Environ. Sci. Technol. **1998**, *32,* 3574−3578

NAPL Compositional Changes Influence Partitioning Coefficients

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Partitioning interwell tracer tests (PITTs) that were developed by the petroleum industry are being used to characterize the extent and amount of subsurface contamination by nonaqueous phase liquids (NAPLs). A promising application of PITTs is to estimate the volume of contamination removed by various remediation technologies by conducting the tests before and after remediation efforts. Laboratory experiments with a light NAPL from Hill Air Force Base, UT, the site of the SERDP demonstration of innovative technologies, indicate that the type of remediation technology used changes the partitioning of the tracer compounds between the NAPL and the aqueous phase. Partitioning coefficients (K_{nw}) that were measured by static and dynamic methods showed a statistically significant change in value after the NAPL was treated in batchwise washes with a cosolvent that simulated enhanced dissolution. In contrast, the value of K_{nw} showed little change before and after the NAPL was treated in a column with a cosolvent that simulated mobilization. The results indicate that PITTs could significantly underestimate the volume remaining of a complex NAPL like the Hill AFB material for an operation that employs the solubilization mechanism without a corrected K_{nw} for the post-treatment test.

Introduction

Partitioning interwell tracer tests (PITTs) have been adopted from the petroleum industry by environmental scientists and engineers as a method to estimate volumes of nonaqueous phase liquids (NAPLs) in the subsurface. The Strategic Environmental Research and Development Program (SERDP) sponsored by the Department of Energy, Department of Defense, and the Environmental Protection Agency used PITTs as one method to evaluate the performance of several innovative technologies to remove NAPL from a contaminated aquifer at Hill Air Force Base, UT (*1*).

The utility of PITTs relies on the determination of coefficients for the partitioning of tracer compounds between the groundwater and the NAPL. A suite of partitioning tracers and at least one nonpartitioning tracer are injected at one location and extracted from wells at another location. Analysis of the breakthrough curves of the tracers and knowledge of their partitioning coefficients allow calculation of the volume of NAPL swept by the tracers through the method of moments (*2*).

The composition of the NAPL may affect the partitioning behavior of the tracer compounds. Reports indicate that many of the NAPLs that are denser than water (DNAPLs) consist of simple mixtures, such as trichloroethane (TCE) and tetrachloroethene (PCE). However, NAPLs that are less dense than water (LNAPLs) are often complex mixtures of hydrocarbons and other components, which is the case for the LNAPL at Hill AFB. It would appear that major changes in the composition of a NAPL result in a change in the partitioning coefficient that would affect the volume estimate. Several of the remediation technologies investigated by SERDP can potentially change a NAPL that is a complex mixture. The NAPL at Hill AFB consists of jet fuel, chlorinated solvents, and various oils that have weathered in place for more than 30 years (*3*). Air sparging, surfactant flooding, and cosolvent flooding will selectively remove components from a NAPL that contains compounds with a range of vapor pressures and aqueous solubilities.

Air sparging will remove volatile organic compounds, which will generally include low molecular weight compounds with Henry's law constants of greater than 10^{-4} L atm mol^{-1}. The specific compounds removed by surfactant or cosolvent flooding will depend on the properties of the selected cosolvent or surfactant. Cosolvent flooding operates through a reduction of interfacial tension that can be accomplished by two different mechanisms (*4*). If the reduced interfacial tension occurs due to the cosolvent partitioning mainly in the aqueous phase, then enhanced dissolution will result. Components will be removed according to their solubility in the specific cosolvent that is influenced by molecular weight, functional groups, and polarity of the cosolvent and of the NAPL components. If the reduction in surface tension occurs mainly due to the paritioning of the cosolvent to the NAPL phase, then mobilization will result. Mobilization of the NAPL as a separate phase is likely to change the overall composition of the NAPL to a lesser extent than enhanced dissolution.

The objective of this study was to determine the influence of NAPL compositional changes on the partitioning coefficients for alcohols that were used as partitioning tracers as part of the SERDP study at Hill AFB. Information from this paper can be used to improve the volume estimates by PITTs and the design of remediation technologies through increased understanding of partitioning coefficients (K_{nw}) and how remediation strategies affect compositional changes.

