulse of tracer solution was stopped and a washout solution was started plus the volume correction.

The PV pulse is the influent volume pulse divided by the pore volume

The influent and effluent flux is the effluent flow rate during the pulse of the tracer solution (influent flux) and the washout solution (effluent flux).

The columns notes, date, and time are used as necessary to record the time and date of sample collection and to record any unusual observations.

FC = the fraction collector setting (min) for each sample tube.

Sample # = the sample tube number.

Dry wt. = actual weight of each empty sample tube. It was necessary to weight each empty tube because such a small volume of solution was being collected in each tube.

Wet weight = the weight of the sample tube once effluent solution was collected in it.

Volume = (wet weight) – (dry weight) = total volume of effluent solution collected in each sample tube.

ml / hour = (volume) / (FC / 60)

Cum Vol = cumulative volume of effluent solution collected throughout the experiment.

Note that the first volume is corrected for the pre- and post-column tubing volume by subtracting the correction from the volume of solution collected yielding a negative value. The rest of the cumulative volumes = (volume at that sample) + (previous samples cum. Vol).

PV = [(volume / 2) + (previous sample cum. Vol)] / (Pore volume at top of datasheet).

APPENDIX C – Example of pore volume calculation datasheet for saturated packed column experiments.

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Worksheet for column pore volume calculation			Column:	Hanford Fm - 4.5 cm column - SrEDTA-2 0.1M NaCl, 0.228 mM SrEDTA, 2.0 mM Br		
Beaker + dry sand:	38.5708 g					
- Beaker tare:	31.9189 g					
	6.6519 g (mass sand in column)					
	(A)					
Glass column + 'u	r ends + saturated porous media	66.54 g				
	- Glass Column, dry	32.7706 g				
	- Influent plunger end, wet	16.5 g				
	- Effluent Plunger end, wet	9.4252 g				
	- dry sand (A)	6.6519 g				
		1.1923 g (mass water in column)				
Column dimensions						
length:	4.5 cm					
radius	0.5 cm		6/15/04:	WC =	0.336772	
	0 cm ³					
Tot. Volum	3.540375 cm ³		WC = Volume water / Volume total			
	(C)		1.1923	This is pore volume,		
Column water content =						
	volume water (B)	0.336772235 cm ³ /cm ³		1.1923	= pore volume (cm ³)	
	total volume (C)	(D)				
Bulk Density =						
	mass sand (A)	1.878868764 g/cm ³				
	total volume (C)	(E)				
Density of the solid =						
	bulk density (E)	1.246117932 g/cm ³	Ratio calculated : expected (2.65 g/cm ³)			
	1 - water content(D)	(F)	1.331953			

			Volume Correction:				
Influent plunger end, wet	16.5	g		0.4629	mL		
- Influent plunger end, dry	16.3978	g	(G)				
	0.1022	g					
Effluent plunger end, wet	9.4252	g					
- effluent plunger end, dry	9.2055	g					
	0.2197	g					
PEEK effluent tubing	0.104	ml					
Quick switch valve	0.022	mL					
Volume of flow-through cell	0.015	mL					

EXPLANATION

The first two lines contain descriptive information about the datasheet and experiment.

Beaker + dry sand = the weight of the glass beaker and the dry sand used in the column.

- Beaker tare = the weight of the empty glass beaker.

(mass sand in column) = (Beaker + dry sand) – (Beaker tare) = grams of sand in packed column.

Glass column + plunger ends + saturated porous media = total weight of the assembled saturated packed column (g)

Glass column (dry) = the dry weight of the glass column only (grams).

Influent plunger end, wet = the wet weight of the influent plunger end (on the bottom of the column through which solution enters the column) (grams).

Effluent plunger end, wet = wet weight of the effluent plunger end (at the top of the packed column through which solution leaves the packed column) (grams).

Dry sand = weight of dry sand in the column (grams)

Mass water in column = (Glass column + plunger ends + saturated porous media) – (Glass column (dry)) – (Influent plunger end, wet) – (Effluent plunger end, wet) – (Dry sand).

Column dimensions

Length = length of glass column

Radius = radius of glass column

o-ring volume = negligible

Total volume = (radius)² * (3.14) * (length) = total column volume

Column water content = (mass of water in column) * (1cm³/g) / (total column volume)

Bulk density = (mass of dry sand in column) / (total column volume)

Density of the solids = (bulk density) * (1-column water content)

WC = column water content

The second part of this table is used to calculate the volume correction needed for each experimental setup.

Influent plunger end, wet = wet weight of the influent plunger end.

Influent plunger end, dry = dry weight of the influent plunger end.

Volume of water contained in the influent plunger end = (wet weight) – (dry weight)

Effluent plunger end, wet = wet weight of the effluent plunger end.

Effluent plunger end, dry = dry weight of the effluent plunger end.

Volume of water contained in the effluent plunger end = (wet weight) – (dry weight)

PEEK effluent tubing = volume of the PEEK tubing used to connect the effluent plunger end to the fraction collector.

Quick switch valve = estimation of the volume of water contained in the switching valve on the bottom of the influent plunger end.

Volume correction = summation of the volume of water contained in the influent plunger end, the effluent plunger end, the PEEK tubing, and the switching valve.

APPENDIX D – Example of a datasheet for the undisturbed core experiments

HH2 - Hanford Horizontal 2			diameter =	22 cm								
MNP			length =	23.5 cm								
Unsat - U/Co(II)EDTA - 190			flow rate =	7.457373								
2/16/2004			pulse =	1159.953 cm3								
unsat wt	69.38 lbs			0.379136 PV								
est. pore vol	3059.46 cm3			1.54 L	on tape							
start time	10:00 AM			1.159953 L	vol collected							
bulk density	1.61											
	date	time	notes	FC (min)	sample	dry wt	wet wt	vol.	ml/hr	cum vol	pore vol.	Time (h)
	2/16/2004	10:08	start exp	40	3	3.3047	9.0917	5.787	8.6805	5.787	0.000946	0.67
				40	4	3.3047	9.6138	6.3091	9.46365	12.0961	0.002923	1.33
			7.456767417	40	5	3.3047	6.5225	3.2178	4.8267	15.3139	0.00448	2.00
				40	6	3.3047	9.3562	6.0515	9.07725	21.3654	0.005994	2.67
				40	7	3.3047	9.48	6.1753	9.26295	27.5407	0.007993	3.33
				40	8	3.3047	9.4078	6.1031	9.15465	33.6438	0.009999	4.00
				40	9	3.3047	9.0067	5.702	8.553	39.3458	0.011928	4.67
				40	10	3.3047	8.8928	5.5881	8.38215	44.9339	0.013774	5.33
				40	11	3.3047	9.1236	5.8189	8.72835	50.7528	0.015638	6.00
				0	12	3.3047	3.3047	0		50.7528	0.016589	6.00
				40	13	3.3047	9.0391	5.7344	8.6016	56.4872	0.017526	6.67
				40	14	3.3047	8.8366	5.5319	8.29785	62.0191	0.019367	7.33
				40	15	3.3047	8.8203	5.5156	8.2734	67.5347	0.021173	8.00
				40	16	3.3047	8.9709	5.6662	8.4993	73.2009	0.023	8.67
				0	17	3.3047	3.3047	0		73.2009	0.023926	8.67
				0	18	3.3047	3.3047	0		73.2009	0.023926	8.67
				40	19	3.3047	8.6895	5.3848	8.0772	78.5857	0.024806	9.33
				40	20	3.3047	8.8379	5.5332	8.2998	84.1189	0.02659	10.00
				40	21	3.3047	8.6852	5.3805	8.07075	89.4994	0.028374	10.67

				40	22	3.3047	11.4935	8.1888	12.2832	97.6882	0.030592	11.33
				0	23	3.3047	3.3047	0		97.6882	0.03193	11.33
				0	24	3.3047	3.3047	0		97.6882	0.03193	11.33
				40	25	3.3047	8.6157	5.311	7.9665	102.9992	0.032798	12.00
				40	26	3.3047	8.6874	5.3827	8.07405	108.3819	0.034545	12.67
				40	27	3.3047	7.8001	4.4954	6.7431	112.8773	0.03616	13.33
				0	28	3.3047	3.3047	0		112.8773	0.036894	13.33
				0	29	3.3047	3.3047	0		112.8773	0.036894	13.33
				0	30	3.3047	3.3047	0		112.8773	0.036894	13.33
				40	31	3.3047	8.5319	5.2272	7.8408	118.1045	0.037749	14.00
				40	32	3.3047	8.4322	5.1275	7.69125	123.232	0.039441	14.67
				40	33	3.3047	5.1968	1.8921	2.83815	125.1241	0.040588	15.33
				0	34	3.3047	3.3047	0		125.1241	0.040897	15.33
				0	35	3.3047	3.3047	0		125.1241	0.040897	15.33
				0	36	3.3047	3.3047	0		125.1241	0.040897	15.33
				40	37	3.3047	8.7798	5.4751	8.21265	130.5992	0.041792	16.00
				40	38	3.3047	8.6639	5.3592	8.0388	135.9584	0.043563	16.67
				0	39	3.3047	3.3047	0		135.9584	0.044439	16.67
				40	40	3.3047	7.1058	3.8011	5.70165	139.7595	0.04506	17.33
				0	41	3.3047	3.3047	0		139.7595	0.045681	17.33
				0	42	3.3047	3.3047	0		139.7595	0.045681	17.33
				40	43	3.3047	8.2029	4.8982	7.3473	144.6577	0.046482	18.00
	2/17/2004	9:30	collect tubes	40	44	3.3047	8.2299	4.9252	7.3878	149.5829	0.048087	18.67
				40	45	3.3047	8.1979	4.8932	7.3398	154.4761	0.049692	19.33
				40	46	3.3047	7.5818	4.2771	6.41565	158.7532	0.05119	20.00
				40	47	3.3047	7.9383	4.6336	6.9504	163.3868	0.052646	20.67
				0	48	3.3047	3.3047	0		163.3868	0.053404	20.67
				0	49	3.3047	3.3047	0		163.3868	0.053404	20.67
				0	50	3.3047	3.3047	0		163.3868	0.053404	20.67

