Partitioning Tracer Tests for Evaluating Remediation Performance

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Abstract

Partitioning tracer tests (PTTs) are being used in environmental systems for the detection and estimation of nonaqueous phase liquid (NAPL) saturations in contaminated aquifers. A series of such studies was recently conducted at Hill Air Force Base, Utah, in two hydraulically isolated test cells of an aquifer contaminated by light nonaqueous phase liquids (LNAPL). These experiments were performed before and after two remediation efforts, a complexing sugar flush (CSF) and a recirculating in-well aeration (IWA) system. The breakthrough curves obtained from monitoring tracer concentrations in the extraction wells indicated the presence of an immiscible phase, and the LNAPL saturation values determined from the pre- and post-PTTs allowed the estimation of remediation efficiencies for both test cells. These remediation efficiencies, a removal of 43% of the LNAPL for the CSF and an increase of 32% for the IWA system, are consistent with data obtained from cores collected from within the experiment zones. The apparent increase in contamination for the IWA cell is likely due to a significant change in the LNAPL distribution caused by the flow system associated with the IWA technology. Several factors influenced the interpretation of the PTT data. Physical heterogeneities at the site caused significant tailing of the tracer concentrations and required the use of a simple extrapolation technique to account for the concentrations below analytical quantification limits. Degradation affected selected nonreactive and reactive tracers, causing the overestimation and underestimation of LNAPL saturations, respectively.

Introduction

The presence of nonaqueous phase liquids (NAPLs) in subsurface systems has been and is a significant problem for many contaminated sites. These slightly soluble organic liquids can dissolve into ground water and volatilize into the soil gas, thereby greatly increasing the volume of contaminated media. Furthermore, considering the various constraints to mass transfer and the generally low maximum contaminant levels, NAPLs have proven to be long-term sources of subsurface contamination (National Research Council 1994).

Light nonaqueous phase liquids (LNAPLs) are less dense than water and tend to float along the top of the capillary fringe. However, fluctuations in the water table can create a "smear zone" of residual NAPL entrapped within the upper portions of the saturated zone. Although this type of NAPL contamination allows easier detection with traditional site characterization techniques, there can still be significant uncertainty as to the volume of LNAPL present and the full extent of contamination. Dense nonaqueous phase liquids (DNAPLs), being denser than water, can migrate downward to depths well below the water table. In the saturated zone, DNAPLs can exist as pools and discrete isolated ganglia, or "residual" DNAPL, and can migrate large distances from the source zone in directions dominated by site geology rather than ground water flow.

These factors cause NAPLs to be extremely difficult to detect and quantify in the subsurface with traditional "point estimate" means of site characterization, such as soil coring, ground water sampling, and soil gas surveys. These methods sample a relatively small volume of the subsurface. Thus, a large number of samples are required to accurately characterize a given domain. More spatially extensive site characterization methods, such as geophysical techniques, are often difficult to use as a means of determining the amount of NAPL present without first knowing the initial geophysical properties of the site before it was contaminated.

Partitioning tracer tests (PTTs), originally developed in the petroleum industry for the characterization of oil reservoirs, have been proposed as a means to characterize NAPL-contaminated sites (Jin et al. 1995; Wilson and Mackay 1995; Nelson and Brusseau 1996). This method uses suites of chemical tracers to detect the presence of a NAPL phase and provide an estimate of its effective saturation (S_n) or volume within the swept zone of a flow field. The term "swept zone" refers to the volume of aquifer that is contacted by the tracer pulse during the course of the test. This characterization technique has a principal advantage of detecting and quantifying the amount of NAPL in a much larger portion of aquifer, compared with point-sampling methods.

The PTT method appears to have great promise for enhancing our ability to characterize NAPL-contaminated sites. Furthermore, by comparing the results of tests conducted before and after the operation of a remediation project, the extent of remediation achieved by a given technology can be quantified. However, the efficacy of the method may be constrained by many factors. For example, rate limited mass transfer, heterogeneities, and solute degradation can all impact the estimation of NAPL saturations. The PTT method needs to be evaluated under different field conditions to determine the extent to which its performance is influenced by such factors. The purpose of this paper is to present an analysis for an LNAPL- contaminated site, with a specific focus on the importance of site heterogeneity, solute degradation, and type of remediation system upon the determination of LNAPL saturations.

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Interwell partitioning tracer tests were conducted during the summer of 1996 at operable unit one (OU1) in Hill Air Force Base, Utah, before and after the application of a cyclodextrin complexing sugar flush (CSF) and an in-well aeration (IWA) system. These tests were performed as one means by which to determine the extent of LNAPL removal accomplished by each technology. The remediation systems were operated within two hydraulically isolated test cells. Additional details of the cyclodextrin flushing experiment are presented elsewhere (McCray and Brusseau 1998; Brusseau et al. 1999a; McCray et al. 1999). Details of the IWA experiment are presented in Blanford et al. (1999). The surficial aquifer at the site is heavily contaminated with a complex LNAPL mixture comprising numerous organic compounds ranging from petroleum products to chlorinated solvents. The primary purpose of conducting the partitioning tracer tests was to provide an estimate of the effective LNAPL saturation within each test cell. A comparison of the saturations determined from PTTs conducted before and after remediation efforts provided a measure of the amount of LNAPL removed, or a remediation efficiency. For comparison purposes, core materials collected before and after the remediation systems were also used to estimate contaminant removal. The performance, accuracy, and problems encountered during the application of the partitioning tracer method are addressed herein.

Theory and Analysis Techniques

Although partitioning tracer studies can also be conducted in the vadose zone (commonly with an advecting gas phase), the theory presented here will focus on their use in the saturated zone. Partitioning tracer theory is based on the chromatographic separation of two or more selected tracers as they travel with the advecting ground water through a NAPL-contaminated aquifer. The tracers are typically injected as a single pulse, and the degree of temporal separation occurring between the solutes at monitoring locations is dependent on the extent of reversible partitioning of the tracers between the advecting water and the immobile NAPL phase. In essence, the partitioning of the tracers into the NAPL phase retards their transport.

