FIELD STUDY OF THE PARTITIONING TRACER METHOD FOR
DETECTION OF DENSE NONAQUEOUS PHASE LIQUID IN A
TRICHLOROETHENE-CONTAMINATED AQUIFER

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DEDICATION

This work is dedicated to my family and friends. Without these people and their unwavering support I would not have been able to achieve what I have or become the person I am. Most significantly this work is dedicated to mother and father.

EATON'S
PARCHMENT
LINEN
USA
BERKSHIRE
100% COTTON FIBRE

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ABSTRACT

Tracer experiments were conducted at a trichloroethene-contaminated Superfund site located in southern Arizona. Two tracers were used, SF₆ (partitioning) and bromide (conservative). Because SF₆ partitions into immiscible-liquid phases, it can be used to detect the possible presence of residual-phase (liquid) trichloroethene in the aquifer. Breakthrough curves for SF₆ and bromide were obtained at several wells located within the hydraulic influence of an injection/extraction well couplet, which was used to generate flow through a 6 m thick semi-confined aquifer 42 m below ground surface. SF₆ appears to have been used successfully as a partitioning tracer for potential detection of dense nonaqueous phase liquid (DNAPL) saturation in the aquifer. Moment analysis of breakthrough curves allowed mass recovery, retardation, and apparent DNAPL saturation to be calculated. Assuming that partitioning to DNAPL is the only mechanism for retention of SF₆, the results indicate the presence of DNAPL saturation in some portions of the aquifer.

1. INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

The contamination of soil and groundwater by hazardous organic chemicals and the associated risks to humans and the environment have become issues of great interest and importance. Much of the research motivated by subsurface contamination has been focused on dissolved constituents in aqueous systems. However, nonaqueous phase liquids (NAPLs) are also of great concern and may occur at many contaminated sites. Spills and leaks of petroleum-based liquids such as gasoline, fuel oil, and jet fuel are a major source of NAPL. Coal-tar and creosote associated with manufactured-gas plants and wood-treatment facilities are another major source of NAPL. Chlorinated solvents used in industrial and commercial activities is a third major source of NAPL. For example, it is estimated that approximately 310,200 metric tonnes of waste solvents were produced by degreasing operations (Mercer and Cohen, 1990). It is now widely accepted that NAPL saturation in the subsurface can be a long-term source of both vapor-phase and groundwater contamination.

According to the National Research Council, the presence of NAPL is the single most important factor limiting site clean-up. In fact, groundwater restoration to health-based goals is considered infeasible with existing technologies (e.g., pump and treat) at most sites contaminated by dense NAPL (NRC, 1994). The development 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, accurate risk assessments can not be made for a contaminated site without knowing if NAPL is present at the site.

Current characterization methods, such as analysis of soil gas, core sampling, cone penetrometer testing, and monitor well sampling, are often not capable of providing the level of data required for effective risk assessment or remediation planning. A major weakness of these methods is that they provide data at discrete points, such that the probability of sampling a zone of localized NAPL is quite small. In addition, data taken at discrete points within an aquifer can not accurately be used to make predictions about the overall distribution without a cost-prohibitive amount of sampling because the distribution of NAPL is complex and highly variable.

1.2 INTRODUCTION TO THE PARTITIONING TRACER METHOD

The purpose of this thesis is to explore and test an alternative, the partitioning tracer method, for measuring the quantity and distribution of NAPL in the subsurface. The partitioning tracer method is based on conducting a tracer experiment 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 can reversibly retain the partitioning tracers, which retards their transport with respect to that of the conservative tracer. Thus, retardation of the partitioning tracers indicates the possible existence of NAPL saturation somewhere within the zone through which the tracer solution moved (swept zone). When other potential sources of tracer retention, such as sorption by the solid phase, are negligible or have been accounted

for, the magnitude of the measured retardation of the partitioning tracer can be translated to a quantitative measure of the NAPL saturation.

1.3 REVIEW OF THE LITERATURE

The theoretical basis for the partitioning tracer method was established in the chromatography field by Martin and Synge (1941), who developed the liquid-liquid chromatography technique. In this technique, compounds dissolved in a mobile liquid are separated as they pass through a column containing an immobile, immiscible liquid, which retains the solutes to different degrees. The use of partitioning tracers to measure NAPL saturation in porous media was pioneered in the petroleum field as a means to determine residual oil saturation in oil fields (Cooke, 1971; Deans, 1971). Since that time, upwards of 300 hundred partitioning tracer tests have been conducted, as reviewed by Tang (1995). In the environmental field, the retention of dissolved solutes by immobile, immiscible-liquid phases and the resultant impact on solute (tracer) transport was initially described by Bouchard et al. (1989) and Brusseau (1990; 1992).

The application of this method in the environmental field will be briefly reviewed below, followed by some illustrative examples. Practical considerations as well as limitations of the method will also be discussed.

As mentioned previously, the retention of dissolved solutes by immobile, immiscible-liquid phases and the resultant impact on solute (tracer) transport was initially described by Bouchard et al. (1989) and Brusseau (1990; 1992). Using miscible-displacement experiments, Bouchard et al. (1989) demonstrated that the retardation of toluene and three

other gasoline constituents was greater when the aquifer material contained a residual saturation of aviation gas. Brusseau (1990) reported similar results for the transport of naphthalene in a column containing aquifer material contaminated with a residual saturation of tetrachloroethene. The influence of the magnitude of NAPL saturation and the magnitude of the liquid-liquid partition coefficient on the retardation of a tracer was illustrated with numerical-model simulations reported by Brusseau (1992). For example, the influence of 0, 1, and 10% saturation of a hypothetical NAPL on the transport of a hypothetical tracer is illustrated in Figure 1.