	40	51	3.3047	8.7657	5.461	8.1915	168.8478	0.054296	21.33
	0	52	3.3047	3.3047	0		168.8478	0.055189	21.33
	0	53	3.3047	3.3047	0		168.8478	0.055189	21.33
	0	54	3.3047	3.3047	0		168.8478	0.055189	21.33
	0	55	3.3047	3.3047	0		168.8478	0.055189	21.33
	40	56	3.3047	8.3725	5.0678	7.6017	173.9156	0.056017	22.00
	40	57	3.3047	8.9109	5.6062	8.4093	179.5218	0.057761	22.67
	40	58	3.3047	8.8576	5.5529	8.32935	185.0747	0.059585	23.33
	0	59	3.3047	3.3047	0		185.0747	0.060493	23.33
	0	60	3.3047	3.3047	0		185.0747	0.060493	23.33
	40	61	3.3047	8.713	5.4083	8.11245	190.483	0.061376	24.00
	40	62	3.3047	8.7488	5.4441	8.16615	195.9271	0.06315	24.67
	40	63	3.3047	8.7287	5.424	8.136	201.3511	0.064926	25.33
	40	64	3.3047	8.3703	5.0656	7.5984	206.4167	0.06664	26.00
	40	65	3.3047	8.5711	5.2664	7.8996	211.6831	0.068329	26.67
	0	66	3.3047	3.3047	0		211.6831	0.06919	26.67
	40	67	3.3047	8.5311	5.2264	7.8396	216.9095	0.070044	27.33
	40	68	3.3047	8.5003	5.1956	7.7934	222.1051	0.071747	28.00
	40	69	3.3047	8.453	5.1483	7.72245	227.2534	0.073437	28.67
	40	70	3.3047	8.4435	5.1388	7.7082	232.3922	0.075119	29.33
	40	71	3.3047	8.4777	5.173	7.7595	237.5652	0.076804	30.00
	0	72	3.3047	3.3047	0		237.5652	0.077649	30.00
	40	73	3.3047	8.4347	5.13	7.695	242.6952	0.078488	30.67
	40	74	3.3047	8.2213	4.9166	7.3749	247.6118	0.08013	31.33
	40	75	3.3047	8.3805	5.0758	7.6137	252.6876	0.081763	32.00
	40	76	3.3047	8.7783	5.4736	8.2104	258.1612	0.083487	32.67
	40	77	3.3047	8.4478	5.1431	7.71465	263.3043	0.085222	33.33
	0	78	3.3047	3.3047	0		263.3043	0.086062	33.33
	40	79	3.3047	8.1322	4.8275	7.24125	268.1318	0.086851	34.00
	40	80	3.3047	8.1624	4.8577	7.28655	272.9895	0.088434	34.67

			40	2408	3.3047	8.9151	5.6104	8.4156	10081.59	3.294296	1351.48
			40	2409	3.3047	8.4686	5.1639	7.74585	10086.75	3.296057	1352.15
			40	2410	3.3047	8.6193	5.3146	7.9719	10092.06	3.297769	1352.82
			40	2411	3.3047	8.7807	5.476	8.214	10097.54	3.299533	1353.48
			40	2412	3.3047	8.4351	5.1304	7.6956	10102.67	3.301266	1354.15
			40	2413	3.3047	8.3838	5.0791	7.61865	10107.75	3.302935	1354.82
			40	2414	3.3047	8.3715	5.0668	7.6002	10112.82	3.304593	1355.48
			40	2415	3.3047	8.5051	5.2004	7.8006	10118.02	3.306271	1356.15
			40	2416	3.3047	8.3528	5.0481	7.57215	10123.06	3.307946	1356.82
			40	2417	3.3047	8.2878	4.9831	7.47465	10128.05	3.309585	1357.48
			40	2418	3.3047	8.3349	5.0302	7.5453	10133.08	3.311222	1358.15
			40	2419	3.3047	8.3530	5.0483	7.57245	10138.13	3.312869	1358.82
			40	2420	3.3047	8.3603	5.0556	7.5834	10143.18	3.31452	1359.48
			40	2421	3.3047	8.2832	4.9785	7.46775	10148.16	3.31616	1360.15
			40	2422	3.3047	8.3223	5.0176	7.5264	10153.18	3.317793	1360.82
			40	2423	3.3047	8.3162	5.0115	7.51725	10158.19	3.319432	1361.48
			40	2424	3.3047	8.3353	5.0306	7.5459	10163.22	3.321074	1362.15
			40	2425	3.3047	8.1555	4.8508	7.2762	10168.07	3.322688	1362.82
			40	2426	3.3047	8.3264	5.0217	7.53255	10173.09	3.324302	1363.48
			40	2427	3.3047	8.3860	5.0813	7.62195	10178.17	3.325953	1364.15
			40	2428	3.3047	8.3786	5.0739	7.61085	10183.25	3.327613	1364.82
			40	2429	3.3047	8.6348	5.3301	7.99515	10188.58	3.329313	1365.48
			40	2430	3.3047	8.3878	5.0831	7.62465	10193.66	3.331015	1366.15
			40	2431	3.3047	8.3404	5.0357	7.55355	10198.7	3.332668	1366.82
			40	2432	3.3047	8.2015	4.8968	7.3452	10203.59	3.334292	1367.48
			40	2433	3.3047	8.3030	4.9983	7.49745	10208.59	3.335909	1368.15
			40	2434	3.3047	8.1504	4.8457	7.26855	10213.44	3.337518	1368.82
			40	2435	3.3047	8.2611	4.9564	7.4346	10218.39	3.339119	1369.48
			40	2436	3.3047	8.1265	4.8218	7.2327	10223.22	3.340718	1370.15
	4/14/2005	10:15 collect tubes	40	2437	3.3047	8.0070	4.7023	7.05345	10227.92	3.342274	1370.82

EXPLANATION

The first couple of lines are identification information indicating the core used in the experiment, who conducted the experiment, unsaturated conditions, date, core dimensions, pulse of tracer solution, influent flow rate, estimated unsaturated pore volume, and core bulk density.

The date, time, and notes columns represent the day the core is checked and tubes collected from the internal fraction collector in the vacuum chamber.

FC = fraction collector setting (minutes).

Sample = effluent sample tube number collected in the internal fraction collector in the vacuum chamber.

Dry wt. = weight of empty sample tube determined from the average of many measured empty tube weights in grams.

Wet wt. = weight of full sample tube containing effluent solution in grams.

Vol. = Wet wt. – Dry wt. = the volume of solution collected in each sample tube.

ml/hr = effluent flow rate = $[(\text{vol.}) / (\text{FC})] * 60$

cum. Vol. = cumulative effluent solution volume collected = sum(vol.).

Pore vol. = relative volume collected = $[(\text{vol.})/2 + (\text{previous samples cum vol.})] / (\text{est. unsat. PV})$.

Time (h) = $[\text{sum}(\text{FC})]/60$ = time of each sample tube since the start of the experiment.

APPENDIX E – Example of a spreadsheet used to determination of the unsaturated V_w (pore volume) for the undisturbed core experiments

Water Content									
Vt =	8928.59	cm3							
Pvsat =	3506.26	cm3	est. from moisture retention						
9/30/2003			same as the sat. flow experiment						
Date		Tube	Comments	Core Wt (lbs)	Core Wt (kg)	WC	VC	% sat	PV
9/15/2003	#####		unsat wt	65.17	29.561112	0.0625			
9/30/03 0:00	0:00:00		start satflow exp						
10/1/03 0:00	24:00:00		sat wt.	71.67	32.509512	0.3927		100.00	3506.26
11/25/03 14:40	1358:40:00			68.16	30.917376	0.2144	-175	54.59	1914.124
12/12/03 15:45	1767:45:00			67.25	30.5046	0.1682	-191	42.82	1501.348
12/31/03 11:15	2219:15:00			65.86	29.874096	0.0975	-171	24.84	870.844
2/16/04 9:00	0:00:00	2	unsat wt	69.38	31.470768	0.2764	-190	70.37	2467.516
3/9/04 9:45	528:45:00	938		70.82	32.123952	0.3495	-191	89.00	3120.7
4/7/04 9:35	1224:35:00	2151		71.18	32.287248	0.3678	-190	93.66	3283.996
4/16/04 15:00	4791:00:00	2531	end of exp	71.36	32.368896	0.3770	-191	95.99	3365.644
	#####		AVERAGE		0	0.3427		87.26	3059.464

EXPLANATION

The first couple of lines identify what this spreadsheet is used to calculate, the total volume of the core, and the saturated V_w .