To produce the greatest degree of separation between tracer pairs and gain greater knowledge of the physical properties of the aquifer, sets of nonreactive (nonpartitioning) and reactive tracers are commonly used. When comparing the travel time of a partitioning tracer to that of a nonreactive tracer, the degree of effective NAPL saturation can be calculated from the ratio of tracer travel times, or the retardation factor of the reactive tracer:

$$\frac{t_p}{t_n} = R = 1 + \left(\frac{\rho_b}{\theta_w}\right) K_d + \left[\frac{S_n}{(1 - S_n)}\right] K_{nw} \qquad (1)$$

where t_p = the travel time of the partitioning tracer, t_n = the travel time of the nonpartitioning tracer, ρ_b = bulk density of porous media, θ_w = water-filled porosity, K_d = water-aquifer solids partition coefficient, K_{nw} = NAPL-water partition coefficient, and S_n = effective NAPL saturation. Given that the partitioning tracers were selected such that the K_{nw} values are much greater than the K_d values for this site, it is assumed that sorption, the second term on the right-hand side of Equation 1, can be neglected. This assumption is further supported by the fact that the large volume of LNAPL present at this site would cause NAPL-water partitioning to dominate solute retardation. A more detailed description of the equations describing partitioning tracer theory can be found in Brusseau (1992) and Jin et al. (1995).

A more general approach, based on using multiple partitioning tracers, can be given in terms of tracer travel times. Solving for S_n, the equation becomes

$$S_n = \frac{t_2 - t_1}{t_1 (K_{nw2} - 1) - t_2 (K_{nw1} - 1)} \qquad (2)$$

where t_1 = the characteristic travel time for each tracer. Note that when a nonreactive tracer is used, K_{nw1} is zero, and the equation simplifies.

The volume of NAPL present in a contaminated aquifer can be calculated by multiplying S_n by the total void volume (V_t) [L^3] of the tracer test's swept zone. The total void volume of the swept zone is defined as the water-filled pore volume (V_w) plus the NAPL-filled pore volume (V_n). It is often useful to calculate V_n values when determining the remediation efficiency for a site. If contaminant mass removal is large, the change in the swept zone between pre- and post-partitioning tracer tests can be significant. Comparing the volume of NAPL removed to the change in V_w helps determine if the total swept volume of the study changed. This information will help indicate whether the post-PTT flow regime adequately reproduced that of the pre-PTT.

Tracer travel times are usually determined by moment analysis of tracer breakthrough curves for each sampling location. The travel time of a tracer is defined as the first normalized temporal moment of the breakthrough curve (T) minus one-half the time of injection. Early reports of partitioning tracer studies in the petroleum industry suggest that the "first arrival" of a tracer or "landmarks" selected along a breakthrough curve can also be used as characteristic transport times (Cooke 1971; Deans 1971; Tang 1992, 1995). However, these methods, while useful in some applications, are sensitive to nonideal transport and variations in experimental conditions and, therefore, are rarely used for complex, heterogeneous sites.

Due to the effects of physical heterogeneities and rate-limited mass transfer between NAPL and aqueous phases, it may be difficult for the tracers to be completely flushed from the system. Thus, the elution wave of breakthrough curves can exhibit extensive tailing. A substantial portion of the tail of the breakthrough curve can be below analytical detection and quantification limits. If this "lost" tracer mass is not included in the moment analysis, the first temporal moment for the curve will be erroneously small, and the resultant saturation estimate will be incorrect. This effect is more severe for solutes that have experienced greater degrees of nonideal transport. In the analysis presented herein, it was necessary to extrapolate the curves of all tracers to "zero concentration" by fitting an exponential function to the final portions of the breakthrough curves using an approach as discussed by Skopp (1984) and Pope et al. (1994). The technique essentially consists of the linear extrapolation of the breakthrough curves when expressed in log-linear format. Only the final portion of the measured data was used to calculate the best-fit equation because the change in tracer concentrations did not always follow an ideal exponential decline.

This simple approximation method produced the most consistent and reliable NAPL saturation values. The correction technique can be applied to data collected under different conditions, includ-

Table 1
Representative Components of Site LNAPL

Benzene	Trichloroethane
Decane	Trichloroethylene
Dichlorobenzene	Trimethylbenzene
Ethylbenzene	Undecane
Naphthalene	m,p-Xylene
Toluene	o-Xylene

ing systems with homogeneous conditions and equilibrium mass transfer. However, changes in travel times will likely be minimal for the latter case. More detailed discussions on the application of PTTs can be found in several references (Jin et al. 1995, 1997; Brusseau et al. 1996b; Annable et al. 1998a, 1998b; Brusseau et al. 1999b; Nelson et al. 1999; Young et al. 1999).

It should be recognized that the mechanisms causing tailing in heterogeneous porous media, especially at the field scale, are often complex processes that may be difficult to adequately fit with a simple log-linear function. Numerical models can also be used to estimate tracer travel times and solute concentrations at late study times (e.g., Jin et al. 1997); however, care must be taken to ensure that the model fits are acceptable and the model assumptions are valid for the experimental system. Furthermore, data from field systems may not produce tracer profiles that are readily described by traditional, simplified transport codes. Thus, the log-linear extrapolation technique serves as a simple means to extend the use of moment analysis for calculating tracer travel times.

Experimental Conditions

The partitioning tracer tests were conducted in a surficial aquifer consisting of interbedded sand and gravel alluvium with silt and clay stringers. From tracer test results, the average hydraulic conductivity for the test cells is 4.5×10^{-2} cm/s. The water-filled porosities for the CSF and IWA cells are 0.2 and 0.18, respectively. A thick clay confining unit, located approximately 8 m below ground surface (bgs), underlies the alluvium, and provides a relatively impermeable barrier for the base of the cells.

Both test cells are located in the vicinity of a former chemical disposal pit and within the boundaries of the site's former fire training facility. Consistent with its operational history, the complex NAPL at the site is composed of petroleum hydrocarbons from JP-4 jet fuel and various chlorinated hydrocarbons. A listing of a representative set of "target" NAPL components is presented in Table 1. The LNAPL was readily collected from extraction wells that intersected pools. Water table fluctuations have smeared the LNAPL into a thick residual zone that extends to the confining unit.

