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INNOVATIVE TRACERS FOR SUBSURFACE CHARACTERIZATION

by

Nicole Terese Nelson

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES
In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY
WITH A MAJOR IN HYDROLOGY

In the Graduate College

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1999
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DEDICATION

This work is dedicated to my family and close friends. Without these people and their unwavering support and encouragement I would not have been able to achieve what I have or become the person I am. Most significantly this work is dedicated to my mom, who always listened patiently and helped me see humor even in unfortunate circumstances and to my dad, who taught me not to make important decisions rashly and not to close doors too quickly, but not to regret my choices once I’ve made them.
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ABSTRACT

Proper site characterization is a critical component in making risk-based decisions and in selecting an appropriate action for a site, whether it is active remediation, containment or natural attenuation. The overall purpose of this work is to investigate innovative techniques for characterizing the factors controlling the transport and fate of organic chemicals at contaminated sites. It is expected that results from this work will lead to improved and more cost-effective methods for characterizing contamination at hazardous waste sites. The information gained from using these methods may lead to a better understanding of factors controlling contaminant transport at sites and therefore more informed risk-based decision making and selection of remediation strategies. The results indicate that (1) the presence of porous media heterogeneity and distinct zones of dense nonaqueous liquid (DNAPL) saturation lead to reduced performance (reduced accuracy) of the partitioning tracer test for measuring DNAPL saturation in saturated subsurface systems, (2) gas-phase tracer tests have the potential to accurately measure water contents for a system with uniform water content and homogeneous porous media, (3) the diffusivity-tracer test method can be used to determine whether diffusion-mediated processes are significant at a particular site, and (4) for a 2-dimensional flow cell flushing experiment the magnitude of trichloroethene concentration and the shape of the trichloroethene elution curves varied as a function of location and sampling type and that the less than solubility concentrations observed at almost all ports were caused by the nonuniform NAPL distribution and porous media heterogeneity, rather than by rate-limited interphase mass transfer at the pore-scale.
CHAPTER 1. INTRODUCTION

Introduction

The fate and transport of contaminants emanating from hazardous waste sites, landfills, and other sites of chemical use and disposal has become one of the predominant environmental issues in the nation. Effective risk assessment and remediation of such sites is limited by our ability to determine the factors controlling contaminant transport and fate. A large number of methods are being evaluated for their potential to clean up contaminated sites. "Pump and treat" is currently the most widely used remediation method for contaminated aquifers and one of the few with a documented operational history upon which an assessment of its effectiveness can be based. Analogously, Soil Vapor Extraction (SVE) is currently the most widely used method for remediating volatile compounds from the vadose zone. It has been shown that pump and treat can control the spread of dissolved contaminant plumes and remove dissolved contaminant from the subsurface. However, pump and treat has generally not been capable of restoring sites to pristine conditions. Due to this limited effectiveness, the time required to reach low target concentrations (such as Maximum Contaminant Levels) may be impractical or infeasible. Two phenomena commonly observed during pump-and-treat operations that reflect the impact of limited effectiveness are: (1) tailing, a term describing the reduced rate of contaminant removal that occurs over time, which results in a leveling of contaminant concentration above the target concentration, and (2) rebound, which describes the increase in contaminant concentration observed after an extraction well is turned off for some time.
The limited effectiveness observed for many pump-and-treat systems may be caused by a number of factors. These include factors related to well-field hydraulics, such as (1) the desaturation of contaminated zones due to drawdown, (2) the presence of stagnation zones, and (3) the relationship between well-screen interval and the vertical distribution of contamination. These factors can, in some cases, be addressed by modifying the operation of the well-field system. Factors related to contaminant transport also have a major influence on the performance of pump and treat and are much more difficult to address. For example, factors such as subsurface heterogeneity (e.g., spatially variable hydraulic conductivity, spatially variable sorption), rate-limited diffusion, rate-limited desorption, and rate-limited immiscible-liquid dissolution may inhibit the removal of contaminants from the subsurface. The greater the difficulty in removing contaminants, the longer the time required to reach the clean up target. Uncontrolled source zones, another major constraining factor, can serve as long term sources of contamination, which if not removed or controlled, can greatly extend the time required to clean a site.

Proper site characterization is a critical component in making risk-based decisions and in selecting an appropriate action for a site, whether it is active remediation, containment or natural attenuation. The overall purpose of this work is to investigate innovative techniques for characterizing the factors controlling the transport and fate of organic chemicals at contaminated sites. It is expected that results from this work will lead to improved and more cost-effective methods for characterizing contamination at hazardous waste sites. The information gained from using these methods may lead to a
better understanding of factors controlling contaminant transport at sites and therefore more informed risk-based decision making and selection of remediation strategies.

**Objectives**

The specific, primary objectives of this research are to:

1. Examine the effect of porous media heterogeneity, nonuniform distribution of dense nonaqueous phase liquid (DNAPL), and sampling method on the performance of the partitioning tracer method for measuring DNAPL saturation in water-saturated subsurface systems.

2. Design and test a gas-phase partitioning tracer method for the in-situ measurement of water content and to illustrate its application and test its performance in well-defined systems.

3. Explore the use of the diffusivity tracer test-method to investigate the impact of scale on solute transport influenced by diffusion-mediated processes.

4. Investigate the factors controlling the elution behavior of chlorinated organic compounds in heterogeneous systems.

**Overview of Chapters**

Chapter 2 contains theory, background, and literature review related to all three innovative tracer techniques explored in this work (aqueous-phase and gas-phase partitioning tracer methods and the diffusive tracer method.) It also contains a section on TCE dissolution in heterogeneous systems. Chapter 3 is the basis for a manuscript that is
being reviewed for publication in the journal *Environmental Science and Technology* (Nelson et al., 1999a). It presents results from partitioning tracer tests conducted in an intermediate flow-cell located at Pacific Northwest National Laboratory to examine the influence of heterogeneity and sampling method on the performance of the tracer method (objective 1). Chapter 4 is the basis for a manuscript that is being reviewed for publication in the journal *Water Resources Research* (Nelson et al., 1999b). It presents the results of laboratory and intermediate scale experiments conducted to test the use of a gas-phase partitioning tracer method for measuring water content (objective 2). Chapter 5 reports the results of laboratory and field investigations conducted to examine the influence of scale on the dispersion of different sized solutes (objective 3).

Chapter 6 examines the elution behavior of chlorinated organic compounds in two heterogeneous systems (objective 4). The first system is a 2-dimensional flow cell equipped with point and vertically integrated sampling ports. The purpose of the flow-cell experiment is to examine the influence of porous media heterogeneity and DNAPL distribution on the aqueous dissolution and removal of trichloroethene (TCE) during a well-controlled water flushing experiment. The influence of sampling method on the overall elution curves is also examined. These results were presented at the 1998 Fall Meeting of the American Geophysical Meeting (Nelson et al., 1998). The second system is a source zone at a Superfund site in Tucson, Arizona. The primary objectives of the project were to characterize the transport and fate behavior of contaminants at the site, to identify the factors controlling contaminant removal for the currently operating pump-and-treat system, and to provide information useful for improving the remediation
program. The project consisted of several components, including site characterization activities, field tracer experiments, laboratory experiments conducted with core material collected from the site, and mathematical modeling. The results of one component of the overall project, the contaminant monitoring, are reported herein. This data is included in a manuscript currently being reviewed by the journal, *Journal of Contaminant Hydrology* (Brusseau et al., 1998).
Aqueous-Phase Partitioning Tracer Method

Introduction. Nonaqueous phase organic liquids (NAPLs) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both vapor-phase and groundwater contamination. According to a recent report released by the National Research Council, the presence of NAPL is the single most important factor limiting clean-up of organic-contaminated sites. In fact, groundwater restoration to health-based goals is considered infeasible with existing technologies (e.g., pump and treat) at most sites contaminated by DNAPL (National Research Council, 1994). Thus, new technologies continue to be developed in an attempt to address this problem. The development and application of new remediation technologies requires an understanding of the mechanisms that control the transport and fate of NAPLs, as well as the nature and distribution of the NAPL in the subsurface. Knowledge of NAPL occurrence and distribution is also critical for the planning and implementation of "source control" strategies. Additionally, appropriate risk based decisions can not be made for a contaminated site without knowing if NAPL is present at the site.

Current methods used for characterizing sites potentially contaminated with a NAPL phase include analysis of soil gas, core sampling, cone penetrometer testing, and monitoring well sampling. These methods provide data for relatively small volumes of the subsurface and require the use of a dense sampling network and application of spatial statistics to determine the overall contaminant distribution. Spatial variability of the
subsurface environment and of contaminant distribution can further complicate proper description. The partitioning tracer test is an alternative, larger-scale method for locating and quantifying NAPL saturation in the subsurface (Jin et al., 1995; Wilson and Mackay, 1995; Nelson and Brusseau, 1996). This method involves the use of partitioning tracers, which distribute into NAPLs, and are thus retarded and separated from non-partitioning tracers during transport.

There are several factors that can constrain the implementation and analysis of partitioning tracer tests. These factors include the presence of subsurface heterogeneity, variable distribution of DNAPL, rate-limited mass transfer, tracer mass loss, and sampling method. Although these factors have been discussed qualitatively (Nelson and Brusseau, 1996; Brusseau et al., 1998), the magnitude and nature of their influence on the method has not been investigated in detail. The purpose of this work is to examine the effect of three of these factors (porous media heterogeneity, variable NAPL distribution, and sampling method) on the performance of the partitioning tracer method. The approach involves intermediate-scale flow cell experiments conducted using heterogeneous porous media, variable DNAPL distribution, and three sampling methods.

**Background.** The partitioning tracer test is based on conducting a tracer test in the targeted zone of the subsurface. The potential presence of NAPL is evaluated by comparing the transport of one or more partitioning tracers to that of a conservative (nonpartitioning) tracer. Organic-fluid phases retain the partitioning tracers, which retards their transport with respect to that of a conservative tracer. The procedure for estimating $S_n$, NAPL saturation, involves calculation of a retardation factor (R) for the
partitioning tracer, which is done by a comparative temporal moment analysis with the conservative tracer. Skopp (1985) summarized many useful properties of time moments. The retardation factor is defined as the mean travel time of water (conservative tracer) divided by the mean travel time of the partitioning tracer. The mean travel times are acquired by calculating the first temporal moments normalized by the zeroth temporal moment for each breakthrough curve. Since tracer tests involve pulse-type inputs, the size of the pulse must be accounted for to correctly calculate travel times (Sardin et al. 1991). This is accomplished by subtracting $\frac{1}{2}$ of the pulse width from the first normalized temporal moment. Using the retardation factor acquired from the moment analysis and with knowledge of $K_{nw}$ (NAPL-water partition coefficient), $K_d$ (sorption coefficient), $\rho_b$ (dry soil bulk density), and $\theta_w$ (volumetric water content), $S_n$ can be calculated by use of:

$$R = 1 + \left( \frac{\rho_b}{\theta_w} \right) K_d + \left[ (S_n/1 - S_n) \right] K_{nw}$$  \hspace{1cm} (2.1)$$

The terms on the right-hand side of the equation describe retention of the tracer by the aqueous, solid phase, and NAPL phases, respectively. For a tracer with no sorption to the porous media:

$$R = 1 + \left[ (S_n/1 - S_n) \right] K_{nw} \hspace{1cm} (2.2)$$
Martin and Synge (1941), who developed the liquid-liquid chromatography technique, established the theoretical basis for the partitioning tracer method in the chromatography field. The petroleum industry was the first group to use partitioning tracers for measuring subsurface NAPL saturations (Cooke, 1971; Deans, 1971; Tang, 1995). More recently, the environmental field began to examine the retention of dissolved solutes by immobile, immiscible liquid phases and the resultant impact on solute (tracer) transport (Bouchard et al., 1989; Brusseau, 1990, 1992). For example, the influence of the magnitude of NAPL saturation and the magnitude of the liquid-liquid partition coefficient on the retardation of a partitioning tracer was illustrated with numerical-model simulations reported by Brusseau (1992).

The use of the partitioning tracer method for measuring NAPL saturation in environmental systems was introduced and tested in the laboratory by Jin et al. (1995) and Wilson and Mackay (1995). Jin et al. (1995) demonstrated the ability of a partitioning tracer test to estimate the amount of liquid tetrachloroethylene in columns packed with Ottawa sand. Wilson and Mackay (1995) used sulfur hexafluoride (SF₆) to successfully predict the amount of TCE saturation in columns packed with Borden sand.

The application of the partitioning tracer method at the field scale has recently been demonstrated at several contaminated sites. Pilot-scale field experiments were conducted at Hill Air Force Base in Utah to test the use of several alcohol tracers for measuring the amount of petroleum-based NAPL contained within 3 m by 5 m fully enclosed cells. Results indicate that the NAPL saturation values obtained from the
partitioning tracer tests are in good agreement with values obtained from core analysis (Annable et al. 1998; Brusseau et al., 1998).

In the applications discussed above, partitioning tracers were used to measure quantities of known NAPL contamination. However, it is feasible that partitioning tracers may also be useful as "detectors" of NAPL saturation. Nelson and Brusseau (1996) demonstrated such a use for a chlorinated-solvent contaminated aquifer at a Superfund site in Tucson, AZ. The results of the partitioning tracer tests indicated the probable presence of NAPL saturation within the swept zone of the tests. These results were in accordance with other lines of evidence, such as the removal of large volumes of solvent during the operation of a soil venting system in the vadose zone directly above the location of the tracer tests.

The effectiveness of the partitioning tracer test can be influenced by the presence of heterogeneity in the subsurface. For example, groundwater may flow around (bypass) zones of high NAPL saturation due to the reduced relative permeabilities associated with these zones. This bypass flow may reduce the potential for contact between the tracers and the NAPL, thereby resulting in an underestimate of NAPL saturation. Porous media heterogeneity may also constrain the performance of the partitioning tracer tests. For example, at a site that has been undergoing active remediation, NAPL saturation may persist in low permeability zones (silt and clay layers or lenses), even after most of the NAPL has been removed from high permeability zones. The NAPL in low permeability zones may be difficult to measure with the partitioning tracer test due to preferential flow that occurs in such systems. The experiments described below were designed to
investigate the impact of porous media heterogeneity, variable NAPL distribution, and sampling method on the efficacy of the partitioning tracer method.

Gas-Phase Partitioning Tracer Method

Introduction. Characterizing soil-water content is critically important to many activities associated with agriculture, forestry, hydrology, and engineering. For example, knowledge of soil-water content is especially important for management of agricultural resources, for flood control, and for predicting contaminant transport. Several methods are available to measure water content, such as neutron moderation, time domain reflectometry (TDR), and gravimetric analysis of core samples. The majority of the methods in current use provide what can be considered as point values of water content due to the relatively small sample volumes (10⁻¹ m scale). While this is an advantage for obtaining accurate information at small scales, it is a disadvantage for determining water contents for larger (field) scales. Using current methods to determine the three-dimensional distribution of water content at the field scale requires the use of a dense sampling network and application of spatial statistics. This approach is constrained by varying levels of uncertainty, and is relatively costly and time consuming. A method that could accurately measure water contents for larger scales would be very useful, and would be a valuable tool to complement the smaller-scale methods.

The partitioning tracer method is an innovative technique for the in-situ measurement of water content at the field scale. The method is based on the use of both nonpartitioning and partitioning tracers introduced into the system in the gas phase. The
partitioning tracers dissolve into the water, which retards the gas-phase transport of the partitioning tracers relative to that of the nonpartitioning tracers. The retardation of the partitioning tracers is a function of the amount of water present. The purpose of this research is to describe this new method and test its performance in laboratory column experiments and at the field-scale in a large weighing lysimeter.

**Partitioning Tracers: Previous Work.** The theoretical basis for the partitioning tracer method and its use in the environmental field for measuring NAPL saturations is saturated subsurface systems is discussed above. A similar concept can be applied to determine water content. However, the use of aqueous-phase tracers for determination of vadose zone water content is problematic, because water movement in the vadose zone is generally very slow. The use of gas-phase tracers would provide for much more rapid measurement. Brusseau et al. (1997a) have examined the potential use of gas-phase partitioning tracers for measuring water content and air-water interfacial area, and have demonstrated success based on their initial experiments. They used a suite of phase-selective partitioning tracers, in combination with conservative tracers, as a method for measuring water content and the gas-water interfacial area. In this initial laboratory scale work, CO₂ was used successfully to measure the bulk water content of the system. The retardation of CO₂ due to partitioning to bulk water is illustrated in Figure 2.1, wherein the breakthrough curve for CO₂ is delayed compared to that of helium (a conservative tracer). Based on the retardation of CO₂ as compared to helium, the water content in a column packed with silica sand was estimated to be 0.14 cm³/cm³. This value is similar
Figure 2.1 Breakthrough curves measured for the gas transport of helium and CO₂ tracers.
to the gravimetrically measured value of 0.16 cm$^3$/cm$^3$, which indicates that the partitioning tracer method was able to provide an accurate estimate of the water content.

Theory of Partitioning Tracers. The experimental and theoretical basis for the retention of dissolved solutes by immobile, immiscible liquid phases and the resultant impact on solute (tracer) transport has been described previously (Brusseau, 1992; Jin et al., 1995). An immobile and immiscible fluid retains the partitioning tracer, which retards its transport with respect to that of conservative tracers. For the present application, water is considered to be essentially immobile relative to the rate of gas flux associated with induced-gradient gas tracer tests.

The procedure for determining volumetric water content, $\theta_w$, involves measurement of a retardation factor, $R$, for the gas-phase partitioning tracer. This is usually done by a comparative moment analysis with a gas-phase conservative tracer (resides only in the soil gas). The retardation factor is defined as the quotient of the partitioning tracer's and the conservative tracer's mean travel times. The retardation factor for gas-phase transport is defined in equation 2.3 and contains terms describing retention of the tracer by the gas, aqueous, sorbed, and gas-water interface phases, respectively.

$$R = 1 + \frac{\theta_w}{\theta_s K_H} + \frac{\rho_o K_{Dm}}{\theta_s K_H} + \frac{K_{IA} A_{IA}}{\theta_s}$$  \hspace{1cm} (2.3)
where $\theta_w$ (cm$^3$ water cm$^{-3}$ total) is volumetric water content, $\theta_a$ (cm$^3$ air cm$^{-3}$ total) is air-filled porosity, $K_H$ (cm$^3$ water cm$^{-3}$ air) is Henry's Law constant (dimensionless), $K_{Dsat}$ (cm$^3$ g$^{-1}$) is the sorption coefficient, $\rho_b$ (g cm$^{-3}$) is the dry soil bulk density, $K_{IA}$ (cm) is the adsorption coefficient between the gas phase and the gas-water interface, and $A_{IA}$ (cm$^2$ cm$^{-3}$) is the specific surface area of the gas-water interface. When sorption and interfacial accumulation of the partitioning tracer are negligible:

$$R = 1 + \frac{\theta_w}{\theta_a} K_H = 1 + \frac{\theta_w}{(\theta_t - \theta_w) K_H} = 1 + \frac{S_w}{(1 - S_w) K_H}$$  \hspace{1cm} (2.4)$$

From the above equation, it is clear that a gas-phase tracer experiment conducted with conservative and partitioning tracers can provide a measurement of $\theta_w$ with knowledge of $K_H$ and values of $\theta_a$ or total porosity $\theta_t$ (cm$^3$ pore space cm$^{-3}$ total). Henry's Law constants can be measured in the laboratory, and are often available in the literature. Values of $\theta_a$ can be determined from analysis of the transport of a conservative gas tracer. Values of $\theta_t$ can be estimated from the bulk density and particle density of the soil. Water saturation ($S_w$, cm$^3$ water cm$^{-3}$ pore space) can be determined without knowledge of $\theta_a$ or $\theta_t$. In this case, the only parameter that must be known is $K_H$.

