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Single-Well "Push−Pull" Partitioning Tracer Test for NAPL Detection in the Subsurface

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Previous environmental applications of partitioning tracer tests to detect and quantify nonaqueous phase liquid (NAPL) contamination in the subsurface have been limited to well-to-well tests. However, theory and numerical modeling suggests that single-well injection−extraction ("push−pull") partitioning tracer tests can also potentially detect and quantify NAPL contamination. In this type of test, retardation factors for injected partitioning tracers are estimated from the increase in apparent dispersion observed in extraction-phase breakthrough curves in the presence of NAPL. A series of laboratory push−pull tests was conducted in physical aquifer models (PAMs) packed with natural aquifer sediment prepared with and without the presence of trichloroethene (TCE) NAPL. Field tests were conducted in an aquifer contaminated with petroleum hydrocarbon NAPL. Injected test solutions contained a suite of partitioning and conservative (nonpartitioning) alcohol tracers. Laboratory push−pull partitioning tracer tests were able to detect and quantify sorption of partitioning tracers to aquifer sediment (in the absence of NAPL) and to detect NAPL when it was present. NAPL saturations computed from estimated retardation factors bracketed those computed from known volumes of emplaced NAPL in the sediment pack. However, numerical modeling with assumed homogeneous NAPL distribution and linear equilibrium partitioning of tracers between aqueous and NAPL phases was unable to reproduce all features of observed breakthrough curves. Excavation of the sediment pack after all tests indicated that a portion of the emplaced NAPL had sunk to the bottom of the PAM invalidating the modeling assumption of homogeneous NAPL distribution. Moreover, the apparent dispersion in extraction-phase breakthrough curves decreased when the injection−extraction pumping rate was decreased, suggesting that mass transfer limitations existed during laboratory tests. Field push−pull partitioning tracer tests were able to detect NAPL in a portion of the aquifer known to contain NAPL; computed NAPL saturations were comparable to those obtained from sediment coring and the results of a partitioning interwell tracer test conducted in the same location. This study clearly demonstrates that the single-well partitioning tracer test can detect NAPL under both laboratory and field conditions. However, additional research is needed to verify the ability of the test to quantify NAPL saturations.

Introduction

Effective characterization and remediation of nonaqueous phase liquid (NAPL) contamination in the subsurface requires accurate information on the location and amount of NAPL present (*1*). However, obtaining this information by direct sampling is difficult because of the high expense of drilling and sediment coring, the typically "patchy" nature of NAPL releases, and the heterogeneous nature of the subsurface. Partitioning tracer tests were developed as field methods to complement soil coring as a means for detecting and quantifying NAPL contamination. Although originally developed in the petroleum industry to detect crude oil (*2, 3*), partitioning tracer tests are also proving useful for environmental cleanup applications (*4*−*6*). To date environmental applications of partitioning tracer tests have been conducted only as well-to-well tests (called partitioning interwell tracer tests or PITTs). In a PITT, a suite of tracers selected to have varying affinities for water and NAPL is injected and caused to flow through a zone of potential NAPL contamination. By comparing breakthrough curves obtained at downgradient monitoring wells for partitioning tracers with those obtained for co-injected conservative (i.e., nonpartitioning) tracers, retardation factors may be estimated using the method of moments (*4, 7*). The average NAPL saturation in the interrogated portion of the aquifer, S_{NAPL} (volume NAPL/volume pore space) can then be computed using

$$S_{\mathrm{NAPL}} = \frac{R-1}{R+K-1} \tag{1}$$

where $R =$ (velocity of the conservative tracer)/(velocity of the partitioning tracer) is the retardation factor and K is the partitioning tracer's NAPL/water partition coefficient (*4*). An analysis of the various assumptions and potential sources of error involved in estimating NAPL saturations using PITT results is given in Dwarakanath et al. (*8*). For example, eq 1 assumes that partitioning is instantaneous so that tracer concentrations in the aqueous and NAPL phases are in local equilibrium (*9*) and can be described by a linear isotherm

$$C^* = KC \tag{2}$$

where C^* and C are the partitioning tracer concentrations in the NAPL and aqueous phases, respectively.

While soil cores provide data on NAPL saturation on a small scale (limited by the size and number of cores), PITTs can provide data on a much larger scale (limited only by the distance between injection and extraction wells). Unfortunately, soil cores may not be representative of subsurface conditions because of their small size, while PITTs may be logistically difficult to conduct because they typically involve injection of large quantities of tracer solution and subsequent treatment of the large volume of extracted groundwater.

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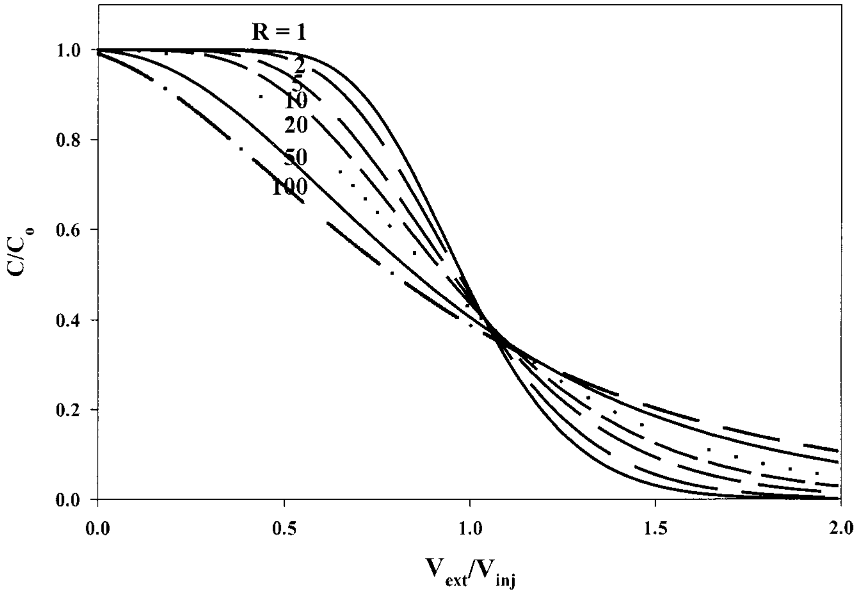

FIGURE 1. Simulated extraction-phase breakthrough curves for push−pull test showing the increased apparent dispersion that occurs for injected partitioning tracers in the presence of NAPL (from ref *11*).

Clearly, there is a need for an intermediate-scale technique for detecting and quantifying NAPL saturation.