A schematic of a test cell is provided in Figure 1. The 2.7 × 4.6 m cells were created by driving corrugated steel sheet piling into the underlying clay unit and grouting the interlocking joints of the piles to prevent leakage. Each test cell was leak tested by raising the water level within the cell above that of the surrounding water table and then monitoring the head difference for several days. The water table exterior to the cell remained at approximately 6.25 m bgs during the tracer tests. The cells were positioned such that the direction of flow within the cell was aligned with the natural ground water gradient. A line of four injection wells and a line of three extraction wells were installed along opposite ends of each cell

Table 2
Test Cell Properties and Experimental Summary

Site geology	Deltaic alluvium with braided channels Sand and gravel with silt lenses Clay confining unit located 8.25 m bgs
Cell porosity/pore volumes	CSF cell: 0.20 / ~8500 L IWA cell: 0.18 / ~5500 L
Average hydraulic conductivity	~ 4.5×10^{-2} cm/s
Cell dimensions	2.7 m × 4.6 m (plan view)
Saturated thickness	CSF cell: 3 m IWA cell: 2 m
Cumulative flow rates	CSF cell: 3.8 L/min IWA cell: 3 L/min
Tracers (concentrations in mg/L)	CSF pre-PTT: bromide (291), ethanol (1017), hexanol (983), 2,2-dimethyl-3-pentanol (531) CSF post-PTT: bromide (304), ethanol (1081), hexanol (871), 2,2-dimethyl-3-pentanol (619), 6-methyl-2-heptanol (604) IWA pre-PTT: bromide (370), ethanol (997), hexanol (946), 2,2-dimethyl-3-pentanol (395) IWA post-PTT: Pentafluorobenzoic acid (PFBA) (262), ethanol (1107), hexanol (991), 2,2-dimethyl-3-pentanol (406), 6-methyl-2-heptanol (604)
Tracer pulse volumes	CSF pre-PTT: 1230 L (0.15 pore volumes) CSF post-PTT: 1325 L IWA Post-PTT: IWA post-PTT: 871 L (0.16 pore volumes) IWA pre-PTT: 871 L (0.16 pore volumes)

using auger drilling methods. All wells were 5.1 cm in diameter and consisted of PVC casing above the water table, and 3.05 m of stainless steel 0.010 slot screen spanning the saturated thickness. The bottoms of the wells were set evenly along the top of the clay confining unit.

Saturated thicknesses of approximately 3 m and 2.1 m were maintained within the CSF and IWA test cells, respectively. Peristaltic pumps (Cole Parmer Master Flex I/P with Tygon LFL tubing) with separate heads for each well were used to generate flow. Equal injection and extraction flow rates of 3.8 Lpm for the CSF cell and 3 Lpm for the IWA cell were maintained, with the flow divided evenly among the three extraction wells and four injection wells. Flowmeters (Dwyer, 3.8 Lpm capacity), periodically calibrated at discharge points, were used to help maintain constant flow rates for each well. Tracer-free water was flushed through the cells for approximately two pore volumes (Table 2) to establish steady-state conditions. The tracer pulses were then injected followed by the injection of tracer-free water once again. A constant flow rate was maintained during the flow establishment, tracer injection, and water flushing portions of each test.

A listing of the cumulative flow rates, nonreactive and partitioning tracers used, injection concentrations, and tracer pulse sizes for both test cells is presented in Table 2. Note that bromide and PFBA (pentafluorobenzoic acid) were used as the primary nonreactive tracers. Similar to bromide and PFBA behavior, ethanol transport was not retarded by the LNAPL. However, significant loss of ethanol mass occurred, presumably due to biodegradation. Hexanol and 2,2-dimethyl-3-pentanol (DMP) were the partitioning tracers for the preliminary PTTs. However, degradation of hexanol

Table 3
NAPL-Water Partition Coefficients

Tracer	CSF Cell Values	IWA Cell Values
PFBA	0.0	0.0
Bromide	0.0	0.0
Ethanol	~0.0	~0.0
Hexanol	2.52	2.44
2,2-dimethyl-3-pentanol	8.60	7.77
2-methyl-6-heptanol	27.8	—

prohibited its use for determination of LNAPL saturations. During the post-technology PTTs, 6-methyl-2-heptanol was also used as a partitioning tracer. This compound has a higher partition coefficient than the other tracers and would be expected to more accurately detect and measure the reduced volumes of LNAPL remaining in the cell after application of the CSF remediation technology. However, 6-methyl-2-heptanol was not used to estimate LNAPL saturations for the IWA system post-PTT because the large volume of LNAPL still present retarded the tracer's breakthrough such that complete breakthrough was not achieved. The tracer pulses were approximately 0.15 and 0.16 pore volumes for the CSF and IWA cells, respectively.

Samples collected from the tracer tests were placed in chilled coolers and shipped overnight to the University of Arizona. Ethanol, hexanol, DMP, and 6-methyl-2-heptanol were analyzed using a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID). Direct liquid injection of 1 μL aliquots was performed on an SPB-624 capillary column (Supelco), 0.53 mm, 30 m long. The analytical quantification limit for all of the alcohols was approximately 0.5 mg/L. Bromide was analyzed using a colorimetric analysis method. Pentafluorobenzoic acid was analyzed using a Waters HPLC unit equipped with a UV-Vis detector. A Phenomenex Luna 5 μ C18(2) column (150 × 1.40 mm) was used in the analysis. The analytical quantification limit for both bromide and PFBA was approximately 0.1 mg/L.

The NAPL-water partition coefficients, determined for each tracer using batch methods, are presented in Table 3. Free-phase LNAPL collected from the site was placed in contact with a tracer solution at a known initial aqueous-phase concentration. The samples were then placed in a rotater for approximately 24 hours. Each sample was centrifuged in an inverted position at 2400 rpm for 20 minutes to separate the two phases. A glass syringe with sampling needle, used to pierce the vial septa, allowed for subsampling an aqueous aliquot of the final tracer solution. The equilibrium aqueous phase tracer concentration compared to the respective initial tracer concentration was then used to determine the partition coefficient.

Results and Discussion

Complexing Sugar Flush Test Cell Results

A 10% solution of cyclodextrin, a complexing sugar, was used in the CSF test to significantly enhance the solubilities of the LNAPL constituents. Detailed analysis of the results indicated that solubility enhancement of NAPL components, and not mobilization, was the primary mechanism of mass removal (McCray and Brusseau 1998). The solubility enhancement of the various chemical species constituting the site's LNAPL mixture varied substantially among the target compounds; however, it was assumed that changes in the composition of the bulk LNAPL were small enough that the partition coefficients could be considered constant. Approximately eight pore volumes of cyclodextrin solution were pumped through the cell at the same flow rate as the tracer tests and using the same well configuration. The cell's saturated thickness was maintained at approximately 2.5 m for both the PTTs and the CSF.