Materials and Methods

NAPL Composition. The NAPL used in this study was collected on September 6, 1996, from an extraction well 6 ft east of monitoring wells U1-659 and U1-658 located in Operable Unit 1 Hill AFB, UT. The NAPL was black with a density of 0.86 mg mL^{-1} at 22 °C and a viscosity of 9.16 cS at 40 °C. It was stored in an amber, glass bottle at 4 °C. Composition was keyed to compounds selected from the hundreds of components present in the NAPL (Figure 1). To represent the jet fuel, total xylenes, naphthalene, decane, undecane, and tetradecane were selected; to represent chlorinated compounds, 1,2-dichlorobenzene was selected (Table 1). Selections were based in part on ease of analytical determination and on suggested analytes from the EPA regarding monitoring the effluent.

Selected compounds were initially identified and quantified by gas chromatography with mass selective detection (GC/MSD) using a Hewlett-Packard 5890A gas chromato-

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10.1021/es980261x CCC: $15.00

TABLE 1. Chemical and Physical Properties of NAPL Components[a]

compound	molecular wt	boiling point (°C)	aqueous solubility (mol L^{-1})	log K_{ow}	density (g/mL)
o-xylene	106.17	144	1.65×10^{-3}	3.13	0.88
naphthalene	128.17	218	2.45×10^{-4}	3.36	1.16
decane	142.29	174[b]	2.69×10^{-7}	na[e]	0.73[b]
1,2-dichlorobenzene	147.00	180	6.31×10^{-4}	3.38	1.30
undecane	156.31	196	2.81×10^{-8} [c]	6.94	0.74
tetradecane	198.39	254[b]	na	7.20[d]	0.76[b]

[a] Values as cited in refs *5* and *6* unless otherwise noted. [b] Values as cited in ref *7*. [c] Value as cited in ref *8*. [d] Value as cited in ref 9. [e] na, not applicable.

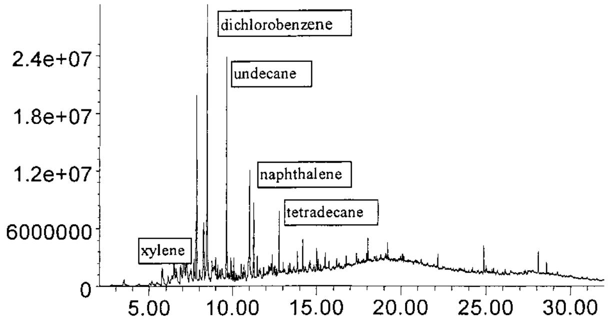

FIGURE 1. GC/MSD chromatogram of free phase Hill NAPL.

graph and a HP 5971A MSD with a 30 m × 0.25 mm i.d. HP-5MS capillary column with a 0.25 μm 5% phenylmethyl silicone film. The following chromatographic conditions were used: 1.0 μL injection; inlet at 280 °C; detector at 320 °C; 3 min at 40 °C; temperature programming at 10 °C/min to 300 °C where the temperature was held for 5 min. MSD was turned on at 2 min to avoid solvent peak. Subsequent analysis was performed with a HP 5890 series II+ GC equipped with a 30 m × 0.25 mm i.d. DB-5 column and flame ionization detector (FID). The inlet and detector temperatures were the same as the GC/MSD method. The initial oven temperature was held at 50 °C for 3 min followed by temperature programming at 10 °C/min to 160 °C and then 30 °C/min to 300 °C held for 5 min. 2-Pentanol was used as an internal standard. Concentrations were determined from relative response factors generated by calibration with a standard stock solution. NAPL samples were diluted with hexane to bring the concentrations into the 10−400 mg/L range of the calibration curve.