An intermediate-scale technique that may be able to complement soil coring and PITTs is the single-well "push−pull" partitioning tracer test that has been used to estimate residual crude oil saturations in petroleum reservoirs (*10*). In a push−pull test, the tracer solution is first injected ("pushed") into the aquifer using a single injection well and then extracted ("pulled") from the same location. Push−pull partitioning tracer tests have several potential advantages for characterizing NAPL contamination, including the need for only a single well, the typically smaller injection and extraction volumes, logistical simplicity, and lower cost. However, to date, there have been no reported applications of the push−pull partitioning tracer test for characterizing NAPL contamination in the subsurface.

In previous petroleum-related applications of the push−pull tracer test, injected solutions contained a *reactive* partitioning tracer that produced a conservative tracer in situ so that the method of moments could be used to interpret extraction-phase breakthrough curves. For example, Tomich et al. (*10*) injected a test solution containing the reactive partitioning tracer ethyl acetate, which partially hydrolyzed to produce the conservative tracer ethanol within the oil reservoir during the rest phase. During the extraction phase, unreacted ethyl acetate transport to the injection−extraction well was retarded relative to ethanol because ethyl acetate has a greater affinity for the stationary oil phase than that of ethanol (which is essentially insoluble in oil). Thus, extraction-phase breakthrough curves for the two tracers were separated in time (ethanol arriving at the well first), and a retardation factor for ethyl acetate could be computed by the difference in arrival times for ethyl acetate and ethanol at the well. The approach of injecting a reactive partitioning tracer to produce a conservative tracer in situ has not been applied to the characterization of NAPL for environmental applications because suitable tracers have not been identified and characterized (note that rapid ethyl acetate hydrolysis requires the elevated temperatures of deep oil reservoirs that do not typically occur in groundwater aquifers). However, the need to use reactive partitioning tracers in a push−pull test is predicated on the assumption that test data will be interpreted using the method of moments. While the methods of moments can be used with reactive partitioning tracers in a push−pull test, it cannot be used to interpret push−pull test breakthrough curves obtained for nonreactive partitioning tracers in a push−pull test because of the flow reversal that occurs between injection and extraction phases which causes the arrival times of partitioning and conservative tracers at the well to be identical (*11*).

Recently, an alternative approach for interpreting push−pull test breakthrough curves to estimate retardation factors was developed by Schroth et al. (*11*). In that study, flow and transport simulations were used to evaluate the effect of varying retardation factor on push−pull test extraction-phase breakthrough curves. Simulated breakthrough curves showed increased apparent dispersion with increasing retardation factor (Figure 1), which is a result of the spatially variable flow field that occurs near the well during a push−pull test. The theoretical analysis of Schroth et al. (*11*) indicates that it should be possible to conduct push−pull partitioning tracer tests to estimate retardation factors and NAPL saturations by analyzing extraction-phase breakthrough curves for a suite of injected partitioning (but nonreactive) and conservative tracers. This hypothesis was tested in a series of laboratory push−pull tests conducted in physical aquifer models packed with natural aquifer sediment prepared with and without trichloroethene (TCE) NAPL and in a series of field push−pull tests conducted in an aquifer containing petroleum NAPL, which had previously been characterized using PITTs (*13*).

Experimental Methods

Laboratory Tests. Laboratory tests were conducted in a physical aquifer model (PAM) constructed in a wedge shape to approximate the radial flow field near an injection−extraction well during a push−pull test (Figure 2a). The PAM was constructed of polypropylene with interior dimensions of 5 cm (width at narrow end), 50 cm (width at wide end), 125 cm (length), 20 cm (height), and a total internal volume of 0.069 m^3 (Figure 2b). Preliminary batch experiments indicated that sorption of the partitioning tracers to polypropylene was negligible. The PAM was packed with sediment from the Hanford Formation, an alluvial deposit of sands and gravels of mixed basaltic and granitic origin. Prior to packing, the sediment was homogenized by manual mixing, air-dried to a water content between 2 and 3 wt %, and sieved to remove particles >0.5 cm in diameter. The sieved sediment

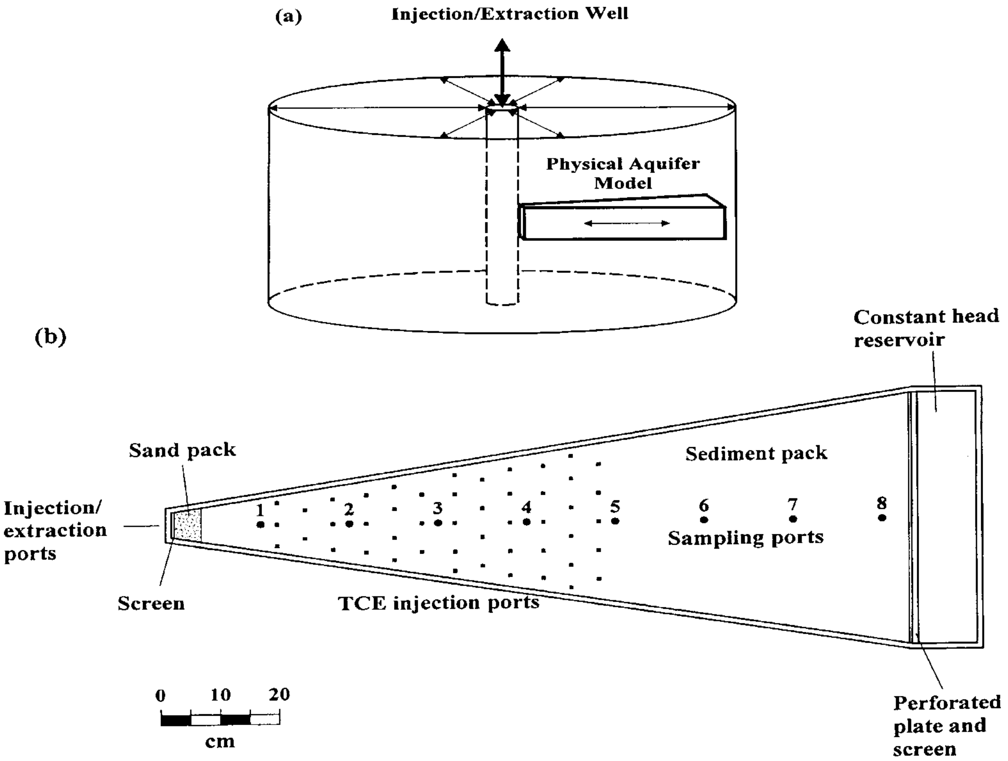

FIGURE 2. Schematic indicating (a) the portion of the flow field near an injection−extraction well represented by physical aquifer models used in laboratory push−pull tests and (b) plan view of a physical aquifer model.

is classified as a clean sand with approximately 30% fine gravels and less than 5% silt and clay. The sediment contains less than 0.001 wt % organic matter and has a particle density of 2.9 g/cm^3. The porosity and bulk density of the packed sediment were 0.39 and 1.77 g/cm^3, respectively. Tap water was used in all laboratory experiments. The narrow end of the PAM had a series of injection−extraction ports covered with screen and a 2.5-cm thick sand pack that allowed it to function as an injection−extraction well.