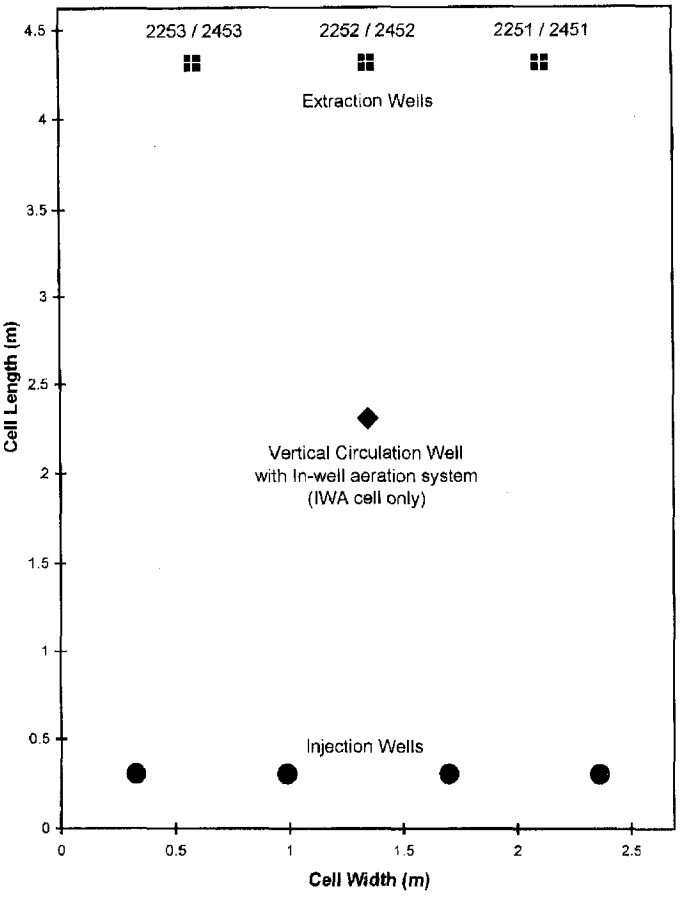

Figure 1. Schematic of a test cell.

Examples of the tracer breakthrough curves for the three extraction wells are presented in Figure 2. Clearly, these solute profiles demonstrate that the transport of the partitioning tracer (DMP) was retarded relative to the nonreactive tracer. It is not as apparent that the partitioning tracers exhibited less retention in the post-PTT than in the pre-PTT. Nonetheless, moment analysis of the data does produce such a decrease in the retardation of the reactive tracers. Note that moment analysis includes the entire portion of the breakthrough curve, not just the arrival and elution fronts. Often, a significant portion of a tracer's mass can be within the long elution tail at late study times; thereby significantly increasing the travel time of the solute. Thus, it is important to consider the entire breakthrough curve distribution before drawing conclusions regarding the degree of retardation in separate tracer tests.

Mass loss, presumably due to biodegradation, prohibited the use of several tracers for the accurate estimation of NAPL saturations. The mass loss observed for ethanol (nonpartitioning) and hexanol (partitioning) caused overestimation and underestimation of S_n values, respectively. The most reliable tracer pair in the preliminary PTT (pre-PTT) consisted of bromide as the nonreactive tracer and 2,2-dimethyl-3-pentanol (DMP) as the partitioning tracer. This pair was also included in the post-PTT tracer suite and again proved dependable. The partitioning tracer, 6-methyl-2-heptanol, included in the post-PTT, also provided robust results. All three of

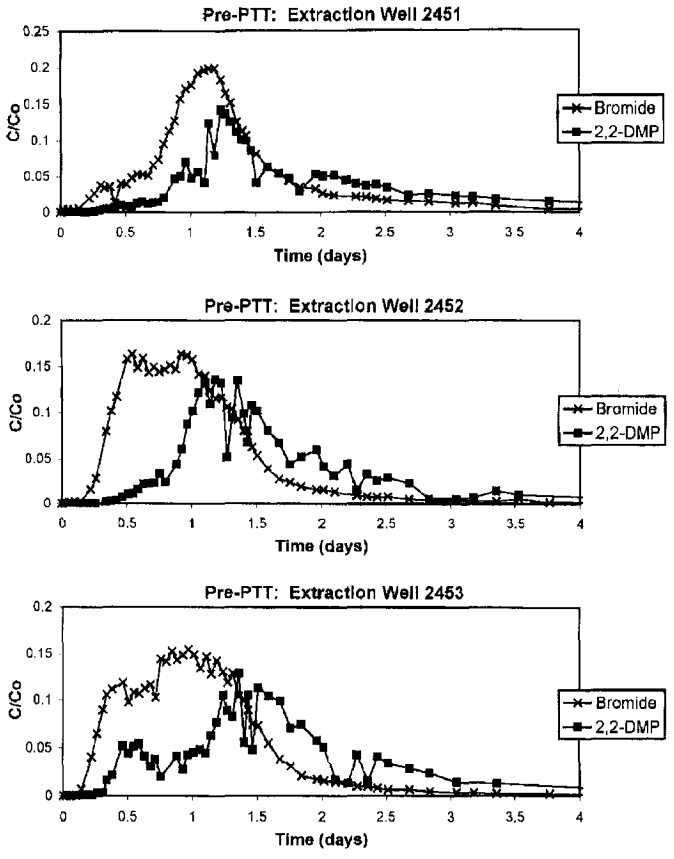

Figure 2a. CSF cell pre-partitioning tracer test breakthrough curves.

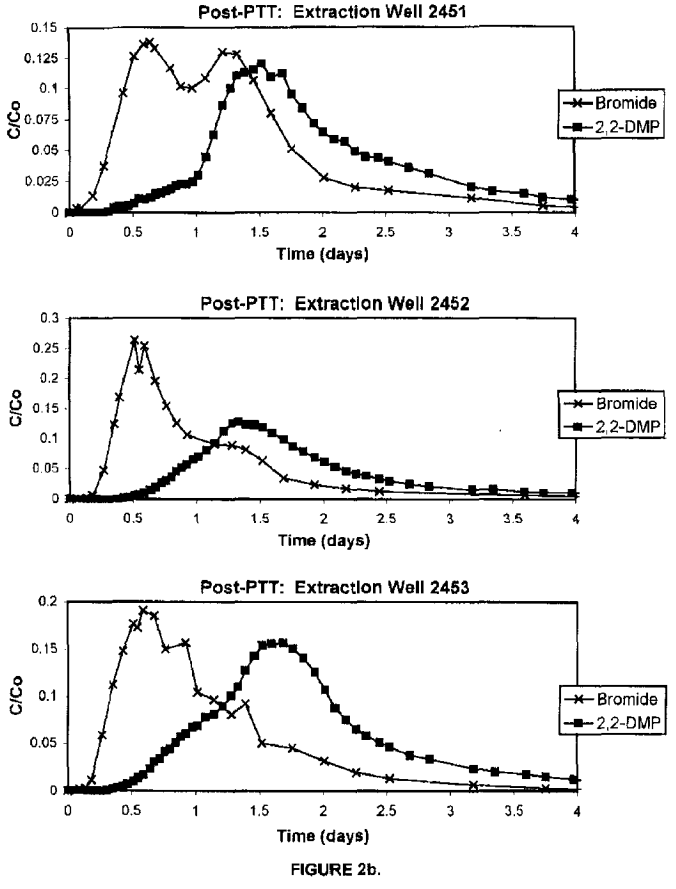

Figure 2b. CSF cell post-partitioning tracer test breakthrough curves.