Batch Washing Experiments. Portions of the NAPL were washed with a solution of 60% *tert*-butyl alcohol (TBA) and 40% synthetic groundwater to simulate changes in composition that would result from cosolvent flooding dominated by enhanced dissolution. TBA was selected as one of the cosolvents for use at Hill AFB after an extensive investigation of several potential cosolvents. In the field, TBA (80%), hexanol (15%), and water (5%) were used to remove the NAPL through mobilization and dissolution (*10*). Details of the selection process are included in a separate publication to be submitted. Water with salts ($CaCl_2{\cdot}2H_2O$, $NaHCO_3$, $MgCl_2{\cdot}6H_2O$, $MgSO_4{\cdot}7H_2O$, and $KHCO_3$) added in similar proportions as the groundwater at Hill AFB was prepared as synthetic groundwater to use in all experiments. The NAPL and washing solution were mixed in Corex centrifuge tubes on a mechanical rotator for 8−10 min, and the phases were separated by centrifugation at 4500 rpm for 15 min at 25 °C. The aqueous phase was carefully removed, and the volume was measured with 4 mL reserved for analysis. Additional washing solution was mixed with the NAPL and the process was repeated. Once the NAPL had been washed the desired number of times, a saturated NaCl aqueous solution, which prevented the formation of emulsions, was used to remove TBA. The NAPL phase was sampled and analyzed for the six selected components after 1, 3, 5, 8, 11, and 14 washes. Dynamic partitioning coefficients were determined for the NAPL that had been washed 3, 8, and 14 times (NAPL 3, NAPL 8, and NAPL 14).

Static Partitioning Tests. Ten milliliters of NAPL and 10 mL of aqueous tracer solution containing methanol as the nonpartitioning tracer and 1-hexanol, 2,2-dimethyl-3-pentanol, and 3-methyl-3-hexanol as the partitioning tracers were placed in a 50-mL Teflon centrifuge tube. To ensure linear partitioning behavior, initial partitioning tests were conducted at three concentrations of tracers: 200, 400, and 600 mg/L. After linearity was established, all static partitioning tests were conducted at 400 mg/L. Detailed procedures can be found in Meyers (*10*). The samples were inverted by hand 30 times. After being mixed, the samples were allowed to sit for 1 h to separate the phases. The mixing process was repeated twice more to ensured equilibrium partitioning had been achieved. After the third mixing, the phases were allowed to separate overnight followed by centrifugation. During the batch static tests, emulsions formed in the NAPL samples that were washed with cosolvent. Emulsions did not form during the tests with the untreated NAPL. Centrifugation removed the emulsions. The aqueous phase was analyzed for tracer concentrations with a HP 6890 GC equipped with a 75 m × 0.53 mm i.d., 3.0 μm film Rtx-624 column (Restek) and FID. The inlet temperature was 200 °C, and the detector temperature was 240 °C. The initial column temperature was 40 °C, which was held for 1 min before ramping at 30 °C/min to 200 °C where it was held for 3 min. Concentrations of the tracers in the NAPL phase were determined by difference. Partition coefficients were calculated from the following:

$$K_{\mathrm{nw}} = \frac{C_{\mathrm{n}}}{C_{\mathrm{w}}} \tag{1}$$

where C_n is the concentration of the tracer compound in the NAPL phase (mg/L) and C_w is the concentration of the tracer compound in the water phase (mg/L).

Dynamic Partitioning Tests. Tracer tests were conducted with clean sand packed into 30 cm × 25 mm glass columns and spiked with NAPL. Details are provided by Meyers (*11*) and Wright (*12*). Air was removed from the column by flooding with CO_2 that in turn was removed by flooding with degassed, distilled/deionized water. Approximately one pore volume of synthetic groundwater was pumped through the column to displace the distilled/deionized water. Tests with the conservative tracer indicated that one pore volume was enough to reliably replace the fluid in the column. The saturated column was contaminated with 10 mL of NAPL injected at the head of the column. The NAPL that was added to the columns consisted of untreated NAPL or treated NAPL that was washed with TBA in batch systems as described above. To reduce the NAPL to residual saturation, synthetic groundwater was recirculated through the column in the downward direction at about 1 mL min^{-1} until all visible downward motion of the NAPL had ceased. Analysis confirmed that no dissolution of the six selected NAPL components was occurring above the detection limit of 1.0 ppm. The column was inverted, and synthetic groundwater was pumped in the upward direction at about 1.5 mL min^{-1} to use the buoyancy of the NAPL to continue to distribute it throughout the column. When movement ceased, the column was inverted again.