After the sediment pack was water-saturated, the PAMs were sealed with a lid containing sampling ports (Figure 2b) that were connected to "well" screens that fully penetrated the saturated thickness of the sediment pack. Additional "wells" were connected to manometers to measure hydraulic head. Experiments were performed under confined conditions. The saturated hydraulic conductivity of the sediment pack was determined periodically from head and pumping rate measurements and was nearly constant ($1.0 \times 10^{-2} \pm 0.6 \times 10^{-3}$ cm/s) during all tests.

During the injection phase of a test, flow was directed from the injection−extraction ports at the model's narrow end toward the model's wide end; during the extraction phase, flow was reversed. A "constant head" reservoir was connected to the model's wide end to allow pore fluids to leave the sediment pack during the injection phase and to allow tap water to enter the sediment pack during the extraction phase. The volume of test solution was selected to ensure that no injected test solution left the sediment pack through the constant head reservoir.

Three tests were performed in a single sediment pack. In Test 1, the sediment pack contained no NAPL. In Tests 2 and 3, the sediment pack contained a known initial quantity of TCE NAPL that was introduced by first draining the sediment pack and then injecting equal aliquots of neat TCE at four depths using 52 injection ports located in the model lid between sampling ports 1 and 5 (Figure 2b). A total of 208 mL (304 g) of neat TCE was injected, which is equivalent to an average NAPL saturation of ~2% of the pore volume within the treated portion of the sediment pack. After TCE injection, the sediment pack was flushed for ~24 h with tap water in an attempt to entrap NAPL within the pore space. Aqueous TCE concentration measurements and mass balance calculations indicated that only 2.9 g (1.4%) of TCE were removed from the PAM during flushing of the sediment pack prior to Test 2 and that an additional 3.4 g (1.6%) of TCE were removed from the PAM during Test 2 (prior to Test 3).

TABLE 1. Properties of Partitioning Tracers Used in Laboratory and Field Tests

property	1-hexanol	1-heptanol	2-ethyl-1-hexanol
K_{oc}	10.2[a]	15[a]	105[b]
S (mg/L)	6262[c]	1798[c]	880[c]
K (TCE NAPL)[d]	18.2	89.5	227
K (petroleum NAPL)[e]	5.05	27.7	82.4

[a] K_{oc} value obtained from ref *18*. [b] The K_{oc} value is estimated from a water solubility of 6.8×10^{-3} M (*19*) using the regression equation $\log K_{oc} = -0.55 \log S + 3.64$ (S in mg/L) obtained for a wide variety of chemicals (*20*). [c] Solubility obtained from ref *19*. [d] K(TCE NAPL) reported in ref *21*. [e] K (petroleum NAPL) reported in ref *13*.

Injected test solutions consisted of tap water containing ~800 mg/L 1-pentanol, which served as a conservative tracer, and ~800 mg/L 1-hexanol, ~ 350 mg/L 1-heptanol, and ~ 100 mg/L 2-ethyl-1-hexanol, which served as partitioning tracers (Table 1). In each test, ~12 L of test solution was injected and ~24 L was extracted. Injection and extraction pumping rates were constant and were either ~100 mL/min (Tests 1 and 2) or ~25 mL/min (Test 3). During each test, water samples were collected from the sampling ports (Figure 2b) using a syringe needle inserted to the mid-depth of the well screens through a septum in the sampling port cap. Additional water samples were collected from the injection−extraction ports.

Field Tests. Field push−pull tests were conducted in wells located at a former petroleum refinery near Cincinnati, OH.