Table 4
CSF Test Cell LNAPL Saturation Values (S_n)

Pre-Technology Partitioning Tracer Results

Extraction Well	Tracer Pair	S_n	Cell-Averaged S_n[3]
2451	Bromide/DMP[1]	10.1%	
2452	Bromide/DMP	12.9%	**12.1%**
2453	Bromide/DMP	14.8%	

Post-Technology Partitioning Tracer Results

Extraction Well	Tracer Pair	S_n	Well-Averaged S_n	Cell-Averaged S_n
	Bromide/DMP	5.7%		
2451	Bromide/M-Hept.[2]	6.1%	6.1%	
	DMP/M-Hept.	6.6%		
	Bromide/DMP	7.9%		
2452	Bromide/M-Hept.	7.3%	7.2%	**7.0%**
	DMP/M-Hept.	6.5%		
	Bromide/DMP	7.7%		
2453	Bromide/M-Hept.	7.7%	7.7%	
	DMP/M-Hept.	7.8%		

[1]DMP = 2,2-deimethyl-3-pentanol
[2]M-Hept. = 6-methyl-2-heptanol

$$^{3}S_{n,\text{cell averaged}} = \sum_{i=1}^{3\ \text{wells}} S_{n,i}\left[\frac{\left(\frac{V_{w,i}}{(1-S_{n,i})}\right)}{V_t}\right]$$

these tracers had recoveries above 90%.

Data from the PTTs were used to calculate a single S_n per extraction well for the pre-PTT and three separate S_n estimates per extraction well for the post-PTT. The determination of multiple S_n estimates for the post-PTT is due to the use of two partitioning tracers instead of one. This allows the separate determination of an S_n value by comparing the results obtained from each partitioning tracer with those of the nonreactive tracer, and also by comparing the results obtained for the two partitioning tracers. The post-PTT S_n values were averaged arithmetically for each well to produce a "well-averaged" value. For all of the tests, a "cell-averaged" value was determined as the weighted average of the three individual-well values. This calculation was done by weighting the S_n value determined for each well by the fraction of total void volume accessed by the tracer sampled at each well. Note that the total void volume includes both the water-filled pore volume and the NAPL-filled pore volume. This weighting method was deemed appropriate because the three extraction wells in both cells exhibited substantial differences in swept volumes.

The NAPL saturation values for the CSF test cell, as well as an equation describing the above weighting method, are presented in Table 4. The value of S_n varied somewhat with the tracer pair used in the calculations for the post-PTT. However, the maximum range in values did not exceed 20% of the well-averaged saturation. Local S_n values, determined from total organic carbon (TOC) analysis of soil core material collected during preliminary coring activities, ranged from 11.9% to 17.6% saturation. Note that as

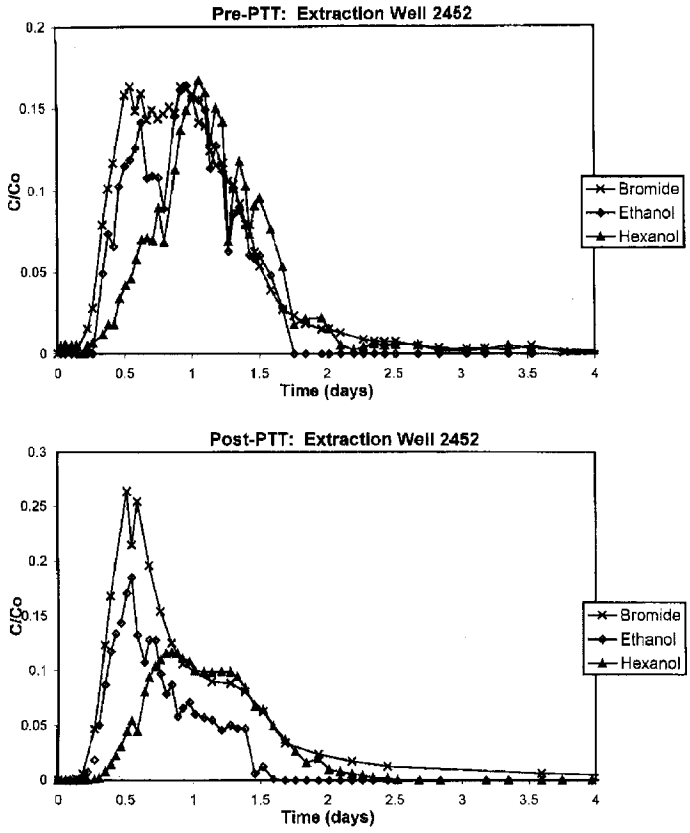

Figure 3a. Mass loss of ethanol and hexanol in CSF cell.

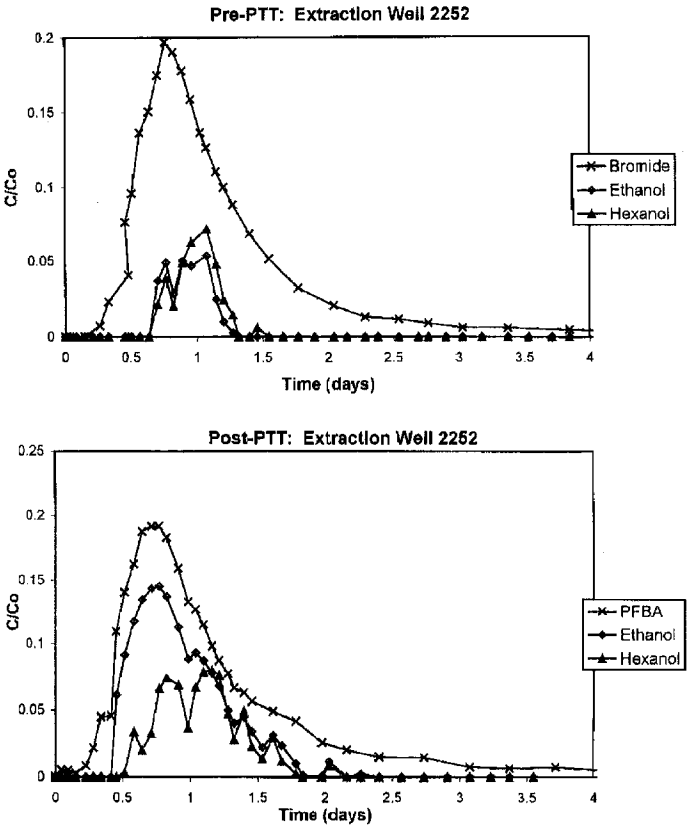

Figure 3b. Mass loss of ethanol and hexanol in IWA cell.