Tracer solution was injected through a Teflon-coated septum at the head of the column with a gas-tight syringe. Testing indicated no background separation of the tracers due to the sand alone. Synthetic groundwater was pumped through the column at about 0.65 mL/min, and effluent was collected in 8-mL aliquots for the first hour and in 4-mL aliquots until exponential decline in the tracer concentration was evident at which time 8-mL aliquots were collected. Effluent was analyzed using the GC/FID conditions described for the static partitioning tests and breakthrough curves were plotted. Using the centroids of the breakthrough curves as calculated by the method of moments, dynamic NAPL/water partition coefficients were calculated using

$$K_{\mathrm{nw}} = \frac{V_1 - V_2}{V_{\mathrm{n}}} \tag{2}$$

where V_1 is the centroid for the partitioning tracer, V_2 is the centroid of the nonpartitioning tracer (methanol), and V_N is the volume of NAPL. V_1, V_2, and V_N are all in milliliters.

Column Flooding Experiments. NAPL was added to four sand columns as described above in the dynamic partitioning studies and remediated with one pore volume of 95%TBA/5% synthetic groundwater solution. The percentage of TBA used for the flood was higher than the percentage used in the batch washing procedure to optimize the removal process. Tracer tests were conducted in the manner described previously before the TBA flood and after the flood when synthetic groundwater flushing decreased the TBA concentrations to less than 500 mg/L. A Soxhlet extraction method based on EPA method 3540 was used to quantify any NAPL remaining on the sand column (*13*). The method used 400 mL of methylene chloride to extract the sand for 20 h. After drying with anhydrous sodium sulfate, the extract was concentrated with a Kuderna–Danish apparatus. The volume of NAPL removed by Soxhlet extraction was determined by subtracting the volume of methylene chloride found by GC analysis from the total volume after concentrating.

Results

The amount of TBA remaining in the NAPL after the batch washing was monitored to ensure that TBA would not affect the solubility of the tracer compounds in the batch partitioning experiments. Equation 3 was used to estimate the solubility enhancement of 1-hexanol by TBA (*14*):

$$\log\left(\frac{C_{\mathrm{mix}}^{\mathrm{sat}}}{C_{\mathrm{w}}^{\mathrm{sat}}}\right) = \frac{0.5(\sigma_{\mathrm{t:w}} - \sigma_{\mathrm{t:c}})/(N\cdot\mathrm{HSA}\cdot f_{\mathrm{c}})}{2.303RT} \tag{3}$$

where $C_{\mathrm{mix}}^{\mathrm{sat}}$ is the solubility of compound in mixture, $C_{\mathrm{w}}^{\mathrm{sat}}$ is the aqueous solubility, $\sigma_{\mathrm{t:w}}$ is the interfacial tension between tetradecane and water, $\sigma_{\mathrm{t:c}}$ is the interfacial tension between tetradecane and TBA, N is Avogadro's number, HSA is hydrophobic surface area of hexane, f_{c} is the volume fraction of TBA, R is the universal gas constant, and T is temperature.

Our estimate using eq 3 indicates that more than 10 000 mg/L TBA would be necessary to increase the aqueous solubility of 1-hexanol in the aqueous phase. In all cases, the TBA concentrations in the aqueous phase of the washes were less than 200 mg/L, which is considerably less than the estimated concentration.

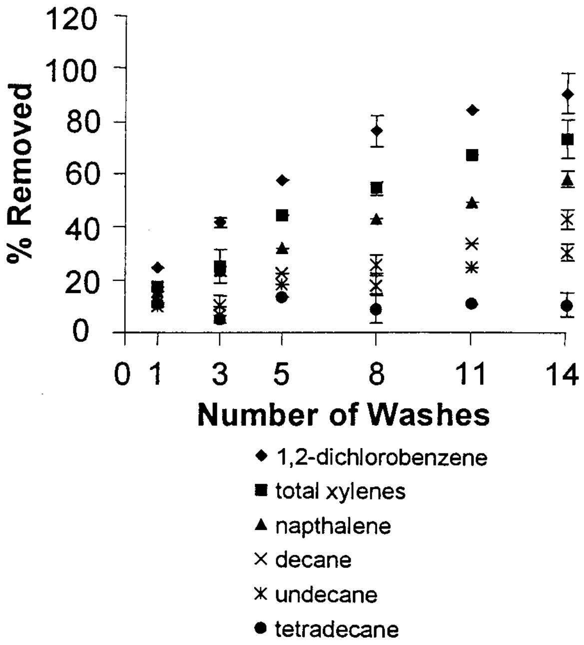

FIGURE 2. Compositional changes in NAPL after batch washing.