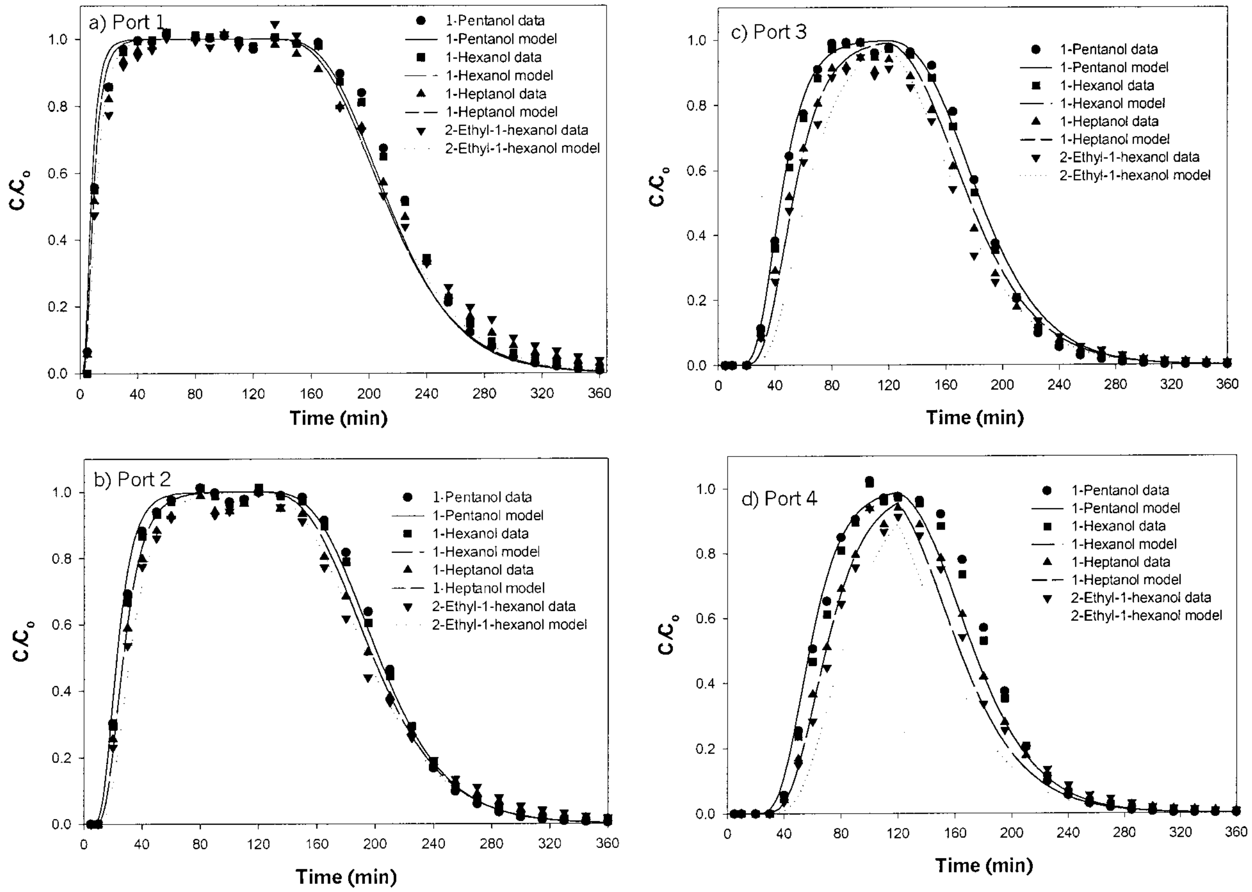

FIGURE 3. Relative concentrations for injected alcohol tracers at sampling ports 1−4 during the injection and extraction phases of Test 1 in the absence of TCE NAPL The duration of the injection phase was 2 h, and the duration of the extraction phase was 4 h.

The unconfined aquifer is formed in sand and gravel glacial outwash deposits and the groundwater depths ranges from 3 to 10 m below the land surface. Regional groundwater velocity is estimated at 25 cm/day. Releases of heating oil, jet and aviation fuel, and automotive gasoline resulted in an extensive zone of NAPL contamination. Test 1 was conducted in a portion of the aquifer where historical groundwater sampling data indicated the absence of NAPL contamination so that sorption of injected alcohol tracers to aquifer sediment could be assessed. The well diameter was 5.1 cm, and the length of the screened interval was 2 m. Test 2 was conducted in a portion of the aquifer that contained NAPL and had been previously characterized by PITTs, sediment sampling, and cone penetrometer testing (*13*). The well diameter was 5.1 cm, and the length of the screened interval was 2.5 m. PITT test results in this portion of the aquifer indicated NAPL saturations ranging from 1.7% to 2.1% (*13*). For each test, 250 L of tap water, containing ~800 mg/L 2-butanol as a conservative tracer and ~800 mg/L 1-hexanol, ~350 mg/L 1-heptanol, and ~100 mg/L 2-ethyl-1-hexanol as partitioning tracers, was injected at approximately 2 L/min. The injected test solution penetrated a radial distance (computed using a porosity of 0.25) of approximately 40 cm in Test 1 and approximately 36 cm in Test 2. Extraction-phase pumping began immediately after the end of the injection phase and continued at 2 L/min until ~500 L of the test solution/groundwater mixture was extracted. Samples were collected during the extraction phase and used to develop breakthrough curves for all tracers. NAPL/water partition coefficients for the partitioning tracers for the NAPL at the field site (Table 1) were measured by combining equal volumes of NAPL and water in a closed vessel, adding known quantities of the partitioning tracers, shaking and allowing time for equilibration, and then analyzing partitioning tracer concentrations in the aqueous phase (*13*).

Tracer Analysis. Tracer analyses were performed using modified method EPA 8015B with direct aqueous injection into a gas chromatograph equipped with flame ionization detection. Approximately 1 μL of the aqueous sample was directly injected into a 15 m × 5 μm film thickness Carbowax column. Helium (10 mL/min) was the carrier gas. The initial temperature of the oven was 45 °C for 6 min followed by a ramp at 10 °C/min until 140 °C, at which the temperature was held for 10 additional min.

Numerical Simulations. Numerical simulations of tracer transport during laboratory and field tests were performed using the subsurface transport over multiple phases (STOMP) code (*14*). STOMP is a fully implicit volume-integrated finite-difference simulator which has been extensively tested and validated against published analytical solutions as well as other numerical codes (*15*). For these simulations, we assumed that tracer transport was described by the one-dimensional (radial) form of the advection−dispersion equation

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n}\frac{\partial S}{\partial t} = \alpha_{\mathrm{L}}|v|\frac{\partial^2 C}{\partial r^2} - v\frac{\partial C}{\partial r} \qquad (3)$$

where t is time; ρ_b, n, and α_{L} are the bulk density, effective porosity, and longitudinal dispersivity, respectively; v is the pore water velocity; and r is radial distance. Equation 3 assumes that sediment properties are homogeneous, that mechanical dispersion is a linear function of v, and that molecular diffusion is negligible (*16*). Note that in a radial