Table 5
Effect of Tracer Mass Loss on LNAPL Saturation Values for CSF Test Cell

Extraction Well	Tracer Pair	% Recovery of Degraded Tracer	S_n	Cell-Averaged S_n
Pre-Technology Partitioning Tracer Results				
2451	Ethanol*/DMP	47%	20.6%	**18.9%** (12.1%)
2452	Ethanol*/DMP	76%	17.5%	
2453	Ethanol*/DMP	55%	17.4%	
2451	Bromide/Hexanol*	71%	4.9%	**11.4%** (12.1%)
2452	Bromide/Hexanol*	84%	17.6%	
2453	Bromide/Hexanol*	77%	14.8%	
Post-Technology Partitioning Tracer Results				
2451	Ethanol*/DMP	48%	16.7%	**19.6%** (7.0%)
2452	Ethanol*/DMP	46%	22.5%	
2453	Ethanol*/DMP	54%	19.8%	
2451	Ethanol*/M-Hept.	48%	12.6%	**14.7%** (7.0%)
2452	Ethanol*/M-Hept.	46%	16.3%	
2453	Ethanol*/M-Hept.	54%	15.4%	
2451	Bromide/Hexanol*	57%	–7.0%	**–7.0%** (7.0%)
2452	Bromide/Hexanol*	53%	–9.9%	
2453	Bromide/Hexanol*	70%	–4.1%	

(LNAPL saturation values from nondegraded tracers in parentheses)
*Degraded tracer.

expected, these values bracket the cell-averaged value of 12.1% obtained from the preliminary PTT. Furthermore, the range of local S_n values determined by TOC analysis compares well with the range of pre-PTT values for individual extraction wells, 10.1% to 14.8%. These results suggest that the partitioning tracer method provided robust estimates of NAPL saturation.

As was discussed, these tests allowed a much larger volume of aquifer to be characterized relative to more traditional means of NAPL quantification. Accordingly, it should be noted that the NAPL saturation estimates derived from the extraction well breakthrough curves are reflective of the entire swept volume of the contaminated zone. Thus, Sn values determined from the PTTs are effective values that represent entire cell pore volumes (in the case of cell-averaged values). Core data from the site indicates that the majority of the LNAPL mass is within the first few feet of the saturated zone. Therefore, it is probable that the NAPL saturation values for localized points decrease significantly with increasing depth below the capillary fringe. Thus, it is to be expected that localized portions of the test cell may exhibit NAPL saturation levels both greater and less than the "cell-averaged" values.

A comparison of the water-filled pore volumes for the pre- and post-PTTs reveals an increase of 592 L. This increase in the volume of water can be primarily explained by the reduction in NAPL volume of 484 L associated with the CSF. Water table fluctuations, improved access to previously isolated portions of the contaminated aquifer, and experimental uncertainty likely account for the remainder of the difference in the tracer-measured volumes.

The estimates of NAPL saturations obtained from the preliminary and final PTTs were used to determine a remediation efficiency for the cyclodextrin flushing technology. From the results of the partitioning tracer tests, the CSF reduced the effective NAPL saturation from 12.1% to 7.0%. This corresponds to a 43% decrease in the volume of LNAPL within the test cell. This volume (or mass) removal percentage compares well to the 41% contaminant-removal value

Table 6
IWA Test Cell LNAPL Saturation Values (S_n)

Extraction Well	Tracer Pair	S_n	Cell-Averaged S_n
Pre-Technology Partioning Tracer Results			
2251	Bromide/DMP[1]	9.7%	
2252	Bromide/DMP	9.3%	8.9%*
2253	Bromide/DMP	7.4%	
Post-Technology Partitioning Tracer Results			
2251	PFBA[2]/DMP	16.7%	
2252	PFBA/DMP	7.7%	11.7%**
2253	PFBA/DMP	14.0%	

[1]DMP = 2,2-dimethyl-3-pentanol.
[2]PFBA = pentafluorobenzoic acid.
*Note: Without the biotracer correction, the pre-PTT cell averaged S_N value was 4.3%.
**Note: Without the biotracer correction, the post-PTT cell averaged S_N value was 6.0%.

derived independently from analysis of core samples collected before and after cell remediation (Brusseau et al. 1999a; McCray and Brusseau, 1998). This indicates that the PTT method provided an accurate measure of the change in NAPL saturation within the cell and suggests that it produced robust estimates of saturation.

As previously stated, ethanol and hexanol experienced significant mass loss during the tests. Previous studies conducted at this site also experienced similar degradation of these compounds (Annable et al. 1998b). Given the nature of these compounds, and considering the test cell was completely enclosed and monitoring did not detect cell leakage, the majority of the mass loss was attributed to biodegradation. The loss of mass for these tracers is readily visible in Figure 3. Often, the elution waves of the breakthrough curves were degraded to levels below detection limits, which resulted in reduced tailing compared with the mass-conservative tracers. This loss of tracer mass at later times caused a shift in the normalized first moment, or travel time, of the tracers. From Equation 2 it is readily apparent that shifts in the characteristic transport times of the tracers have an impact on the calculation of effective NAPL saturations. The effect of tracer biodegradation on S_n determination for the CSF cell is presented in Table 5.

The use of ethanol as a nonreactive tracer yields travel times that are erroneously small, thereby, given Equation 2, producing S_n values that are erroneously large. Likewise, the use of hexanol as the partitioning tracer (and bromide as the nonreactive tracer) yields travel times that are erroneously small, producing average S_n values that are erroneously small. In the case of the post-PTT, the negative values indicate that the travel time of hexanol was smaller than that of the nonreactive tracer. The large degree of uncertainty in travel times derived from data influenced by degradation supports the careful selection of tracers for a microbially active site.