The date column indicates what date and time the core was weighed.

The next column represents the time between the start of the experiment and the individual core weights.

The tube column identifies the effluent sample tube that the fraction collector was on when the core was weighted.

The comments column was used to list observations that may have been important during the flow and transport experiment.

Core wt. (lbs) was recorded from a large triple beam balance.

Core wt. (kg) = [Core wt (lbs)] * 0.4536

WC = unsaturated water content = [sat PV (cm^3) - ((sat Core wt (kg) - unsat Core wt (kg)) * 1000 g/kg * $1\text{cm}^3/\text{g}$)] / total core volume (cm^3).

VC = vacuum chamber tension. (-cm).

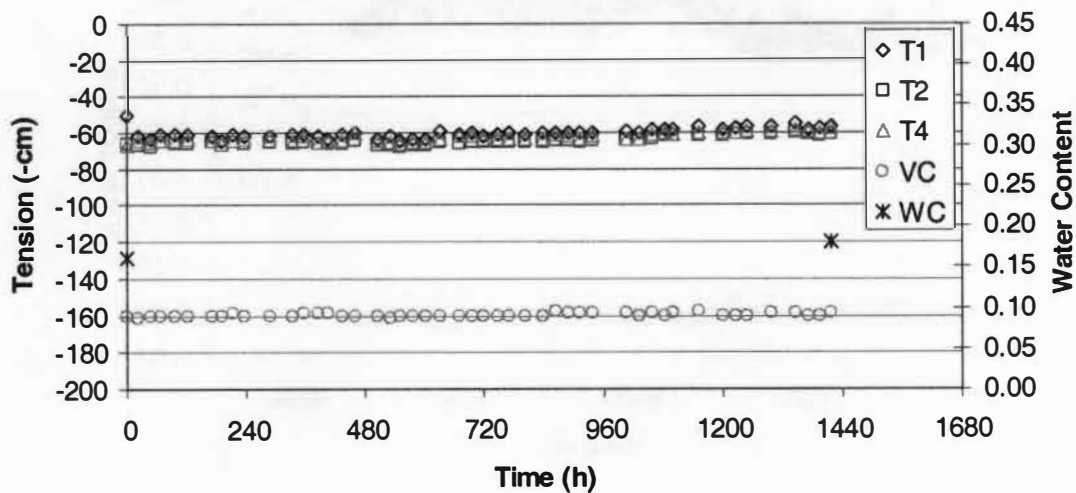
% sat = [unsaturated water content / saturated water content] * 100

PV = [sat PV (cm^3) - ((sat core wt (kg) - unsat core wt (kg)) * 1000 g/kg * $1\text{cm}^3/\text{g}$)]

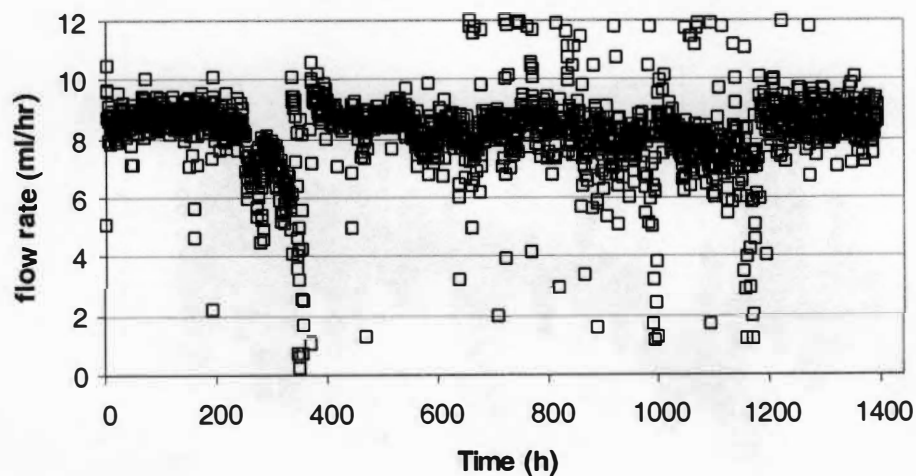
APPENDIX F – Core tensions, water content, and effluent flow rate measurements.

HV1 – 42% saturated - U(VI) and Co(II)EDTA experiment

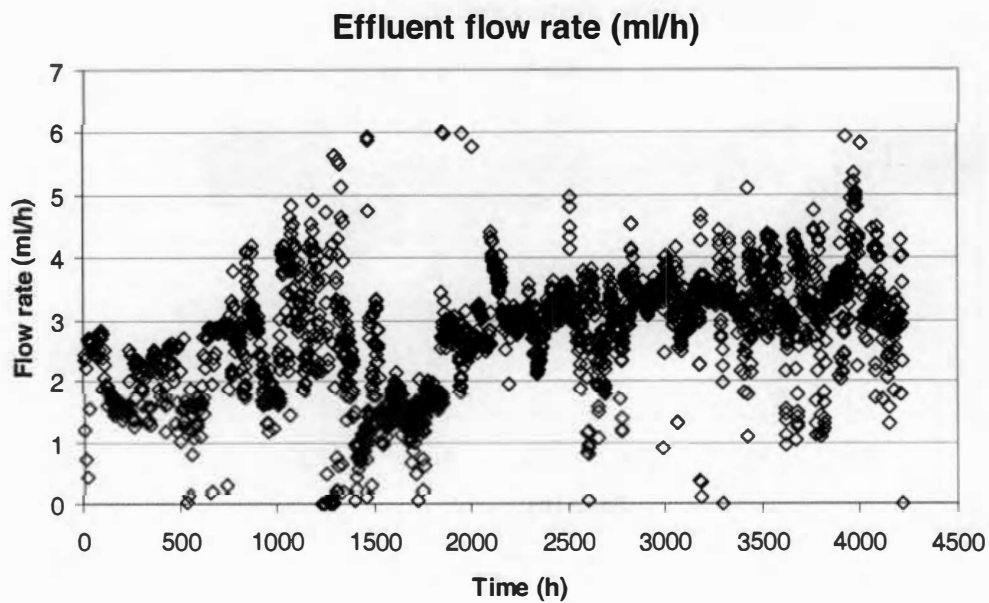
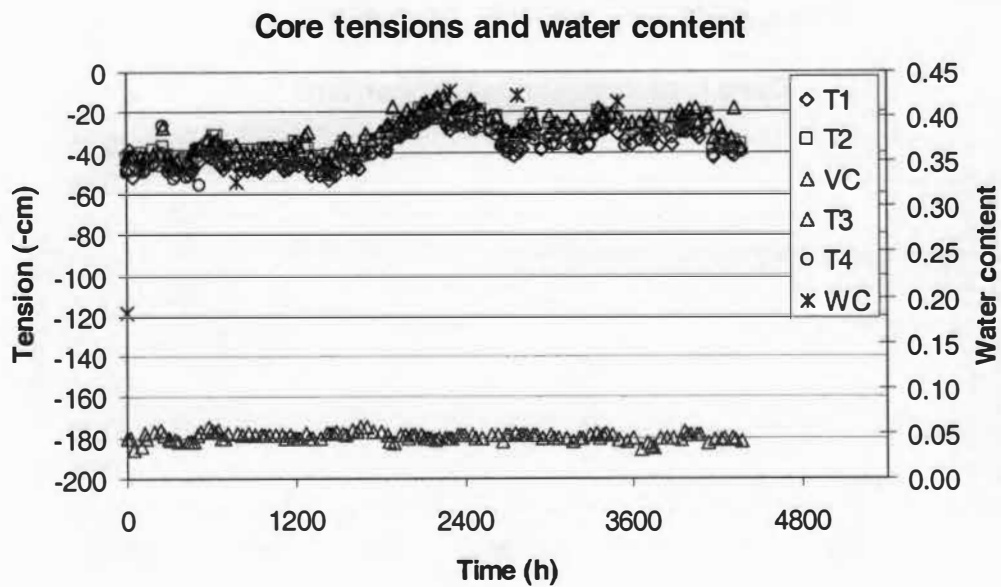
Core tensions and water content



Effluent Flow Rate (ml/hr)