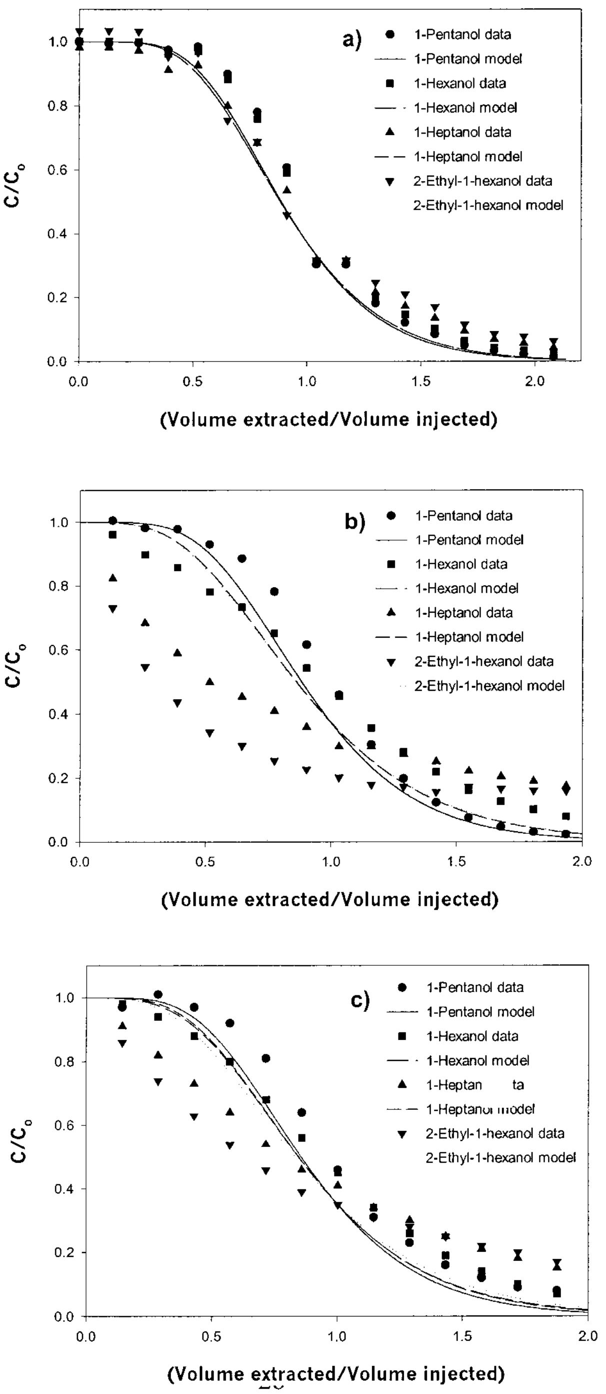

FIGURE 4. Extraction-phase breakthrough curves for injected alcohol tracers during (a) Test 1 in the absence of TCE NAPL, (b) Test 2 in the presence of TCE NAPL, and (c) Test 3 in the presence of TCE NAPL where injection and extraction rates are $^1/_4$ those in Test 2.

TABLE 2. Estimated Retardation Factors, Sorption Adjusted Retardation Factors, and Computed NAPL Saturations for Laboratory Push−Pull Tests

	1-hexanol	1-heptanol	2-ethyl-1-hexanol
	Test 1		
estimated R	1.1	1.2	1.4
	Test 2		
estimated R	1.4	2.8	3.0
sorption adjusted R	1.3	2.6	2.6
NAPL saturation (%)	1.6	1.7	0.7
	Test 3		
estimated R	2.0	3.0	4.0
sorption adjusted R	1.9	2.8	3.6
NAPL saturation (%)	4.9	2.0	1.1

flow field the pore water velocity is a function of r

$$v(r) = Q/(2\pi rnb) \qquad (4)$$

where Q is the pumping rate (positive during the injection phase, negative during the extraction phase) and b is the saturated thickness.

Equation 3 is solved in STOMP using a modified Newton−Raphson method. Initial conditions were $C = 0$ for all solutes. Time-varying third-type (Neumann) boundary conditions were used to represent pumping at the injection−extraction ports (laboratory tests) or well (field tests); constant head and zero solute flux boundary conditions were used to represent flow conditions at the wide end of the PAM (laboratory tests) or far from the well (field tests). For the laboratory tests, the value of α_L was estimated by minimizing the combined sum of squared differences between simulated and observed relative concentrations for the conservative tracer at sampling ports 1−4. Then, retardation factors for each partitioning tracer were estimated by minimizing the combined sum of squared differences between simulated and observed relative concentrations of that tracer at sampling ports 1−4. For the field tests, values of α_L were estimated by minimizing the sum of squared differences between simulated and observed extraction-phase breakthrough curves for the conservative tracer. Retardation factors were then estimated for each partitioning tracer.

Results and Discussion

Laboratory Tests. Relative concentrations (C/C_0, where C is the tracer concentration and C_0 is the tracer concentration in the injected test solution) for all tracers increased smoothly from 0 to 1 at sampling ports 1−4 during the injection phase of Test 1, which was conducted in the absence of TCE NAPL (Figure 3a−d). Observed arrival times (the time when $C/C_0 = 0.5$) for 1-pentanol were essentially identical with those predicted from the PAM geometry, sediment pack porosity, and pumping rate. In addition, the arrival times were consistent with those observed in preliminary tracer tests conducted in this sediment pack with only Br^- (data not shown), confirming conservative transport of 1-pentanol in the absence of NAPL. Observed arrival times for 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol were slightly larger than those for 1-pentanol, which is attributed to sorption of these tracers to sediment organic matter (Figure 3a−d). Sorption resulted in a "chromatographic separation" of the injected partitioning tracers in an order that is consistent with K_{oc} values (Table 1) with arrival times as 1-pentanol < 1-hexanol < 1-heptanol < 2-ethyl-1-hexanol during the injection phase.

Relative concentrations for all tracers at the sampling ports gradually decreased to zero during the extraction phase as the test solution was displaced from the sediment pack by tap water entering from the constant head reservoir (Figure 3a−d). Chromatographic separation of the injected tracers due to sorption was also observed during the extraction phase. However, due to the flow reversal that occurs during the extraction phase of a push−pull test, the order of arrival of injected tracers at the sampling was reversed to that observed during the injection phase (Figure 3a−d).

Retardation of injected tracers was also apparent in extraction-phase breakthrough curves measured at the injection−extraction ports for Test 1 (Figure 4). In Figure 4, volume extracted (V_{ext}) is the cumulative volume of water extracted at the time the sample was collected and volume injected (V_{inj}) is the volume of injected test solution. Mass balance calculations indicated essentially complete removal