IWA Test Cell Results

A standard IWA system creates a vertical flow field that brings contaminated ground water into the lower portion of a dual-screened vertical circulation well, which is equipped with an in situ air-stripping system. Volatile contaminants are stripped from the ground water into a gas phase that is drawn out of the well casing into a contaminant collection system. The treated water then moves back into the aquifer through an upper screen. Note that this sys-

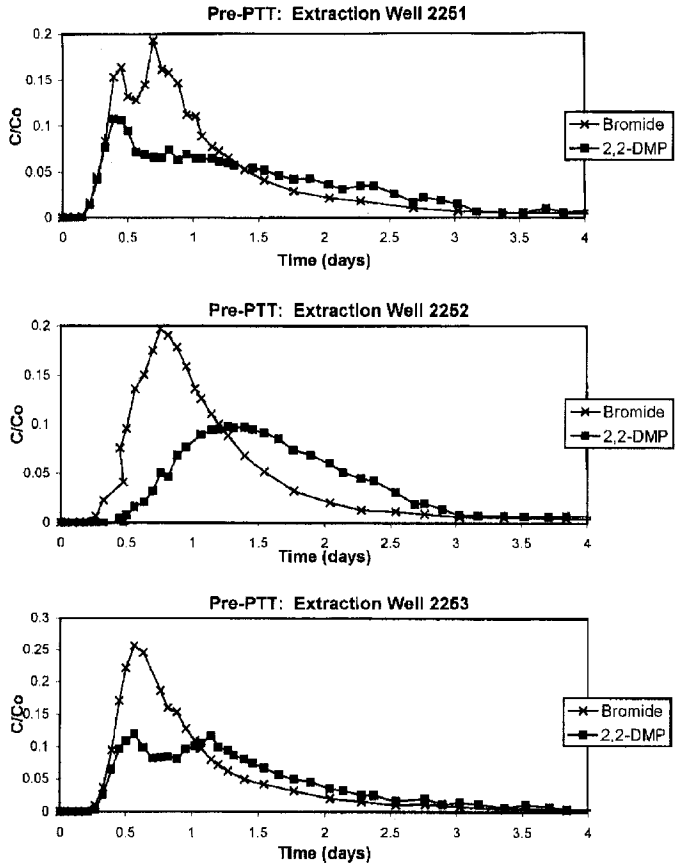

Figure 4a. IWA cell pre-partitioning tracer test breakthrough curves.

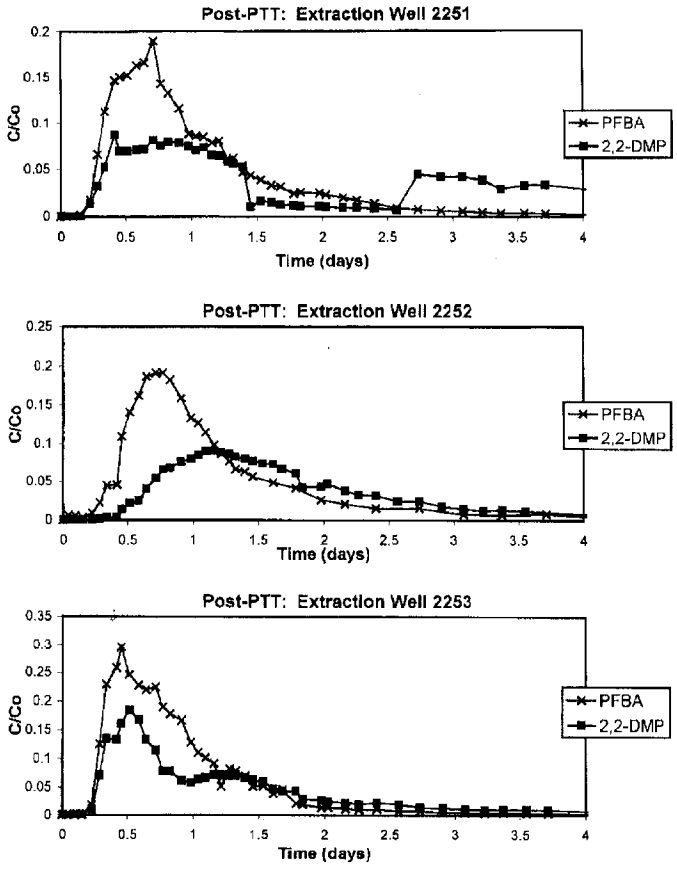

Figure 4b. IWA cell post-partitioning tracer test breakthrough curves.

tem does not enhance the solubilities of the LNAPL components, nor is it designed to mobilize the LNAPL to the well and volatilize it. Due to the low solubilities and dissolution rates of many organic compounds, the remediation efficiency of this technology was expected to be much lower than that of the CSF.

The IWA well was operated for 62 days at an estimated flow rate of approximately 5 L/min. The average saturated thickness of the test cell was maintained at approximately 2.1 m during the study. However, during the operation of the IWA unit, significant water table mounding was observed near the IWA well.

Examples of tracer breakthrough curves measured for the three extraction wells are presented in Figure 4. The use of PFBA as an additional nonreactive tracer during the IWA post-PTT was the only significant difference between the tracer suites used for the two cells (Table 2). Once again, the transport of the reactive tracers was retarded relative to the nonreactive tracers. Note that for well 2251 during the post-PTT, portions of the breakthrough curves for DMP exhibit anomalous behavior between 1.4 days and 2.7 days. Accordingly, the results from this well are considered to be uncertain. The mass loss of hexanol and ethanol again prevented their use in S_n estimation. For the IWA cell PTTs, the most reliable tracer pairs were bromide (94% recovery) and DMP (82% recovery) in the pre-PTT and PFBA (100% recovery) and DMP (75% recovery) in the post-PTT. Analytical problems prohibited the use of bromide as a nonreactive tracer for the post-PTT. The breakthrough curves were analyzed in the same manner as that for the CSF cell, and cell-averaged S_n values were weighted as described earlier.

The LNAPL saturation values for the IWA test cell are presented in Table 6. Note that for this test cell there is an increase in the cell-averaged S_n from the pre-PTT to the post-PTT. Given that the test cells were separated from the surrounding contaminated aquifer, there is no apparent mechanism for an actual increase in NAPL volume within the cell. However, as previously stated, the operation of the IWA remediation system created significant vertical flow and caused temporal fluctuations in the elevation of the water table. It is possible that these flow transients altered the NAPL distribution. Thus, the post-technology PTT may not have experienced the same conditions as the pre-PTT. This inconsistency between tracer tests may constrain the accurate determination of a remediation efficiency.

The IWA system created a vertical flow field by drawing contaminated water through a lower screen and reinjecting "stripped" water through an upper screen. This single-well flow field is substantially different from the horizontal flow system associated with the PTTs. During the operation of the IWA a large mound of water, initially a 1.2 m rise, was created at the centrally located IWA well, and large volumes of LNAPL, up to 0.4 m in depth, were subsequently detected with a dual-phase liquid level probe in the seven tracer study wells. These observations suggest that significant quantities of LNAPL were mobilized and pooled during the operation of the IWA system. The detected change in the distribution of the LNAPL is also reflected in the results of the PTTs and may explain the changes in well-averaged S_n values between the pre-PTT and post-PTT.