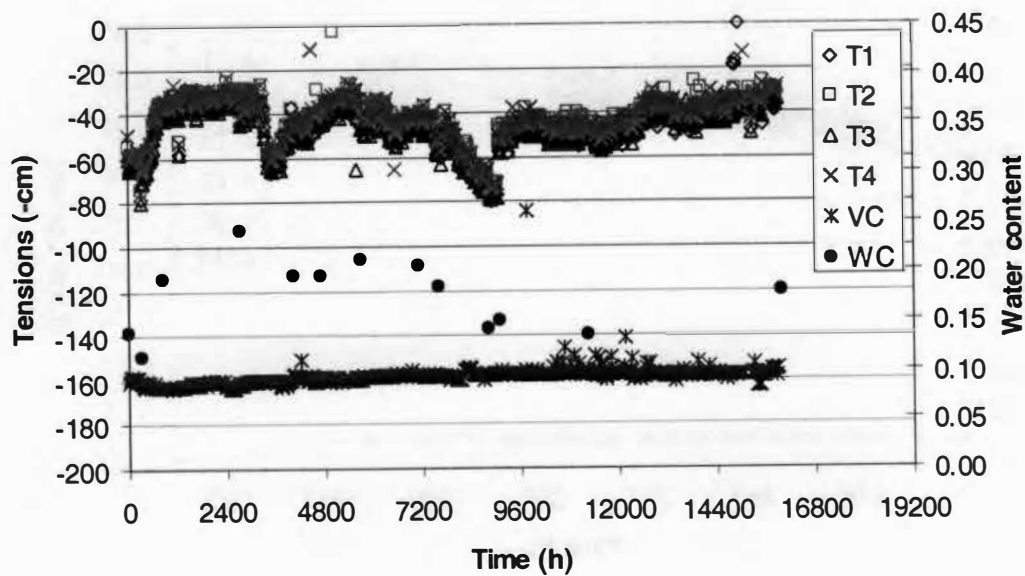


HV2 – Variable saturation - U(VI) and Co(II)EDTA experiment

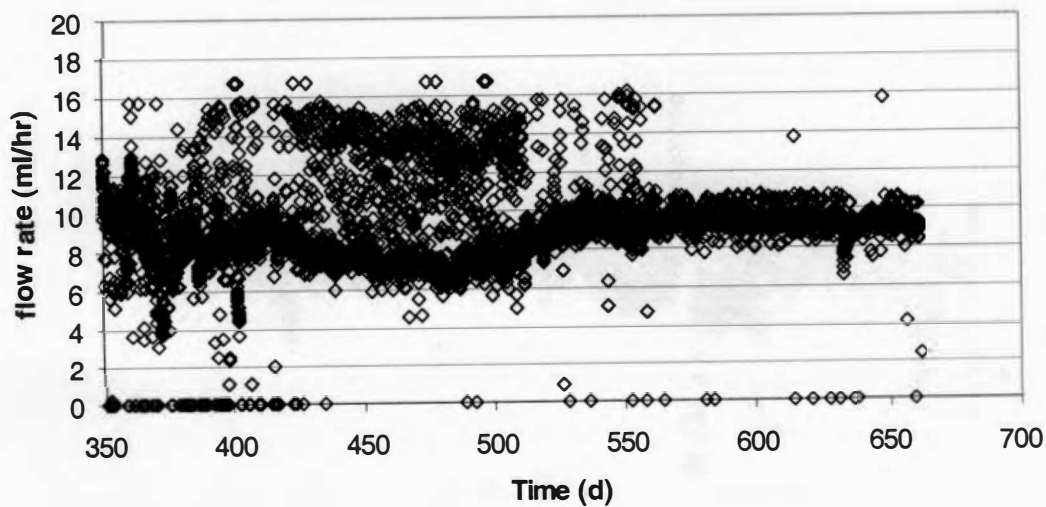


HH1 – 54% saturated – Strontium transport experiment

Core tensions and water content

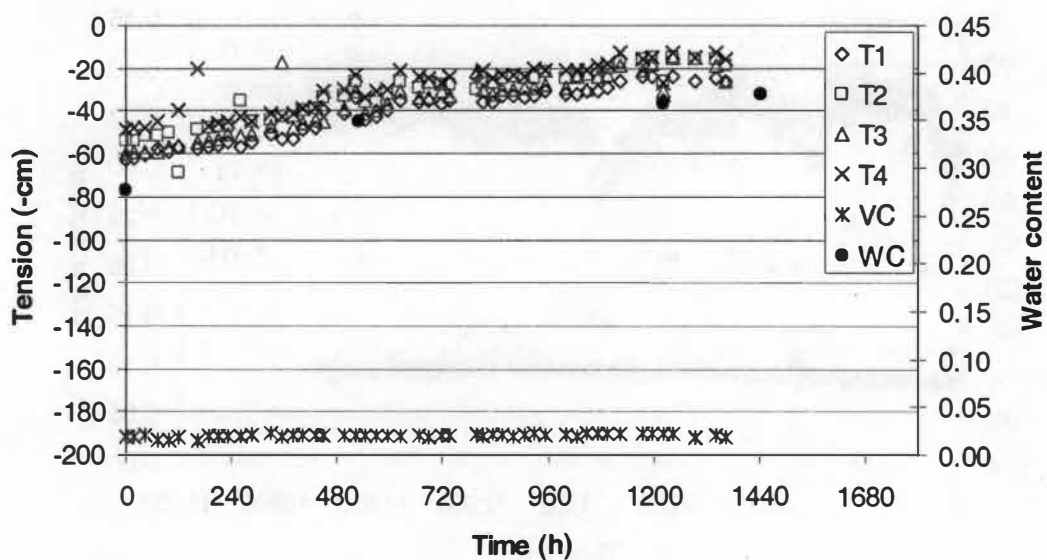


Effluent Flow Rate (ml/hr)

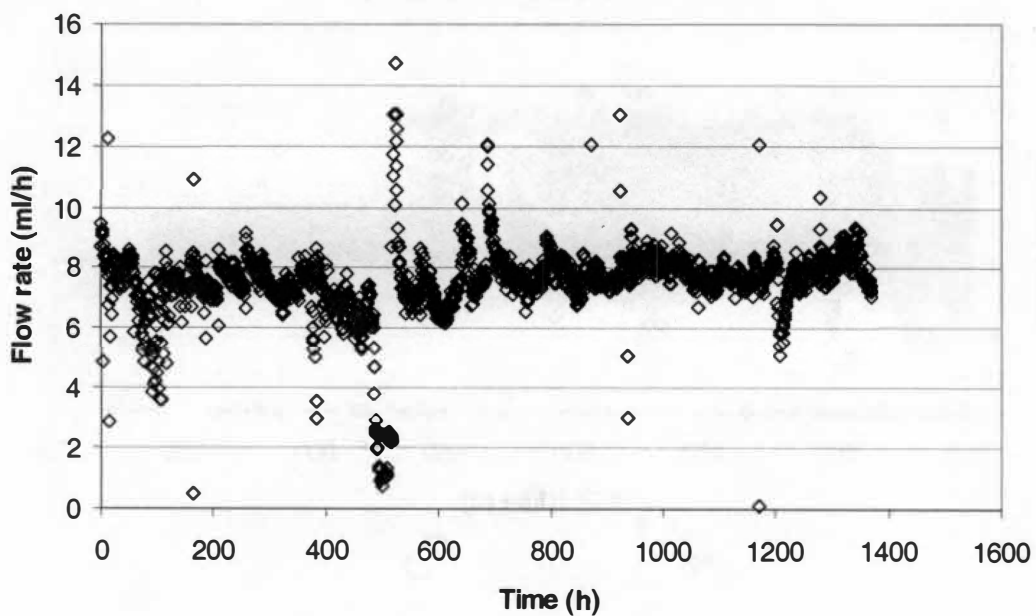


HH2 – 87% saturated – U(VI) and Co(II)EDTA experiment

Core tensions and water content

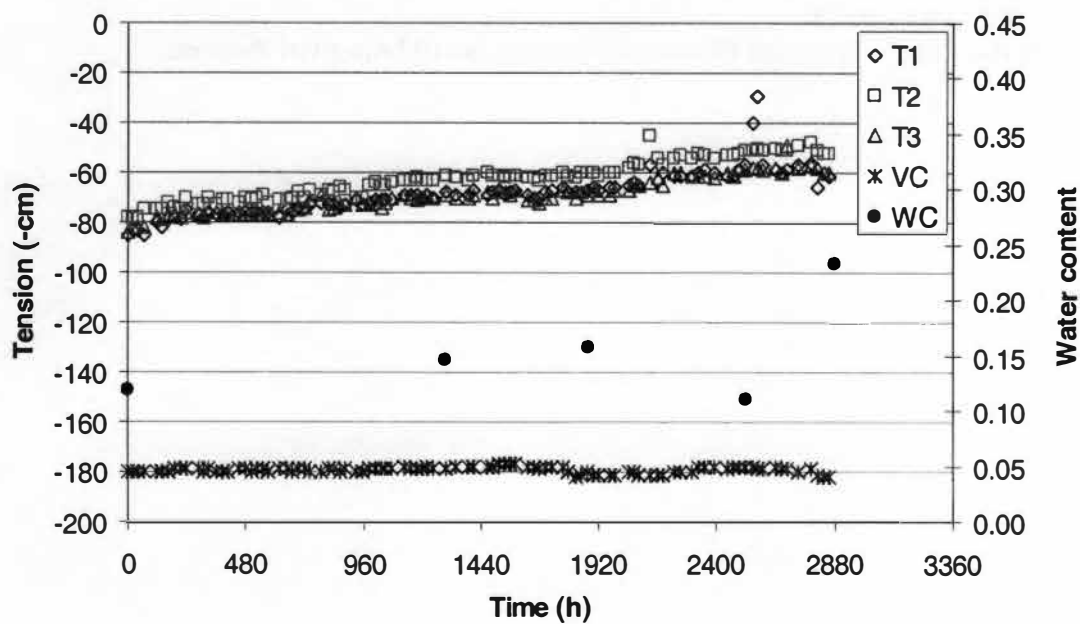


Effluent Flow Rate (ml/h)