With column experiments using Ottawa sand, Jin et al. (1995) demonstrated that partitioning tracer tests using two alcohols provided good estimates of the known amount of liquid tetrachloroethene in the columns. Wilson and Mackay (1995) used sulfur hexafluoride as a partitioning tracer to successfully predict the known amounts of trichloroethene residual saturation in the columns. Bai and Brusseau (1996) examined the transport of several potential partitioning tracers through sand containing a residual saturation of hexadecane. The transport of benzoic acid is illustrated in Figure 2, where a small but measurable retardation due to partitioning into the hexadecane is evident.

The use of partitioning tracers at the field scale has recently been demonstrated at two contaminated sites. Pilot-scale field experiments involving several investigators are being conducted at an Air Force base in Utah to test the use of several alcohol tracers for measuring the amount of petroleum-based NAPL contained within 5 m by 3 m fully enclosed cells (Enfield et al, 1996). Results to date indicate that the NAPL saturation values obtained from

Figure 1: Influence of NAPL Saturation on Breakthrough Curves

Benzoic Acid

Figure 2: Retardation of a Partitioning Tracer by NAPL Residual
(Bai and Brusseau, 1996)

the partitioning tracer tests is in good agreement with values obtained from core analysis (Annable et al., 1996).

This work, as well as previous research, has used partitioning tracers to measure quantities of known NAPL contamination. However, it is feasible that partitioning tracers may also be useful as "detectors" of NAPL saturation. The purpose of this work is to test the use of partitioning tracers as detectors of potential DNAPL saturation in a trichloroethene-contaminated aquifer at a Superfund site.

1.4 INTERPRETATION OF PARTITIONING TRACER TESTS

Partitioning tracer tests can be used to detect the presence of NAPL saturation. By virtue of sampling a much larger volume of the subsurface in comparison to cores or monitoring wells, the partitioning tracer method has a much greater chance of detecting NAPL saturation. This greater effectiveness for detection of NAPL saturation is a major advantage of the method. The sensitivity of the partitioning tracer method for NAPL detection is a function of the area of influence of the tracer test (swept volume), the mass of NAPL in that swept volume, the NAPL-water partitioning coefficient of the tracer, and constraining factors (rate-limited mass transfer, heterogeneity, mass loss). If the ratio of NAPL saturation to swept volume is too small, the influence of the NAPL saturation on tracer retardation could be lost within the normal uncertainty associated with field data.

Partitioning tracer tests can also be used to measure or quantify the amount of NAPL saturation located within a target zone. The procedure for estimating S_n , NAPL saturation, involves calculation of a retardation factor, R , for the partitioning tracer, which can be done

in a number of ways, as will be discussed below. With knowledge of the NAPL-water partition coefficient (K_{nw}), soil-water partition coefficient (K_d), bulk density of the porous medium (ρ_b), and volumetric water content (θ_w), S_n can be calculated by use of:

$$R = 1 + (\rho_b/\theta_w)K_d + [(S_n)/(1-S_n)]K_{nw} \quad (1)$$

When there is negligible sorption of the tracer by the soil, $K_d = 0$ and:

$$R = 1 + [(S_n)/(1-S_n)]K_n \quad (2)$$

The magnitude of the observed retardation, and thus of S_n , is a function of the NAPL saturation-swept volume ratio. Because of factors such as bypass flow (water flows around a NAPL zone due to reduced relative permeability), rate-limited mass transfer, and mass loss, the measured S_n values may often be underestimates of the true values. Thus, NAPL saturation measurements obtained with the partitioning tracer method must, at least initially, be considered as underestimates of actual values. In addition, when interpreting the results of a partitioning tracer test, it is important to realize that the S_n values obtained from the test are "global" values, representing an averaging across the measured domain. Retardation of the partitioning tracer indicates (possible) saturation somewhere within the swept volume, but its exact location is not revealed.

The retardation factor, R , can be calculated through a comparative moment analysis of the conservative and partitioning tracers, where R is defined as the ratio of mean travel

time for the partitioning tracer breakthrough to the mean travel time of the conservative tracer. Arrival time, t_a , is defined as:

$$t_a = \frac{\sum t \bar{C}_d \Delta t}{\sum \bar{C}_d \Delta t}$$

where,

$\sum t \bar{C}_d \Delta t =$ first moment of breakthrough curve of tracer normalized concentration plotted against time.

$\sum \bar{C}_d \Delta t =$ zero-th moment of breakthrough curve of tracer normalized concentration plotted against time.

t = time of measurement (T)

$\bar{C}_d =$ average dimensionless concentration

t_a = mean arrival time, or mean residence time for an instantaneous tracer pulse (T)

When the tracer pulse is finite, the size of that pulse must be accounted for:

$t_l = t_a - \frac{1}{2}$ the pulse width

where, t_l = mean travel time, or corrected mean residence time for a finite tracer pulse.

Thus:

$$R = t_{dp}/t_{dn}$$

where,

t_{tp} = mean travel time for partitioning tracer.

t_{tn} = mean travel time for nonpartitioning tracer.