Generally, the analysis of a partitioning tracer test involves calculating mean travel times of the tracers by conducting a comparative temporal moment analysis of the partitioning and conservative tracers (as described above). However, travel times or
retardation factors can also be obtained by other methods. For example, with the "landmark" method (Tang, 1995), calculation of travel times is based on comparing specific points of the respective breakthrough curves, such as the times of first arrival or the times of peak arrival. The advantage of the moment method is that it may be less sensitive to nonideality factors (rate-limited mass transfer, heterogeneity effects) than the landmark method. Mathematical models can also be used to obtain retardation factors. In many cases modeling-based analyzes depend on a suite of assumptions such as physical and chemical homogeneity and chemical equilibrium. Although the moment method is based on the premise that the tracers fully contact the system, the moment method is not dependent on the same types of assumptions as mathematical modeling is. However, as will be discussed below, the moment method is susceptible to error, especially when breakthrough curves are incomplete, when mass transfer constraints are extreme and, in some cases, when mass loss occurs.

Other parameters that can be estimated from the gas-phase tracer test are the "effective" air and total porosities. The "effective" air porosity ($\theta_{ea}$) is the fraction of the true air porosity contacted by the tracer gas (the "mobile" air phase). It can be calculated based on the conservative tracer data as $\theta_{ea} = Q/vA$; where $Q =$ volumetric flow rate ($l^3/T$), $v =$ linear velocity ($L/T$), $A =$ cross-sectional area of the swept volume ($l^2$). The linear velocity is calculated as the travel length divided by the conservative tracer's mean travel time. The "effective" total porosity ($\theta_{et}$) represents the portion of the total porosity (both air and water filled) contacted by the tracer gas. It can be calculated as $\theta_{et} = \theta_{ea} + \theta_{ew}$; where $\theta_{ew}$ is the water content measured from the partitioning tracer test. The
"effective" air and total porosities measured by transport experiments can be compared to values measured independently by methods that measure the entire water content or porosity (e.g. neutron probe, TDR, gravimetric analysis of core samples).

**Relationship to Other Methods.** A variety of methods are available for measuring water content in soils. Each of these methods relies on the measurement of a different physical condition that corresponds to water content, usually at different measurement scales. Thermogravimetric analysis of core samples collected from the field provides the only direct measure of soil-water content. The scale of these measurements obviously corresponds to the size of the sample. Time domain reflectometry measures soil dielectric constant. The range of influence is a volume confined by the length of the waveguides, with a distance of one or two cm outside the outer waveguide, depending on probe geometry (Knight et al., 1994). The neutron probe method measures the presence of hydrogen ions in a spherical volume of soil with a radius that varies from approximately 7 to 20 cm, depending primarily on the soil-water content (de Vries and King, 1961). Other non-intrusive methods, such as electromagnetic induction can be used to measure spatial variations of water content (Kachanoski et al. 1988) to a depth of up to 6 m. Alternatively, remote sensing techniques (e.g. radiometry or radar) can provide regional values averaged across 10-100 square meters. However, these methods measure only the top one cm and thus can not provide water content values at depth.

The water content values obtained from tracer experiments are "global" values, representing an averaging across the measured domain. The magnitude of the observed
retardation, and thus of water content, is a function of the areal influence of the tracer test (swept zone) and the volume of water in the swept zone. The scale of measurement corresponds to the size of the swept zone, which is controlled by the placement of the injection and sampling points. Thus, the tracer method provides a measure of water content at scales that can be considered as intermediate to the methods discussed above. Advantages of the tracer technique are the absence of depth limitations and the ability to vary the scale of measurement.

**Tracer Selection.** A tracer selected for use should have the following characteristics: (1) low toxicity, (2) relatively inexpensive, (3) low background levels, (4) no biodegradation or other transformation reactions, (5) no sorption to porous media or to materials comprising the tracer experiment infrastructure such as PVC and stainless steel, (5) low detection levels such that it can be injected at concentrations several orders of magnitude higher than its detection limit, and (6) an appropriate $K_H$ value. The Henry's Law constant controls the magnitude of retardation for any given water content. A gas with a suitable $K_H$ value would yield a retardation factor large enough to be measurable with some level of certainty, but small enough such that the duration of the test remains practical.

The expected transport behavior of three representative tracers with different Henry's Law constants in systems with water contents of 0.03 and 0.15 cm$^3$/cm$^3$ are shown in Figure 2.2A and Figure 2.2B, respectively. The breakthrough curves were produced using a visualization program that plots an analytical solution to the one dimensional advection-dispersion equation based on user input of retardation factor,
Peclet number, and pulse width. The solution is based on the initial condition that the concentration is zero along the system length, an upper flux-type boundary condition, and a lower boundary condition that the concentration is zero at a great distance from the end of the system. Figure 2.2A indicates that tracers with $K_H$ values between 0.02 and 0.2 would yield $R$ values that are of an acceptable magnitude for a system with $\theta_w=0.03 \text{ cm}^3/\text{cm}^3$. However, for a larger $\theta_w$ of 0.15 $\text{ cm}^3/\text{cm}^3$ (Figure 2.2B), tracers with $K_H$ values between 0.2 and 2 would be appropriate. In general, Figure 2.2 demonstrates that a suitable choice of tracers can not always be made without an a priori estimate of water content. Therefore, it may be desirable to choose several tracers, with a range of $K_H$ values to ensure satisfactory results.

Constraints. Nonideal transport behavior, caused by factors such as rate-limited mass transfer, variable distribution of water, pneumatic-related factors, and subsurface heterogeneity, can lead to difficulties in interpreting partitioning tracer tests. For example, extreme rate-limited mass transfer can cause extensive concentration tailing, which in turn can prevent the accurate calculation of moments (Brusseau, 1992). The impact of these complicating factors on the partitioning-tracer method has not yet been examined in detail.

Mass transfer between the gas and water phases may be constrained by rate-limited diffusion of the tracer within the water. Diffusive mass transfer in water is usually considered to be relatively rapid for aqueous-phase systems. However, residence times associated with gas-phase advection are generally much smaller than those for
Figure 2.2a Selection of appropriate tracers ($K_{H}$ Values) at a water content of 0.03.
Figure 2.2b Selection of appropriate tracers ($K_H$ Values) at a water content of 0.15.
aqueous-phase advection. Thus, the time-scale of aqueous diffusion coupled with the short residence times of gas-phase transport can cause diffusion within water to be significantly rate limited (Popovičová and Brusseau, 1998). As a result, mass transfer between the gas and water phases may be rate limited, which could lead to under estimation of the water content.

Several authors have examined the impact of diffusion within immobile water on gas-phase transport. Brusseau (1991) developed a model for gas transport through structured porous media that accounted for multiple rate-limited mass transfer processes, and used the model to describe data collected from the literature. It was found that diffusion within immobile water significantly influenced transport. Gierke et al. (1992) found that although mass transfer across the gas-water interface could be considered instantaneous, diffusion in immobile water contained within intraaggregate pores caused nonideal gas-phase transport. Grathwohl and Reinhard (1993) and Conklin et al. (1995) conducted column experiments with sandy materials and suggested that intraparticle diffusion in micropores filled with immobile water controlled gas-phase removal of volatile organic compounds. Popovičová and Brusseau (1998) found that diffusion within immobile water contributed to nonideal gas-transport of TCE and benzene in unsaturated homogeneous porous media.

The partitioning of a tracer between two immiscible fluids is generally considered to be reversible at the microscopic scale. However, there are several processes that can cause the partitioning to appear to be non-reversible at the field scale (Nelson and Brusseau, 1996). Consider, for example, a zone of high water saturation that is relatively
thick in the dimension normal to gas flow. When a partitioning tracer first contacts the water zone, a concentration gradient drives the tracer into the water. The concentration gradient reverses when the tracer pulse is followed by tracer-free gas, which causes the tracer to transfer back to the advecting gas. However, if the size of the pulse is insufficient to allow the tracer to fully equilibrate with the water-filled zones prior to the elution step, an inward concentration gradient will still exist in the interior of those zones. This could significantly delay the return of some of the tracer mass to the advecting gas. Depending on the time scale of the experiment and the morphology and distribution of the water, this behavior could cause reduced mass recovery and, thus, the appearance that partitioning was non-reversible. This "apparent" mass loss of the tracer can influence the calculation of water content.

Recovery of the tracer can also be influenced by pneumatic-related factors, such as failure to capture all injection-well flow lines. While the impact of pneumatic factors on tracer recovery should be considered, one purpose of using a conservative tracer is to attempt to account for such factors. True mass loss processes, such as biodegradation and abiotic transformations can also influence tracer recovery. The degree of impact will depend on the nature of the mass loss.

The impact of mass loss on performance of the partitioning tracer test is due to the influence of mass loss on the solute travel time (first temporal moment) (Srivastava and Brusseau, 1999). When the mass loss is nonlinear with time or with location, the measured travel time may differ from what it would have been without mass loss. An example of such behavior was illustrated by Brusseau et al. (1997b), who showed that the
travel times measured for tracers undergoing nonlinear biodegradation were smaller than those measured for a nonbiodegradable tracer under identical conditions. If either of the tracers experiences a nonlinear mass loss, the measured travel times, and hence the estimated water content, may be incorrect. If the partitioning tracer is preferentially degraded, water content would be underestimated, whereas water content would be overestimated if the conservative tracer was preferentially degraded.

Under many conditions, however, travel time is not significantly affected when mass loss is linear and uniform, i.e., when the proportional mass loss is constant at all times and for all locations (e.g., Srivastava and Brusseau, 1999). Hence, the results of a partitioning tracer test may not be significantly influenced by mass loss if the mass-loss mechanism is linear. It is important to evaluate the potential causes of mass loss for each specific case.

The sampling method used can also influence the performance of the tracer test. For example, the swept volume is relatively small for monitoring wells, such that a small zone of high water content can be easily "measured". However, the swept volume of an extraction well can be enormous in comparison. Thus, a small zone of high water content within a region of lower water content may have little impact on retardation as measured at an extraction well. In general, because of factors such as bypass flow, rate-limited mass transfer, and mass loss, the measured water content values may often be underestimates of the true values. Thus, water content measurements obtained with the partitioning tracer method should, at least initially, be considered as underestimates of actual values.
Diffusive Tracer Test

Background. The relative contribution of diffusion-mediated processes for solute transport and for groundwater remediation is a subject of debate and importance. For example, it has recently been suggested that one of the main factors inhibiting the clean-up of groundwater by pump and treat is diffusion of contaminants out of low permeability layers (National Research Council, 1994). It is also accepted that vertical "mixing" contributes to the overall dispersion of solute plumes. Although diffusion-mediated processes are generally considered to play some role in solute transport, it is often difficult to determine their relative contribution to field-scale solute transport.

Mechanisms that lead to dispersion of nonreactive solutes include: (1) hydrodynamic dispersion, (2) physical nonequilibrium resulting from a heterogeneous flow domain at the local scale, and (3) macrodispersion resulting from spatial variability of hydraulic conductivity at scales larger than local. The relative significance of these mechanisms can be evaluated by examining the magnitude of the dispersivities obtained over a range of scales. The dispersivity value determined for transport of a nonreactive tracer through a column of homogeneously packed porous media represents the contribution of hydrodynamic dispersion, assuming longitudinal diffusion is insignificant. The dispersivity value determined for transport of a nonreactive tracer through a core of undisturbed porous media would represent the effect of both hydrodynamic dispersion and local-scale heterogeneity. In this case, the parameter is often referred to as an apparent dispersivity to distinguish this lumped value from the one representing solely local-scale hydrodynamic dispersion. The apparent dispersivity value determined for
transport of a nonreactive tracer in an aquifer would represent the effect of hydrodynamic dispersion, local-scale heterogeneity, and macrodispersion, and is sometimes referred to as a macrodispersivity. In general, the apparent dispersivity values will increase as scale increases due to an increase in the number and scale of factors causing dispersion.

The role of diffusive mass transfer in the transport of nonreactive solutes depends on the conditions and physical nature of the system including the residence time, the characteristic time(s) of mass transfer, and the type and extent of physical heterogeneity (e.g., aggregated soil, layered aquifer systems). For homogeneous systems, the contribution of diffusive mass transfer to solute dispersion is generally considered negligible, except at low velocities (i.e. less than 0.1 cm/hr) (Hu and Brusseau, 1994). For systems that contain mobile and immobile regions, such as aggregated soil systems and fractured rock systems, interregion diffusion can contribute significantly to the overall dispersion (Grisak and Pickens, 1980; Lever et al., 1985; Hu and Brusseau, 1995). In layered systems or systems that contain zones of high and low hydraulic conductivity, two processes, in addition to local-scale hydrodynamic dispersion, contribute to dispersion. These processes are vertical mixing due to flow variation (spatial variability in advection) and diffusion between layers or zones of varying hydraulic conductivity. Sampling methods may be carefully designed to help determine the relative importance of these two processes.

For example, vertical mixing due to spatial variability in advection may contribute significantly to the spreading of breakthrough curves for depth-integrated sampling, whereas it may not be important for depth-specific sampling (especially where flow is
Diffusion between layers will impact spreading of breakthrough curves when depth-specific sampling is used. However, the relative contribution of diffusion between layers may be small in comparison to the contribution of spatial variability in advection when the sampling method is depth-integrated. It has been suggested that the relative contributions of flow variation and inter-layer diffusion depends on velocity for layered soils (flow parallel to layering) (Li et al., 1994). At lower velocities local flow variation was shown to dominate dispersion, whereas at higher velocities interregion diffusion was more important.

Several types of experiments can be conducted to determine the importance of diffusion-mediated processes for solute transport. At the laboratory scale, the primary method used to date involves conducting tracer experiments at two or more pore-water velocities. Because diffusion is a rate-controlled process, changes in residence time (pore-water velocity) will influence the impact of a diffusion-mediated process on solute transport. Two other methods that can be used to examine the influence of rate-controlled processes on solute transport are the “flow-interruption” method (Brusseau et al., 1989; 1997) and the diffusivity tracer-test method (a suite of tracers of different sizes) (Brusseau, 1993).

TCE Dissolution in Heterogeneous Systems

Literature Review. The presence of NAPL contamination at many hazardous-waste sites has contributed greatly to widespread and persistent subsurface contamination. Aqueous concentration data often serve as the basis for decisions
regarding remedial investigations, risk assessments, and performance evaluations of remediation systems. However, aqueous concentrations of NAPL compounds are often several orders of magnitude less than their solubility, even at sites where the presence of NAPL has been confirmed. Thus, the use of aqueous-concentration data is often problematic for determining contaminant-mass distributions, and may lead to inaccurate decision making. Knowledge of the mechanisms controlling NAPL dissolution is critical for conducting risk assessments at and selecting and designing appropriate remediation strategies for NAPL contaminated sites.

Factors that may contribute to less than solubility concentrations, an apparently rate-limited behavior, include heterogeneous NAPL distribution, nonuniform flow and associated physical nonequilibrium, dilution, diffusion mediated mass transfer, and rate-limited mass transfer between the NAPL and aqueous phases. A majority of current literature on NAPL dissolution involves investigating the rate of interphase mass transfer between a single-component NAPL and aqueous phases at the laboratory scale. Some of these experimental investigations have suggested that the local equilibrium assumption is valid for laboratory columns (Fried et al., 1979; Miller et al. 1990). Batch style experiments indicate that aqueous concentrations often approach solubility values in minutes to hours depending on the NAPL/water volume ratio (Shiu et al., 1988; Poulsen et al., 1992).

For example, Miller et al. (1990) investigated the effect of pore water velocity, aqueous and NAPL saturations, and porous media characteristics on the interphase mass transfer rate using homogeneous one-dimensional columns packed with glass beads and
toluene. To examine the effect of particle size uniform distributions of three different sized glass beads, 200-, 400-, and 650-μm nominal particle diameter, were used. NAPL saturations ranging from 2.6 to 21.5% were established by mixing the NAPL with the glass beads to achieve uniform distributions of NAPL in the column. Pore-water velocities varied from 0.25 to 15.6 m/d. The authors concluded that the interphase mass transfer rate was a function of pore-water velocity and NAPL saturation, but not of mean particle size. High values of experimentally determined mass transfer rate coefficients indicate that equilibrium is reached relatively quickly and that the local equilibrium assumption is valid in systems similar to the ones studied.

Other investigations have shown that interphase mass transfer processes may be rate-limited under certain conditions (Hunt et al., 1988b; Geller, 1990; Powers et al., 1991; Powers et al., 1992; Geller and Hunt, 1993; Imhoff et al., 1993; Powers et al., 1994). For example, Powers et al. (1991) use a one-dimensional, steady state form of the advection-dispersion mass balance equation that incorporates a first-order interphase mass transfer relationship and temporal changes in blob configuration to model NAPL dissolution. The sensitivity of the model is explored by varying porosity, Darcy velocity, blob shape and size, residual saturation, dispersivity, mass transfer coefficient correlation, aquifer type (well graded vs. well sorted) and exposed surface area. The results indicate that the aqueous phase solute concentration profiles depend on NAPL blob shape and size, Darcy velocity, lateral dimensions of the exposure zone and the mass transfer coefficient correlation used. The authors also use the model to evaluate the efficiency of
various pump-and-treat schemes. The results indicate that nonequilibrium effects could impact NAPL dissolution for large blob sizes and relatively high velocities.

Results of column-scale NAPL dissolution experiments conducted using a homogeneous packing of Ottawa sand and various blends of Wagner soil, Darcy velocities ranging from 0.5 - 6.5 cm/hr, and residual saturations ranging from 8.4 to 18.5% are presented in Powers et al., 1992. Most of the experiments used Styrene, a light NAPL, which could be polymerized, separated, and examined following the dissolution experiments. This allowed blob shapes and sizes to be characterized for each column. The experimental results from many of the experimental conditions indicate nonequilibrium conditions. Dissolution rates were determined to depend on the distribution pattern of the entrapped NAPL and on the aqueous phase velocity. The results of this work indicate that dissolution of NAPL is rate-limited at the pore-scale and conflict with the results of Miller et al. (1990). This may be due, in part, to different methods used to emplace the NAPL saturation. Miller et al. (1990), mixed the NAPL with glass beads, whereas NAPL was flowed into the columns in this work.

A majority of the published literature focuses on the dissolution of NAPL from systems containing homogeneous porous media and a uniform distribution of NAPL. However, in recent years, researchers have begun to examine the dissolution of NAPLs in systems containing a nonuniform distribution of NAPL and/or heterogeneous porous media theoretically (Anderson et al., 1992; Soerens et al., 1998) and experimentally (Anderson et al., 1992; Manivannan et al., 1996). Dissolution of NAPL from fractured
permeable media has been investigated through the use of mathematical models by Rubin et al., 1997.

Soerens et al. (1998) used two-domain and parallel column models to demonstrate the effects of nonuniform NAPL distribution and flow bypassing on apparent interphase mass transfer. The model that incorporated the two-domain concept to represent heterogeneity was able to reproduce the time-scale dependency of mass transfer coefficients that have often been observed. In the parallel column model, the porous media column was modeled as a collection of parallel columns with the residual saturation distributed between the columns by a probability distribution. Therefore, each individual column had a different NAPL mass, relative permeability, and fraction of flow passing through it. Interestingly, the parallel column models, with equilibrium partitioning assumed within each column, were able to reproduce the concentration drop-off and tailing observed in published column studies of NAPL dissolution (Imhoff et al., 1994). The results of this research suggest that much of the apparent rate-limited interphase mass transfer can be described by heterogeneity in NAPL distribution and in porous media properties.

In the work of Manivannan et al., 1-dimensional column experiments and a two-dimensional flow cell experiment were conducted to examine dissolution of single-component NAPL (styrene, toluene or TCE) entrapped in a coarse sand lens at a high NAPL saturation. In both the column experiment and in the flow cell experiment the coarse sand lens (cylindrical for column and rectangular for flow cell) was surrounded by a finer medium. The results from the heterogeneously packed column were compared to
results from a homogeneously packed column. During the early phase of the two column experiments, effluent concentrations remained near their equilibrium concentrations for approximately 250-300 pore volumes. The effluent concentration in the homogeneously packed column continued to decrease slowed, whereas effluent concentration for the heterogeneously packed column actually began to increase.