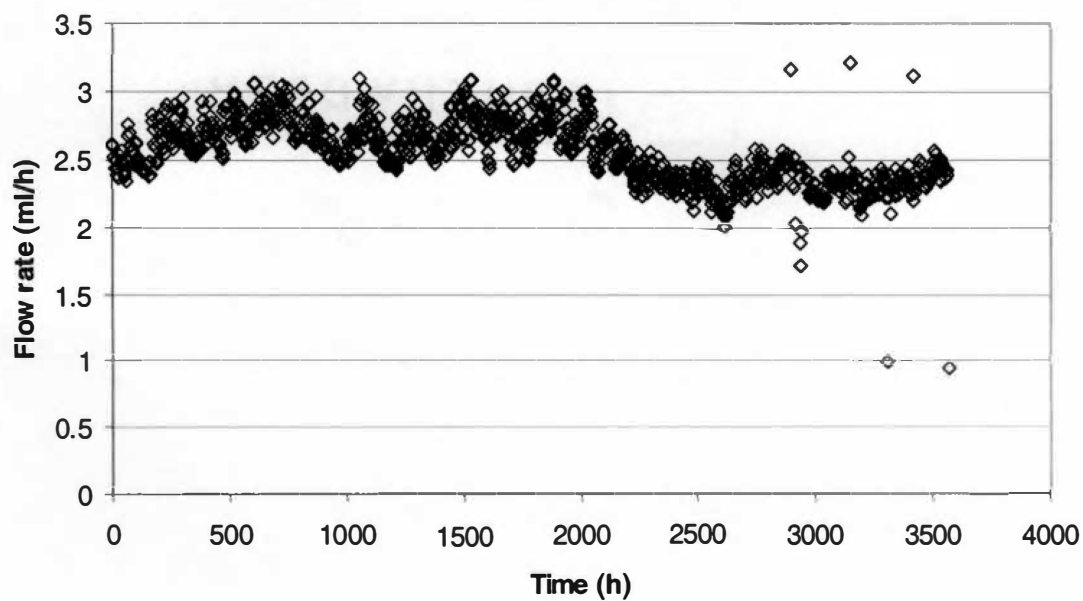


HH3 – 39% saturated - U(VI) and Co(II)EDTA experiment

Core tensions and water content



Effluent Flow Rate (ml/h)



Explanation

T# = tension (-cm) read from tensionmeters in the core.

VC = vacuum chamber tension

WC = core water content

Effluent flow rate = flow rate of solution coming out of bottom of the core.

APPENDIX G – Examples of CXTFIT input files

CDE model

```

1
*** BLOCK A: MODEL DESCRIPTION *****
Molly HV1-160-Br Unsat
unit, cm, h, micro g)
INVERSE  MODE  NREDU
1         1         3
MODC     ZL
1         21.0
*** BLOCK B: INVERSE PROBLEM *****
MIT      ILMT  MASS
100      0      0
*** BLOCK C: TRANSPORT PARAMETERS *****
V  D  R  Beta  omega  Mu1  Mu2
0.146  0.1  1.0  0.0  0.00  0  0
0  1  0  0  0  0  0
*** BLOCK D: BVP; MODB=0 ZERO; =1 DIRAC; =2 STEP; =3 A PULSE *****
MODB (Reduced Conc.& time) =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
3
1.0 1.35
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
0
*** BLOCK G: DATA FOR INVERSE PROBLEM *****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
1
21.0
      TIME      CONC  (Give "0 0 0" after last data set.)
0.0076 0.0008
0.0259 0.0008
0.1166 0.0003
0.2396 0.0008
0.3654 0.0008
0.4776 0.0003
0.6014 0.0039
0.7199 0.0420
0.7896 0.0930
0.8411 0.1543
0.8977 0.2197
1.0143 0.3870
1.0837 0.4813
1.2012 0.6206
1.3195 0.7133
1.4365 0.7803
1.5628 0.8249
1.6761 0.8524
1.7805 0.8730

```

1.8641	0.8867
1.9580	0.8884
2.0541	0.8283
2.1382	0.7099
2.2228	0.5657
2.2905	0.4232
2.4874	0.3048
2.5451	0.2645
2.5803	0.2403
2.6574	0.1991
2.7235	0.1743
2.8892	0.1299
3.0172	0.1097
3.1238	0.0955
3.2393	0.0894
3.3473	0.0798
3.4635	0.0712
3.5821	0.0641
3.6969	0.0560
3.7917	0.0530
3.8540	0.0499
3.9589	0.0420
4.0708	0.0390
4.1704	0.0339
4.2811	0.0329
4.3736	0.0294
4.4790	0.0294
4.5942	0.0234
4.6952	0.0214
4.8085	0.0254
4.9334	0.0164
5.1084	0.0139
5.3017	0.0129
5.4387	0.0109
5.6879	0.0089
5.8177	0.0079
6.0040	0.0069
6.0926	0.0064
0 0 0	

MIM (two-region model)

```

1
*** BLOCK A: MODEL DESCRIPTION *****
Molly HH2-160-Br Unsat
unit, cm, h, micro g)
INVERSE  MODE      NREDU
  1         2          3
MODC      ZL
  1       23.5
*** BLOCK B: INVERSE PROBLEM *****
MIT      ILMT      MASS
100      0         0
MNEQ     MDEG
  0       0
*** BLOCK C: TRANSPORT PARAMETERS *****
  V      D      R      Beta  omega  Mu1    Mu2
0.0573  0.002  1.0   0.7   0.5   0      0
  0      1      0    1     1     0      0
*** BLOCK D: BVP; MODB=0 ZERO; =1 DIRAC; =2 STEP; =3 A PULSE *****
MODB (Reduced Conc.& time) =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  3
  1.0 0.379
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR INVERSE PROBLEM *****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
  1
  23.5
      TIME      CONC      (Give "0 0 0" after last data set.)
0.0230 0.0051
0.0578 0.0026
0.1141 0.0036
0.1721 0.0036
0.2286 0.0031
0.2867 0.0046
0.3435 0.0192
0.4017 0.0563
0.4576 0.1168
0.5157 0.2031
0.5735 0.2865
0.6304 0.3777
0.6893 0.4543
0.7442 0.5314
0.8043 0.6143
0.8600 0.6099
0.9163 0.5826
0.9752 0.5728
1.0309 0.4982
1.0890 0.4285

```

1.1462	0.3485
1.2598	0.3036
1.3179	0.2660
1.3749	0.2270
1.4331	0.1909
1.4909	0.1763
1.5536	0.1212
1.6032	0.1114
1.6635	0.0982
1.7183	0.0865
1.7758	0.0787
1.8341	0.0660
1.8913	0.0631
1.9471	0.0514
2.0855	0.0475
2.2342	0.0412
2.3666	0.0417
0 0 0	

MIM (two-site model)

```

1
*** BLOCK A: MODEL DESCRIPTION *****
Molly HH2-190_U Unsat
unit, cm, h, micro g)
INVERSE  MODE    NREDU
1          2      3
MODC     ZL
1        23.5
*** BLOCK B: INVERSE PROBLEM *****
MIT      ILMT    MASS
100      0        0
MNEQ     MDEG
2         0
*** BLOCK C: TRANSPORT PARAMETERS *****
V         D      R    Beta  omega  Mu1    Mu2
0.0573  0.0982  1.0   0.516  0.610   0      0
0         0      1    1      1      0      0
*** BLOCK D: BVP; MODB=0 ZERO; =1 DIRAC; =2 STEP; =3 A PULSE *****
MODB (Reduced Conc.& time) =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
3
1.0 0.379
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
0
*** BLOCK G: DATA FOR INVERSE PROBLEM *****
INPUTM =0; Z,T,C =1; T,C FOR SAME Z =2; Z,C FOR SAME T
1
23.5
      TIME    CONC    (Give "0 0 0" after last data set.)
0.1176 0.0000
0.1176 0.0000
0.2273 0.0000
0.3451 0.0000
0.3451 0.0000
0.4560 0.0000
0.4560 0.0000
0.5770 0.0000
0.5770 0.0002
0.6249 0.0093
0.6249 0.0122
0.6875 0.0325
0.6875 0.0415
0.7426 0.0699
0.8027 0.1034
0.8618 0.1359
0.9736 0.2100
1.0363 0.2589
1.0905 0.2701
1.1474 0.2143