Compositional Changes. Six components of the weathered NAPL from Hill AFB were identified, quantified, and tracked throughout the treatments that consisted of washing the NAPL up to 14 times with 60% TBA/40% synthetic groundwater. Figure 2 shows the removal of the six components in terms of the percentage removed with each wash. 1,2-Dichlorobenzene was removed to the greatest extent by the batch washing procedure with less than 10% of the original concentration remaining after 14 repetitions. Tetradecane was removed to the least extent with nearly 90% remaining after 14 repetitions. The compounds were removed in the following order, from most removed to least: 1,2-dichlorobenzene, total xylenes, naphthalene, decane, undecane, and tetradecane, which follows the trend of increasing molecular weight and decreasing aqueous solubility with the exception of 1,2-dichlorobenzene. The polarity of 1,2-dichlorobenzene is the most likely reason it is removed to a greater extent than would be predicted by molecular weight alone. Enhanced dissolution as simulated by the batch washing method substantially changes the composition of the Hill NAPL.

In contrast, if mobilization is the primary mechanism of cosolvent flooding, then the compositional changes are not as significant. Figure 3 compares the removal of the compounds by flooding a contaminated sand column with 95% TBA/5% synthetic groundwater with the batch washing procedure. The order of removal for the column cosolvent flood differs from the removal by the batch washing procedure. For the column flood the removal was in the following order, from most to least: total xylenes, 1,2-dichlorobenzene, decane, naphthalene, undecane, and tetradecane. In all cases, except for the most polar component, 1,2-dichlorobenzene, the column flood removed a greater percentage than the batch washing procedure. For example, the column flood removed 48% of the tetradecane while the batch washing removed only about 10%. The reasons for the greater removal and different order are likely due to an increased concentration of TBA (95% vs 60%) and to mobilization as well as dissolution occurring in the column flood. Supporting evidence for the removal mechanisms includes observations of drops of separate phase NAPL in the column effluent that indicated mobilization. The

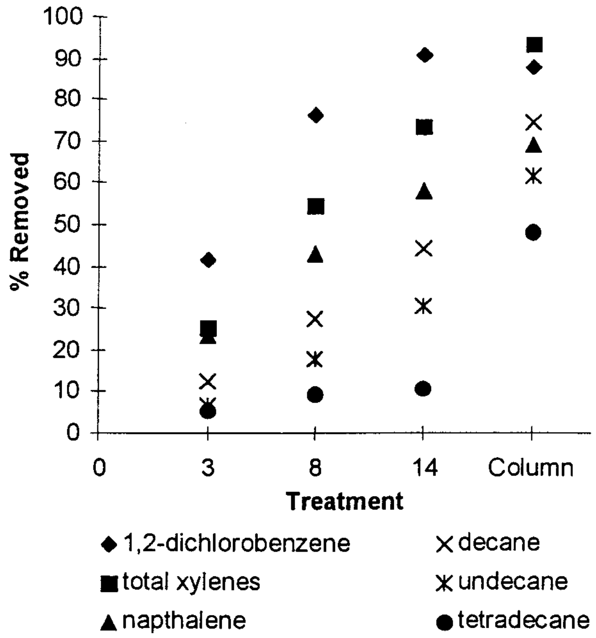

FIGURE 3. Comparison of batch washed and column flooded NAPL.

TABLE 2. Static NAPL/Water Partition Coefficients

	1-hexanol	3-methyl-3-hexanol	2,2-dimethyl-3-pentanol
untreated	3.65 (1.37)[a]	5.51 (1.27)[a]	12.19 (1.31)[a]
3 washings	3.02	4.60	10.28
8 washings	2.93	4.51	10.27
14 washings	2.79 (11.47)[a]	4.19 (11.69)[a]	9.46 (10.15)[a]
mean of washed	2.88 (6.07)[b]	4.37 (6.73)[b]	9.87 (6.19)[b]

[a] Relative percent difference ($n = 2$). [b] Coefficient of variation ($n = 4$).