1.5 CONTRIBUTION OF AUTHOR

The contributions of the author include the main design of the partitioning tracer test, including the SF₆ injection mechanism, SF₆ sampling and handling protocol, and the analysis of water samples for SF₆. The author analyzed the SF₆ data and wrote this thesis and the appended manuscript. Significant editing and comments were made by the student's advisor, Mark L. Brusseau. Jon Rohrer managed and designed a majority of the general tracer test, including the selection of major experimental parameters and implementation of the bromide tracer test.

The following chapter describes the methods, results, and conclusions of the research. The manuscript entitled "Field Study of the Partitioning Tracer Method for Detection of Dense Nonaqueous Phase Liquid in a Trichloroethene-Contaminated Aquifer" published in Environmental Science and Technology, Volume 30, Number 9, pages 2859-2863, 1996, is appended.

2. PRESENT STUDY

The general methods, results, and conclusions of this study are presented in the paper appended to this thesis. The following includes a summary of the most important findings in the paper along with additional details of the experimental design and the analytical methods.

2.1 PROJECT ORGANIZATION

This work is part of a larger, cooperative investigation involving the U.S. Air Force, Hughes Missile Systems Co., and several University of Arizona personnel. The overall problem is that the effectiveness of the pump-and-treat system at Air Force Plant-44 has decreased in recent times. The purpose of the project is to help improve the remediation operation at Air Force Plant-44 by conducting an advanced characterization study of the site. The project includes field, laboratory, and modeling components. The specific purpose of this thesis was to design and implement a field scale test of the partitioning tracer method at Air Force Plant-44. Additional details regarding the overall project can be found in Brusseau, 1996. Information about the regional geology, plume scale hydrogeology, and bromide tracer experiment can be found in Rohrer, 1996. Information about the transport behavior of the resident contaminants can be found in Decker, 1995.

2.2 PURPOSE OF PARTITIONING TRACER TEST

The purpose of the partitioning tracer test is to determine the possible presence of liquid phase TCE within the study area. The procedure for estimating the TCE residual saturation involves calculation of a retardation factor for the partitioning tracer, which is the ratio of the velocity of the conservative tracer (bromide) to the velocity of the partitioning tracer. A retardation factor larger than one indicates that the partitioning tracer is being slowed during its passage through the aquifer most likely due to contact with a NAPL phase. Determination of the presence or absence of a NAPL phase has important remediation significance because pump-and-treat systems generally are inadequate to remove such

phases.

2.3 SITE DESCRIPTION

The tracer experiment was conducted at Air Force Plant-44 which is located in the southern portion of the Tucson International Superfund Site. A large, multi-source plume of trichloroethene and dichloroethene exists in the upper portion of the the regional aquifer where the test was conducted (Figure 3). The study site is coincident with the former location of a large unlined solvent disposal pit. A large-scale pump-and-treat system has been operating at the site for about 9 years. In addition to the pump-and-treat system, a pilot-scale soil vapor extraction system was operated in the vadose zone directed above the saturated zone wherein the test was conducted. The system removed about 1000 kg of liquid chlorinated solvents during a 2 month operation time.

2.4 EXPERIMENT DESIGN

The experimental design of the tracer experiment included the use of an extraction-injection well couplet, separated by 7.5 m (Figure 4). A multilevel sampling device was placed in a centerline monitoring well, located approximately equal distances from the injection and extraction well. The extraction well, the monitoring well, and several fully screened monitoring wells surrounding the couplet were sampled during the experiment (Figure 5). Sulfur hexafluoride was used as the partitioning tracer at a concentration of 3.9 mg/l,. Bromide was used as the conservative tracer at a concentration of 56 mg/l. Equal injection and extraction rates of 140 l/m were used to generate steady flow through a 20 ft. thick semi-confined aquifer unit beginning at 140 ft. BGS. The unit grades downward from a fine-medium sand to a clayey gravel with cobbles up to 4 inches in nominal diameter. Groundwater velocities were estimated from the conservative tracer data to range between 1 and 11 m/day during the experiment. A pulse of tracer solution was injected for 49.5 days, and consisted of 416,000 liters of solution. Following the tracer pulse, tracer free water was pumped for 58 days. The volume of tracer free water injected was 11,355,000 liters which

Pre-remediation distribution (April 1987)

Distribution (June 1994)

Figure 3: Map of TCE Plume (after Brusseau et al., 1995)

Figure 4: Site Cross Section

Figure 5: Site Map

is equivalent to 71 pore volumes . Additional experiment parameters and aquifer properties are reported in Table 1.

TABLE 1. Experiment Parameters and Aquifer Properties. ¹

Sampling Zones in M72	A: 42.4 - 43.0 m
	C: 43.7 - 44.5 m
	D: 44.5 - 45.3 m
	B: 45.3 - 50.0 m
Pre-experiment groundwater gradient	~ 0.01 meters/meter
Pre-experiment groundwater velocity	~ 0.26 m/day
Experiment groundwater velocity	0.9 to 11.6 m/day
Experiment maximum groundwater gradient	0.32 meters/meter
Average hydraulic conductivity	10 ⁻² cm/s
Average depth to groundwater	37 m
Depth lower confining unit	48.4 m
Bromide injection concentration	56 mg/l
SF ₆ injection concentration	3.9 mg/l
Bromide mass recovery at SVE7	73%
SF ₆ mass recovery (SVE7) relative to bromide	73%
Total pumpage	11,863 cubic meters
Grain size analysis (cuttings from M72: 44.2 m - 45.7 m)	
Gravel	26.4 %
Sand	65.9 %
Silt	3.0 %
Clay	4.7 %
Fraction organic carbon	0.03

¹ Data from reference 14.