```

1.2029	0.2334
1.3197	0.2434
1.3734	0.2661
1.3805	0.2649
1.4346	0.2505
1.4889	0.2084
1.5520	0.2317
1.6075	0.2185
1.6618	0.1944
1.7216	0.1836
1.7838	0.1671
1.8391	0.1505
1.8949	0.1353
1.9489	0.1256
2.0054	0.1126
2.0656	0.0998
2.1208	0.0908
2.1762	0.0834
2.2359	0.0737
2.2893	0.0723
2.3524	0.0612
2.4057	0.0591
2.4689	0.0573
2.5236	0.0515
2.5236	0.0512
2.6406	0.0422
2.6406	0.0413
2.7531	0.0409
2.7531	0.0406
2.8689	0.0348
2.8689	0.0331
2.8689	0.0374
2.9804	0.0293
2.9804	0.0279
2.9804	0.0304
3.0983	0.0239
3.0983	0.0266
3.2067	0.0192
3.2067	0.0228
3.2591	0.0149
3.2591	0.0184
3.2793	0.0161
0 0 0	

APPENDIX H – Examples of CXTFIT Output files

CDE

\$

```
*****
*
* CXTFIT VERSION 2.1 (4/17/99)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* Molly HV1-160-Br Unsat
* unit, cm, h, micro g)
*
* DATA INPUT FILE: hv1-160-br.dat
*
*****
```

MODEL DESCRIPTION

```
=====
DETERMINISTIC EQUILIBRIUM CDE (MODE=1)
FLUX-AVERAGED CONCENTRATION
REDUCED TIME (T), DIMENSIONAL POSITION(Z)
(ALL PARAMETERS EXCEPT D AND V ARE DIMENSIONLESS)
CHARACTERISTIC LENGTH = 21.0000
FOR DIMENSIONLESS PARAMETERS
```

INITIAL VALUES OF COEFFICIENTS

```
=====
NAME      INITIAL VALUE  FITTING
V.....  .1460E+00      N
D.....  .1000E+00      Y
R.....  .1000E+01      N
mu.....  .0000E+00      N
```

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS

```
=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = 1.3500
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM
```

PARAMETER ESTIMATION MODE

```
=====
MAXIMUM NUMBER OF ITERATIONS = 100
```

```
ITER  SSQ    D....
0 .4218E+00 .100E+00
```

1 .3788E+00 .143E+00
 2 .3760E+00 .157E+00
 3 .3759E+00 .160E+00
 4 .3759E+00 .160E+00
 5 .3759E+00 .160E+00

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .92396292
 (COEFFICIENT OF DETERMINATION)

MEAN SQUARE FOR ERROR (MSE) = .6713E-02

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

95% CONFIDENCE LIMITS				
NAME	VALUE	S.E.COEFF.	LOWER	UPPER
D....	.1600E+00	.2554E-01	.1088E+00	.2112E+00

-----ORDERED BY COMPUTER INPUT-----

		CONCENTRATION		RESI-		DUAL
\$	NO	DISTANCE	TIME	OBS	FITTED	
	1	21.0000	.0076	.0008	.0000	.0008
	2	21.0000	.0259	.0008	.0000	.0008
	3	21.0000	.1166	.0003	.0000	.0003
	4	21.0000	.2396	.0008	.0000	.0008
	5	21.0000	.3654	.0008	.0009	-.0001
	6	21.0000	.4776	.0003	.0135	-.0132
	7	21.0000	.6014	.0039	.0730	-.0691
	8	21.0000	.7199	.0420	.1902	-.1482
	9	21.0000	.7896	.0930	.2795	-.1865
	10	21.0000	.8411	.1543	.3501	-.1958
	11	21.0000	.8977	.2197	.4285	-.2088
	12	21.0000	1.0143	.3870	.5803	-.1933
	13	21.0000	1.0837	.4813	.6592	-.1779
	14	21.0000	1.2012	.6206	.7684	-.1478
	15	21.0000	1.3195	.7133	.8484	-.1351
	16	21.0000	1.4365	.7803	.9030	-.1227
	17	21.0000	1.5628	.8249	.9415	-.1166
	18	21.0000	1.6761	.8524	.9633	-.1109
	19	21.0000	1.7805	.8730	.9715	-.0985
	20	21.0000	1.8641	.8867	.9592	-.0725
	21	21.0000	1.9580	.8884	.9113	-.0229
	22	21.0000	2.0541	.8283	.8214	.0069
	23	21.0000	2.1382	.7099	.7176	-.0077
	24	21.0000	2.2228	.5657	.6026	-.0369
	25	21.0000	2.2905	.4232	.5112	-.0880
	26	21.0000	2.4874	.3048	.2861	.0187
	27	21.0000	2.5451	.2645	.2358	.0287
	28	21.0000	2.5803	.2403	.2087	.0316
	29	21.0000	2.6574	.1991	.1581	.0410
	30	21.0000	2.7235	.1743	.1234	.0509
	31	21.0000	2.8892	.1299	.0642	.0657

32	21.0000	3.0172	.1097	.0378	.0719
33	21.0000	3.1238	.0955	.0240	.0715
34	21.0000	3.2393	.0894	.0145	.0749
35	21.0000	3.3473	.0798	.0090	.0708
36	21.0000	3.4635	.0712	.0053	.0659
37	21.0000	3.5821	.0641	.0031	.0610
38	21.0000	3.6969	.0560	.0018	.0542
39	21.0000	3.7917	.0530	.0012	.0518
40	21.0000	3.8540	.0499	.0009	.0490
41	21.0000	3.9589	.0420	.0005	.0415
42	21.0000	4.0708	.0390	.0003	.0387
43	21.0000	4.1704	.0339	.0002	.0337
44	21.0000	4.2811	.0329	.0001	.0328
45	21.0000	4.3736	.0294	.0001	.0293
46	21.0000	4.4790	.0294	.0000	.0294
47	21.0000	4.5942	.0234	.0000	.0234
48	21.0000	4.6952	.0214	.0000	.0214
49	21.0000	4.8085	.0254	.0000	.0254
50	21.0000	4.9334	.0164	.0000	.0164
51	21.0000	5.1084	.0139	.0000	.0139
52	21.0000	5.3017	.0129	.0000	.0129
53	21.0000	5.4387	.0109	.0000	.0109
54	21.0000	5.6879	.0089	.0000	.0089
55	21.0000	5.8177	.0079	.0000	.0079
56	21.0000	6.0040	.0069	.0000	.0069
57	21.0000	6.0926	.0064	.0000	.0064

MIM (two-region model)

\$

```
*****
*                                     *
* CXTFIT VERSION 2.1 (4/17/99)         *
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE      *
* NON-LINEAR LEAST-SQUARES ANALYSIS          *
*                                     *
*   Molly HH2-160-Br Unsat              *
*   unit, cm, h, micro g)                *
*                                     *
* DATA INPUT FILE: hh2-190-br.dat        *
*                                     *
*****
```

MODEL DESCRIPTION

=====

DETERMINISTIC NONEQUILIBRIUM CDE (MODE=2)
FLUX-AVERAGED CONCENTRATION
REDUCED TIME (T), DIMENSIONAL POSITION(Z)
(ALL PARAMETERS EXCEPT D AND V ARE DIMENSIONLESS)
CHARACTERISTIC LENGTH = 23.5000
FOR DIMENSIONLESS PARAMETERS

INITIAL VALUES OF COEFFICIENTS

=====

NAME	INITIAL VALUE	FITTING
V.....	.5730E-01	N
D.....	.2000E-02	Y
R.....	.1000E+01	N
beta.....	.7000E+00	Y
omega....	.5000E+00	Y
mu1.....	.0000E+00	N
mu2.....	.0000E+00	N

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS

=====

SINGLE PULSE OF CONC. = 1.0000 & DURATION = .3790
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

PARAMETER ESTIMATION MODE

=====

MAXIMUM NUMBER OF ITERATIONS = 100
TWO-REGION PHYSICAL NONEQUILIBRIUM MODEL

ITER	SSQ	D....	beta.	omega
0	.5142E+00	.200E-02	.700E+00	.500E+00
1	.2805E+00	.635E-02	.680E+00	.749E+00
2	.1922E+00	.178E-01	.672E+00	.718E+00
3	.1583E+00	.397E-01	.708E+00	.431E+00
4	.1293E+00	.631E-01	.756E+00	.178E+00
5	.8099E-01	.973E-01	.812E+00	.100E-06
6	.7763E-01	.995E-01	.802E+00	.100E-06
7	.7676E-01	.996E-01	.797E+00	.100E-06
8	.7626E-01	.993E-01	.794E+00	.100E-06
9	.7591E-01	.990E-01	.793E+00	.100E-06
10	.7567E-01	.987E-01	.793E+00	.100E-06
11	.7552E-01	.985E-01	.792E+00	.100E-06
12	.7542E-01	.984E-01	.792E+00	.100E-06
13	.7536E-01	.983E-01	.792E+00	.100E-06
14	.7532E-01	.982E-01	.792E+00	.100E-06
15	.7530E-01	.982E-01	.792E+00	.100E-06

COVARIANCE MATRIX FOR FITTED PARAMETERS

```
=====
D.... beta. omega
D.... 1.000
beta. .463 1.000
omega -.572 -.310 1.000
```

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .94951708
(COEFFICIENT OF DETERMINATION)