The total volume of LNAPL detected by the post-PTT was 215 L greater than that detected by the pre-PTT. The total water-filled pore volume (swept volume) for the post-PTT was 200 L greater than that of the pre-PTT, which was primarily due to slightly higher water levels (approximately 1 cm) during the post-PTT. If the increase in LNAPL volume is due solely to the rise in water levels, without any change in NAPL distribution, an effective S_n of approximately 53% would be required for the additional pore volume accessed in the post-PTT. It seems unlikely that a 1 cm vertical increase in the saturated thickness of the post-PTT would have such a large, and previously undetected, volume of LNAPL. Because LNAPLs tend to float along the top of the capillary fringe, any minor fluctuations in the capillary fringe would cause a similar vertical movement of the floating LNAPL. Thus, it would be unlikely that much "undetected" LNAPL would be brought into contact with the advecting ground water for such a minor change in the level of the saturated zone. Furthermore, because the test cell was isolated from the surrounding aquifer, it is not feasible that additional LNAPL entered the cell from the surrounding aquifer during the remediation study. Thus, it is probable that it was the IWA flow system that altered the LNAPL distribution and caused a larger portion of the LNAPL to be accessible to the flowlines of the post-PTT. This finding suggests that the design of a partitioning tracer study to determine a remediation efficiency should include a flow system similar or identical to that of the remediation technology. If this condition is not met, the results of the tracer study could reflect regions of the aquifer not accessed by the technology, or vice versa. Likewise, if the remedial system significantly alters the distribution of the NAPL, it would be difficult if not impossible to directly compare post remediation data with that of a pre-PTT.

Pore volumes and S_n values for individual wells further support this argument. Preliminary PTT results indicate an increasing trend in the well-averaged NAPL saturation values from well 2253 to well 2251 (west to east). However, unlike the CSF tracer tests, the same trend is not seen in the results from the post-PTT. Instead, the well-averaged S_n values are much larger for the two corner extraction wells and smaller for the middle well. The S_n values for the two extraction wells closest to the cell walls (wells 2251 and 2253) increase from 9.7% to 16.7% and 7.4% to 14.0%, respectively, while the S_n for the central extraction well (2252) is reduced from 9.3% to 7.7%. These values may reflect the observed preferential redistribution of the floating LNAPL from the relatively uniform initial distribution to a nonuniform distribution wherein it accumulated at the sides of the cell. The large initial mounding of water in the center of the cell caused the LNAPL to flow downward to the corners and sides of the test cell. This shift in LNAPL distribution is also reflected in the increased swept volume of the central extraction well (2048 L to 2784 L) and the reduced swept volumes of the corner wells (1800 L to 1500 L for well 2251 and 1519 L to 1270 L for well 2253).

The change in the LNAPL distribution is further supported by data obtained from analysis of core samples. There was a 27% increase in the weighted average contaminant mass based on comparing core samples collected before and after cell remediation (Blanford et al. 1999). This increase compares well with the 32% increase in cell-averaged LNAPL saturations obtained from the PTTs (from 8.9% to 11.7%).

The effect of tracer mass loss on estimated S_n values was also significant for the PTTs conducted in the IWA test cell. Severe degradation of the organic solutes necessitated the use of a correction technique to accurately estimate the first moments for DMP, the least degraded tracer. Included in the suite of tracers injected into the post-PTT were two tracers that were to be used to characterize biodegradation (Brusseau et al. 1999c). These "biotracers," benzoate and salycilate, were then used to determine a linear best-fit equation

describing the percent change in the solute's first moment, or travel time, versus percent degradation. This equation provided a consistent and site-specific means to account for the impact of biodegradation on the tracer data. The effects of tracer biodegradation and the biotracer correlation technique are noted in Table 6. While it is better to select tracers that will not undergo significant mass loss during transport, the use of a biotracer correction may allow the calculation of a reasonable estimate of S_n from tracer data influenced by biodegradation. It should be noted that this technique is limited. Severely degraded tracers, such as ethanol and hexanol in these experiments, can exhibit so much mass loss that they fall outside of the range of the biotracer correction correlation.

Conclusions

The use of interwell partitioning tracer tests at Operable Unit One in Hill AFB, Utah, to determine remediation efficiencies for a complexing sugar flush and an in-well aeration system provided results of varying usefulness. The PTT-derived remediation efficiency for the CSF test was similar to the value determined using core samples. This is encouraging, as the partitioning tracer method adequately characterized the cell, while minimizing the use of invasive measures that could have disturbed or spread the subsurface contamination. However, while the absolute LNAPL saturations and their relative decreases or increases agree in magnitude with independent analyses based on core materials, it is clear that careful analysis of the breakthrough curves is required to produce reliable results. Furthermore, it is important to consider the many possible problems when planning, conducting, and analyzing the results of a partitioning tracer study.

Site heterogeneity as well as rate-limited partitioning between the NAPL and aqueous phases can cause tailing of solute breakthrough curves. For this site, the degree of heterogeneity within the test cells was large relative to the scale of the experiment. Thus, it was necessary to extrapolate all of the tracer response curves to zero to produce results that were more consistent and accurate. Biodegradation precluded the use of several tracers for determining NAPL saturations. The historical presence of hydrocarbons in the subsurface appears to have produced an active population of microbes that readily used both contaminants and partitioning tracers as a carbon source. The loss of mass from the tails of the breakthrough curves caused erroneous saturation estimates. Only the branched alcohols had mass recoveries large enough to be useful in moment analysis. For the IWA system post-PTT, even the branched alcohols underwent significant biodegradation, and "biotracer" correction of the first moments was necessary for estimation of NAPL saturations.

Finally, the operational specifics of the remediation system should be considered when planning a partitioning tracer study. The CSF was conducted using the same wells, flow alignment, flow rates, and water levels as the PTTs. Thus, both PTTs accessed essentially the same volume of the contaminated aquifer. Furthermore, no additional LNAPL was mobilized into or out of the swept zone of the tracer tests. Accordingly, the remediation efficiency determined from the PTTs (43%) corresponded closely to that determined by extensive core collection and analysis (41%). Conversely, the IWA system mobilized large volumes of LNAPL, as seen in both the partitioning tracer data and dual-phase probe measurements. This substantial change in the LNAPL distribution likely caused the apparent increase in contaminant mass.

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