A concentrated stock solution of bromide was prepared in a 4543-liter tank located near the injection well. The stock solution was then metered into the injection flow line at a rate of 1.9 liters per minute (Figure 6). Due to its high volatility, SF₆ could not be mixed

Figure 6: Tracer Injection System

in the tank with the bromide. Instead it was metered into the injection line as a gas to yield a final concentration of 3.9 mg/l (9% of solubility) (Figure 7). A stainless steel pipe with an injection port was fit into the PVC injection line. The SF_6 was then metered into the injection port through a stainless steel porous cup which caused the gas to disperse into small bubbles. The flow was controlled by a gas flow meter. Due to high summer temperatures of up to 110°F, the SF_6 gas tank was contained in a refrigerator for the two days of injection. A total of 1.6 kg of SF_6 was injected.

After both tracers were metered into the flow line, the tracer solution was injected through an approximately 39 meter long, 3.8-cm (1.5 inch) PVC pipe (schedule 40) in the injection well. A rubber packer, 19.6-cm diameter, was used to control injection into the well bore. The packer performed correctly in the laboratory and field. The packer was located 42.7 meters below ground surface, causing the solution to be injected over 6.1 meter interval (42.7 - 48.8 meters below ground surface). A constricting orifice was added to the injection pipe to avoid de-gassing of SF_6 during the injection. Two holes[0.95 cm (3/8-inch) and 0.635 cm (1/4-inch diameter)] were drilled into the PVC end cap on the injection pipe. Flows of 117.7 liters per minute and 52.2 liters per minute result from these orifice diameters at a head of 38.7 meters, for a total flow of 169.9 liters per minute (Parmley, 1992).

The depths of sampler ports and packers spacing of the multi-level sampling device are illustrated in Table 2. The zones were designated A2, C2, D2, and B2 respectively with increasing depth. Zone A2 was located in a clayey unit, zone B2 was in a fine-grained cemented material, and zones C2 and D2 were located in sandy gravelly units. The sampler was located over a vertical distance of 5.2 meters and the sample ports were approximately zone A2 - 42.7 meters, zone C2 - 44.2 meters, zone D2 - 45.1 meters, and zone B2 - 47.55 meters. The four zones had large variations in hydraulic conductivities, concentration of contaminants, and soil properties.

Figure 7: SF₆ Injection System

Table 2: Port and Packer Depth Settings.

Zone ID	Upper packer depth (meters BGS)	Sample port depth (meters BGS)	Lower packer depth (meters BGS)
A2	42.42	42.71	42.97
C2	43.75	44.15	44.55
D2	44.55	45.04	45.33
B2	45.33	47.60	---

2.5 PROPERTIES OF SF₆

Sulfur hexafluoride (M.W. = 146 g/mol) is a colorless, odorless, tasteless, noncombustible gas at room temperature. SF₆ has many of the characteristics desirable in an ideal partitioning tracer. It: (1) is nontoxic even at high concentrations (Lester and Greenberg, 1950); (2) behaves conservatively in typical sandy saturated media and in media with high percentages of organic carbon (Biggin, D.S., 1991; Wilson and Mackay, 1993 and 1996); (3) has a low, but significant octanol-water partition coefficient, K_{ow} (Wilson and Mackay, 1996); and (4) has been shown to partition into liquid-phase TCE (Wilson and Mackay, 1995). Previous tests have shown SF₆ to be resistant to chemical degradation in the presence of NH₃, F₂, Cl₂, Br₂, I₂, HCL, and elemental carbon (Mellor, 1939) and resistant to microbial degradation (Watson et al, 1991). Vapor pressures, solubility values, and dimensionless Henry's law constants are compiled in Table 3.

TABLE 3. Properties of Sulfur Hexafluoride.

Solubility	35.2 mg/l	Wilson & Mackay, 1993
Vapor Pressure	23.9 atm	Wilson & Mackay, 1993
Henry's Law Constant at 25°C	169.7 (conc./conc.)	calculated
K _{ow} to TCE at 22°C	32 ±1.33 (conc./conc.)	Wilson & Mackay, 1995
log K _{ow}	1.14±0.03 (conc./conc.)	Wilson & Mackay, 1996

Henry's Law Constant calculated as $(1 \text{ atm} \div \text{solubility}) \div RT$; R = Ideal gas constant, and T = temperature Kelvin.

2.6 SAMPLING PROTOCOL AND SAMPLE HANDLING

Because of SF₆'s high volatility special care was taken to reduce losses of SF₆ during sampling. The head of the multi-level sampler at the monitoring well and the discharge line on the extraction well were equipped with two-way valves ending in luer type fittings for SF₆ sampling and in teflon tubing for bromide and TCE/DCE sampling. A 20 ml glass syringe with an on/off valve and a luer end was attached to the luer fitting on the sample port and a sample was extracted. The 20 ml sample was then inserted from the syringe into an 80 ml aluminum aerosol canister through a specialized stainless steel fitting. The aerosol canisters were pre-evacuated by suction to form a vacuum. After the 20 mls of sample was injected, a negative pressure still existed within the canisters, which inhibited losses and allowed for an extended holding time of two months (personal communication, Tracer Research Corp, Tucson, Arizona). All 80 ml aerosol canisters were labeled and weighed prior to use. The samples were refrigerated at 10°C until analyzed. The canisters were purchased from Tracer Research Corp, Tucson, Arizona.