MEAN SQUARE FOR ERROR (MSE) = .2215E-02

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

```
=====
                      95% CONFIDENCE LIMITS
NAME  VALUE  S.E.COEFF. T-VALUE  LOWER  UPPER
D.... .9821E-01 .1074E-01 .9145E+01 .7639E-01 .1200E+00
beta. .7918E+00 .1592E-01 .4973E+02 .7594E+00 .8241E+00
omega .1000E-06 .4044E-01 .2473E-05 -.8218E-01 .8218E-01
```

-----ORDERED BY COMPUTER INPUT-----

\$	NO	DISTANCE	CONCENTRATION		RESI-		DUAL
			TIME	OBS	FITTED		
	1	23.5000	.0230	.0051	.0000	.0051	
	2	23.5000	.0578	.0026	.0000	.0026	
	3	23.5000	.1141	.0036	.0000	.0036	
	4	23.5000	.1721	.0036	.0000	.0036	
	5	23.5000	.2286	.0031	.0004	.0027	
	6	23.5000	.2867	.0046	.0041	.0005	
	7	23.5000	.3435	.0192	.0176	.0016	

8	23.5000	.4017	.0563	.0486	.0077
9	23.5000	.4576	.1168	.0978	.0190
10	23.5000	.5157	.2031	.1670	.0361
11	23.5000	.5735	.2865	.2490	.0375
12	23.5000	.6304	.3777	.3350	.0427
13	23.5000	.6893	.4543	.4190	.0353
14	23.5000	.7442	.5314	.4814	.0500
15	23.5000	.8043	.6143	.5230	.0913
16	23.5000	.8600	.6099	.5339	.0760
17	23.5000	.9163	.5826	.5209	.0617
18	23.5000	.9752	.5728	.4874	.0854
19	23.5000	1.0309	.4982	.4438	.0544
20	23.5000	1.0890	.4285	.3920	.0365
21	23.5000	1.1462	.3485	.3396	.0089
22	23.5000	1.2598	.3036	.2432	.0604
23	23.5000	1.3179	.2660	.2011	.0649
24	23.5000	1.3749	.2270	.1652	.0618
25	23.5000	1.4331	.1909	.1340	.0569
26	23.5000	1.4909	.1763	.1081	.0682
27	23.5000	1.5536	.1212	.0850	.0362
28	23.5000	1.6032	.1114	.0699	.0415
29	23.5000	1.6635	.0982	.0550	.0432
30	23.5000	1.7183	.0865	.0440	.0425
31	23.5000	1.7758	.0787	.0347	.0440
32	23.5000	1.8341	.0660	.0272	.0388
33	23.5000	1.8913	.0631	.0214	.0417
34	23.5000	1.9471	.0514	.0169	.0345
35	23.5000	2.0855	.0475	.0093	.0382
36	23.5000	2.2342	.0412	.0049	.0363
37	23.5000	2.3666	.0417	.0027	.0390

MIM (two-site model)

\$

```

*****
*
* CXTFIT VERSION 2.1 (4/17/99)
* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE
* NON-LINEAR LEAST-SQUARES ANALYSIS
*
* Molly HH2-190_U Unsat
* unit, cm, h, micro g)
*
* DATA INPUT FILE: hh2-190-u.dat
*
*****

```

MODEL DESCRIPTION

```

=====
DETERMINISTIC NONEQUILIBRIUM CDE (MODE=2)
FLUX-AVERAGED CONCENTRATION
REDUCED TIME (T), DIMENSIONAL POSITION(Z)
(ALL PARAMETERS EXCEPT D AND V ARE DIMENSIONLESS)
CHARACTERISTIC LENGTH = 23.5000
FOR DIMENSIONLESS PARAMETERS

```

INITIAL VALUES OF COEFFICIENTS

```

=====
NAME      INITIAL VALUE  FITTING
V.....  .5730E-01      N
D.....  .9820E-01      N
R.....  .1000E+01      Y
beta..... .5160E+00      Y
omega..... .6100E+00      Y
mu1.....  .0000E+00      N
mu2.....  .0000E+00      N

```

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS

```

=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = .3790
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

```

PARAMETER ESTIMATION MODE

```

=====
MAXIMUM NUMBER OF ITERATIONS = 100
TWO-SITE CHEMICAL NONEQUILIBRIUM MODEL

```

ITER SSQ R.... beta. omega

0	.1973E+01	.100E+01	.516E+00	.610E+00
1	.5141E+00	.151E+01	.273E+00	.222E+01
2	.2351E+00	.131E+01	.199E+00	.556E+01
3	.7447E-01	.142E+01	.100E-03	.186E+02
4	.4149E-01	.147E+01	.751E+00	.342E+01
5	.3443E-01	.145E+01	.735E+00	.247E+01
6	.2684E-01	.147E+01	.802E+00	.827E+00
7	.1858E-01	.155E+01	.821E+00	.358E+00
8	.1313E-01	.178E+01	.735E+00	.261E+00
9	.9508E-02	.204E+01	.641E+00	.327E+00
10	.8373E-02	.209E+01	.639E+00	.332E+00
11	.8370E-02	.210E+01	.638E+00	.329E+00
12	.8370E-02	.210E+01	.637E+00	.329E+00

COVARIANCE MATRIX FOR FITTED PARAMETERS

```
=====
R.... beta. omega
R.... 1.000
beta. -.989 1.000
omega -.267 .212 1.000
```

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .98219523
(COEFFICIENT OF DETERMINATION)

MEAN SQUARE FOR ERROR (MSE) = .1419E-03

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

```
=====
                        95% CONFIDENCE LIMITS
NAME  VALUE  S.E.COEFF. T-VALUE  LOWER  UPPER
R... .2097E+01 .1133E+00 .1850E+02 .1870E+01 .2324E+01
beta. .6374E+00 .3183E-01 .2003E+02 .5738E+00 .7011E+00
omega .3289E+00 .2206E-01 .1491E+02 .2847E+00 .3730E+00
```

-----ORDERED BY COMPUTER INPUT-----

\$	NO	DISTANCE	CONCENTRATION		RESI-	DUAL
			TIME	OBS	FITTED	
	1	23.5000	.1176	.0000	.0000	
	2	23.5000	.1176	.0000	.0000	
	3	23.5000	.2273	.0000	.0000	
	4	23.5000	.3451	.0000	.0001	
	5	23.5000	.3451	.0000	.0001	
	6	23.5000	.4560	.0000	.0022	
	7	23.5000	.4560	.0000	.0022	
	8	23.5000	.5770	.0000	.0150	
	9	23.5000	.5770	.0002	.0150	
	10	23.5000	.6249	.0093	.0257	
	11	23.5000	.6249	.0122	.0257	
	12	23.5000	.6875	.0325	.0456	

13	23.5000	.6875	.0415	.0456	-.0041
14	23.5000	.7426	.0699	.0687	.0012
15	23.5000	.8027	.1034	.0989	.0045
16	23.5000	.8618	.1359	.1317	.0042
17	23.5000	.9736	.2100	.1930	.0170
18	23.5000	1.0363	.2589	.2217	.0372
19	23.5000	1.0905	.2701	.2413	.0288
20	23.5000	1.1474	.2143	.2560	-.0417
21	23.5000	1.2029	.2334	.2643	-.0309
22	23.5000	1.3197	.2434	.2646	-.0212
23	23.5000	1.3734	.2661	.2585	.0076
24	23.5000	1.3805	.2649	.2574	.0075
25	23.5000	1.4346	.2505	.2479	.0026
26	23.5000	1.4889	.2084	.2362	-.0278
27	23.5000	1.5520	.2317	.2209	.0108
28	23.5000	1.6075	.2185	.2065	.0120
29	23.5000	1.6618	.1944	.1921	.0023
30	23.5000	1.7216	.1836	.1764	.0072
31	23.5000	1.7838	.1671	.1606	.0065
32	23.5000	1.8391	.1505	.1472	.0033
33	23.5000	1.8949	.1353	.1345	.0008
34	23.5000	1.9489	.1256	.1231	.0025
35	23.5000	2.0054	.1126	.1121	.0005
36	23.5000	2.0656	.0998	.1013	-.0015
37	23.5000	2.1208	.0908	.0924	-.0016
38	23.5000	2.1762	.0834	.0843	-.0009
39	23.5000	2.2359	.0737	.0765	-.0028
40	23.5000	2.2893	.0723	.0703	.0020
41	23.5000	2.3524	.0612	.0637	-.0025
42	23.5000	2.4057	.0591	.0588	.0003
43	23.5000	2.4689	.0573	.0536	.0037
44	23.5000	2.5236	.0515	.0497	.0018
45	23.5000	2.5236	.0512	.0497	.0015
46	23.5000	2.6406	.0422	.0427	-.0005
47	23.5000	2.6406	.0413	.0427	-.0014
48	23.5000	2.7531	.0409	.0374	.0035
49	23.5000	2.7531	.0406	.0374	.0032
50	23.5000	2.8689	.0348	.0331	.0017
51	23.5000	2.8689	.0331	.0331	.0000
52	23.5000	2.8689	.0374	.0331	.0043
53	23.5000	2.9804	.0293	.0299	-.0006
54	23.5000	2.9804	.0279	.0299	-.0020
55	23.5000	2.9804	.0304	.0299	.0005
56	23.5000	3.0983	.0239	.0271	-.0032
57	23.5000	3.0983	.0266	.0271	-.0005
58	23.5000	3.2067	.0192	.0250	-.0058
59	23.5000	3.2067	.0228	.0250	-.0022
60	23.5000	3.2591	.0149	.0242	-.0093
61	23.5000	3.2591	.0184	.0242	-.0058
62	23.5000	3.2793	.0161	.0239	-.0078\$