To help elucidate this behavior, experiments were conducted in a flow-cell to qualitatively examine NAPL dissolution from the coarse sand lens. Visual observations of the flow cell experiment showed that initially the NAPL was selectively removed around the periphery of the coarse lens. At later times, an overall reduction in the intensity of color (the NAPL phase was dyed with a red organic dye) was observed throughout the entire lens. This evidence suggests that the increase in effluent concentration observed for the heterogeneously packed column was likely due to an increase in relative permeability of the NAPL zone following significant removal of NAPL.

**Rate-Limited Dissolution of Single-Component NAPLs.** In general, NAPLs can occur as residual zones and as pools on top of low permeability layers. In residual zones NAPL is present as immobile blobs and ganglia that generally occupy 10% or less of the pore space. In pools the NAPL may occupy much more of the pore space (up to 50 – 70%) thereby significantly restricting flow through the pool region. In general, pools will tend to have much lower relative permeabilities than residual zones. As groundwater flow occurs through the remaining pore space in the residual zone or pool, dissolution of the NAPL occurs.
The rate of NAPL dissolution is a function of several factors including the aqueous solubility and diffusivities of the NAPL, the physical distribution of the NAPL in the porous (or fractured) medium, and the rate of groundwater flow through and around the NAPL. There are several physical scenarios that are characterized by low NAPL-water contact area. The presence of a nonuniform distribution of NAPL residual can lead to "bypass flow" as the groundwater flows around a zone of isolated NAPL residual due to reduced relative permeability. When bypass flow occurs the contact area between the NAPL and flowing water will be reduced leading to reduced aqueous concentration. In some cases, NAPL saturation may exist within a low permeability zone. Preferential flow can occur around this layer or zone of reduced hydraulic conductivity also leading to reduced NAPL-water contact area. A third scenario that is characterized by low NAPL-water contact area, is the presence of a NAPL pool. In this case dissolution of the NAPL occurs primarily along the top and sides of the pool.

Mathematically, the rate of dissolution is expressed as a function of a mass transfer coefficient, a linear driving force, and the interfacial contact area between the NAPL and aqueous phases: \( \frac{dC}{dt} = A \ k \ (C - C_s) \) where \( \frac{dC}{dt} \) is the rate of interphase mass transfer (\( M/L^3T \)), \( A \) is the specific NAPL-water interfacial area (\( L^1 \)), \( k \) is the mass transfer coefficient (\( L/T \)), and the linear driving force is the difference between \( C \) (\( M/L^3 \)), the actual aqueous concentration, and \( C_s \) (\( M/L^3 \)), the aqueous phase concentration that would be in thermodynamic equilibrium with the pure organic liquid. Since the parameter \( A \) is difficult to measure or approximate, \( k \) and \( A \) are often lumped into an effective mass transfer coefficient, \( k_{eff} \ (1/T) = k \ A \).
In general, dimensionless numbers, which are correlated to mass transfer coefficients, are reported in the literature rather than the mass transfer coefficients directly. The most common dimensionless number reported in hydrologic literature related to NAPL dissolution is the Sherwood number ($S_h = kL/D$), where $L$ is a characteristic length of mass transfer (L) and $D$ is the diffusion coefficient (free-liquid diffusivity) ($L^3/T$). The Sherwood number represents the relationship between the interphase mass transfer rate and the diffusion rate. Other common dimensionless numbers are the Stanton number, which represents the relationship between the interphase mass transfer rate and the flow rate, the Schmidt number, which represents the relationship between the diffusivity of momentum and the diffusivity of mass, and the Reynolds number, which represents the relationship between inertial forces and viscous forces.
CHAPTER 3. THE PARTITIONING TRACER METHOD FOR THE IN SITU MEASUREMENT OF DNAPL SATURATION: INFLUENCE OF HETEROGENEITY AND SAMPLING METHOD

Objective

The objective of this study is to examine the effect of porous media heterogeneity, nonuniform distribution of dense nonaqueous phase liquid (DNAPL), and sampling method on the performance of the partitioning tracer method for measuring DNAPL saturation in water-saturated subsurface systems. This method involves the use of partitioning tracers, which distribute into NAPLs, and are thus retarded and separated from non-partitioning tracers during transport. Experiments were conducted in an intermediate-scale flow cell packed with heterogeneous porous media and a variable trichloroethene (TCE) distribution. Aqueous samples were collected using three methods. A dual-energy gamma radiation system was used to determine a two-dimensional image of DNAPL distribution both before and after the tracer experiment. This allowed the results from the tracer experiment to be compared to a previously tested method.

Materials and Methods

Experimental Apparatus. The experiments were conducted in a 2.20-m-long by 1.10-m-high by 0.053-m-wide intermediate-scale flow cell. The flow cell has a 0.64 cm thick glass front to allow flow visualization and a 0.64 cm thick Kynar® back plate to allow for installation of sampling ports. The bottom and side pieces of the cell were made out of 2.54 cm thick stainless steel. A steel frame consisting of vertical 3.18 cm
rectangular bars spaced approximately 22 cm apart, welded to 2.54 cm angle iron at the top and bottom, provided rigidity to the assembly.

The flow cell is equipped with eight "point" sampling ports, which are integrated across the 0.05-m width, and two "vertically integrated" sampling ports, which are integrated across the 0.05-m width and a 0.3-m height. The point sampling ports emulate multi-level samplers whereas the vertically integrated sampling ports emulate monitoring wells with relatively large screened intervals. The point sampling ports consist of laser-drilled stainless steel tubing (0.18-cm OD and 4.8-cm length), which are inserted through holes drilled into the Kynar® back and terminate in PEEK® push valves (Kloehn, Las Vegas). The vertically integrated sampling ports consist of three lengths of the same type of stainless steel tubing inserted through the top of the flow cell at the same X coordinate (length) but spaced evenly along the Z coordinate (width). The three tubes are connected via a manifold that terminates in a PEEK® push valve. A schematic of the flow cell, including the location of the two zones with residual TCE, injection and extraction wells, point (A-G), and vertically integrated (J-K) samplers is presented in Fig. 3.1.

An injection well and an extraction well, each consisting of 0.88 cm ID Schedule 40 PVC pipe slotted over a 71 cm length, were installed at opposite ends of the flow cell. To help reduce dead-volume, solid aluminum rods with 0.63 cm OD were placed within the PVC. A zone of pea gravel was packed around the PVC wells to ensure uniform tracer injection. A cotton cloth sleeve was wrapped around the slots to reduce clogging. The flow cell was designed to be compatible with a state-of-the-art dual-energy gamma radiation system.
Figure 3.1: Schematic of flow cell.

- **Zone 1**: 70-mesh sand; 11.1% residual TCE
- **Zone 2**: 20/30-mesh sand; 9.2% residual TCE

Injection Well

Extraction Well

20/30 mesh sand
**Materials.** Two conservative tracers (pentafluorobenzoic Acid [PFBA] and calcium bromide [bromide]) and two partitioning tracers (2,4-dimethyl-3-pentanol [DMP] and 6-methyl-2-heptanol [MH]) were chosen for this study. Trichloroethylene [TCE] was the NAPL used in this study. The TCE was dyed with a hydrophobic red dye, Sudan IV, to allow visualization of the TCE phase. Fluorescein dye [sodium salt form] was used to conduct visualization experiments to help characterize the flow field. Research grade PFBA, bromide, TCE, and fluorescein dye [~70% dye content] were purchased from Aldrich Chemical Company, Inc., Wisconsin. Research grade DMP and MH were purchased from Lancaster Chemicals. The partitioning tracers were chosen based on preliminary batch experiments conducted to measure the TCE-water partition coefficients. The measured TCE-water partition coefficients were 46.5 and 222.3 for DMP and MH, respectively. The porous media used in this study were a medium-grained 20/30-mesh and a fine-grained 70-mesh (ASTM, 1990) sand (Unimin Corporation, Le Sueur, MN). Information on the particle diameter and the uniformity coefficient of the sands is listed in Table 3.1.

**Experimental Procedures.** Two distinct zones containing TCE residual were established in the flow cell. Zone 1 consisted of TCE residual within 70-mesh sand to examine the effect of preferential flow associated with physical heterogeneity. Zone 2 consisted of TCE residual within the same material as the matrix (20/30 mesh sand) to examine the effect of bypass flow associated with a localized zone of TCE saturation. The materials, except for the two zones with residual TCE, were packed under saturated
Table 3.1. Physical Properties of the 20/30- and 70- mesh Sands

<table>
<thead>
<tr>
<th></th>
<th>70-Mesh</th>
<th>20/30-Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Diameter d50 (mm)</td>
<td>0.724±0.031</td>
<td>0.213±0.011</td>
</tr>
<tr>
<td>Uniformity Coefficient d60/d10</td>
<td>1.210±0.034</td>
<td>1.184±0.039</td>
</tr>
<tr>
<td>Particle Density kg/m³</td>
<td>2658</td>
<td>2657</td>
</tr>
</tbody>
</table>

Note: Five sieve analysis were performed for each sand.

conditions. The two TCE-residual zones (0.8-m-long by 0.1-m-high by 0.053-m-wide blocks) were emplaced in the flow cell as follows. First, the flow cell was packed under saturated conditions with 20/30-mesh sand to a height coincident with the lower boundary of each of the planned inclusions. The water table was then lowered until the upper 1 cm of the 20/30-mesh sand had drained. The TCE-residual zones were then emplaced within the designated locations, the space for which was maintained temporarily during the packing with vertical support slats. For each zone, the sand/TCE mixture was prepared by thoroughly mixing a pre-determined amount of dry sand with an amount of liquid TCE that would yield an approximate 10% saturation of the pore space. The amount of sand required for each zone was computed from porosities obtained for the same sands in prior experiments (Oostrom et al., 1998b). The partially saturated sand was then saturated with CO₂-gas before the water table was raised to minimize air entrapment. Based on the amount of sand and liquid TCE packed in each zone, average bulk density, porosity, and TCE saturation values were computed (Table 3.2). After packing of the cell was completed, a 1-cm-layer of a kaolinite-clay paste was placed on
Table 3.2. Average Properties of the Two TCE Zones

<table>
<thead>
<tr>
<th></th>
<th>Zone 1</th>
<th>Zone 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Computed Gravimetrically and Volumetrically</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Bulk Density, kg/m$^3$</td>
<td>1637</td>
<td>1759</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.384</td>
<td>0.338</td>
</tr>
<tr>
<td>TCE Saturation</td>
<td>0.104</td>
<td>0.099</td>
</tr>
<tr>
<td><strong>Computed from Gamma Data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Path length, cm</td>
<td>5.29±0.08</td>
<td>5.28±0.07</td>
</tr>
<tr>
<td>Dry Bulk Density, kg/m$^3$</td>
<td>1659</td>
<td>1764</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.376±0.012</td>
<td>0.336±0.017</td>
</tr>
<tr>
<td>TCE Saturation</td>
<td>0.111±0.010</td>
<td>0.092±0.011</td>
</tr>
</tbody>
</table>

...top of the sand to create an impermeable cap.

After the flow-cell was packed and an initial set of dual-energy gamma measurements were collected, steady-state flow was established by flushing a 750 mg/L solution of CaCl$_2$ through the flow cell using two Masterflex peristaltic pumps. The injection and extraction flow-rates were gradually increased to and remained at 50 ± 0.7 mL/min, which corresponds to one pore volume per 14.4 hours (as measured at the extraction well). Once steady-state conditions were achieved, a one pore-volume pulse of tracer solution containing 170 mg/L bromide, 170 mg/L PFBA, 180 mg/L DMP, and 151 mg/L MH was injected. The tracer solution also contained 112 mg/L CaCl$_2$ to match the
density of the electrolyte solution. Following the tracer pulse, nine additional pore volumes (130 hours) of tracer-free water were flushed through the system.

The eight point and two vertically integrated sampling ports described above and the flow-cell effluent were sampled approximately every hour for the first 2.6 pore volumes. The sampling interval gradually decreased as the experiment progressed. The point and vertically integrated ports were sampled by attaching a gas-tight ten-mL syringe with a glass barrel (Kloehn, Las Vegas or Hamilton) to the push valve connected to a particular port. A one-mL purge volume was discarded prior to taking a sample. Following the purge, a six-mL sample was withdrawn. Two mL were used to completely fill glass VOA vials with teflon-lined septum for analysis of DMP, MH, and TCE. Four mL were expelled into polyethylene scintillation vials for analysis of bromide and PFBA. The elution stream was sampled by allowing the stream to completely fill the VOA vials and partially fill the polyethylene vials. The samples were chilled at 5°C prior to analysis.

A transport experiment using the fluorescent dye fluorescein was conducted in the flow-cell to qualitatively examine the uniformity of packing and the effect of the heterogeneities on the flow field. This dye enabled visualization by using ultraviolet (black) light sources. The experiment was conducted after the tracer test to avoid potential interaction of the dye with the porous media or NAPL phase. Steady-state flow was maintained between the tracer test and the dye experiment. The experiment was implemented by injecting a pulse of water containing 200 mg/L fluorescein through the
flow cell at 50 mL/min, followed by continuous injection of dye-free water. Photographs were taken at regular intervals as the dye traveled through the flow cell.

**Dual-Energy Gamma Radiation System.** The fully automated dual-energy (280 mCi Americium and 100 mCi Cesium) gamma radiation system was used to determine TCE saturations in the two zones. Each zone was calibrated at 792 measurement locations according to procedures adapted from Oostrom and Dane (1990) and Oostrom et al. (1998a). The horizontal and vertical distance between measurement locations is 1 cm except where vertical support bars were present. The horizontal distance between locations at either side of a vertical support bar was 5 cm. Count rates were obtained at all locations when the flow cell was empty, filled with water, and three times when filled with saturated sand. The three times include just before the tracer solution was injected into the flow cell, after injection/extraction was terminated, and after clean up of both zones with a 4% T-MAZ-80 solution, which is an anionic POE (20) sorbitan monooleate surfactant. Because the TCE was added to the flow cell concurrent with packing, it was necessary to remove all TCE from the two zones after the tracer experiment to obtain gamma counts without liquid TCE present (i.e., background). The counting times for all scans were 60 seconds per location.

**Analytical Methods.** The DMP, MH, and TCE were analyzed at the University of Arizona using a Shimadzu Gas Chromatograph with flame ionization detector (model 14A) equipped with a Shimadzu auto injector (model AOC-17). The detection limit of the alcohols and TCE were 1.4 mg/L and 0.3 mg/L, respectively. The bromide and PFBA were analyzed at the Environmental Molecular Science Laboratory at Pacific
Northwest National Laboratory. The bromide was analyzed using a Dionex Ion Chromatograph (model DX-500) with suppressed conductivity detector. The detection limit was 100 \( \mu g/L \). The PFBA was analyzed using a Hewlett Packard Liquid Chromatograph (model 1100) with a Diode array detector and a Phenomenex Luna 2 column. The detection limit was 200 \( \mu g/L \).

Results

Dual-Energy Gamma Measurements. The count rates yielded path lengths, dry bulk densities, porosities, and TCE saturations at the start and end of the injection/extraction experiment, which are listed in Table 3.2. The average porosity and dry bulk density values computed from the gamma radiation count rates are similar to the gravimetrically obtained data. Plots of the initial and final TCE saturation distribution are shown in Fig. 3.2 a,b and in Fig. 3.3 a,b, for Zone 1 and 2, respectively. In making the plots, it was assumed that each measurement location represented an area of 1 cm\(^2\). The TCE values in the area behind the vertical support bars are an average of the two values obtained for the locations adjacent to each bar. The average saturations computed from gamma count rates compare well to those computed from the volume of TCE mixed into each zone. The maximum probable error in the computed TCE saturation as a result of the randomness of the gamma radiation is 0.006 (Oostrom et al., 1995).
Figure 3.2 TCE saturation distribution for zone 1.
Figure 3.3 TCE saturation distribution zone 2.
Tracer Transport: Conservative Tracer and Dye Transport. The dye pulse was characterized by a sharp front as it traveled through the region upgradient of the heterogeneities, indicating uniform packing. However, the behavior of the pulse indicated nonuniform flow associated with Zones 1 and 2. The dye was delayed slightly by Zone 2 and significantly by Zone 1. Dye-free regions persisted downgradient of both zones, indicating areas of no or low flow.

Breakthrough curves measured for bromide, DMP, and MH at the two point sampling ports located upgradient from the TCE zones (Ports A and B) are shown in Figure 3.4 a,b. The bromide breakthrough curves are sharp and symmetrical indicating that packing was uniform. This is consistent with the results of the dye experiment.

The positions and general shapes of the DMP breakthrough curves are very similar to those of bromide at these locations. Although the MH breakthrough curves indicate that a mass loss mechanism may be affecting MH recovery, the positions of the MH breakthrough curves are also similar to those of bromide. This indicates that DMP and MH experienced no measurable sorption by the solid phase and also that their dispersive behavior was similar to that of bromide. The data for the tracers were analyzed by calculating the zeroth and first temporal moments to quantify mass recovery and retardation (e.g., Fischer et al., 1979). The results from the moment analysis are presented in Table 3.3.

Tracer Transport: Point Sampling Ports (Zone 2). Breakthrough curves measured for bromide, DMP, and MH at two point sampling ports located downgradient from zone 2 (Ports E and G) are shown in Figure 3.5 a,b. The arrival of the DMP and
Table 3.3: Moment Analysis Results

<table>
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<tr>
<th></th>
<th>Bromide</th>
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<th>PFBA</th>
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<tbody>
<tr>
<td></td>
<td>$O^h$ (hr)</td>
<td>Travel Time</td>
<td>$O^h$ (hr)</td>
<td>Travel Time</td>
</tr>
<tr>
<td>A</td>
<td>13.96</td>
<td>3.69</td>
<td>15.27</td>
<td>2.69</td>
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<tr>
<td>B</td>
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<td>2.41</td>
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<td>2.96</td>
</tr>
<tr>
<td>C</td>
<td>14.25</td>
<td>7.13</td>
<td>14.00</td>
<td>7.22</td>
</tr>
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<td>D</td>
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<td>15.89</td>
<td>7.28</td>
</tr>
<tr>
<td>E</td>
<td>15.40</td>
<td>7.82</td>
<td>14.96</td>
<td>8.14</td>
</tr>
<tr>
<td>F</td>
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<td>13.09</td>
<td>10.97</td>
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<tr>
<td>G</td>
<td>15.40</td>
<td>8.43</td>
<td>15.04</td>
<td>8.44</td>
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<tr>
<td>H</td>
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<td>12.70</td>
<td>14.01</td>
<td>11.95</td>
</tr>
<tr>
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<td>7.31</td>
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<tr>
<td>K</td>
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<td>14.61</td>
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</tr>
<tr>
<td>EXT</td>
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<td>14.82</td>
<td>15.86</td>
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<table>
<thead>
<tr>
<th></th>
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<th>Travel Time</th>
<th>MH</th>
<th>Travel Time</th>
</tr>
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<tbody>
<tr>
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<td>$O^h$ (hr)</td>
<td>Travel Time</td>
<td>$R$</td>
<td>$S_n$</td>
</tr>
<tr>
<td>A</td>
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<tr>
<td>B</td>
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<td>2.75</td>
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<td>3.5</td>
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<tr>
<td>C</td>
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<td>6.364</td>
<td>0.89</td>
<td>10.06</td>
</tr>
<tr>
<td>D</td>
<td>14.14</td>
<td>7.134</td>
<td>0.99</td>
<td>12.27</td>
</tr>
<tr>
<td>E</td>
<td>13.91</td>
<td>18.10</td>
<td>2.31</td>
<td>33.78</td>
</tr>
<tr>
<td>F</td>
<td>13.08</td>
<td>17.00</td>
<td>1.30</td>
<td>20.61</td>
</tr>
<tr>
<td>G</td>
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<td>24.74</td>
<td>3.05</td>
<td>60.11</td>
</tr>
<tr>
<td>H</td>
<td>16.19</td>
<td>13.40</td>
<td>1.29</td>
<td>23.52</td>
</tr>
<tr>
<td>J</td>
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<td>7.04</td>
<td>0.96</td>
<td>7.30</td>
</tr>
<tr>
<td>K</td>
<td>12.08</td>
<td>14.86</td>
<td>1.02</td>
<td>15.68</td>
</tr>
<tr>
<td>EXT</td>
<td>14.15</td>
<td>17.55</td>
<td>1.18</td>
<td>15.85</td>
</tr>
</tbody>
</table>

MH breakthrough curves are clearly delayed in comparison to bromide at these two ports. Given that partitioning into the immiscible liquid phase of TCE is the only mechanism causing retention of DMP and MH, apparent residual TCE saturations can be calculated using equation 2.1. The values of residual saturation so obtained for Port E based on DMP and MH are 1.9% and 1.5% respectively. The values of residual saturation obtained for Port G based on DMP and MH are 2.9% and 2.7%, respectively.
Figure 3.4 Tracer breakthrough curves; port a (A) and port b (B)
Figure 3.5 Tracer breakthrough curves; port e (A) and port g (B)
These values are lower than the average $S_n$ of 9.2% measured with the dual-energy gamma instrument prior to the tracer experiment. However, this value must be averaged over the entire zone swept by the tracers to directly compare it to the $S_n$ values determined by the tracer experiment. Assuming horizontal flow and that $S_n=0$ for the area upgradient from the distinct residual zone, the spatially averaged value is calculated to be 5.0%. Additionally, the $S_n$ estimated from the tracer data should be compared to a measured $S_n$ value that is temporally averaged, given that the $S_n$ is decreasing due to TCE dissolution as the tracer experiment progresses. A final average $S_n$ value of 6.2%, corresponding to a spatially averaged value of 3.3% as described above, was measured after the tracer experiment. While it is not possible to determine the actual temporally averaged $S_n$ value based on these two values, they do provide the upper and lower limits.