Five piezometers (P-6, P-7, P-8, P-9, and P-10) and well E-14 were also sampled for the tracers during the experiment. These wells were sampled by bailing. Twenty ml

glass VOA vials with teflon septums were filled approximately half-way with water from the bailer. The VOA vials were immediately capped and turned upside down. The SF_6 partitions from the water to the air phase and the layer of water hinders SF_6 's diffusion through the septum. These VOA vials were all preweighed and labeled. The samples were refrigerated at 10°C until analyzed.

2.7 ANALYSIS OF WATER SAMPLES FOR SF_6

The canisters and the VOA vials were weighted after sampling to determine the exact mass of sample added. A mass balance calculation using Henry's Constant and Henry's Law reveals that 99% of the available SF_6 mass will be in the air phase at equilibrium. Immediately prior to analysis the canisters were allowed to warm to room temperature and were pressurized with nitrogen to 16 pounds per square inch (psi) to allow headspace samples to be extracted. A 1 ul aliquot was drawn from the canister headspace and immediately injected onto the GC for SF_6 analysis. The ECD response to the air sample represents the mass of SF_6 in the air, rather than the mass in the water. When the sample is withdrawn from the canister, the air expands in response to an atmosphere of lower pressure. Both of these factors are accounted for in the following equations:

$$C_{\text{hs}} = (A)(2.02 \times 10^{-4})$$

$$C_{\text{w}} = (C_{\text{hs}})(V_{\text{hs}})/(V_{\text{w}})$$

$$C_{\text{wp}} = C_{\text{w}} + (C_{\text{hs}}/170)$$

where:

C_{hs} = concentration in the headspace.

A = ECD response area [2.02×10^{-4} = response factor for ECD calculated from a 5-point calibration curve]

C_{w} = concentration in the water not accounting for partitioning.

V_{hs} = volume of headspace = $(V_{\text{a}})(16 \text{ psi}/13.5 \text{ psi}) + V_{\text{a}}$

[the canisters were pressurized to 16 psi]

[13.5 psi is atmospheric pressure in Tucson, Arizona]

(for the VOA vials $V_{hs} = V_a$ since the VOA vials are not pressurized)

V_a = volume of air = 80 mls - V_w

V_w = volume of water = $M_f - M_i$ [assuming a density of water = 1 g/cm³]

M_i = initial mass

M_f = final mass

C_{wp} = concentration in the water accounting for partitioning.

H = henry's constant = $C_{hs}/C_w = 170$ dimensionless.

SF₆ analysis was performed at Tracer Research Corp., Tucson, Arizona on a model 3300 Gas Chromatograph with an electron capture detector from Varian Associates, Sugar Land, Texas. The GC was equipped with a 6 foot long, 1/8"OD stainless steel column with liquid phase SB-1000 1%, and solid phase Carbopack B 60/80 mesh. The ECD signal was acquired and integrated using a Spectra Physics 4400 integrator. SF₆ eluted from the gas chromatograph in 0.59 minutes, allowing quick processing of samples. Air blanks eluted at 0.41 minutes. The concentration that resulted in a peak height 3 times the back ground noise was defined as the detection limit. The height of the background at high attenuation was 0.4 cm. The lowest detectable height would be defined at 1.2 cm which corresponds to 2,570 area units and a concentration of 0.05 ug/l. The low detection limit allows for three orders of magnitude resolution when SF₆ is injected at a few mg/l.

2.8 RESULTS

Sulfur hexafluoride and bromide samples were taken at all the wells previously mentioned, but the tracers were observed only at M72, SVE7, P6, P8, and E14. A summary of the results (mass recovery and retardation of SF₆ and estimates of TCE residual saturation) are shown in Table 4.

Table 4: Mass Recoveries, Retardation Factors, and Residual Saturations.

	Mass Recovery (%) ¹	Retardation ²	S _n
M72-B	2.9	1.0	-
M72-C	11.0	1.2	0.006
M72-D	12.1	1.9	0.027
P6	53.3	1.8	0.024
P8	1.8	2.7	0.050
E14	55.1	1.0	-
SVE7	73.0	1.0	-

¹ Mass recovery of SF₆ normalized by bromide mass recovery.

² Retardation factor calculated for SF₆.

Breakthrough curves measured for bromide and SF₆ at the centerline monitoring well (M72B2) and at perimeter monitoring well (E14) are shown in Figure 8 and 9. The positions and general shapes of the SF₆ breakthrough curves are very similar to those of bromide at these locations. This indicates that SF₆ experienced no measurable sorption by the solid phase and also that its dispersive behavior was similar to that of bromide. These results are consistent with the results of laboratory experiments (Wilson and Mackay, 1993 and 1996). The non-retardation of SF₆ also indicates the absence of trapped gas phases within the aquifer that could serve as a source of retention. The data for bromide and SF₆ were analyzed by calculating the zeroth and first temporal moments to quantify mass recovery and retardation according to the procedure described above.

Breakthrough curves for bromide and SF₆ measured at two other perimeter monitoring wells (P6 and P8) are shown in Figures 10 and 11. The arrival of the SF₆ breakthrough curves is clearly delayed in comparison to bromide at these two wells. The primary question to resolve is the cause of the retardation. Given that sorption by the solid

Figure 8: M72-B Breakthrough Curve

Figure 9: E14 Breakthrough Curve

Figure 11: P8 Breakthrough Curve

phase and retention by trapped gas phases are not occurring, as discussed above, partitioning into immiscible liquid phases appears to be the only other likely process that could cause retardation of SF_6 .