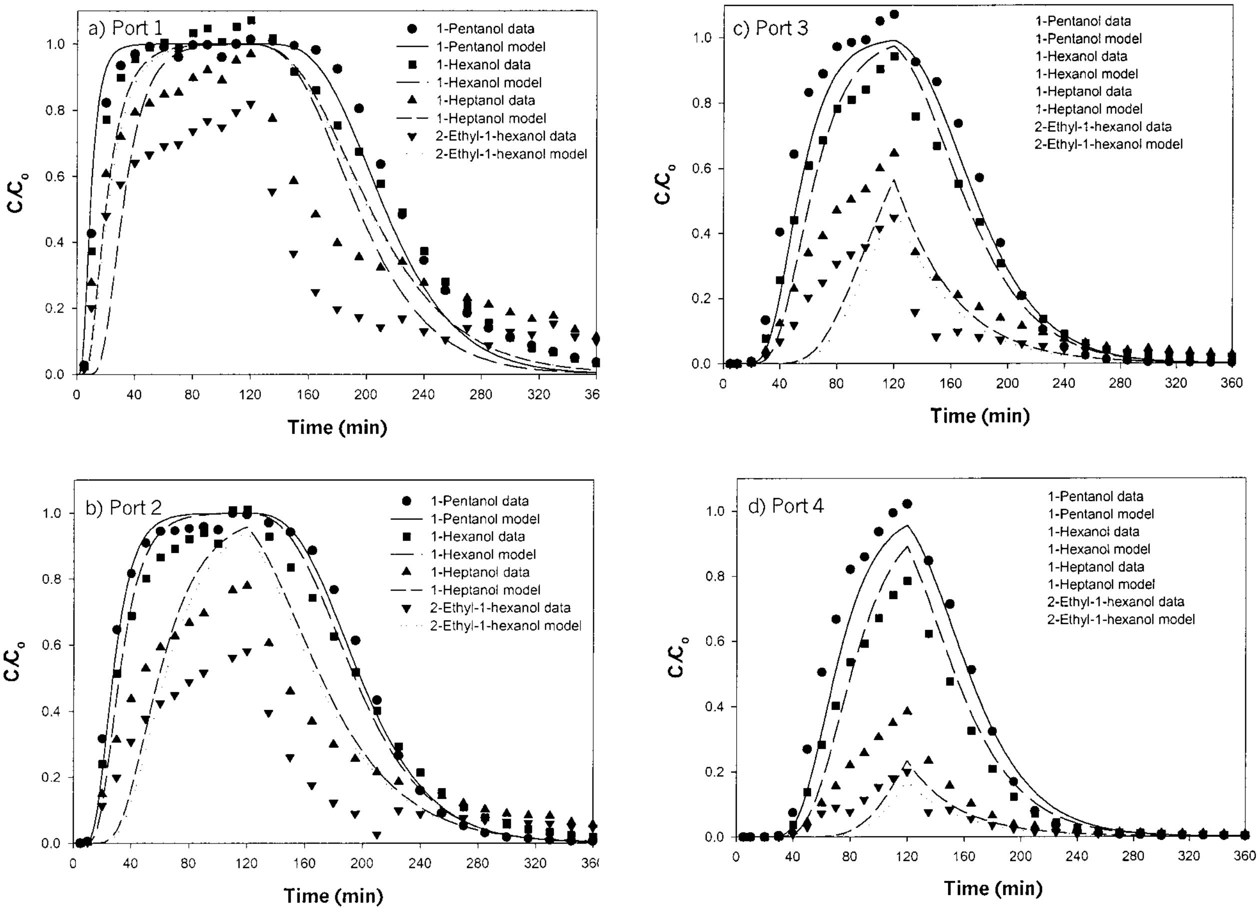

FIGURE 5. Relative concentrations for injected alcohol tracers at sampling ports 1–4 during the injection and extraction phases of Test 2 in the presence of TCE NAPL. The duration of the injection phase was 2 h, and the duration of the extraction phase was 4 h.

(>95%) of all injected tracers during the extraction phase of Test 1. Extraction-phase breakthrough curves are, of course, the only data that can be obtained during field push–pull tests.

Using STOMP, eq 3 was fit to the injection-phase breakthrough curves for 1-pentanol to estimate α_L assuming conservative transport ($R = 1$). Then, eq 3 was fit to the injection-phase breakthrough curves for 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol to estimate retardation factors for the partitioning tracers. Fits for ports 1–4 were generally very good for all tracers during Test 1 (Figure 3a–d). The estimated value of $\alpha_L = 3.0$ cm is identical with that obtained for bromide and is consistent with other tracer tests performed in similar sediment packs in our laboratory. Estimated retardation factors ranged from 1.1 to 1.4 and increased in the order 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol (Table 2), which is consistent with the trend in published K_{oc} values (Table 1). Simulated extraction-phase breakthrough curves at the injection–extraction ports (performed using fitted α_L and R values from ports 1–4) provided a reasonable match to observed breakthrough curves (Figure 4). Because push–pull tests can be used to detect sorption of injected partitioning tracers to sediment, they can be used to account for sorption at field sites and thus to avoid overestimating NAPL saturations.

A substantial increase in arrival times and chromatographic separation of injected partitioning tracers was observed during the injection phase of Test 2 conducted in the presence of TCE NAPL (Figure 5a–d). Estimated retardation factors were also larger than those during Test 1, ranging from 1.2 to 3.0 and increased in the order 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol (Table 2), which is consistent with the trend in these tracers K values for TCE (Table 1). Port data for 1-pentanol and 1-hexanol were generally well fit by eq 3, but port data for 1-heptanol and 2-ethyl-1-hexanol displayed substantially more tailing than could be accounted for using eq 3 (Figure 5a–d).

A comparison of Figure 4, parts a and b, clearly illustrate the potential of the push–pull partitioning tracer test to detect the presence of NAPL, at least under laboratory conditions. Increased retardation of partitioning tracers in the presence of NAPL resulted in increased apparent dispersion in the extraction-phase breakthrough curves at the injection–extraction ports (Figure 4b). However, simulated extraction-phase breakthrough curves (with fitted R values obtained from the port data) only poorly matched observed breakthrough curves, especially for 1-heptanol and 2-ethyl-1-hexanol (Figure 4b).

The relatively poor fits obtained for 1-heptanol and 2-ethyl-1-hexanol during Test 2 could potentially have resulted from diffusion-limited mass transfer of these tracers between aqueous and NAPL phases (*17*). The alternating diverging–converging flow fields near the injection–extraction ports during a push–pull test results in pore water velocities that vary as a function of radial distance according to eq 4. For example, for tests 1 and 2, computed pore velocities ranged from 2.58×10^{-2} cm/s at port 1 to 1.01×10^{-2} cm/s at port 4. In an attempt to reduce the effect of potential mass transfer limitations on the transport behavior of injected tracers, Test 3 was conducted at injection and extraction pumping rates equal to $^1/_4$ those used in Tests 1 and 2. The reduced pumping rates resulted in smaller pore water velocities, ranging from 6.35×10^{-3} cm/s at port 1 to 2.48×10^{-3} cm/s at port 4. Observed chromatographic