An estimate of the mass of TCE removed from the flow cell can be determined by integrating under the TCE elution curve at the extraction well. The total mass removed by the extraction well at 30 hours was used to specify a more precise temporally averaged $S_n$ given that most of the tracers had passed by most of the ports by 30 hours. This total mass removed was proportioned between Zone 1 and 2 by comparing the relative mass removed from the two zones according to the dual-energy gamma data. Given that the temporally and spatially averaged value determined using this method is 4.6%, the DMP breakthrough curve yields an estimate of $S_n$ that is 41% of the true value for Port E. The MH breakthrough curve yields an estimate of $S_n$ that is 33% of the true value for Port E. For Port G, the DMP and MH breakthrough curves yield $S_n$ estimates that are 63% and 59% of the true value, respectively.
The MH breakthrough curves may be yielding lower estimates of $S_n$ compared to DMP due to the increased residence time of MH combined with continued depletion of TCE saturation. The higher $S_n$ values measured by the partitioning tracer breakthrough curves at Port G compared to Port E may be due in part to higher $S_n$ values at the bottom of the zone as measured by the dual-energy gamma system. Hydraulic factors, such as the presence of a possible low flow region at Port E as suggested by the results of the fluorescein dye experiment, may also help explain the lower values at Port E.

**Tracer Transport: Point Sampling Ports (Zone 1).** Breakthrough curves measured for bromide, DMP, and MH at two point sampling ports located downgradient from Zone 1 (Ports F and H) are shown in Figure 3.6 a,b. For both locations, the bromide breakthrough curves are asymmetrical and contain multiple peaks in the tail region, indicating that a nonuniform flow field is significantly influencing tracer transport. The degree of flow field nonuniformity associated with the region downgradient of Zone 1 would be expected to be greater than that associated with the region downgradient of Zone 2 due to the larger difference in hydraulic conductivity between Zone 1 and the coarser matrix. This would account for the distinct difference in the shapes of the bromide breakthrough curves at Ports E and G compared to those at Ports F and H. The difference in the degree of flow field nonuniformity is supported by the results of the fluorescein dye experiment. Although the dye experiment highlighted regions of essentially no flow downgradient of both NAPL zones, the region downgradient of Zone 1 was more persistent and had sharper boundaries.
Figure 3.6 Tracer breakthrough curves; port f (A) and port h (B)
The frontal sections of the DMP and MH breakthrough curves at Port F are slightly delayed in comparison to bromide. This is especially apparent at higher concentrations (i.e. $C/C_0$ between 0.6 and 0.8). The DMP and MH breakthrough curves exhibit more concentration tailing than bromide. Additionally, a set of two concentration peaks located between 1.25 and 2 hours for bromide is visibly shifted to between 2.25 and 3.25 hours for DMP. The two peaks appear to merge into one peak located between 3.5 and 6 hours for MH. Although the data is more scattered at Port H, similar behavior is observed.

Apparent $S_n$ values calculated using equation 2 for port F based on the retardation of DMP and MH are 0.4 % and 0.3%, respectively. The values of residual saturation so obtained for Port H based on DMP and MH are 0.4% for both tracers. For Zone 1, the average $S_n$ value measured with the dual-energy gamma instrument following the tracer experiment was almost the same as the value measured before the tracer experiment [10.1 vs. 11.1%]. As described above, to compare the tracer results to the dual-gamma measurement, the $S_n$ value acquired from the dual-gamma instrument needs to be spatially and temporally averaged. Following the reasoning explained above, the spatially and temporally averaged value for this port is estimated to be 5.9%. The $S_n$ values measured by the partitioning tracers at Ports F and H are thus approximately 7% of the measured value.

The lower values of $S_n$ determined from the tracer results at Ports F and H relative to Ports E and G indicate that the tracer method was less effective at measuring NAPL retained within the lower intrinsic permeability zone. This reduced performance is likely
caused by the larger degree of nonuniform flow and related physical nonequilibrium associated with Zone 1 relative to Zone 2. The transport of the partitioning tracers through Zone 1 would be greatly influenced by diffusion-mediated mass transfer due to extreme preferential flow of the tracer solution around the zone. As discussed above, the larger degree of nonuniform flow is supported both by the asymmetrical breakthrough curves and by the dye experiment.

**Tracer Transport: Vertically Integrated Ports.** Breakthrough curves measured for bromide, DMP, and MH at the vertically integrated port located downgradient from Zone 2 (Port K) are shown in Figure 3.7a. The positions and general shapes of the DMP and MH breakthrough curves are very similar to those of bromide. The bromide breakthrough curve, as well as the partitioning tracers breakthrough curves, exhibit concentration tailing associated with spatially variable hydraulic conductivity, which is a common characteristic of vertically integrated samples.

The moment analysis yielded a slight retardation of the tracers, with retardation values of 1.02 for DMP and 1.07 for MH. From equation 2, these correspond to $S_n$ values of 0.03% for both tracers. This value severely underestimates the true value, which is between 3.3%-5.0% (as explained above). The lack of retardation of the partitioning tracers is likely due to severe dilution by streamlines that have not contacted the NAPL phase. In addition, when suction is placed on the sampling port, a gradient is formed toward the port and the flow of water entering the port from a given region will depend on that region's hydraulic conductivity. Therefore, the sample is flux-averaged and will be biased towards areas of higher conductivity. Because the zone containing the NAPL
Figure 3.7 Tracer breakthrough curves; port k (A) and port j (B)
has a lower hydraulic conductivity than the surrounding areas, its contribution will be less than its areal size would indicate. Although this biasing can potentially occur for the point sampling ports, the degree of biasing would be much less because the vertical ports span a much greater vertical domain.

Breakthrough curves measured for bromide, DMP, and MH at the vertically integrated port (Port J) located downgradient from Zone 1 are shown in Figure 3.7b. The positions and general shapes of the DMP and MH breakthrough curves are very similar to those of bromide. The breakthrough curves do not exhibit the same degree of concentration tailing that was exhibited for Port K. Although this is also a vertically integrated port, it is possible that the difference in hydraulic conductivity between this NAPL zone (low intrinsic permeability) and the surrounding sandy matrix is so extreme that almost all the water entered the port from the surrounding coarser matrix. This is supported by the complete lack of retardation of the partitioning tracers.

**Tracer Transport: Extraction Well.** Breakthrough curves measured for bromide and DMP at the extraction well are shown in Figure 3.8. The MH curve is not used due to severe mass loss. Although the fronts arrive at the same time, DMP exhibits more tailing than bromide. The $S_n$ calculated from equation 2 based on DMP is 0.3%. The swept-volume for the extraction well consists of the entire flow cell. Therefore, the $S_n$ values for the two NAPL zones measured from the dual-gamma instrument must be averaged over the entire flow cell. This spatially averaged $S_n$ is 1.1% before the tracer experiment and 0.9% at the end of the tracer experiment, which translates to a temporally
Figure 3.8 Tracer breakthrough curves, extraction well.
and spatially averaged $S_n$ of 1.0% (as explained above). The extraction well DMP data therefore provides a value that is 30% of the true value.

**Discussion**

The results demonstrate that physical nonequilibrium and preferential flow associated with zones of lower intrinsic and relative permeability have a significant impact on the performance of the partitioning tracer test. The results also show that the effect of physical nonequilibrium on the tracer breakthrough curves and on the performance of the method varies as a function of sampling method. The highest $S_n$ estimates were obtained from data collected at the point sampling ports. The saturations were highest for the point sampling ports downgradient from the higher intrinsic permeability zone (Ports E and G). The underestimation at these ports is likely related to the tracers bypassing areas within Zone 2 that had high saturations of TCE. In general, the bromide breakthrough curves at these locations are sharper and more symmetrical than those at other locations, indicating relatively ideal transport. The lower values of TCE saturation obtained for Zone 1 are likely caused by preferential flow phenomena associated with the lower intrinsic permeability. The bromide breakthrough curves at these locations exhibit concentration tailing and asymmetry associated with nonuniform flow.

The lowest values of NAPL saturation were obtained from the breakthrough curves collected at the integrated sampling ports. In fact, the partitioning tracer breakthrough curves at the integrated port downgradient from Zone 1 (Port J) exhibit
retardation factors of approximately one, which translates to a TCE saturation of zero. The tracer breakthrough curves at the integrated port downgradient from Zone 2 yield a TCE saturation an order of magnitude less than the extraction well and Ports F and K and two orders of magnitude less than Ports E and F.

The extraction well breakthrough curves yielded a NAPL saturation estimate that was about 1/3 of the measured value. In contrast to the vertically integrated port data, which samples a selected part of the domain as discussed above, the extraction well data represents an averaging of all the streamlines in the flow cell. Due to this difference, the breakthrough curves at the extraction well may yield a higher value of TCE saturation than the vertically integrated ports, as was the case in this experiment. In contrast to the extraction well in this experiment, an extraction well in the field may fail to capture all injection-well flow lines. In addition, the flow lines associated with low hydraulic conductivity regions may have effective travel times that exceed the time scale of the tracer test. Therefore an extraction well in the field may not represent an averaging of all the injection streamlines and may yield results that are biased by flow from high conductivity zones. The potential significance of this affect can be determined by examining the mass recovery and travel times of the conservative tracer.

The values of NAPL saturation obtained from the point sampling port data ranged from approximately 5% (Ports F and H) to 63% (Port G) of the actual spatially and temporally averaged values measured by the dual energy gamma instrument. However, the results from the pilot-scale field experiments conducted at Hill Air Force Base indicate that the NAPL saturation values obtained from the partitioning tracer tests are
within 90% of values obtained from core analysis (Annable et al. 1998 and Brusseau et al., 1998). The reduced performance associated with the flow-cell experiment may be due to the nature of the NAPL distribution and porous media heterogeneity. In this experiment, the NAPL was constrained to very discrete zones, and comprised a cell-wide average $S_n$ of 1%. In addition, the porous medium was characterized by abrupt and large changes in permeability. At Hill Air Force Base, the NAPL phase was distributed fairly evenly throughout the 3 m by 5 m cells, at an average $S_n$ of 10%. Furthermore, the material consists primarily of medium to coarse sand and gravel, with very few low permeability regions within the zone swept by the tracer tests. Thus, the greater performance of the tracer tests conducted at Hill Air Force Base is likely due to a combination of the higher NAPL saturation and the ideal tracer transport associated with the relatively homogeneous nature of the porous media and NAPL distribution.

The results of the flow-cell experiment indicate that the presence of porous media heterogeneity and distinct zones of NAPL saturation lead to reduced performance (reduced accuracy) of the partitioning tracer test. The reduced performance can be improved, in part, by using depth-specific sampling. In fact, NAPL within lower intrinsic permeability zones may not be measurable by the partitioning tracer method without depth-specific sampling ports. The breakthrough curves show a strong correlation between the performance of the partitioning tracer test and the amount of nonideal transport associated with the conservative tracer data. This correlation may be used to qualitatively examine whether the values of NAPL saturation obtained by the tracer test
should be considered to be underestimates due to heterogeneity and physical nonequilibrium.

Despite these results, the partitioning tracer test can still be a valuable tool for characterizing sites that may be contaminated by a NAPL phase. At sites where the presence of NAPL is suspected, but not confirmed, partitioning tracers may be useful as "detectors" of NAPL source zones. Partitioning tracers may also be useful as "performance indicators" of a chosen remedial action. Tracer tests can be conducted before, during, and after site clean-up to judge the efficacy of the remediation. Additional research in this area is certainly justified due to a continued need to characterize the large number of sites contaminated by complex and persistent NAPL phases.
CHAPTER 4. THE PARTITIONING TRACER METHOD FOR THE IN SITU MEASUREMENT OF WATER CONTENT

Objective

The objective of this study is to test a gas-phase partitioning tracer method for the in-situ measurement of water content and to illustrate its application and test its performance in well-defined systems. The method is based on the use of both nonpartitioning and partitioning tracers introduced into the system in the gas phase. The partitioning tracers dissolve into the water, which retards the gas-phase transport of the partitioning tracers relative to that of the nonpartitioning tracers. The retardation of the partitioning tracers is a function of the amount of water present. The method provides an integrated field-scale value that complements the smaller-scale methods, such as neutron moderation, and the regional-scale methods, such as remote sensing. Tracer experiments were conducted in the laboratory and in a large weighing lysimeter to test the performance of the method.

Laboratory Experiment

Description of Laboratory System. The partitioning tracer method was tested in laboratory-scale column experiments. The experimental setup is similar to the modified gas chromatographic system described by Brusseau et al. (1997a). Gases containing the tracer of interest are introduced into the system via high pressure gas cylinders and passed through a 500mL gas washing bottle (Pyrex, Ace Glass, Vineland, NJ) for humidification to prevent desaturation of the porous medium. Separate humidification
bottles are used for the carrier gas (nitrogen) and the tracers (reactive and conservative) to avoid background contamination. A 10.5 cm long (5.08 cm i.d.) stainless steel column (MODcol, St. Louis, MO) was used, with diffusion plates fitted at both ends to allow an even distribution of vapor across the column cross-section. Stainless steel three-way valves (Whitey, Arizona Valve and Fittings Co., Phoenix, AZ) are used to switch between the tracer and the carrier gas. The column effluent stream passes directly to an online flame ionization detector (FID) (Varian 3700, Varian Associates, Inc., Walnut Creek, CA) for analysis. All system components through which the gases flow are connected with 1/8" stainless steel tubing and 1/8" stainless steel Swagelok fittings (Arizona Valve and Fitting Co., Phoenix, AZ). The FID signal is routed to a digital voltmeter (Micronta, Fort Worth, TX), which is interfaced to a personal computer using Wedge software. This allows concentration (voltage) versus time data to be collected real-time at any specified time interval.

**Methods.** The tracer experiments were conducted on uniformly wetted homogeneous Vinton fine sand (sandy, mixed thermic Typic Torrifuvent). The sand was mixed with a known amount of water and packed wet. Dibromodifluoromethane (BFM) was used as the water-partitioning tracer and methane served as the conservative tracer. Both conservative and reactive tracers were custom mixed in a balance of nitrogen (Air Products, Long Beach, CA and Spectra Gases, Alpha, NJ, respectively). Nitrogen was used as the background gas to establish steady-state flow and a steady FID baseline prior to each tracer experiment. Pertinent properties of the tracers used in both the laboratory experiments and in the lysimeter experiments are listed in Table 4.1.
Because the water in the humidification system retains the water-partitioning tracer, the BFM was passed through the tracer humidification bottle via a column bypass prior to each experiment. The tracer-humidification water was assumed to be saturated with BFM once a constant FID signal was obtained. Flow rates were regulated by adjusting the gas cylinder regulator pressure and stainless steel high resolution metering valves at both the column inlet and outlet (Cole-Parmer, Vernon Hills, IL). Flows were established at approximately 30.0 mL min\(^{-1}\) using a 25 mL bubble flowmeter (Kimble-Kontes, Vineland, NJ) inserted at the detector outlet. This corresponds to an average pore velocity of 3.4 cm min\(^{-1}\).

Multi-tracer experiments could not be conducted due to the use of flow-through detection. Thus, sequential experiments were conducted, using the same column and identical conditions. Conservative tracer experiments were conducted at least in duplicate and reactive tracer experiments were conducted in triplicate. Tracer
experiments were also conducted to evaluate the retention of BFM by the system apparatus, including sorption to the stainless steel surfaces and retention by the water films created associated with these surfaces. This effect was evaluated by conducting experiments as method described above, but with no porous media in the column.

Water content was measured before and after each experiment. Prior to the experiment, the water content is calculated based on the known amount of water added to a known mass of sand. After the experiment, the column is unpacked, and water content is measured thermogravimetrically. Small aliquots (<15g) are taken from the column inlet, midpoint, and outlet to determine spatial distribution. The remaining sand (≈300g) is used to gravimetrically measure a composite water content.

**Measurement of Henry’s Law Constants.** The value of water content estimated with the partitioning tracer method is a linear function of the partitioning tracer’s Henry’s Law constant (assuming a constant value of gas porosity). Clearly, the actual value used for $K_H$ can significantly influence the accuracy of the results. Measured values for $K_H$ are often available in the literature. However, literature values should be used with caution because experimental conditions that influence air-water partitioning, such as temperature, may differ between the laboratory and field.

Values of $K_H$ are also commonly estimated, because measurements are difficult to make for many compounds (see Schwarzenbach et al., 1993 for a discussion of the Henry’s Law constant and methods for estimation). Henry’s Law constants are most commonly estimated from vapor pressure and solubility data. These estimates can differ from experimental ones by less than 10% to more than 300% (Schwarzenbach et al.,
Hine and Mookerjee (1975) proposed a Henry's Law constant estimation method based on molecular structure contributions. This method is usually only within a factor of 2 or 3 of experimentally derived values. Thus, in many cases, using an estimated value can lead to erroneous calculations of water contents.

We determined $K_H$ for BCF and BFM, as follows. An aliquot of a gas standard was injected into a 21 mL crimped headspace vial containing 10 mL of Nanopure water. Five different sized aliquots were used to produce five different concentrations within the headspace vial. This was done in triplicate. The vials were placed on a shaker table for 24 hours to equilibrate. A 2.5 mL aliquot of the headspace was then subsampled and placed in a headspace vial. The gas in the headspace vial was then analyzed using gas chromatography (Shimadzu, GC-17) using an electron capture detector and a headspace autosampler (Tekmar). The difference between the initial mass of the sample gas injected into the vial and the final mass of the sample gas in the headspace was assumed to have partitioned to the water phase. The Henry's Law constant was calculated as the resulting slope of the concentration in the water plotted against the concentration in the headspace.