There are four additional sets of data that indicate the possible presence of liquid-phase TCE within the aquifer. (1) Samples from the extraction well showed a rapid, 50% reduction in TCE concentration at the start of the tracer experiment. However, TCE concentrations did not continue to decline, even though TCE-free water was flushed through the aquifer for an additional 60 days (Brusseau, 1996)). (2) Concentrations of TCE at M72 returned to approximately the initial starting concentrations after the extraction well was turned off at the end of the tracer experiment (Brusseau, 1996). (3) During a pilot-scale soil-vapor extraction operation, several hundred gallons of liquid TCE were removed from the vadose zone directly above the saturated zone wherein our tracer experiment was conducted (Decker, 1995). The extensive tailing and rebound behavior of TCE and the large mass of TCE removed from the vadose zone are additional evidence of the possible presence of liquid-phase TCE in the aquifer and support the results of the partitioning tracer experiment. (4) The location of the tracer experiment is coincident with an identified source zone, as discussed previously. These factors are additional evidence of the possible presence of liquid-phase trichloroethene in the aquifer and support the results of the partitioning tracer experiment.

Assuming that partitioning into immiscible liquid phases is the only mechanism causing retention of SF_6 , apparent residual trichloroethene can be calculated using equation 2 for those locations where the transport of SF_6 was retarded. The values of residual saturation so obtained range from 0.6% to 5.0%. These values are at the lower range of laboratory measurements of S_n for trichloroethene in sandy media (Cohen and Mercer, 1993) and match the "large-scale average" values of about 1% reported by Poulsen and Kueper (1992) for measurements made of a controlled release of tetrachloroethene into a sandy vadose zone.

The breakthrough curves for bromide and SF₆ measured at the extraction well (SVE7) are shown in Figure 12. The curves are quite similar in shape, which again indicates similar advective and dispersive behavior. The measured retardation factor for SF₆ was 1.0. As discussed previously, the partitioning tracer method most likely provides underestimates of retardation and residual saturation values measured at an extraction well can be much smaller than those measured at monitoring wells because of the great differences in swept volumes. These factors are most likely the reason for the apparent lack of retardation measured for SF₆ at the extraction well.

2.9 DISCUSSION OF LOW MASS RECOVERY

The moment analysis data indicates lower mass recovery of SF₆ compared to bromide at all locations. Several factors may lead to low recovery, including: sampling methods (multi-level sampler vs. bailing), sample containers (glass vials vs. canisters), miscalculation of initial concentration, degassing during injection, and transport behavior of SF₆ in the aquifer.

Losses of SF₆ during sampling with the multi-level sampler (M72) could occur due to diffusion through the teflon tubing and across the air-water interface in both the sample chamber and in the tubing. Losses due to diffusion are a function of concentration gradient. Samples with higher concentration would therefore have higher losses compared to samples with lower concentrations. Since M72-B had significantly lower SF₆ concentrations than M72-C, lower losses should have been observed for M72-B. However M72-B had significantly higher losses than M72-C, indicating that the sampling method is not the main mechanism of low recovery for M72. Preliminary laboratory experiments conducted with trichloroethene indicate 92% recovery during operation of the multi-level sampler.

Two of the wells sampled by bailing showed fairly good recovery of SF₆ (E14 and P6), whereas low recovery was obtained at P8. This wide range of recoveries indicates that bailing is also not the main mechanism of loss. This is supported by results of laboratory

Figure 12: SVE7 Breakthrough Curve

experiments, which indicate less than 2% loss associated with bailing. Mass loss experiments were also conducted for both the glass vials and the aerosol canisters. These experiments indicate less than 2% loss for a one week holding time for both container types.

Initial concentration of SF_6 was calculated by mass balance of the SF_6 gas cylinder. The difference in mass of the cylinder before and after the experiment was taken to be the mass injected. This mass was then divided by the amount of water injected (based on an average flow-rate of $8.4 \text{ m}^3/\text{hour}$) to yield an input concentration of 3.9 mg/l . Assuming that all the gas that left the cylinder entered the aquifer, this is an acceptable technique for calculating initial concentration. However, if some of the SF_6 did not enter the aquifer (e.g. due to degassing in the well), this method would give erroneously low values for relative concentration and lead to erroneously low mass recovery values. However, since the extraction well had a mass recovery of 73%, no more than 27% of the low recovery can be due to potential degassing and the resultant miscalculation of initial concentration.

Another possible mechanism for the low mass recovery is the transport behavior of SF_6 in the aquifer. The liquid-liquid partitioning of the tracer is a reversible process at the microscopic scale. However, there are several processes that can cause the partitioning to appear to be nonreversible at the field scale. Consider, for example, a NAPL phase that is relatively thick in the dimension normal to water flow. When a partitioning tracer first contacts the NAPL phase, there is a concentration gradient driving the tracer into the NAPL. The concentration gradient reverses when the tracer pulse is followed by tracer-free water, which causes the tracer to transfer back to the advecting water. However, if the length of the pulse is short enough such that the tracer has not fully saturated the NAPL phase prior to the elution step, an inward concentration gradient will still exist in the interior of the NAPL phase. This could significantly delay the return of some of the tracer mass to the water. Depending on the time scale of the experiment and the nature of the NAPL, this hysteretic behavior could cause reduced mass recoveries and, thus, apparent non-reversible partitioning. Given the elimination of other possible sources of mass loss, as discussed above, the transport behavior of SF_6 in the aquifer appears to be the most likely primary cause of the

reduced mass

2.10 CONCLUSIONS

In summary, SF_6 was used successfully as a partitioning tracer in a TCE-contaminated aquifer. Moment analysis of breakthrough curves allowed mass recovery, retardation, and apparent TCE residual saturation to be calculated. Assuming that partitioning to DNAPL is the only mechanism for retention of SF_6 , the data indicates the presence of DNAPL in the area near P6, P8, and possibly M72. The data does not indicate the presence of DNAPL between the injection well and E14. The lack of significant retardation at SVE7 does not negate the presence of DNAPL within its zone of capture, since it is an extraction well and therefore integrates across the entire domain. Future laboratory and field experiments will be conducted to elucidate the effect of rate-limited mass transfer and porous-media heterogeneities on the behavior of partitioning tracers.