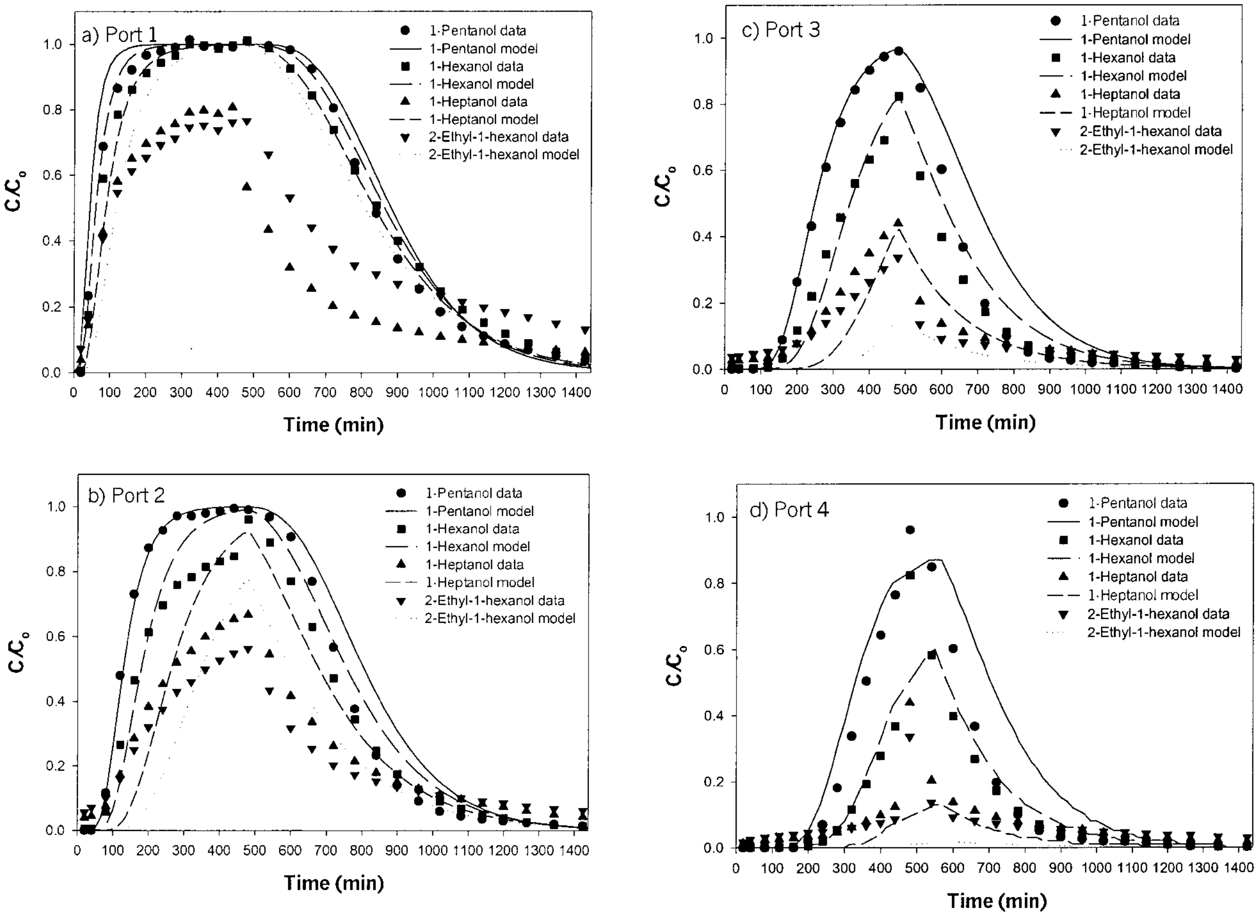

FIGURE 6. Relative concentrations for injected alcohol tracers at sampling ports 1−4 during the injection and extraction phases of Test 3 in the presence of TCE NAPL. Injection and extraction rates are $^1/_4$ those in Test 2. The duration of the injection phase was 2 h, and the duration of the extraction phase was 4 h.

separation and arrival times for all tracers at ports 1−4 increased relative to those observed in Test 2 (Figure 6a−d). Fits to eq 3 did not generally improve during Test 3 with data showing more tailing then predicted, especially for 1-heptanol and 2-ethyl-1-hexanol in ports 3 and 4. Estimated retardation factors for all tracers increased during Test 3 (Table 2). Interestingly, the apparent dispersion of partitioning tracers observed at the injection−extraction ports was reduced in Test 3 (Figure 4c) as compared to Test 2 (Figures 4b). Observed breakthrough curves also more closely approximated simulated breakthrough curves during Test 3; however, observed breakthrough curves still displayed greater apparent dispersion than numerical simulations (Figure 4c).

NAPL saturations were computed by first adjusting estimated retardation factors obtained during Tests 2 and 3 for the effects of sorption observed during Test 1

$$R_{\mathrm{adjusted}} = 1 + (R - 1) - (R_{\mathrm{Test1}} - 1) \tag{5}$$

where R_{adjusted} is the sorption-adjusted retardation factors for a partitioning tracer and $\mathrm{R}_{\mathrm{Test1}}$ is the retardation factor estimated for the same tracer during Test 1.

Computed NAPL saturations ranged from 0.7% to 1.6%, which are relatively close to the value of 2%, which was used to compute NAPL volumes added to the sediment pack (Table 2). For Test 3, computed NAPL saturations increased to between 1.1% and 4.7%. Note that estimation errors for retardation factors (computed from the mean squared differences between simulated and observed breakthrough curves) ranged from 10% to 20%. Thus, computed NAPL saturations for each tracer also have errors of from 10% to 20%.

Excavation of the sediment pack after completion of the laboratory tests indicated that a portion of the TCE NAPL had sunk to the bottom of the PAM. Heterogeneity in NAPL saturation may account for underestimation of NAPL saturation in Tests 2 and 3. Moreover, the existence of high NAPL saturation regions (i.e., "NAPL pools") may have also contributed to the apparent mass transfer limitations on partitioning inferred from the results of Tests 2 and 3.

Field Tests. Extraction-phase breakthrough curves for both field tests (Figure 7) indicated an increased dispersion of all injected tracers that is attributed to the increased heterogeneity of aquifer sediments as compared to the prepared sediment packs used in laboratory push−pull tests. Estimated values of dispersivity ranged from 120 to 200 cm for all tests; for Field Tests 1 and 2, identical estimated values of α_L = 167 cm were obtained using the extraction-phase breakthrough curve for the conservative tracer 2-butanol. Estimated retardation factors for the partitioning tracers in Field Test 1, conducted in a portion of the aquifer containing no NAPL, were all close to 1, indicating only weak sorption of injected partitioning tracers to aquifer sediments (Table 3). Estimated retardation factors for the partitioning tracers in Field Test 2, conducted in a portion of the aquifer where NAPL had previously been detected, were larger, ranging from 1.1 to 2.7 (Table 3), and increased in an order consistent with the partitioning tracer's K values for site NAPL (Table 1). NAPL saturations computed from sorption-adjusted retardation factors ranged from 1.4 to 2.0 (Table 3). Field Test 2 was conducted in a monitoring well within the zone of influence of a partitioning interwell tracer test conducted at this site and is near locations where NAPL saturations