**Data Analysis.** The tracer breakthrough curves were analyzed by calculating the zeroth and first temporal moments to quantify mass recovery, travel time and retardation (Fischer et al., 1979). For the column systems, travel time was corrected for the known system dead volume. Additionally, the total observed retardation factor was corrected for BFM retention by the apparatus.
Intermediate-Scale Experiments

Description of Site. The partitioning tracer method was tested in controlled experiments conducted in a large weighing lysimeter located at The University of Arizona's Karsten Center for Research. The lysimeter is 4.0 m deep, 2.5 m in diameter, and contains a homogeneous packing of Vinton fine sand (the same material used in the column experiments). The lysimeter is equipped with 6 tensiometers, 21 TDR probes, a neutron-probe access tube, 3 thermocouples, and 48 porous stainless steel cups for gas injection and sampling. The weighing scales have a capacity of 45 Mg and can detect a 200-g mass change, equivalent to ± 0.04 mm of water on the surface. The instrumentation allows the values of water content estimated from the partitioning tracer experiment to be compared to known values obtained with established methods. Pressure transducers (model 136PC15G2, Microswitch, Freeport, IL) installed in the injection line, extraction line, and at 50 cm increments along the lysimeter allow pressure to be monitored throughout the entire system. All instrumentation (excluding TDR) is connected to a data logger (Model CR7, Campbell Scientific, Inc. Logan, UT) for data collection and storage. Software (PC208W, Campbell Scientific) for a personal computer connected to the data logger allows real time monitoring of all data during the experiment. Additional information about the lysimeter is available in Young et al. (1996) and Zou et al. (1998).

Methods. Three tracer experiments were conducted in the lysimeter. For the first experiment, a nonreactive tracer (SF₆) was used to test the flow system and gas-sampling techniques, and to obtain estimates of travel times. For the second experiment, SF₆ was
used as the nonreactive tracer and bromochlorodifluoromethane (BCF) was used as the water-partitioning tracer. For the third experiment, SF₆ was used as the nonreactive tracer and dibromodifluoromethane (BFM) was used as the water-partitioning tracer. The tracers were analyzed by gas chromatography (Shimadzu, GC-17) using an electron capture detector. Pertinent properties of the tracers are listed in Table 4.1 (above).

Steady state flow was established by injecting air into the lysimeter through a length of stainless steel tubing. This stainless steel tubing was manifolded to 18 lengths of 6.4 mm Kynar tubing embedded horizontally within a layer of pea gravel at the bottom of the lysimeter. The tubing terminated in porous stainless steel cups (50-mm long, 12.5 mm in diameter, with an air-entry pressure of 20 cm). A 5 horsepower air compressor was used to inject air at 15 liters per minute (first experiment), 32.2 liters per minute (second experiment), or 38.8 liters per minute (third experiment). A 3/4 horsepower vacuum pump was used to extract air, at the same rate as it was injected, through four ports drilled into an aluminum lid at the top of the lysimeter. Injection and extraction flow-rates were controlled using gate-valves and monitored using gas flow rotameters (Dwyer Instruments Inc. or Omega).

The air stream was humidified to greater than 95% by passing the stream through a water tower prior to injection. The water tower consisted of schedule 40 PVC (0.3 m OD and 1.8 m length) and was capped at both ends. Wire mesh was placed inside the tower to increase the area of mass transfer, and the tower was filled with 66 liters of water. This configuration provided an average residence time of two minutes for the air stream. The tracer pulse was not passed through the water tower because the water
would retain the partitioning tracer. However, calculations assuming equilibrium conditions indicate that a maximum of 0.063 liters of water (0.0032% of the total water) could be removed from the lysimeter due to evaporation during the tracer pulse.

A vacuum test was conducted before the tracer experiment to check for air leaks. The test showed minimal leakage (approximately 0.29 liters per minute, 0.7-1.9% of the flow-rate during the experiment) using a vacuum of 51.6 cm, which is 25 times higher than the vacuum used during the tracer test (2.1 cm) and therefore provides an overestimate of the actual leakage expected during the tracer test. A helium leak test was conducted in addition to the vacuum tests. Helium was pumped into the lysimeter and a helium-leak detector was used to check for leaks at all fittings and connections.

The gas tracers were contained in a 6.2 m$^3$ gas cylinder and injected directly into the lysimeter using the method described above for air injection. Two 2-way valves were used to switch between the tracer and tracer-free gas sources. Tracer injection began once steady state gas flow was established. During the first experiment, the tracer was injected for 1.02 hours, corresponding to 0.12 pore volumes. Following the tracer injection, tracer-free air was injected for an additional 13.6 hours, corresponding to 1.6 pore volumes. During the second experiment, the tracers were injected for two hours, corresponding to approximately 0.5 pore volumes. Tracer-free air was then flushed through the lysimeter for an additional 18.6 hours, corresponding to 4.3 pore volumes. During the third experiment, the tracers were injected for two hours, corresponding to approximately 0.6 pore volumes. Tracer-free air was then flushed through the lysimeter for an additional 19.3 hours, corresponding to 5.9 pore volumes.
In-situ samples were collected from two horizontal planes located at 1.75 m (bottom) and 3.1 m (top 1) from the bottom of the lysimeter. The samples were collected from ports located near the center of the lysimeter (Figure 4.1). For the third experiment, a second in-situ port was sampled (top 2). This port is located near the lysimeter wall, 3.1 m from the bottom of the lysimeter (top 2). The influent- and effluent-gas streams were also sampled. The sampling ports consist of septum injector nuts (Valco Instruments Co. Inc., Houston, TX), connected to 6.4 mm OD Kynar tubing embedded horizontally within the soil. Inside the lysimeter, the Kynar tubing terminated in porous stainless steel cups at various distances from the lysimeter wall. The tubing passed through the lysimeter wall through an airtight fitting. A septum sampling port was also attached to the effluent-gas stream. Gas samples were taken by withdrawing samples through the septum into a needle-tipped syringe. The gas samples were then injected from the syringe into evacuated 80 ml aerosol canisters (Tracer Research, Tucson, AZ). The first volume of gas withdrawn was expelled as a purge volume.

**Independent Measures of Water Content.** Core samples (1.3 cm x 30 cm) were removed from the lysimeter at 50 cm intervals for gravimetric analysis of water content. The samples were placed in airtight containers, weighed, oven dried for 48 hours, and weighted again. The gravimetric water content was converted to volumetric water content by using the global average of bulk density. The tension data collected by the data logger was converted to volumetric water content by use of the soil characteristic properties (Zou et al., 1998). However, small errors in measured tension lead to relatively large errors in the estimated water content due to the large slope of the water
Figure 4.1 Orientation of gas-sampling ports within the lysimeter.
characteristic curve measured for Vinton fine sand. The TDR probes were individually connected to a cable tester (Model 1502C, Tektronix Corp., Beaverton OR) and wave forms read, in duplicate, using software (TACQ, Dynamax, Inc., Houston, TX) on a personal computer. The wave forms were reduced to volumetric water content using the Topp equation (Topp et al., 1980).

Results and Discussion

Laboratory Results. Breakthrough curves for the Methane and BFM are shown in Figure 4.2a. The curves are symmetric with sharp arrival and elution waves, indicating ideal transport. The BFM arrival is retarded relative to methane, due to retention by partitioning to water. Good precision was achieved in the replicate runs, with a relative standard deviation of 0.6% in retardation for BFM replicates. Reproducibility is demonstrated visually by the overlap of BFM replicate arrival fronts shown in Figure 4.2b.

As discussed above, a measurement of $\theta_{\text{ew}}$ can be provided by a gas-phase tracer experiment using either values of $\theta_t$ or using values of $\theta_{ea}$ obtained from the conservative tracer. Values of $\theta_{\text{ew}}$ obtained by using $\theta_t$ are designated $\theta_{\text{ew1}}$, whereas those obtained by using $\theta_{ea}$ are designated $\theta_{\text{ew2}}$. The estimated water content using the known air-filled porosity of 0.38 is 0.058. This value represents 96.6% of the actual total water content of the system (0.060). Using the methane-transport derived porosity, 0.34, the estimated water content is 0.053 or 87.9% of the actual value.
Figure 4.2a Breakthrough curves measured for the gas transport of methane and BFM.

Figure 4.2b Triplicate breakthrough curves measured for the gas transport of BFM.
The ratio of $\theta_t$ to $\theta_{ea}$ indicates that methane contacted only 90% of the total air-filled porosity. Assuming the BFM experienced this same air-filled volume, underestimation of the water content by the water-partitioning tracer method would be expected. However, despite this constraint, the tracer method provided estimates that are within 10% of the actual water contents.

**Lysimeter Results.** Average measurements of air porosity ($\theta_t - \theta_w$), water content, and water saturation from gravimetric analysis of soil cores and TDR are reported in Table 4.2. Profiles of water content along the lysimeter length from gravimetric analysis of soil cores and TDR are shown in Figure 4.3. Both profiles exhibit a uniform water content of 0.060 to 0.065 from 50 cm to 300 cm below ground surface and a relatively higher water content below 300 cm.

<table>
<thead>
<tr>
<th>Table 4.2: Physical Measurements of $\theta_a, \theta_w, \text{and } S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_a(\text{cores})$</td>
</tr>
<tr>
<td>Bottom Level (1.65 m)</td>
</tr>
<tr>
<td>Top Level, Center port (3.00 m)</td>
</tr>
<tr>
<td>Effluent Gas Stream (3.85 m)</td>
</tr>
</tbody>
</table>

Breakthrough curves for SF$_6$ at 1.65 m and 3.00 m from the inlet and for the effluent gas stream are shown in Figure 4.4 for the first experiment. The breakthrough
Figure 4.3 Water content distribution in the lysimeter measured using TDR, tension data, and gravimetric measurements.
Figure 4.4 Breakthrough curves measured for the gas transport of SF₆ at the effluent gas-stream in the lysimeter during the first field experiment.
curves are smooth and symmetrical, indicating ideal transport. The curves also show that the tracer pulse is spreading as it travels through the system, as expected.

The breakthrough curves were analyzed using the method of moments to determine retardation factors as described above. Peclet Numbers were determined using a nonlinear least-squares optimization program incorporating the one-dimensional advection-dispersion equation (van Genuchten, 1981). The program uses an analytical solution based on the initial condition that the concentration is zero along the system length, an upper flux-type boundary condition, and a lower boundary condition that the concentration is zero at a great distance from the end of the system. For all cases, the time axis was converted to pore volumes by dividing by the mean travel time (assumed to be the time for one pore volume) determined for SF₆ at the same location. Peclet Numbers, pore-gas velocities, [travel distance/mean travel time] and estimated air-filled porosities [volumetric flow-rate divided by the product of the pore-gas velocity and cross-sectional area] are reported in Table 4.3.

Breakthrough curves for SF₆ and BCF from experiment two and for SF₆ and BFM for experiment three at the effluent gas monitoring location are shown in Figure 4.5a and Figure 4.5b respectively. The Peclet Number obtained for SF₆ transport during the second experiment at the effluent gas stream is essentially identical to the value obtained during the first experiment. This indicates that the experimental methods and therefore conservative tracer transport are reproducible. In addition, the Peclet Numbers obtained from the effluent breakthrough curves are essentially identical for SF₆ and BCF transport, indicating that the two tracers experienced similar levels of nonideal transport.
Table 4.3: SF₆ Results, Experiment 1

<table>
<thead>
<tr>
<th>Location</th>
<th>Peclet #</th>
<th>v (cm/min)</th>
<th>θₑa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom Level</td>
<td>29.45 [28-30.9]</td>
<td>0.87</td>
<td>0.35</td>
</tr>
<tr>
<td>Top Level</td>
<td>62.34 [59.8-64.9]</td>
<td>0.96</td>
<td>0.32</td>
</tr>
<tr>
<td>Effluent Gas Stream</td>
<td>53.94 [48.7-59.2]</td>
<td>1.08</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Inspection of Figure 4.5 shows that the partitioning tracer (BCF or BFM) breakthrough curve is slightly delayed and exhibits concentration tailing in comparison to the SF₆ breakthrough curves. Values of pore-gas velocity (v), effective air porosity (θₑa), retardation factor (R), effective water content (θₑw) and effective water saturation (Sₑw) are reported for all sampling points (Table 4.4a and 4.4b). The measurements of air porosity from all three tracer experiments ranged from 0.035 to 0.045, with a mean of 0.38. The independent measurement of air porosity based on the average gravimetric water content and total porosity ranged from 0.404 to 0.419, with a mean of 0.414. The independent measurement of air porosity based on TDR measurements and total porosity ranged from 0.407 to 0.424, with a mean of 0.414.

The measurements of θₑw₁ (water content calculated using the known value of porosity) from experiments two and three ranged from 0.040 to 0.099, with a mean of 0.065. The measurements of θₑw₂ (water content calculated using the value of air-filled porosity determined from the conservative tracer data) were similar to the measurements of θₑw₁ and ranged from 0.040 to 0.105, with a mean of 0.065. The gravimetric water content measurements ranged from 0.059 to 0.075, with a mean of 0.064. The water
Figure 4.5a Breakthrough curves measured for the gas transport of SF₆ and BCF at the effluent gas-stream in the lysimeter during the second experiment.
Figure 4.5b Breakthrough curves measured for the gas transport of SF₆ and BFM at the effluent gas-stream in the lysimeter during the third experiment.
Table 4.4a: Tracer Results; Experiment 2

<table>
<thead>
<tr>
<th>Level</th>
<th>Tracer</th>
<th>V (cm/min)</th>
<th>$\theta_{ea}$</th>
<th>R</th>
<th>$S_{ew}$</th>
<th>$\theta_{ew1}$</th>
<th>$\theta_{ew2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom Level (1.65 m)</td>
<td>SF$_6$</td>
<td>1.6</td>
<td>0.41</td>
<td>1*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BCF</td>
<td>1.5</td>
<td></td>
<td>1.07</td>
<td>0.134</td>
<td>0.064</td>
<td>0.057</td>
</tr>
<tr>
<td>Top Level (3.00 m)</td>
<td>SF$_6$</td>
<td>1.8</td>
<td>0.36</td>
<td>1*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BCF</td>
<td>1.7</td>
<td></td>
<td>1.06</td>
<td>0.113</td>
<td>0.054</td>
<td>0.043</td>
</tr>
<tr>
<td>Effluent Gas Stream (3.85 m)</td>
<td>SF$_6$</td>
<td>1.9</td>
<td>0.35</td>
<td>1*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BCF</td>
<td>1.8</td>
<td>NA</td>
<td>1.05</td>
<td>0.092</td>
<td>0.044</td>
<td>0.035</td>
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</tbody>
</table>

* assumed

Table 4.4b: Tracer Results; Experiment 3

<table>
<thead>
<tr>
<th>Level</th>
<th>Tracer</th>
<th>$v$ (cm/min)</th>
<th>$\theta_{ea}$</th>
<th>R</th>
<th>$S_{ew}$</th>
<th>$\theta_{ew1}$</th>
<th>$\theta_{ew2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom Level (1.65 m)</td>
<td>SF$_6$</td>
<td>1.98</td>
<td>0.40</td>
<td>1*</td>
<td>0.207</td>
<td>0.099</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td>BFM</td>
<td>1.70</td>
<td></td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Level, Center port (3.00 m)</td>
<td>SF$_6$</td>
<td>1.75</td>
<td>0.45</td>
<td>1*</td>
<td>0.123</td>
<td>0.059</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>BFM</td>
<td>1.63</td>
<td></td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Level, Side port (3.00 m)</td>
<td>SF$_6$</td>
<td>1.85</td>
<td>0.43</td>
<td>1*</td>
<td>0.169</td>
<td>0.081</td>
<td>0.087</td>
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<tr>
<td></td>
<td>BFM</td>
<td>1.63</td>
<td></td>
<td>1.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent Gas Stream (3.85 m)</td>
<td>SF$_6$</td>
<td>1.98</td>
<td>0.40</td>
<td>1*</td>
<td>0.119</td>
<td>0.057</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>BFM</td>
<td>1.82</td>
<td></td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* assumed
contents measured by TDR ranged from 0.054 to 0.071, with a mean of 0.064. The means of both the \( \theta_{ew1} \) and \( \theta_{ew2} \) measurements are close to the means of the independently determined water content measurements, indicating that the tracer test provides a reasonable estimate of water content. Furthermore, the results indicate that most of the air porosity is mobile and that the partitioning tracer contacted a large percentage of the water phase.

The values of water content measured by the two tracer experiments indicate higher water contents at the bottom of the lysimeter. The independently determined gravimetric and TDR measurements also show increasing water content with depth (Figure 4.3). The water content values measured by the tracer tests at the effluent gas stream are smaller than the water content measured at the three point ports. This may be due, in part, to inherent differences between effluent or extraction well samples, which represent transport behavior averaged across the entire swept zone and point samples which represent transport behavior along a flow-line. Although efforts were made to ensure that the lysimeter was homogeneously packed and that water content was spatially constant, the water content profile shown in Figure 4.3 and bulk density profile shown in Figures 4.6 exhibit a small degree of heterogeneity. This heterogeneity may have contributed to the lower values of water content obtained at the effluent gas stream.

Conclusions

The results of the experiments demonstrate that gas-phase tracer tests can be a valuable tool for characterizing the vadose zone. Conservative gas-phase tracers can be
Figure 4.6 Profile of bulk density along the lysimeter.
used to estimate the size of the advective pore volume, which is an important parameter in designing soil vapor extraction systems and in predicting gas-phase transport behavior. A comparative analysis of the conservative and partitioning tracer transport has the potential to provide accurate values of $\theta_w$ at the field scale. Knowledge of $\theta_w$ can be critical in a variety of applications, including crop management, flood control, and the transport of pesticides and other contaminants.

Although the mean value of $\theta_w$ obtained from the tracer tests in the lysimeter agrees with the value obtained from the gravimetric and TDR measurement, it should be noted that the $R$ values of the partitioning tracers [1.05 to 1.13] were at the lower limit of the acceptable range. For a less-controlled experiment, a retardation factor of 1.1 may not have been statistically different from 1.0. The results demonstrate that the lysimeter provides a well-controlled setting for exploring the use of gas-phase tracer tests for measuring water content and indicate that tracer tests have the potential to accurately measure water contents for a system with uniform water content and homogeneous porous media. This method would complement both the traditional, small-scale methods and the regional [watershed] scale methods of measuring water content. The presence of nonuniform water content and porous media heterogeneity may lead to reduced performance of gas-phase partitioning tracer test and merits further investigation.
CHAPTER 5. THE INFLUENCE OF SCALE ON
THE DISPERSION OF DIFFERENT SIZED SOLUTES:
LABORATORY AND FIELD INVESTIGATIONS

Objective

The objective of this study is to explore the use of the diffusivity tracer test-method (tracer test using a suite of tracers of different sizes) to investigate the impact of scale on solute transport influenced by diffusion-mediated processes. This will be examined using three experimental systems: (1) a column packed with homogenized aquifer material, (2) an undisturbed aquifer core and (3) confined alluvial aquifer. Tracer experiments were conducted in the laboratory and field using different sized tracers. Results from flow interruption experiments are compared to results from a diffusivity tracer test conducted using the undisturbed aquifer core. The effect of scale on the calculated apparent dispersivities is also discussed.

Materials and Methods

Tracers. Pentafluorobenzoate (PFBA, purity > 99%) and bromide (as CaBr2) were purchased from Aldrich Chemical Co. \(^3\)H\(_2\)O was purchased from New England Nuclear. Hydroxypropl-beta-cyclodextrin (HPCD) was donated by Cerestar, Inc. PFBA, bromide, and HPCD were used in the homogenized soil column experiments. PFBA and \(^3\)H\(_2\)O were used in the undisturbed aquifer core experiments. Bromide and HPCD were used for the field experiment. Pertinent properties of tracers are listed in Table 5.1.
Table 5.1: Properties of tracers

<table>
<thead>
<tr>
<th>Tracer</th>
<th>MW</th>
<th>D₀, cm²/h</th>
<th>Co- Homogenized Column</th>
<th>Co- Undisturbed Core</th>
<th>Co- Field Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>22</td>
<td>0.0878¹</td>
<td></td>
<td>2 nCi/ml</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>79.9</td>
<td>0.075³</td>
<td>200 mg/L</td>
<td></td>
<td>76 mg/L</td>
</tr>
<tr>
<td>PFBA</td>
<td>212</td>
<td>0.0284²</td>
<td>200 mg/L</td>
<td>100 mg/L</td>
<td></td>
</tr>
<tr>
<td>HPCD</td>
<td>1500</td>
<td>0.0064²</td>
<td>1700 mg/L</td>
<td></td>
<td>175 mg/L</td>
</tr>
</tbody>
</table>

¹From Wang et al. [1953]
²Estimated by use of Hayduk and Laudie approach [Tucker and Nelken, 1982].