TABLE 3. Dynamic NAPL/Water Partition Coefficients

column	1-hexanol	3-methyl-3-hexanol	2,2-dimethyl-3-pentanol
untreated	3.33	4.86	10.92
3 washings	2.92	4.47	9.92
8 washings	2.51	4.03	9.26
14 washings	2.25	3.58	8.10
mean of washed	2.55 (13.26)[a]	4.02 (11.09)[a]	9.09 (10.15)[a]

[a] Coefficient of variation ($n = 3$).

TABLE 4. Mean Dynamic Partition Coefficients for Three Sand Columns before and after Cosolvent Flooding

test	1-hex	3M-3H	2,2-DMP
pre-cosolvent	3.29 (1.56)[a]	5.03 (1.63)	11.29 (1.75)
post-cosolvent	3.48 (25.12)	4.67 (15.89)	10.11 (10.11)

[a] Coefficient of variation.

observed yellow color of the effluent implied that dissolution was also occurring.

Static Partitioning Coefficients. Static NAPL/water partition coefficients were determined for the Hill NAPL and three of the washed NAPL with the results shown in Table 2. With more repetitions of the batch washing procedure, the static partitioning coefficient decreases. As more of the lower molecular weight compounds are removed, the tracer alcohols partition to a lesser extent into the NAPL. The results of a two tailed Student's *t*-test at the 95% confidence level indicate that there is a significant difference for all of the tracer alcohols between the K_{nw} for the untreated NAPL and the mean K_{nw} of the three washed NAPL samples.

We also observed that during the static partitioning tests emulsions formed for the washed NAPL but not for the untreated NAPL, which would indicate a change in the physical characteristics of the NAPL. Landon and Hult (*15*) observed that differential removal of components from a subsurface crude oil spill due to natural weathering caused changes not only in the chemical composition of the oil but also in its specific gravity and viscosity. A change in the specific gravity and viscosity may have affected the emulsifying characteristics of the NAPL.

Dynamic Partitioning Coefficients. Untreated NAPL and washed NAPL from three of the batch washing experiments were spiked onto clean sand columns and partition coefficients measured for the tracer alcohols. The results are shown in Table 3. For the three tracer alcohols tested, the dynamic partitioning coefficients decrease with an increase in the number of washings, which is the same trend observed for the static partitioning coefficients (Table 2). The dynamic partition coefficients are also less than the partitioning coefficients measured by the static batch method. The difference may be an indication of nonequilibrium in the column studies. To test the assumption that the rate-limiting step is transport related, the linear water velocity was decreased from 6.5 m/d to 2.6 m/d, and the dynamic partitioning coefficients were determined. There was little observed difference in the dynamic partitioning coefficients for the two velocities (data not shown). We also observed symmetrical breakthrough curves for the conservative tracer. Therefore, it appears that the rate-limiting step is not transport related. A likely possibility is that diffusion into the residual NAPL is controlling the rate. Brusseau et al. (*16*) suggested that diffusion limitations were responsible for nonequilibrium of sorption of hydrophobic compounds by natural sorbents. In our case, the partitioning tracers may not be diffusing through the entire residual NAPL present in the column.

The mean dynamic NAPL/water partition coefficients determined for the untreated NAPL were compared to the mean NAPL/water partition coefficients determined for the washed NAPL using a two-tailed Student's *t*-test at the 95% confidence level. The test results indicate a statistically significant difference between the dynamic K_{nw} for the untreated NAPL and the washed NAPL.

Partition coefficients were also measured in three other column experiments before and after flooding with 95% TBA (Table 4). The means of the partition coefficients for the three column experiments show little change after the cosolvent flooding. This is another indication that mobilization causes little compositional change in this complex NAPL to alter the partition coefficients as compared to the dissolution of the batch washing experiments.