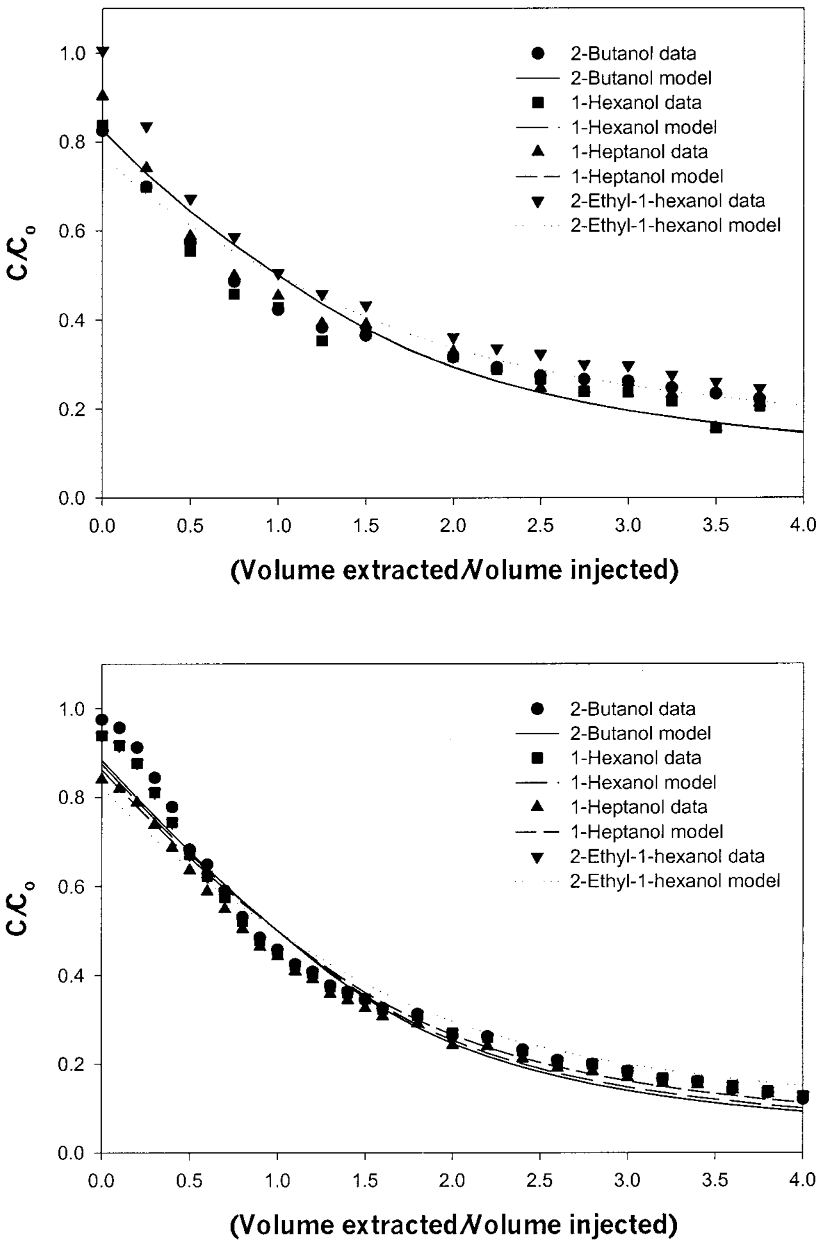

FIGURE 7. Field tests conducted in (a) uncontaminated portion of site showing sorption of injected partitioning tracers to aquifer sediment and (b) in NAPL contaminated portion of site showing increased dispersion of injected partitioning tracers attributed to the presence of NAPL. Lines indicate least-squares fit for eq 6.

TABLE 3. Estimated Retardation Factors, Sorption Adjusted Retardation Factors, and Computed NAPL Saturations for Field Tests 1 and 2

	1-hexanol	1-heptanol	2-ethyl-1-hexanol
	Field Test 1		
estimated *R*	1.0	1.0	1.0
	Field Test 2		
estimated *R*	1.1	1.4	2.7
sorption adjusted *R*	1.1	1.4	2.7
NAPL saturation (%)	1.9	1.4	2.0

were determined by sediment coring and penetrometer testing (*13*). Results obtained by these other methods ranged from 1.7% to 2.1%, which are similar to those obtained from the push–pull test conducted at this site. Similar extraction-phase breakthrough curves were obtained for nine other tests conducted in widely separated (up to 800 m) wells at this site (data not shown). Estimated NAPL saturations ranged from 0% to 4%.

Environmental Significance. To our knowledge, this is the first study to demonstrate the capability of the single-well push–pull test with *nonreactive* partitioning tracers to detect NAPL under both laboratory and field conditions. The presence of NAPL is indicated by an apparent increase in dispersion of the partitioning tracers relative to the non-partitioning (conservative) tracer. This suggests that the push–pull partitioning tracer test should be useful for site characterization and remediation monitoring especially since it provides a low-cost technique for assessing NAPL contamination at intermediate scales (i.e., between small-scale coring and large-scale PITTs). However, the ability of the push–pull partitioning tracer test to *quantify* NAPL saturations was not unequivocally demonstrated in this study. Transport models assuming homogeneous NAPL distributions and linear equilibrium partitioning were unable to describe all features of injection- and extraction-phase breakthrough curves, even under controlled laboratory conditions. In particular, the effects of diffusion-limited mass transfer between aqueous and NAPL phases may be important in the spatially variable velocity field near the injection−extraction well. Moreover, the effects of spatial heterogeneity in NAPL saturation on extraction-phase breakthrough curves has not been studied. In common with all partitioning tracer test methods (e.g., PITTS) as well as pumping tests, slug tests, and most reactive tracer tests, our approach assumes that the interrogated volume of the aquifer is "homogeneous" within the zone of influence of the test. In this application, homogeneity was assumed for both aquifer physical properties (e.g., hydraulic conductivity, porosity, dispersivity) *and* NAPL saturation. Although we recognize that these assumptions are certainly not satisfied across any field site (and NAPL saturations are probably not completely uniform within our sand packs in the laboratory), this approach still is useful. In fact, the single-well test, because it can be performed in any existing well, provides an ideal tool for quantifying spatial variability in NAPL saturations (and other aquifer properties) at the field scale. While it is true that the test offers no information on spatial heterogeneity at scales equal to or smaller than the interrogated volume, it can provide important information on variations of these properties at the larger field scale. Moreover, if a series of tests were conducted in a single well by injecting increasing volumes of test solution, it would be possible to quantify intermediate-scale (∼1−10 m) heterogeneities in NAPL saturations.

Supporting Information Available

Figures of Test 2−11 data for methanol, IPA, 1-butanol, 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol in different well sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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