For column experiments in which PFBA was used, a flow-through, variable-wavelength UV detector (Gilson, Model 115) was used to continuously monitor concentrations of PFBA in the column effluent. Output was recorded on a strip-chart recorder (Fisher, Recordall Series 5000). For column experiments in which bromide or HPCD was used, effluent fractions were collected with an automated fraction collector (Pharmacia RediFrac). Bromide was analyzed using a bromide specific electrode (Cole-Palmer) with a Fisher Scientific Accumet pH meter. HPCD was analyzed by measuring the fluorescence of HPCD complexed with TNS (2-p-toluidinnaphthalene-6-sulfonate) using a Hitachi F-2000 Fluorescence Spectrophotometer (Wang and Brusseau, 1993). Effluent fractions were collected with an automated fraction collector (Pharmacia RediFrac) for column experiments conducted with H₂O. The activity of H₂O in the effluent samples was analyzed by radioassay using liquid scintillation counting (Packard Tri-Carb Liquid Scintillation Analyzer, Model 1600TR). For the field experiment, bromide was analyzed using a colorimetric method (ALPKEM Corporation, Clackmas,
Oregon) and HPCD was analyzed using the same method described above for the column experiments.

**Homogeneously Packed Column.** The homogenized soil column experiments were conducted in a glass column (2.5 cm i.d., and 15 cm in length) packed homogeneously with aquifer material collected from a depth of 43-45 m below ground surface (BGS) during the drilling of a well at the field site. The less than 2-mm fraction was used to pack the column. The results of a sieve analysis conducted on the less than 2-mm fraction showed a composition of 89.5% sand, 4.1% silt, and 6.4% clay. An analysis of the less than 2-mm fraction showed 0.06% total carbon and 0.03% organic carbon.

The apparatus employed for the miscible displacement experiments was a HPLC pump (SSI Acuflow series II) connected to the column by a three-way switching valve placed in-line to facilitate switching between solutions, one of which contained the solute of interest and the other which contained an electrolyte solution \([\text{Ca(NO}_3\text{)}_2, \text{CaCl}_2, \text{MgSO}_4, \text{NaHCO}_3, \text{NaCl}]\) similar to the site groundwater. The electrolyte solution was pumped through the column to obtain complete water saturation and to acclimate the aquifer material to the electrolyte solution. Two separate experiments were conducted. During experiment one, a solution containing 200 mg/L PFBA and 2000 mg/L bromide was pumped into the column at a flow rate of 0.74 mL/min [corresponding to a linear velocity of 25.2 cm/hr]. During experiment two, a 1700 mg/L solution of HPCD was pumped through the column at a flow rate of 0.80 mL/min [corresponding to a linear velocity of 27.2 cm/hr]. The difference in velocities (8%) between the two columns
should not influence the magnitude of dispersion in homogeneously packed columns where dispersion is dominated by local-scale hydrodynamic dispersion.

**Undisturbed Column.** The undisturbed core was obtained by pressing a Plexiglas column (5.08 cm i.d., and 7.62 cm in length) through the 43-45 m BGS section of the field core. This allowed the column to be filled with "undisturbed" porous media, maintaining the structural arrangement of the aquifer material within the column. The column was pressed through the core normal to the vertical axis of the core so that flow generated during the experiments would match the direction of flow at the site.

The apparatus employed for the miscible displacement experiments was the same as used for the homogenized column experiments. Solutions containing 100 mg/L PFBA and \(^3\)H\(_2\)O were pumped separately into the column. Flow rates of 2.2 and 0.22 mL/min, corresponding to pore-water velocities of 1.5 and 15.0 cm/hr, were used for the experiments and are within the range of those observed during the field experiment. Specific activity of tritium in the solution was 2 nCi/mL. Flow interruption was employed to examine the effect of diffusive mass transfer on solute transport.

**Field Site.** The field site is located within a Superfund site in Tucson, Arizona. The tracer test was conducted in a 6 m thick, semi-confined alluvial aquifer, whose upper surface is approximately 42 m below ground surface. One fully screened injection well (170.3 liters/min) and one fully screened extraction well (567.7 liters/min), located 57 m apart, were used to establish flow. Two days before experiment startup, the tracer-stock tank was filled with 3800 liters of water. Calcium bromide and HPCD were then added to the tank. Tracer-free groundwater was used during injection to dilute the stock
solution at a ratio of about 100:1. The tracer was injected at a rate of 170.3 liters/min and extracted at a rate of 266.8 liters/min. The tracer solution containing bromide and HPCD was injected for 53 hours, after which tracer-free groundwater was injected for 60 days. Depth-specific water samples were collected at a centerline monitoring well using a multi-level sampling device. Several fully screened peripheral monitoring wells were bailed to collect depth-integrated samples.

Results

Homogeneously Packed Column. Breakthrough curves for PFBA, bromide, and HPCD are relatively symmetric and similar in shape indicating ideal transport (Figure 5.1). For comparison purposes the data is plotted as relative concentration versus pore volumes normalized by R. Figure 5.1a shows the frontal portions of all three breakthrough curves. Figure 5.1b shows the entire breakthrough curve for PFBA. The breakthrough curves for all three tracers yield the same value of dispersivity, indicating that diffusional processes are not contributing to solute transport. The breakthrough curves were analyzed using the method of moments to determine retardation factors and mass recoveries (Table 5.2). The values of the Peclet Number were determined using a nonlinear least-squares optimization program incorporating the one-dimensional advection-dispersion equation (van Genuchten, 1981).

Generally, the Peclet Number is defined as $P = \frac{vL}{D}$, where $v$ is the average pore-water velocity ($L \cdot T^{-1}$), $L$ is characteristic system length ($L$), and $D$ is the hydrodynamic dispersion coefficient ($L^2 \cdot T^{-1}$). The dispersion coefficient is defined as $D$
Figure 5.1a Breakthrough curves measured for PFBA in homogeneously packed column; frontal portions.
Figure 5.1b Breakthrough curve measured for PFBA in homogeneously packed column.
Table 5.2. Results: Homogeneously Packed Column

| Tracer | L  | v       | R      | P       | α_L     | mass recovery % |
|--------|----|---------|--------|---------|---------|----------------|----------------|
| PFBA   | 15 cm | 25.2 cm/min | 0.85 | 10.32 [9.52-11.1] | 1.45 cm [1.35-1.58] | 101%            |
| Bromide | 15 cm | 25.2 cm/min | 0.85 | 10.69 [9.85-11.5] | 1.40 cm [1.30-1.52] | 100%            |
| HPCD   | 15 cm | 27.2 cm/min | 1.23 | 10.61 [7.78-13.4] | 1.41 cm [1.12-1.93] | 94%             |

\[ D = (D_o/\tau) + \alpha_L v, \]
where \( D_o \) is the aqueous diffusion coefficient (L^2 T^{-1}), \( \tau \) is the tortuosity factor, and \( \alpha_L \) is the longitudinal dispersivity (L). However, when velocity is greater than 1 cm/hr, \( D_o/\tau \) is usually considered negligible and the dispersion coefficient reduces to 
\[ D = \alpha_L v \]
giving a Peclet Number of \( P = L/\alpha_L \). This definition of the Peclet Number should be valid for our experiments since our experimental velocity is a factor of 25 larger than 1 cm/hr. The longitudinal dispersivity was calculated from the fitted Peclet Number, assuming \( P = L/\alpha_L \).

The calculated \( \alpha_L \) values (1.4 cm) are much larger than values measured for other sand-packed columns. For example, Hu and Brusseau (1994) report \( \alpha_L \) values of 0.04 cm for columns packed with silica-glass beads (212-300 \( \mu \)m in diameter). This may be due to the larger grain size distribution of our aquifer material (89.5% sand, 4.1% silt, and 6.4% clay) in comparison to other sand. The aquifer material was mixed prior to packing in an attempt to achieve a homogeneous packing. However the relatively large dispersivities indicate that porous media heterogeneity is present within the column.
Undisturbed Column. Breakthrough curves for transport of PFBA and $^3\text{H}_2\text{O}$ in the undisturbed cores are shown in Figure 5.2. The breakthrough curves are asymmetrical, with extended tailing compared to the homogeneously packed columns. This behavior reflects the impact of core-scale heterogeneity on solute transport. The PFBA solution had to be flushed through the column longer than the $^3\text{H}_2\text{O}$ solution in order to reach a relative concentration of one (42.3 pore volumes for PFBA versus 19.6 pore volumes for $^3\text{H}_2\text{O}$). Thus, PFBA exhibits extended tailing in comparison to $^3\text{H}_2\text{O}$, indicating an impact of solute size (diffusivity) on transport.

Although PFBA shows extended tailing in comparison to $^3\text{H}_2\text{O}$, the fronts are similar in shape and position. PFBA does not show obvious early breakthrough and increased asymmetry in comparison to $^3\text{H}_2\text{O}$, as would be expected for a system whose transport behavior is strongly influenced by diffusional mass transfer between mobile and immobile zones. The lack of obvious early breakthrough and increased asymmetry for PFBA in comparison to $^3\text{H}_2\text{O}$ indicates that the core is not a strong mobile-immobile type system. In this case, advection dominates during flow. However, the enhanced tailing of PFBA in comparison to $^3\text{H}_2\text{O}$, indicates that a diffusional mass transfer process is contributing to solute transport. This process may be associated with mass transfer between zones of lower and higher advection, rather than with diffusion between mobile and immobile zones.

Flow interruption experiments were conducted using both $^3\text{H}_2\text{O}$ and PFBA as an additional technique for examining the impact of diffusion-mediated mass transfer on transport. These experiments have an increased sensitivity in comparison to standard
undisturbed core

* tritiated water (19.6 PV)
O PFBA (42.3 PV)

Figure 5.2 Breakthrough curves measured for PFBA and tritiated water in an undisturbed column.
flow experiments for identifying the occurrence of diffusion-mediated mass transfer. During flow a nonuniform concentration distribution may develop due to a nonuniform velocity distribution (the presence of immobile zones or low permeability zones). For systems dominated by advection (residence time is short in comparison to the time necessary for diffusive mass transfer to occur or there is a relatively small amount of immobile or low permeability zones), the effect of diffusional mass transfer between the zones on transport may not be evident. However, during flow interruption there is more time for the system to reach equilibrium. As discussed above, the undisturbed aquifer core is not a strong mobile-immobile type system and therefore the occurrence of diffusion-mediated mass transfer may be more apparent during flow interruption experiments.

PFBA shows a greater percentage of rebound after the flow interruption compared to $^3\text{H}_2\text{O}$, indicating that it was farther from equilibrium due to a rate-limited diffusional process (Figures 5.3 and 5.4). Flow-interruption experiments were also conducted with PFBA at two different velocities. PFBA shows greater rebound after the flow interruption for the experiment with the larger velocity (Figure 5.4). This is consistent with the increase in the contribution of diffusion-mediated mass transfer to nonideal transport associated with increased velocity and shorter residence time. These results suggest that a diffusive mass-transfer process influenced transport in the undisturbed core. The lack of early breakthrough of PFBA during the flow experiment suggests that the system is not a strong mobile-immobile system, however the extended tailing of PFBA does indicate that a diffusional mass-transfer process is contributing to transport.
Figure 5.3 Elution curve measured for H$_2$O in an undisturbed column showing rebound following flow interruption.
Figure 5.4 Elution curves measured for PFBA in an undisturbed column showing rebound following flow interruption (two velocities).
This evidence, along with the results from the flow-interruption experiment, suggests that the nonideal transport is caused by diffusion between zones of lower and higher advection.

The breakthrough curves were analyzed using a dual-porosity model (DPM) to determine the Peclet Number (P), Omega Parameter (ω), Beta Parameter (β) and first-order mass transfer rate coefficient (α_{mt}) where the parameters are defined as:

\[ P = \frac{vL}{D} \quad (5.1) \]
\[ \omega = \frac{\alpha_{mt}L}{q} \quad (5.2) \]
\[ \beta = \frac{(\theta_a + f\rho_b K_d)}{(\theta + \rho_b K_d)} \quad (5.3) \]

and where q is the Darcy flux (L T^{-1}), \( \theta_a \) is the fraction of porosity in which advection occurs, f is the fraction of sorbent associated with the advection domain, \( \alpha_{mt} \) is the first-order mass transfer coefficient (T^{-1}), \( \rho_b \) is bulk density of the porous media (M L^{-3}), \( \theta \) is the total porosity, and \( K_d \) is the equilibrium sorption coefficient (L^{-1} M^{-1}).

The Peclet Number represents the advection related spreading. The Omega Parameter is the ratio of the effective hydraulic residence time and the characteristic time of mass transfer and represents the impact of inter-region diffusive mass transfer on transport. The larger the magnitude of Omega, the closer the system is to a condition of equilibrium between the advective and nonadvective regions, and the smaller is the impact of inter-region mass transfer on transport (e.g. less tailing). The Beta Parameter
indicates the relative size of the immobile region (e.g. Beta = 1 indicates no immobile region).

The longitudinal dispersivities calculated from the Peclet Numbers obtained using a dual-porosity approach represent the contribution of hydrodynamic dispersion, but not the effect of diffusive mass transfer related to core-scale heterogeneity. Thus, the dispersivities should be independent of diffusive mass transfer. The longitudinal dispersivities calculated from the Peclet Numbers obtained using the dual-porosity model are 0.5 cm [0.32 - 1.02] for $^3$H$_2$O and 0.7 cm [0.52 - 1.1] for PFBA. These $\alpha_L$ values cannot be considered statistically different from each other since the 95% confidence intervals overlap. These numbers are approximately 2.5 times smaller than those obtained for the homogenized column.

To calculate an apparent dispersivity, which is a function of all factors contributing to spreading, an effective Peclet Number is calculated using a method utilized by Lee et al. (1988) where:

$$\frac{1}{P_e} = \frac{1}{P} + (1-\beta)^2/\omega$$  \hspace{1cm} (5.4)

$P_e =$ effective Peclet Number

$P =$ Peclet Number obtained from dual porosity model

The values of $P$, $\beta$, and $\omega$ obtained from the dual porosity model, values of $P_e$ from equation 5.4, values of $\alpha_L$ from $\alpha_L = L/P$, values of $\alpha_a$ from $\alpha_a = L/P_e$, and values of $\alpha_{int}$ from equation 5.2 are shown in Table 5.3.
Table 5.3. Results: Undisturbed Column

<table>
<thead>
<tr>
<th>Tracer</th>
<th>P</th>
<th>β</th>
<th>ω</th>
<th>$\alpha_L$ (DPM)</th>
<th>$P_e$</th>
<th>$\alpha_s$ (cm)</th>
<th>$\alpha_{mt}$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H$_2$O</td>
<td>15.5</td>
<td>0.387</td>
<td>0.542</td>
<td>0.5[0.32-0.5]</td>
<td>1.32</td>
<td>5.8[0.8-1.87]</td>
<td>1.177[0.912-1.433]</td>
</tr>
<tr>
<td></td>
<td>[7.46-23.5]</td>
<td>[0.35-0.43]</td>
<td>[42-0.66]</td>
<td>[-1.02]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBA</td>
<td>10.8</td>
<td>0.473</td>
<td>0.277</td>
<td>0.7[0.52-0.7]</td>
<td>0.91</td>
<td>7.6[5.40-13.37]</td>
<td>0.277[0.2-0.36]</td>
</tr>
<tr>
<td></td>
<td>[6.90-14.7]</td>
<td>[0.43-0.52]</td>
<td>[20-0.36]</td>
<td>[-1.1]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The $\alpha_s$ values for the undisturbed core are five times larger than the $\alpha_L$ calculated for the homogenized column, indicating that additional processes are contributing to solute dispersion in the undisturbed core. In addition, the value of $\alpha_s$ calculated for PFBA is larger than that for $^3$H$_2$O, indicating that a diffusional mass transfer process is contributing to solute transport. Other researchers have shown that dispersivities obtained for undisturbed columns are larger than those obtained for homogeneously packed columns. For example, the dispersivity value obtained for undisturbed cores collected from the aquifer located at the Chalk River experimental site (Champ et al., 1985) is 1 order of magnitude larger than dispersivity values reported for tracer transport in columns homogeneously packed with the Chalk River aquifer material (Pickens and Grisak, 1981). The dispersivity value measured for undisturbed cores collected from the Twin Lake field experiments (Moltyaner and Killey, 1988) is about five times as large as typical longitudinal dispersivities reported in homogenous sandy porous media (Pickens and Grisak, 1981; Lee et al., 1988; Brusseau et al., 1991b; Brusseau and Rao, 1991).
In addition to examining apparent dispersivity values, values of $\alpha_{mt}$ can be compared to determine whether inter-region mass transfer is influencing transport. The first-order mass transfer coefficient is larger for $^{3}$H$_2$O than for PFBA, indicating that the $^{3}$H$_2$O system is closer to a condition of equilibrium between the zones of low and high advection during transport. For a system influenced by a diffusional mass transfer process, it is expected that the solute with the larger diffusion coefficient ($^{3}$H$_2$O) would be closer to a condition of equilibrium than the solute with the smaller diffusion coefficient (PFBA).

**Field Site.** Breakthrough curves for bromide and HPCD measured at the centerline monitoring well (four depths) and at two fully screened peripheral wells were analyzed using the methods of moments and a one-dimensional advection dispersion equation to determine Peclet Numbers using a macrodispersion approach. However, since the flow to the peripheral wells is radial, there is some uncertainty in using a one-dimensional analysis for those wells. Apparent dispersivity values were therefore not calculated for data collected at the peripheral wells. In contrast, the flow in the vicinity of a centerline monitoring well can usually be assumed to be one-dimensional (Chrysikopoulos et al., 1990). In addition, the zeroth moment (area under the breakthrough curve) for bromide ranged between 54 and 59 hours for all four ports of the centerline monitoring well. These values are very similar to the measured length of injection (56 hours), which indicates that the flow between the injection well and the centerline monitoring well is essentially ideal and unidirectional. Apparent dispersivity values were therefore calculated for the four ports of the centerline monitoring wells from.
the fitted Peclet numbers using equation 1. In this case it must be noted that the approach used assumes a constant velocity between the injection and monitoring wells, which is not the actual case. Thus, the dispersivity values are minimum values.

HPCD appears to exhibit a slightly greater degree of spreading than does bromide for all locations (see Figure 5.5 for an example). This is also indicated by the smaller Peclet Numbers obtained for HPCD (see Table 5.4). This suggests that a diffusion-mediated mass transfer process influenced solute transport during the tracer experiment.