Implications for Volume Estimates. To examine how the enhanced dissolution mechanism may influence estimates of residual NAPL volumes in the subsurface, we used data obtained from the column studies that were run with the washed NAPL. A sand column was contaminated with 10 mL of NAPL that had been washed with TBA in a batch system 3, 8, or 14 times. A partitioning tracer test was run for each column. Using the partitioning coefficient obtained with the untreated NAPL, the NAPL volume was calculated using eq 2. The calculations were made using the partitioning coefficients measured by the static method and the dynamic method for each of the three partitioning tracers. As shown in Table 5, the volume estimates are 8–38% less than the actual volume, which clearly indicates that the partitioning coefficients for the washed NAPL are smaller than for the untreated NAPL. Note also that using the partitioning

TABLE 5. Volume Estimates for Enhanced Dissolution (Measured = 10 mL)

	NAPL 3			NAPL 8			NAPL 14		
	1-hex	3M-3H	2,2-DMP	1-hex	3M-3H	2,2-DMP	1-hex	3M-3H	2,2-DMP
dynamic	8.8	9.2	9.1	7.5	8.3	8.5	6.7	7.4	7.4
static	8.0	8.1	8.1	6.9	7.3	7.6	6.2	6.5	6.6

TABLE 6. Volume Estimates for Mobilization (Measured = 2.8 mL)

	1-hex	3M-3H	2,2-DMP
dynamic	3.0	2.8	2.7
static	2.8	2.5	2.4

coefficients obtained by the static method results in a major difference in the volume estimated as compared to using the dynamic partitioning coefficients.

The effect of mobilization on volume estimates was also evaluated. The contaminated sand column that was flooded with 95% TBA/5% synthetic groundwater was Soxhlet extracted to determine that 2.8 mL of NAPL remained after the cosolvent flood. An analysis of the error involved in the Soxhlet extractions indicated that 105.5% of the known volume was recovered for four replicates with a relative standard deviation of 1.88%. The volume remaining in the column was also estimated using partitioning coefficients obtained with the untreated NAPL. Table 6 shows that the estimates using the dynamic partitioning coefficients are similar to the measured amount. The static K_{nw} for 3-methyl-3-hexanol (3M-3H) and for 2,2-dimethyl-3-pentanol (2,2-DMP) result in an underestimate of the measured volume.

Discussion

The compositional changes based on the six compounds monitored in the batch washing studies differed from the changes observed in the column studies. The differences were the order in which the compounds were removed and the percentage removed. For example, decane was removed to a greater extent than naphthalene in the column although decane has a higher molecular weight and lower solubility than naphthalene. The column flooding removed greater quantities of all the compounds (except 1,2-dichlorobenzene) than the batch washing. The differences appear to be a result of mobilization as well as dissolution occurring in the column and only dissolution occurring in the batch studies. The results clearly point to greater compositional changes occurring due to enhanced dissolution than due to mobilization. The column studies produce results that better mirror field conditions when using cosolvents or surfactants chosen for their mobilization mechanisms. For compounds in complex NAPL mixtures such as the Hill AFB NAPL, molecular weight and aqueous solubility were good predictors for removal by enhanced dissolution.

The two methods used for determining partitioning coefficients produced different K_{nw} values. For the untreated NAPL, the static procedure returned values for the partitioning coefficients that were greater than the dynamic procedure. The dynamic partitioning coefficients may represent nonequilibrium due to retarded diffusion of the tracers into the residual NAPL. However, the dynamic partitioning coefficients produced a more accurate prediction of the NAPL volume remaining on the column after mobilization with a cosolvent (Table 6).

Our results indicate that compositional change that significantly affect partitioning coefficients for tracers can be anticipated if enhanced dissolution is the primary mechanism for removal. This in turn means that PITT-generated estimates of the volume removed by enhanced dissolution may be significantly overestimated unless changes in the K_{nw} are taken into account. PITTs may provide more accurate information about NAPL volumes removed with cosolvents and surfactants chosen for their mobilization characteristics.

Acknowledgments

The authors gratefully acknowledge the help of Brett Whitin and Robert Cullom from Clemson University. This study was supported by the U.S. EPA Robert S. Kerr Environmental Research Laboratory under Cooperative Agreement CR-821992-01-0. This paper has not been reviewed by the EPA, and thus no official endorsement should be inferred.

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Received for review March 16, 1998. Revised manuscript received July 29, 1998. Accepted August 7, 1998.

ES980261X