*

*

* CXTFIT VERSION 2.1 (4/17/99)

*

```

* ANALYTICAL SOLUTIONS FOR ONE-DIMENSIONAL CDE *
* NON-LINEAR LEAST-SQUARES ANALYSIS *
*
* Molly HH2-190_U Unsat *
* unit, cm, h, micro g) *
*
* DATA INPUT FILE: hh2-190-u.dat *
*
*****

```

MODEL DESCRIPTION

```

=====
DETERMINISTIC NONEQUILIBRIUM CDE (MODE=2)
FLUX-AVERAGED CONCENTRATION
REDUCED TIME (T), DIMENSIONAL POSITION(Z)
(ALL PARAMETERS EXCEPT D AND V ARE DIMENSIONLESS)
CHARACTERISTIC LENGTH = 23.5000
FOR DIMENSIONLESS PARAMETERS

```

INITIAL VALUES OF COEFFICIENTS

```

=====
NAME      INITIAL VALUE  FITTING
V.....  .5730E-01    N
D.....  .9820E-01    N
R.....  .1000E+01    Y
beta..... .5160E+00    Y
omega....  .6100E+00    Y
mu1.....  .0000E+00    N
mu2.....  .0000E+00    N

```

BOUNDARY, INITIAL, AND PRODUCTION CONDITIONS

```

=====
SINGLE PULSE OF CONC. = 1.0000 & DURATION = .3790
SOLUTE FREE INITIAL CONDITION
NO PRODUCTION TERM

```

PARAMETER ESTIMATION MODE

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=====
MAXIMUM NUMBER OF ITERATIONS = 100
TWO-REGION PHYSICAL NONEQUILIBRIUM MODEL

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ITER  SSQ    R....  beta.  omega
0  .1973E+01 .100E+01 .516E+00 .610E+00
1  .5141E+00 .151E+01 .273E+00 .222E+01
2  .2351E+00 .131E+01 .199E+00 .556E+01
3  .7447E-01 .142E+01 .100E-03 .186E+02
4  .4149E-01 .147E+01 .751E+00 .342E+01
5  .3443E-01 .145E+01 .735E+00 .247E+01
6  .2684E-01 .147E+01 .802E+00 .827E+00

```

7	.1858E-01	.155E+01	.821E+00	.358E+00
8	.1313E-01	.178E+01	.735E+00	.261E+00
9	.9508E-02	.204E+01	.641E+00	.327E+00
10	.8373E-02	.209E+01	.639E+00	.332E+00
11	.8370E-02	.210E+01	.638E+00	.329E+00
12	.8370E-02	.210E+01	.637E+00	.329E+00

COVARIANCE MATRIX FOR FITTED PARAMETERS

```

=====
R.... beta. omega
R.... 1.000
beta. -.989 1.000
omega -.267 .212 1.000

```

RSQUARE FOR REGRESSION OF OBSERVED VS PREDICTED = .98219523
(COEFFICIENT OF DETERMINATION)

MEAN SQUARE FOR ERROR (MSE) = .1419E-03

NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

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=====
                      95% CONFIDENCE LIMITS
NAME  VALUE  S.E.COEFF. T-VALUE  LOWER  UPPER
R.... .2097E+01 .1133E+00 .1850E+02 .1870E+01 .2324E+01
beta. .6374E+00 .3183E-01 .2003E+02 .5738E+00 .7011E+00
omega .3289E+00 .2206E-01 .1491E+02 .2847E+00 .3730E+00

```

-----ORDERED BY COMPUTER INPUT-----

\$	NO	DISTANCE	CONCENTRATION		RESI-		DUAL
			TIME	OBS	FITTED		
	1	23.5000	.1176	.0000	.0000	.0000	
	2	23.5000	.1176	.0000	.0000	.0000	
	3	23.5000	.2273	.0000	.0000	.0000	
	4	23.5000	.3451	.0000	.0001	-.0001	
	5	23.5000	.3451	.0000	.0001	-.0001	
	6	23.5000	.4560	.0000	.0022	-.0022	
	7	23.5000	.4560	.0000	.0022	-.0022	
	8	23.5000	.5770	.0000	.0150	-.0150	
	9	23.5000	.5770	.0002	.0150	-.0148	
	10	23.5000	.6249	.0093	.0257	-.0164	
	11	23.5000	.6249	.0122	.0257	-.0135	
	12	23.5000	.6875	.0325	.0456	-.0131	
	13	23.5000	.6875	.0415	.0456	-.0041	
	14	23.5000	.7426	.0699	.0687	.0012	
	15	23.5000	.8027	.1034	.0989	.0045	
	16	23.5000	.8618	.1359	.1317	.0042	
	17	23.5000	.9736	.2100	.1930	.0170	
	18	23.5000	1.0363	.2589	.2217	.0372	
	19	23.5000	1.0905	.2701	.2413	.0288	

20	23.5000	1.1474	.2143	.2560	-.0417
21	23.5000	1.2029	.2334	.2643	-.0309
22	23.5000	1.3197	.2434	.2646	-.0212
23	23.5000	1.3734	.2661	.2585	.0076
24	23.5000	1.3805	.2649	.2574	.0075
25	23.5000	1.4346	.2505	.2479	.0026
26	23.5000	1.4889	.2084	.2362	-.0278
27	23.5000	1.5520	.2317	.2209	.0108
28	23.5000	1.6075	.2185	.2065	.0120
29	23.5000	1.6618	.1944	.1921	.0023
30	23.5000	1.7216	.1836	.1764	.0072
31	23.5000	1.7838	.1671	.1606	.0065
32	23.5000	1.8391	.1505	.1472	.0033
33	23.5000	1.8949	.1353	.1345	.0008
34	23.5000	1.9489	.1256	.1231	.0025
35	23.5000	2.0054	.1126	.1121	.0005
36	23.5000	2.0656	.0998	.1013	-.0015
37	23.5000	2.1208	.0908	.0924	-.0016
38	23.5000	2.1762	.0834	.0843	-.0009
39	23.5000	2.2359	.0737	.0765	-.0028
40	23.5000	2.2893	.0723	.0703	.0020
41	23.5000	2.3524	.0612	.0637	-.0025
42	23.5000	2.4057	.0591	.0588	.0003
43	23.5000	2.4689	.0573	.0536	.0037
44	23.5000	2.5236	.0515	.0497	.0018
45	23.5000	2.5236	.0512	.0497	.0015
46	23.5000	2.6406	.0422	.0427	-.0005
47	23.5000	2.6406	.0413	.0427	-.0014
48	23.5000	2.7531	.0409	.0374	.0035
49	23.5000	2.7531	.0406	.0374	.0032
50	23.5000	2.8689	.0348	.0331	.0017
51	23.5000	2.8689	.0331	.0331	.0000
52	23.5000	2.8689	.0374	.0331	.0043
53	23.5000	2.9804	.0293	.0299	-.0006
54	23.5000	2.9804	.0279	.0299	-.0020
55	23.5000	2.9804	.0304	.0299	.0005
56	23.5000	3.0983	.0239	.0271	-.0032
57	23.5000	3.0983	.0266	.0271	-.0005
58	23.5000	3.2067	.0192	.0250	-.0058
59	23.5000	3.2067	.0228	.0250	-.0022
60	23.5000	3.2591	.0149	.0242	-.0093
61	23.5000	3.2591	.0184	.0242	-.0058
62	23.5000	3.2793	.0161	.0239	-.0078

VITA

Mary Fairfax Nichols Pace, "Molly", was born in Jackson, MS on October 27, 1971 to Mr. and Mrs. B.W. Nichols, Jr. She graduated from William B. Murrah High School, Jackson, MS in 1989. She earned her B.S. in ACS Chemistry at Millsaps College, Jackson, MS in 1994, graduating Cum Laude. Then she attended graduate school at Texas A&M University where she earned a M.S. in Analytical Chemistry in 1996. While at Texas A&M University she conducted research on age dating ancient pictographs. She and her husband, Chris Pace, then moved to Idaho for his job. Mrs. Pace earned a second M.S. in Hazardous Waste Management, a combined Chemistry and Engineering degree, at Idaho State University while working as a co-op with the USGS. This thesis included research involving ^{90}Sr sorption to geologic material from the Idaho National Engineering and Environmental Laboratory. She then went to work for the Idaho National Engineering and Environmental Laboratory in Idaho Falls, ID. She worked for two years in the Geosciences Research Group conducting various sorption type experiments as well as writing manuscripts and workplans. Then, she and her husband moved to Knoxville, TN where she began work at Oak Ridge National Laboratory in the Environmental Science Division on a post-masters fellowship while she attended graduate school at the University of Tennessee. This dissertation is a result of her work at Oak Ridge National Laboratory. She will graduate with a PhD in Earth and Planetary Science from the University of Tennessee in December 2005.

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