Table 5.4. Results: Field Experiment

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>P - Bromide</th>
<th>P - HPCD</th>
<th>( \alpha_s ) - Bromide</th>
<th>( \alpha_s ) - HPCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centerline Well - M73A</td>
<td>5.15 [3.86 - 6.43]</td>
<td>2.42 [2.04 - 2.80]</td>
<td>2.30 m[1.8-3.1]</td>
<td>4.90 m[4.2-5.8]</td>
</tr>
<tr>
<td>Centerline Well - M73B</td>
<td>6.45 [6.10 - 6.80]</td>
<td>3.95 [3.72 - 4.19]</td>
<td>1.84 m[1.7-1.9]</td>
<td>3.00 m[2.8-3.2]</td>
</tr>
<tr>
<td>Centerline Well - M73C</td>
<td>2.89 [2.45 - 3.34]</td>
<td>2.44 [2.24 - 2.64]</td>
<td>4.10 m[3.5-4.8]</td>
<td>4.86 m[4.5-5.3]</td>
</tr>
<tr>
<td>Centerline Well - M73D</td>
<td>3.10 [2.82 - 3.37]</td>
<td>2.08 [1.87 - 2.28]</td>
<td>3.82 m[3.5-4.2]</td>
<td>5.70 m[5.2-6.3]</td>
</tr>
</tbody>
</table>

The apparent dispersivity values calculated for the centerline monitoring well are in the range of 2.5 m for bromide. This value is larger than dispersivity values determined for other tracer experiments that used point sampling methods. For example, Lee and Pickens (1980) report dispersivity values of 0.5 - 1.2 cm for a natural gradient tracer experiment with a length scale of 0.5 - 4.3 m. Sudicky and Cherry (1979) report
Figure 5.5 Breakthrough curves measured for bromide and HPCD at field site.
dispersivity values of 1.0 - 22.0 cm for a natural gradient tracer experiment with a length scale of 0.75 - 11.5 meters. Our values may be larger due to a larger length scale (17 m) and due to a higher degree of heterogeneity in comparison the aquifers used in other experiments. The grain sizes observed at our field site range between clay and large cobbles. Laminations at the centimeter scale and textural variations between 0.3 and 15 meters in thickness have been observed from borehole cores. In general this heterogeneity is larger than the heterogeneity associated with the Borden aquifer and Chalk River aquifer where the other field tests were conducted.

Discussion

In general the results show an increasing trend in the $\alpha_a$ as the degree of heterogeneity in the system increases. The $\alpha_L$ calculated for the homogenized columns and undisturbed columns [from the Peclet number obtained from the dual-porosity model] are similar, indicating that the contribution of hydrodynamic dispersion is similar in both cases. However the $\alpha_a$ calculated for the undisturbed column [from the effective Peclet Number] are larger than the $\alpha_L$ calculated for the homogenized column, indicating that an additional process (i.e. PNE) is affecting transport in the undisturbed column, which is consistent with the results of the diffusivity and flow-interruption experiments. The $\alpha_L$ numbers calculated for transport in the aquifer include the effect of all factors contributing to dispersion (i.e. hydrodynamic dispersion, PNE, and macrodispersion). These numbers are much larger than the values calculated for the homogenized and
undisturbed columns as is expected given the differences in scale and magnitudes of heterogeneity.

The diffusivity tracer-test method involves comparing the Peclet Numbers calculated from the breakthrough curves of different sized tracers. A larger Peclet Number for the smaller sized tracer (or the effective Peclet Numbers for systems analyzed by the dual-porosity model) would indicate that diffusion-mediated processes (i.e. PNE and macrodispersion) are affecting transport. The Peclet Numbers calculated for the homogenized column are the same (approximately 10.5) for all three tracers. This result is expected since the only factor that should be affecting transport in this system is hydrodynamic dispersion. In contrast, the effective Peclet Numbers calculated for the undisturbed column are larger for the smaller tracer (i.e. $^{3}\text{H}_{2}\text{O}$) indicating that a diffusion-mediated process (PNE) is affecting transport. The larger diffusive mass-transfer coefficient calculated for $^{3}\text{H}_{2}\text{O}$ supports this result. For the field site, the Peclet Numbers calculated for the smaller tracer (bromide) are consistently larger than the values calculated for the larger tracer (HPCD), indicating that diffusion mediated processes (PNE and macrodispersion) are affecting transport.

In summary, the results show that the diffusivity-tracer test method can be used to determine whether diffusion-mediated processes are significant at a particular site. Our results show that diffusion-mediated processes are important for both the field scale and for the undisturbed column, but not for the homogenized column. The data also shows an increasing trend in apparent dispersivities as the degree of heterogeneity increases.
CHAPTER 6. DISSOLUTION OF TCE IN HETEROGENEOUS SYSTEMS

Objective and Approach

The objective of this chapter is to examine the elution behavior of chlorinated organic compounds in two heterogeneous systems. The first system is a 2-dimensional flow cell equipped with point and vertically integrated sampling ports. The purpose of the flow-cell experiment is to examine the influence of porous media heterogeneity and DNAPL distribution on the aqueous dissolution and removal of trichloroethene during a well-controlled water flushing experiment. The influence of sampling method on the elution curves is also examined.

The second system is a source zone at a Superfund site in Tucson, Arizona. The primary objectives of the project were to characterize the transport and fate behavior of contaminants at the site, to identify the factors controlling contaminant removal for the currently operating pump-and-treat system, and to provide information useful for improving the remediation program. The project consisted of several components, including site characterization activities, field tracer experiments, laboratory experiments conducted with core material collected from the site, and mathematical modeling. The results of one component of the overall project, the contaminant monitoring, are reported herein.

Flow Cell Experiment

Materials and Methods: Experimental Apparatus. The experiments were conducted in a 2.20-m-long by 1.10-m-high by 0.053-m-wide intermediate-scale flow
cell. The flow cell has a 0.64 cm thick glass front to allow flow visualization and a 0.64 cm thick Kynar® back plate to allow for installation of sampling ports. The bottom and side pieces of the cell were made out of 2.54 cm thick stainless steel. A steel frame consisting of vertical 3.18 cm rectangular bars spaced approximately 22 cm apart, welded to 2.54 cm angle iron at the top and bottom, provided rigidity to the assembly.

The flow cell is equipped with eight "point" sampling ports, which are integrated across the 0.05-m width, and two "vertically integrated" sampling ports, which are integrated across the 0.05-m width and a 0.3-m height. The point sampling ports emulate multi-level samplers whereas the vertically integrated sampling ports emulate monitoring wells with relatively large screened intervals. The point sampling ports consist of laser-drilled stainless steel tubing (0.18-cm OD and 4.8-cm length), which are inserted through holes drilled into the Kynar® back and terminate in PEEK® push valves (Kloehn, Las Vegas). The vertically integrated sampling ports consist of three lengths of the same type of stainless steel tubing inserted through the top of the flow cell at the same X coordinate (length) but spaced evenly along the Z coordinate (width). The three tubes are connected via a manifold that terminates in a PEEK® push valve. A schematic of the flow cell, including the location of the two zones with residual TCE, injection and extraction wells, point (A-G), and vertically integrated (J-K) samplers is presented in Fig. 6.1.

An injection well and an extraction well, each consisting of 0.88 cm ID Schedule 40 PVC pipe slotted over a 71 cm length, were installed at opposite ends of the flow cell. To help reduce dead-volume, solid aluminum rods with 0.63 cm OD were placed within the PVC. A zone of pea gravel was packed around the PVC wells to ensure uniform
Figure 6.1 Schematic of flow cell.

- **Injection Well**: A
- **Zone 2**: E, G
  - 20/30-mesh sand; 9.2% residual TCE
- **Zone 1**: F, H
  - 70-mesh sand; 11.1% residual TCE
- **Extraction Well**: J

20/30 mesh sand
tracer injection. A cotton cloth sleeve was wrapped around the slots to reduce clogging. The flow cell was designed to be compatible with a state-of-the-art dual-energy gamma radiation system.

**Materials and Methods: Materials.** Bromide was chosen as the conservative tracer and TCE was the NAPL used in this study. The TCE was dyed with a hydrophobic red dye, Sudan IV, to allow visualization of the TCE phase. Fluorescein dye [sodium salt form] was used to conduct visualization experiments to help characterize the flow field. Research grade bromide, TCE, and fluorescein dye [~70% dye content] were purchased from Aldrich Chemical Company, Inc., Wisconsin. The porous media used in this study were a medium-grained 20/30-mesh and a fine-grained 70-mesh (ASTM, 1990) sand (Unimin Corporation, Le Sueur, MN). Information on the particle diameter, the uniformity coefficient, and the hydraulic conductivity of the sands is listed in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>70-Mesh</th>
<th>20/30-Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Diameter d50&quot; (mm)</td>
<td>0.724±0.031</td>
<td>0.213±0.011</td>
</tr>
<tr>
<td>Uniformity Coefficient d60/d10&quot;</td>
<td>1.210±0.034</td>
<td>1.184±0.039</td>
</tr>
<tr>
<td>Particle Density* kg/m³</td>
<td>2658</td>
<td>2657</td>
</tr>
<tr>
<td>Hydraulic Conductivity* m/s</td>
<td>1.97 X 10⁻⁵</td>
<td>1.29 X 10⁻⁵</td>
</tr>
</tbody>
</table>

Note: "Five sieve analysis were performed for each sand.
* Measured by constant head method in a 1-m-long column.
Materials and Methods: Experimental Procedures. Two distinct zones containing TCE residual were established in the flow cell. Zone 1 consisted of TCE residual within 70-mesh sand to examine the effect of preferential flow associated with physical heterogeneity. Zone 2 consisted of TCE residual within the same material as the matrix (20/30 mesh sand) to examine the effect of bypass flow associated with a localized zone of TCE saturation. The materials, except for the two zones with residual TCE, were packed under saturated conditions. The two TCE-residual zones (0.8-m-long by 0.1-m-high by 0.053-m-wide blocks) were emplaced in the flow cell as follows. First, the flow cell was packed under saturated conditions with 20/30-mesh sand to a height coincident with the lower boundary of each of the planned inclusions. The water table was then lowered until the upper 1 cm of the 20/30-mesh sand had drained. The TCE-residual zones were then emplaced within the designated locations, the space for which was maintained temporarily during the packing with vertical support slats. For each zone, the sand/TCE mixture was prepared by thoroughly mixing a pre-determined amount of dry sand with an amount of liquid TCE that would yield an approximate 10% saturation of the pore space. The amount of sand required for each zone was computed from porosities obtained for the same sands in prior experiments (Oostrom et al., 1998b). The partially saturated sand was then saturated with CO₂-gas before the water table was raised to minimize air entrapment. Based on the amount of sand and liquid TCE packed in each zone, average bulk density, porosity, and TCE saturation values were computed (Table 6.2). After packing of the cell was completed, a 1-cm-layer of a kaolinite-clay paste was placed on top of the sand to create an impermeable cap.
Relative permeabilities reported in Table 6.2 were computed following procedures based on the Burdine pore-size distribution model, discussed by Lenhard and Parker (1987). A main assumption in the computations is that the entrapped TCE is uniformly distributed over the whole pore space. Since the TCE was mixed with dry sand initially, this is not a bad assumption.

Table 6.2. Average Properties of the Two TCE Zones

<table>
<thead>
<tr>
<th></th>
<th>Zone 1</th>
<th>Zone 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Computed Gravimetrically and Volumetrically</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Bulk Density, kg/m$^3$</td>
<td>1637</td>
<td>1759</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.384</td>
<td>0.338</td>
</tr>
<tr>
<td>TCE Saturation</td>
<td>0.104</td>
<td>0.099</td>
</tr>
<tr>
<td><strong>Computed from Gamma Data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Path length, cm</td>
<td>5.29±0.08</td>
<td>5.28±0.07</td>
</tr>
<tr>
<td>Dry Bulk Density, kg/m$^3$</td>
<td>1659</td>
<td>1764</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.376±0.012</td>
<td>0.336±0.017</td>
</tr>
<tr>
<td>Initial TCE Saturation</td>
<td>0.111±0.010</td>
<td>0.092±0.011</td>
</tr>
<tr>
<td>Final TCE Saturation</td>
<td>0.101</td>
<td>0.062</td>
</tr>
<tr>
<td><strong>Burdine Pore-size Distribution Model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative permeability</td>
<td>0.71</td>
<td>0.75</td>
</tr>
</tbody>
</table>
After the flow-cell was packed and an initial set of dual-energy gamma measurements were collected, steady-state flow was established by flushing a 750 mg/L solution of CaCl₂ through the flow cell using two Masterflex peristaltic pumps. The injection and extraction flow-rates were gradually increased to and remained at 50 ± 0.7 mL/min, which corresponds to one pore volume per 14.4 hours (as measured at the extraction well). Once steady-state conditions were achieved, a one pore-volume pulse of tracer solution containing 170 mg/L of bromide was injected. The tracer experiment was conducted to qualitatively examine the potential contribution of nonuniform flow and related physical nonequilibrium and dilution-related factors on the measured TCE elution curves. Following the tracer pulse, nine additional pore volumes (130 hours) of tracer-free water were flushed through the system.

The eight point and two vertically integrated sampling ports described above and the flow-cell effluent were sampled approximately every hour for the first 2.6 pore volumes. The sampling interval gradually decreased as the experiment progressed. The point and vertically integrated ports were sampled by attaching a gas-tight ten-mL syringe with a glass barrel (Kloehn, Las Vegas or Hamilton) to the push valve connected to a particular port. A one-mL purge volume was discarded prior to taking a sample. Following the purge, a six-mL sample was withdrawn. Two mL were used to completely fill glass VOA vials with teflon-lined septum for analysis of TCE. Four mL were expelled into polyethylene scintillation vials for analysis of bromide. The elution stream was sampled by allowing the stream to completely fill the VOA vials and partially fill the polyethylene vials. The samples were chilled at 5°C prior to analysis.
Photographs were taken during the flushing experiment to visually show the removal of TCE as a function of time. A transport experiment using the fluorescent dye fluorescein was conducted in the flow-cell to qualitatively examine the uniformity of packing and the effect of the heterogeneities on the flow field. This dye enabled visualization by using ultraviolet (black) light sources. The experiment was conducted after the flushing experiment to avoid potential interaction of the dye with the porous media or NAPL phase. Steady-state flow was maintained between the flushing experiment and the dye experiment. The experiment was implemented by injecting a pulse of water containing 200 mg/L fluorescein through the flow cell at 50 mL/min, followed by continuous injection of dye-free water. Photographs were taken at regular intervals as the dye traveled through the flow cell.

**Materials and Methods: Dual-Energy Gamma Radiation System.** The fully automated dual-energy (280 mCi Americium and 100 mCi Cesium) gamma radiation system was used to determine TCE saturations in the two zones. Each zone was calibrated at 792 measurement locations according to procedures adapted from Oostrom and Dane (1990) and Oostrom et al. (1998a). The horizontal and vertical distance between measurement locations is 1 cm except where vertical support bars were present. The horizontal distance between locations at either side of a vertical support bar was 5 cm. Count rates were obtained at all locations when the flow cell was empty, filled with water, and three times when filled with saturated sand. The three times include just before the tracer solution was injected into the flow cell, after injection/extraction was terminated, and after clean up of both zones with a 4% T-MAZ-80 solution, which is an
anionic POE (20) sorbitan monooleate surfactant. Because the TCE was added to the flow cell concurrent with packing, it was necessary remove all TCE from the two zones after the tracer experiment to obtain gamma counts without liquid TCE present (i.e. background). The counting times for all scans were 60 seconds per location.

**Materials and Methods: Analytical Methods.** The TCE were analyzed at the University of Arizona using a Shimadzu Gas Chromatograph with flame ionization detector (model 14A) equipped with a Shimadzu auto injector (model AOC-17). The detection limit of the TCE was 0.3 mg/L. The bromide was analyzed at the Environmental Molecular Science Laboratory at Pacific Northwest National Laboratory using a Dionex Ion Chromatograph (model DX-500) with a suppressed conductivity detector. The detection limit was 100 μg/L.

**Results**

**Dual-Energy Gamma Measurements.** The count rates yielded path lengths, dry bulk densities, porosities, and TCE saturations at the start and end of the injection/extraction experiment, which are listed above in Tables 6.2. The average porosity and dry bulk density values computed from the gamma radiation count rates are similar to the gravimetrically obtained data. Plots of the initial and final TCE saturation distributions are shown in Fig. 6.2 a,b and in Fig. 6.3 a,b for Zone 1 and 2, respectively. In making the plots, it was assumed that each measurement location represented an area of 1 cm². The TCE values in the area behind the vertical support bars are an average of the two values obtained for the locations adjacent to each bar. The average saturations
Figure 6.2 TCE saturation distribution for zone 1.
Figure 6.3 TCE saturation distribution zone 2.
computed from gamma count rates compare well to those computed from the volume of TCE mixed into each zone. The maximum probable error in the computed TCE saturation as a result of the randomness of the gamma radiation is 0.006 (Oostrom et al., 1995).

**Tracer Transport.** The dye pulse was characterized by a sharp front as it traveled through the region upgradient of the heterogeneities, indicating uniform packing. However, the behavior of the pulse indicated nonuniform flow associated with Zones 1 and 2. The dye was delayed slightly by Zone 1 and significantly by Zone 2. Dye-free regions persisted downgradient of both zones, indicating areas of no or low flow.

Breakthrough curves measured for bromide at the two point sampling ports located upgradient from the TCE zones (Ports A and B) are shown in Figure 6.4 a,b. The bromide breakthrough curves are sharp and symmetrical indicating that packing was uniform. This is consistent with the results of the dye experiment.

Breakthrough curves measured for bromide at two point sampling ports located downgradient from zone 2 (Ports E and G) are shown in Figure 6.5 a,b. Here the breakthrough curves are smooth and symmetrical indicating ideal transport. Breakthrough curves measured for bromide at two point sampling ports located downgradient from Zone 1 (Ports F and H) are shown in Figure 6.6 a,b. In contrast to Ports E and G, at these locations the bromide breakthrough curves are asymmetrical and contain multiple peaks in the tail region, indicating that a nonuniform flow field is significantly influencing tracer transport. The degree of flow field nonuniformity associated with the region downgradient of Zone 1 would be expected to be greater than
Figure 6.4 Bromide breakthrough curves, port a (A) and port b (B).
Figure 6.5 Bromide breakthrough curves, port e (A) and port g (B).
Figure 6.6 Bromide breakthrough curves, port f (A) and port h (B).
that associated with the region downgradient of Zone 2 due to the larger difference in hydraulic conductivity between Zone 1 and the coarser matrix. This would account for the distinct difference in the shapes of the bromide breakthrough curves at Ports E and G compared to those at Ports F and H. The difference in the degree of flow field nonuniformity is supported by the results of the fluorescein dye experiment. Although the dye experiment highlighted regions of essentially no flow downgradient of both NAPL zones, the region downgradient of Zone 1 was more persistent and had sharper boundaries.

The breakthrough curve measured for bromide at the vertically integrated port downgradient from Zone 2 (Port K) is shown in Figure 6.7a. The breakthrough curve exhibits concentration tailing associated with spatially variable hydraulic conductivity, which is a common characteristic of vertically integrated samples. The breakthrough curve measured for bromide at the vertically integrated port (Port J) downgradient from Zone 1 is shown in Figure 6.7b. The breakthrough curve does not exhibit the same degree of concentration tailing that was exhibited for Port K. Although this is also a vertically integrated port, it is possible that the difference in hydraulic conductivity between this NAPL zone (low intrinsic permeability) and the surrounding sandy matrix is so extreme that almost all the water entered the port from the surrounding coarser matrix.

**TCE Elution Curves: Port E.** TCE elution curves measured at port E and F are shown in Figure 6.8 a, b. At Port E, the TCE concentration starts low (400 mg/L), then quickly increases to near solubility. The initial concentration is less than solubility because the TCE was emplaced into the flow-cell 80 hours prior to the start of the flow-
Figure 6.7 Bromide breakthrough curves, port k (A) and port j (B).
Figure 6.8 TCE elution curves, port e and port f.
field, which is not a sufficient time period to allow for equilibration of the TCE NAPL with the aqueous phase. Calculations based on diffusion of TCE indicate that only the region right next to the zones would be at solubility. Once the concentration reaches solubility, it remains at or near solubility (1100 mg/L) for the first 60 hours indicating that the water coming to the sample port is at equilibrium with TCE NAPL. This also suggests that the sample is not being diluted by lower concentrations of TCE at this time.

After 60 hours the TCE concentration begins to decrease. One potential cause of the decreasing concentration is that rate-limited mass transfer is beginning to occur and that system is no longer at local scale equilibrium. This possibility seems unlikely given that the TCE residual within the zones is still high (even at the end of the experiment there was 6.2% residual in this zone). The other possibility is that the flow-field remained the same, but TCE was preferentially removed from the outer edges of the zone. This would effectively cause the dilution factor into Port E to be increased.