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APPENDIX

Field Study of the Partitioning Tracer Method for Detection of Dense Nonaqueous Phase Liquid in a Trichloroethene-Contaminated Aquifer

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Field Study of the Partitioning Tracer Method for Detection of Dense Nonaqueous Phase Liquid in a Trichloroethene-Contaminated Aquifer

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Introduction

Dense nonaqueous phase liquids (DNAPLs) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both vapor-phase and groundwater contamination. Successful remediation and effective risk assessment of DNAPL-contaminated sites is limited by the behavior and current site characterization techniques. DNAPL sources are difficult to identify because they are denser than water, can migrate below the water table, and move along pathways that may be distinct from the direction of water flow. Furthermore, DNAPL is often present as residual saturation and is difficult to observe in soil or groundwater samples. A major weakness of current characterization methods, such as soil-gas analysis, core sampling, and groundwater sampling, is that they provide data at discrete points, and thus the probability of sampling a zone of localized DNAPL saturation is quite small. In addition, given the heterogeneity typical of field sites, constructing an accurate, comprehensive map of DNAPL distribution is usually cost prohibitive using such point values.

A new method of site characterization for NAPL involves the use of partitioning tracers. Partitioning tracers have been employed since the 1970s in the petroleum industry to determine residual oil saturations (1–3). Recently, partitioning tracers have been used successfully to measure NAPL saturations in environmental systems. In column experiments with Ottawa sand, Jin et al. (4) demonstrated that partitioning tracer tests using alcohols provided good estimates of the known amount of liquid tetrachloroethene in the columns. In column experiments with aquifer sand, Johnson and Mackay (5) used sulfur hexafluoride to successfully predict the known amounts of trichloroethene residual saturation in the columns. Pilot-scale field experiments involving several investigators are being conducted at an Air Force base in Utah to test the use of several alcohol tracers for measuring the amount of petroleum-based NAPL

FIGURE 1. Illustration of the impact of NAPL residual saturation on the transport and retardation of a partitioning tracer. Figure from Brusseau (8).

contained within 5 m by 3 m fully enclosed cells (6). Results to date indicate that transport of some of the alcohols is retarded with respect to that of the nonreactive tracers (7).

All of the research referenced above involved the use of partitioning tracers to measure quantities of *known* NAPL contamination. However, it is feasible that partitioning tracers may also be useful as “detectors” of NAPL saturation. The purpose of this work is to test the use of partitioning tracers as detectors of potential DNAPL saturation in a trichloroethene-contaminated aquifer at a Superfund site.

Theory

The experimental and theoretical basis for the retention of dissolved solutes by immobile, immiscible liquid phases and the resultant impact on solute (tracer) transport have been described previously (4, 8). Organic fluid phases reversibly retain the partitioning tracer, which retards the tracer's transport with respect to that of conservative tracers. To illustrate, the influence of three quantities of residual saturation on the transport of a partitioning tracer is shown in Figure 1. These breakthrough curves were produced using a model developed by Brusseau (8).

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 moment analysis with the conservative tracer. The retardation factor is defined as the mean travel time of the partitioning tracer divided by the mean travel time of the conservative tracer. With knowledge of the NAPL–water partition coefficient (K_{nw}), soil–water partition coefficient (K_d), bulk density of porous media (ρ_b), and volumetric water content (θ_w), S_n can be calculated by use of

$$R = 1 + (\rho_b / \theta_w) K_d + [(S_n) / (1 - S_n)] K_{nw} \quad (1)$$

When there is negligible sorption of the tracer to the soil, $K_d = 0$ and

E 2 Tracer Parameters and Aquifer Properties^a

Monitoring zones in M72

	42.4–43.0
	43.7–44.5
	44.5–45.3
	45.3–50.0
Experiment groundwater gradient (m/m)	~0.01
Experiment groundwater velocity (m/day)	~0.26
Experiment groundwater flow direction	west
Experiment groundwater velocity (m/day)	0.9–11.6
Experiment max groundwater gradient (m/m)	0.32
Hydraulic conductivity (cm/s)	10^{-2}
Depth to groundwater (m)	37
Thickness of lower confining unit (m)	48.4
Tracer injection concn (mg/L)	56
Tracer injection concentration (%)	3.9
Tracer mass recovery at SVE7 (%)	73
Mass recovery (SVE7) relative to bromide (%)	73
Tracer pumpage (m ³)	11863
Tracer size analysis (cuttings from M72): 0.2–45.7 m)	
Gravel (%)	26.4
Sand (%)	65.9
Silt (%)	3.0
Clay (%)	4.7
Fraction of organic carbon (%)	0.03

^aData from ref 14.

Immediately capped and turned upside down. The SF₆ concentrations from the water to the air phase and the layer of soil hinders diffusion of SF₆ through the septum. All samples were refrigerated at 10 °C until analyzed.

Analysis of SF₆ was performed at Tracer Research Corp., Phoenix, AZ, using a gas chromatograph with an electron capture detector (Model 3300, Varian Associates, Sugar Land, TX). The GC was equipped with a 1.85 m long, 0.32 mm i.d. stainless steel column with liquid phase SB-1000 and solid phase Carbowax B 60/80 mesh. The ECD signal was acquired and integrated using a Spectra Physics integrator. The detection limit for SF₆ is approximately 0.1 µg/L using this method. The low detection limit allows for orders of magnitude resolution when SF₆ is injected into the aquifer at a few milligrams per liter.

Results and Discussion

Tracer Transport. Breakthrough curves measured for bromide and SF₆ at the centerline monitoring well (M72-B) and at a perimeter monitoring well (E14) are shown in Figure 3. The positions and general shapes of the SF₆ breakthrough curves are very similar to those of bromide at these locations. This indicates that SF₆ experienced no measurable sorption to the solid phase and also that its dispersive behavior was similar to that of bromide. These results are consistent with the results of laboratory experiments (10, 11). The retardation of SF₆ also indicates the absence of trapped gas phases within the aquifer that could serve as a source of retention. The data for bromide and SF₆ were analyzed by calculating the zeroth and first temporal moments to quantify mass recovery and retardation (e.g., ref 4), which are reported in Table 3.

Breakthrough curves for bromide and SF₆ measured at other perimeter monitoring wells (P6 and P8) are shown in Figure 4. The arrival of the SF₆ breakthrough curves is significantly delayed in comparison to bromide at these two wells. A primary question to resolve is the cause of this retardation. Given that sorption by the solid phase and

FIGURE 3. Breakthrough curves for SF₆ and bromide at selected monitoring wells: (A) centerline monitoring well M72-B and (B) perimeter monitoring well E14.

retention by trapped gas phases are not occurring, as discussed above, partitioning into immiscible liquid phases appears to be the only other likely process that could cause retardation of SF₆.

There are four additional sets of data that indicate the possible presence of liquid-phase trichloroethene within the aquifer. First, samples from the extraction well showed a rapid, 50% reduction in trichloroethene concentration at the start of the tracer experiment. However, the concentration did not continue to decline, even though trichloroethene-free water was flushed through the aquifer for 60 days (14). This is equivalent to 71 pore volumes given the flow rate and zone of influence associated with the well. With measured retardation factors of less than 2 for trichloroethene, this extensive tailing is not likely a result of sorption/desorption processes alone.

Second, concentrations of trichloroethene at M72 returned to approximately the initial starting concentrations after the extraction well was turned off at the end of the tracer experiment (14). Third, during a pilot-scale soil-vapor extraction operation conducted for several months (~2 months operating time), about 1000 kg of liquid chlorinated solvent were removed from the vadose zone directly above the saturated zone wherein our tracer experiment was conducted (15). Fourth, the location of the tracer experiment is coincident with an identified source zone, as discussed previously. These factors are additional evidence of the possible presence of liquid-phase trichlo-

the initial concentration of SF₆ was calculated by using a mass balance for the SF₆ gas cylinder. The change in mass of the cylinder before and after the experiment was considered to be the mass injected. This was then divided by the amount of water injected to obtain an input concentration of 3.9 mg/L. Assuming that the gas that left the cylinder entered the aquifer, this is an acceptable technique for calculating initial concentration. However, if some of the SF₆ did not enter the aquifer (due to degassing in the well), this method would give artificially low values for relative concentration and lead to artificially low mass recovery values. However, given the minimum observed mass recovery of 73% (SVE7), no more than 27% of the reduced recovery can be due to potential partitioning and the resultant miscalculation of initial concentration.

Another possible cause of the reduced recovery is the transport behavior of SF₆ in the aquifer. The liquid-liquid partitioning of the tracer is a reversible process at the microscopic scale. However, there are several processes that can cause the partitioning to appear to be nonreversible at the field scale. Consider, for example, a NAPL phase that is relatively thick in the dimension normal to water flow. When a partitioning tracer first contacts the NAPL phase, there is a concentration gradient driving the tracer into the NAPL. The concentration gradient reverses when the tracer pulse is followed by tracer-free water, which causes the tracer to transfer back to the advecting water. However, if the length of the pulse is short enough such that the tracer has not fully saturated the NAPL phase prior to the elution step, an inward concentration gradient will still exist in the interior of the NAPL phase. This could significantly delay the return of some of the tracer mass to the water. Depending on the time scale of the experiment and the nature of the NAPL, this hysteretic behavior could cause reduced mass recoveries and, thus, apparent non-Fickian partitioning. Given the elimination of other possible sources of mass loss, as discussed above, the transport behavior of SF₆ in the aquifer appears to be the most likely primary cause of the reduced mass recoveries. In summary, SF₆ appears to have been used successfully as a partitioning tracer for detection of potential DNAPL contamination in a trichloroethene-contaminated aquifer. Breakthrough analysis of breakthrough curves allowed mass recovery, retardation, and apparent DNAPL saturation to be calculated. Assuming that partitioning to DNAPL is the dominant mechanism for retention of SF₆, the results indicate the possible presence of DNAPL saturation in some portions of the aquifer. Future experiments will be conducted to

substantiate these results and to examine the effect of rate-limited mass transfer and porous media heterogeneities on the behavior of partitioning tracers.

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