There are two lines of evidence to support this theory. The gamma data shows that TCE was removed preferentially from the upper edge of the zone. Sequential photographs taken during the experiment also show that the TCE is preferentially removed from the upper zone. The upgradient and downgradient edges are removed which may be expected as the flow-field bypasses the zone and converges downgradient of the zone. The preferential removal acts to decrease the effective length of contact between the TCE zone and the water flowing by above it. Its also important to note that since the relative permeability started out at 0.75 there was significant flow through the zone at all times.
As discussed above, the bromide breakthrough curve at Port E is smooth and symmetrical indicating ideal transport. The bromide pulse traveled passed Port E in 30 hours which corresponds to the initial portion of the TCE elution curve, which is characterized by concentrations near solubility. The ideal bromide transport indicates that the flow field is uniform and therefore most of the water entering Port E during bromide breakthrough is most likely supplied by the region directly upgradient. The bromide transport is consistent with the high concentrations of TCE at Port E during the first 60 hours of the experiment. The bromide data can not be used to help explain the decrease in concentration demonstrated after 60 hours since the bromide pulse had already passed by Port E.

**TCE Elution Curves: Port F.** The TCE concentration at Port F is much lower than at Port E. This is a reasonable outcome since the intrinsic permeability and the flow of water through Zone 1 is much smaller. Although Port E and F are both point ports, samples taken at Port F are more likely to be impacted by lower concentration water coming from TCE-free regions since the overall hydraulic conductivity of Zone 1 is much less than Zone 2. Although the concentrations are lower, the data shows a similar trend with an initial pulse of high TCE concentration followed by a gradual decrease in TCE concentration. Since the change in residual saturation is small here (i.e. from 11.1 to 10.1 %) is seems unlikely that the slow decrease could be related to rate-limited mass transfer at the pore scale. The photographs and gamma data show that the TCE is removed preferentially from the top of the zone. Therefore, a similar phenomenon,
related to flow lines traveling through regions that no longer contain TCE, is likely leading to the decrease in concentration at this port.

As discussed above the bromide breakthrough curve at Port F is asymmetrical and contains multiple peaks in the tail region, indicating that a nonuniform flow field is significantly influencing tracer transport. In contrast to Port E, the bromide breakthrough curve exhibited extensive tailing at Port F that persisted through the entire TCE flushing experiment. Therefore, the bromide data can be used to help interpret the TCE elution curve even at later times. The high degree of flow field nonuniformity and related physical nonequilibrium indicated by bromide transport is consistent with the theory that the decrease in TCE concentration is due to flow lines traveling through regions which no longer contain TCE.

**TCE Elution Curves: Port K.** The TCE elution curve measured at Port K is shown in Figure 6.9. The concentration of TCE at this port is lower than that Port E, the corresponding point port. Although the concentration is approximately 1/10 of that at Port E, it follows a similar general trend. Given that the vertically averaged port extends above and below the TCE zone and is therefore diluted by TCE-free water, it is expected that the concentration at the vertically integrated would be lower than that at the corresponding point port.

**TCE Elution Curves: Port J.** The TCE elution curve measured at Port J is shown in Figure 6.10. Similar to the relationship between TCE concentrations at Port E and K, the concentration at the vertically integrated Port J is lower than that at its
Figure 6.9 TCE elution curve, port k.
Figure 6.10 TCE elution curve, port j.
corresponding point port, F. It is also approximately 1/10 of the concentration of its corresponding point port due to dilution by TCE-free water.

**TCE Elution Curves: Extraction Well.** The TCE elution curve at the extraction well is low initially, followed by a rapid increase to approximately 350 mg/L (Figure 6.11). This increase represents the arrival of the wave of high concentration TCE that formed adjacent to the zones of TCE during the no-flow period at the beginning of the experiment. The concentration returns to approximately 150 mg/L and then remains constant for the remainder of the experiment. The extraction well data may not have been effected by the same phenomena that caused the other ports to slowly decrease with time. This may be because the effect is diluted by additional TCE-free water coming into the extraction well or because the lower TCE concentration may not have arrived at the extraction well yet.

The concentration at the extraction well is lower than that at the point ports, which is expected, but higher than the integrated ports which was not anticipated. The difference can be explained by considering that when suction is placed on the integrated sampling port, a gradient is formed toward the port and the flow of water entering the port from a given region will depend on that region's hydraulic conductivity. Therefore, the sample is flux-averaged and will be biased towards areas of higher conductivity. Because the zone containing the NAPL has a lower hydraulic conductivity than the surrounding areas, its contribution will be less than its areal size would indicate. In contrast, the extraction well data represents an averaging of all the streamlines in the flow cell. Due to this difference, the elution curves at the extraction well may yield a higher
Figure 6.11 TCE elution curve, extraction well.
value of TCE concentration than the vertically integrated ports, as was the case in this experiment. In fact, a calculation shows that the TCE concentration at the extraction well may be a direct function of the concentrations directly downstream of the TCE zones. A cross section through the flow cell directly downgradient of the TCE zones, can be split into three sections; that associated with Zone 1, that associated with Zone 2, and that associated with the TCE-free porous media. The TCE concentrations associated with these sections can be approximated by 300 mg/L (Port F), 1000 mg/L (Port E), and 0 mg/L. By averaging these three concentrations and taking into account that the two TCE Zones represent about 1/3 of the height of the flow-cell, a concentration of 195 mg/L can be calculated, which is close to the concentration measured at the extraction well.

Conclusions

The results indicate that the magnitude of TCE concentration and the shape of the TCE elution curves varied as a function of location and sampling type. Initially, concentrations were relatively close to aqueous solubility (400 to 1000 mg/L) at point ports located directly downstream from the NAPL zones. At approximately 70 hours, the concentration at point ports began to decrease slowly. This slow decrease in concentration is likely related to increased dilution by low TCE concentration water as the upgradient and downgradient edges of the zones are selectively removed. The decrease is not likely related to rate-limited interphase mass transfer at the pore-scale since there is still significant mass of TCE in the zones at the end of the experiment. Although all ports demonstrated some degree of concentration tailing, the point port
located downstream from the low intrinsic-permeability zone exhibited extensive tailing with TCE concentrations remaining at ~300 mg/L at the end of flushing.

The TCE concentrations were significantly less than solubility at the corresponding vertically integrated ports (50-100 mg/L). The two vertically ports were approximately 1/10 of the concentration at their corresponding point ports. The large difference between the TCE concentrations at the vertically integrated ports and their corresponding point ports emphasizes the importance of considering the type of sampling method used when interpreting or making decisions based upon chlorinated organic compound data.

The TCE concentration at the extraction well remained fairly constant at approximately 150 mg/L following an initial pulse of high concentration water related to the no-flow period prior to experiment start. The extensive concentration tailing is typical of concentrations seen at pump-and-treat extraction wells.

In general, the less than solubility concentration at the point sampling ports is most likely caused by an increase in the amount of flow lines traveling through TCE-free regions. The relatively lower concentrations observed at the vertically integrated ports is related to dilution by TCE-free water as preferential flow around Zone 1 and flow bypassing around Zone 2 occurs. The concentration at the extraction well represents an integration of all of the system flow lines and is affected by both dilution and heterogeneity related factors. The less than solubility concentrations observed at almost all ports is, in general, caused by the nonuniform NAPL distribution and porous media heterogeneity, rather than by rate-limited interphase mass transfer at the pore-scale. The
results reinforce the concept that even at sites with aqueous NAPL concentrations that are only 1% of solubility the presence of a NAPL phase can not be ruled out.

Field Experiment

Site History. The source zone that was the focus of the study is part of the Tucson International Airport Area Superfund site in southern Arizona (Leake and Hanson, 1987). The site was placed on the National Priorities list in August 1983 in response to the detection of TCE in several wells. A large, multiple-source plume of TCE and 1,1-dichloroethene (DCE) exists in the upper portion of the regional aquifer, which is currently the sole source of potable water for Tucson. Contaminants are believed to have entered the subsurface by seepage from unlined pits and ponds used during the late 1950's to mid 1970's to dispose of organic solvents, including TCE. The study site is located within the southern part of the Superfund site, as illustrated in Figure 6.12. The study site coincides with the former location of an unlined pit (18.3 m x 3.7 m deep x 6.1 m wide), which is considered a contaminant source zone. In 1976 the pit was closed, and a percolation pond was built on top of the pit and used for several years.

Various remediation programs have been in operation at different parts of the Superfund site for several years. In 1987 a relatively large pump-and-treat groundwater remediation project, which includes 24 extraction wells and 20 recharge wells, was initiated in the southern part of the study site. The pump-and-treat system has been effective at containing the plume and decreasing its size. As of March 1998, more than 9,000 Kg of TCE have been removed from the groundwater (Hughes, 1998), and the size
Figure 6.12  Location of study site. Contours represent distribution of trichloroethene (ug/L) in groundwater prior to the start of remediation activities in 1987.
of the plume defined by TCE concentrations greater than 100 ug/L had been decreased in area by 96%. However, the system has exhibited reduced efficiency for the past several years, as illustrated by the marked tailing observed for TCE in the composite extracted groundwater entering the treatment plant (Figure 6.13). For the past seven years, the concentration of TCE has remained at approximately 100 ug/L, which is 20 times higher than the drinking water standard. In addition, concentration rebound was been observed for extraction wells located within the source zones.

Materials and Methods. A dual-well, forced-gradient tracer experiment was conducted at the site during the summer of 1996. The injection (SVE-6) and extraction well (E-14) are 57 m apart (Figure 6.14). During the tracer test, the elution of TCE and dichloroethene (DCE) was examined. The injection and extraction flow rates were 170 and 567.7 liters/min, respectively. The tracer solution was injected only into the upper portion of the Upper aquifer, but was extracted from both zones of the aquifer. Preliminary experiments indicated that the upper zone contributes 47% to total flow, which corresponds to an equivalent extraction rate of 266.8 liters/min during the tracer test. After the tracer experiment was completed, the wells were sampled for another month to monitor for rebound. Pumping at SVE-6, E-14, and other wells within the effective radius of influence of SVE-6 and E-14 was stopped 6 weeks prior to the tracer test to allow ambient, “equilibrium” conditions to be established.

Sampling for TCE/DCE was conducted at a centerline monitor well (M-73), at the extraction well, and at several monitoring wells located around the couplet. Samples were collected prior to the initiation of the experiment to establish initial concentrations
Figure 6.13  Concentration of TCE in flow entering the groundwater treatment plant; flow is a composite of all extraction wells used in the pump-and-treat system
Figure 6.14 Study site map.
for TCE/DCE. Samples at the centerline monitoring well were collected using a multi-level gas drive sampling device (Burge Environmental Inc., Tempe, AZ). Extraction well samples were collected from a port on the discharge line, and samples for the peripheral monitor wells were collected by bailing. TCE/DCE samples were collected in 20-mL volatile organic analysis vials. Samples were delivered to an on-site analytical laboratory, where they were quantified by gas chromatography (Hall detector) using standard EPA methods.

Results and Discussion. Representative elution curves for TCE/DCE are shown in Figure 6.15 a,b,c. The concentrations declined rapidly at the beginning of the experiment. However, it is clear that extensive tailing was exhibited for the duration of the experiment. For example, TCE concentrations in extraction well E-14 decreased from approximately 1600 ug/L at the start of the tracer experiment to about 300 ug/L within five days. The concentration remained at this value, however, for the remaining 63 days of the experiment, during which the equivalent of approximately 20 pore volumes of contaminant-free water was flushed through the aquifer.

Samples were collected for an additional month after the injection and extraction wells were turned off. Strong rebounding was observed for TCE and DCE (Figure 6.15 b,c). For several wells, the concentrations rebounded to levels close to, or higher than, the initial concentrations.

The relatively high aqueous concentrations, the extensive elution tailing, and the strong rebound observed for TCE and DCE during the experiment indicate the presence of a significant mass of contaminant within or adjacent to the aquifer that is acting as a
Figure 6.15a TCE and DCE elution curves at E-14 during the field tracer
Figure 6.15b TCE and DCE elution curves at E-14M during the field tracer
Figure 6.15c TCE and DCE elution curves at M72 during the field tracer test.
long-term source. This mass could be associated with the solid phase (sorbed), the low permeability zones, or with a NAPL phase. In principle, some of the observed behavior could also be related to hydraulic phenomena. For example, tailing at the extraction well could be caused in part by a continual supply of contaminant mass from outside the swept zone of the injection well. However, this mechanism is unlikely to have influenced the tailing observed at the monitoring wells, which, given the configuration of the tracer test, are located within the swept zone of the injection well. Concentration rebound observed for unconfined systems can be due, in part, to resaturation of contaminated zones that were dewatered during pumping. However, the aquifer is confined within our study area, and the screened interval of the monitoring wells remained saturated during the tracer experiment. Thus, concentration rebound associated with resaturation is not a factor for this system.

The results and discussion presented above suggest that the tailing and rebound measured during the tracer experiments were caused by factors related to contaminant transport, rather than hydraulic-related factors. In this case, the extensive tailing and rebound indicate that mass transfer between the contaminant “source” and the advecting water is rate limited.
CHAPTER 7. SUMMARY OF CONCLUSIONS

Partitioning Tracer Tests for Measuring DNAPL Saturation.

The results of the flow-cell experiment indicate that the presence of porous media heterogeneity and distinct zones of NAPL saturation lead to reduced performance (reduced accuracy) of the partitioning tracer test. The reduced performance can be improved, in part, by using depth-specific sampling. In fact, NAPL within lower intrinsic permeability zones may not be measurable by the partitioning tracer method without depth-specific sampling ports. The breakthrough curves show a strong correlation between the performance of the partitioning tracer test and the amount of nonideal transport associated with the conservative tracer data. This correlation may be used to qualitatively examine whether the values of NAPL saturation obtained by the tracer test should be considered to be underestimates due to heterogeneity and physical nonequilibrium.

Despite these results, the partitioning tracer test can still be a valuable tool for characterizing sites that may be contaminated by a NAPL phase. At sites where the presence of NAPL is suspected, but not confirmed, partitioning tracers may be useful as "detectors" of NAPL source zones. Partitioning tracers may also be useful as "performance indicators" of a chosen remedial action. Tracer tests can be conducted before, during, and after site clean-up to judge the efficacy of the remediation. Additional research in this area is certainly justified due to a continued need to characterize the large number of sites contaminated by complex and persistent NAPL phases.
Partitioning Tracer Method for the In Situ Measurement of Water Content.

The results of the experiments demonstrate that gas-phase tracer tests can be a valuable tool for characterizing the vadose zone. Conservative gas-phase tracers can be used to estimate the size of the advective pore volume, which is an important parameter in designing soil vapor extraction systems and in predicting gas-phase transport behavior. A comparative analysis of the conservative and partitioning tracer transport has the potential to provide accurate values of $\theta_w$ at the field scale. Knowledge of $\theta_w$ can be critical in a variety of applications, including crop management, flood control, and the transport of pesticides and other contaminants.

Although the mean value of $\theta_w$ obtained from the tracer tests in the lysimeter agrees with the value obtained from the gravimetric and TDR measurement, it should be noted that the R values of the partitioning tracers [1.05 to 1.13] were at the lower limit of the acceptable range. For a less-controlled experiment, a retardation factor of 1.1 may not have been statistically different from 1.0. The results demonstrate that the lysimeter provides a well-controlled setting for exploring the use of gas-phase tracer tests for measuring water content and indicate that tracer tests have the potential to accurately measure water contents for a system with uniform water content and homogeneous porous media. This method would complement both the traditional, small-scale methods and the regional [watershed] scale methods of measuring water content. The presence of nonuniform water content and porous media heterogeneity may lead to reduced performance of gas-phase partitioning tracer test and merits further investigation.
The Influence of Scale on the Dispersion of Different Sized Solutes

In general the results show an increasing trend in the $\alpha_a$ as the degree of heterogeneity in the system increases. The $\alpha_L$ calculated for the homogenized columns and undisturbed columns [from the Peclet number obtained from the dual-porosity model] are similar, indicating that the contribution of hydrodynamic dispersion is similar in both cases. However the $\alpha_a$ calculated for the undisturbed column [from the effective Peclet Number] are larger than the $\alpha_L$ calculated for the homogenized column, indicating that an additional process (i.e. PNE) is affecting transport in the undisturbed column, which is consistent with the results of the diffusivity and flow-interruption experiments. The $\alpha_L$ numbers calculated for transport in the aquifer include the effect of all factors contributing to dispersion (i.e. hydrodynamic dispersion, PNE, and macrodispersion). These numbers are much larger than the values calculated for the homogenized and undisturbed columns as is expected given the differences in scale and magnitudes of heterogeneity.

The diffusivity tracer-test method involves comparing the Peclet Numbers calculated from the breakthrough curves of different sized tracers. A larger Peclet Number for the smaller sized tracer (or the effective Peclet Numbers for systems analyzed by the dual-porosity model) would indicate that diffusion-mediated processes (i.e. PNE and macrodispersion) are affecting transport. The Peclet Numbers calculated for the homogenized column are the same (approximately 10.5) for all three tracers. This result is expected since the only factor that should be affecting transport in this system is hydrodynamic dispersion. In contrast, the effective Peclet Numbers calculated for the
undisturbed column are larger for the smaller tracer (i.e. $^{3}\text{H}_2\text{O}$) indicating that a diffusion-mediated process (PNE) is affecting transport. The larger diffusive mass-transfer coefficient calculated for $^{3}\text{H}_2\text{O}$ supports this result. For the field site, the Peclet Numbers calculated for the smaller tracer (bromide) are consistently larger than the values calculated for the larger tracer (HPCD), indicating that diffusion mediated processes (PNE and macrodispersion) are affecting transport.

In summary, the results show that the diffusivity-tracer test method can be used to determine whether diffusion-mediated processes are significant at a particular site. Our results show that diffusion-mediated processes are important for both the field scale and for the undisturbed column, but not for the homogenized column. The data also shows an increasing trend in apparent dispersivities as the degree of heterogeneity increases.

**Dissolution of TCE in Heterogeneous Systems**

The results indicate that the magnitude of TCE concentration and the shape of the TCE elution curves varied as a function of location and sampling type. Initially, concentrations were relatively close to aqueous solubility (400 to 1000 mg/L) at point ports located directly downstream from the NAPL zones. At approximately 70 hours, the concentration at point ports began to decrease slowly. This slow decrease in concentration is likely related to increased dilution by low TCE concentration water as the upgradient and downgradient edges of the zones are selectively removed. The decrease is not likely related to rate-limited interphase mass transfer at the pore-scale since there is still significant mass of TCE in the zones at the end of the experiment.
Although all ports demonstrated some degree of concentration tailing, the point port located downstream from the low intrinsic-permeability zone exhibited extensive tailing with TCE concentrations remaining at ~300 mg/L at the end of flushing.

The TCE concentrations were significantly less than solubility at the corresponding vertically integrated ports (50-100 mg/L). The two vertically ports were approximately 1/10 of the concentration at their corresponding point ports. The large difference between the TCE concentrations at the vertically integrated ports and their corresponding point ports emphasizes the importance of considering the type of sampling method used when interpreting or making decisions based upon chlorinated organic compound data.

The TCE concentration at the extraction well remained fairly constant at approximately 150 mg/L following an initial pulse of high concentration water related to the no-flow period prior to experiment start. The extensive concentration tailing is typical of concentrations seen at pump-and-treat extraction wells.

In general the less than solubility concentration at the point sampling ports is most likely caused by an increase in the amount of flow lines traveling through TCE-free regions. The relatively lower concentrations observed at the vertically integrated ports is related to dilution by TCE-free water as preferential flow around Zone 1 and flow bypassing around Zone 2 occurs. The concentration at the extraction well represents an integration of all of the system flow lines and is affected by both dilution and heterogeneity related factors. The less than solubility concentrations observed at almost all ports is, in general, caused by the nonuniform NAPL distribution and porous media
heterogeneity, rather than by rate-limited interphase mass transfer at the pore-scale. The results reinforce the concept that even at sites with aqueous NAPL concentrations that are only 1% of solubility the presence of a NAPL phase cannot be ruled out.
REFERENCES


