Laboratory Investigation of Surfactant-Enhanced Trichloroethene Solubilization Using Single-Well, "Push-Pull" Tests

by J.A. Field[a], J.D. Istok[b], M.H. Schroth[b], T.E. Sawyer[a], and M.D. Humphrey[b]

Abstract

The objective of this study was to evaluate the ability of the single-well, "push-pull" test to characterize the enhanced solubilization of trichloroethene (TCE) by a hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactant. Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration characterized by weight- and molar-solubilization ratios of 0.26 and 1.25, respectively. Laboratory push-pull tests were performed in wedge-shaped physical aquifer models to simulate the alternating radially divergent/convergent flow field in the vicinity of an injection/extraction well. Experiments were conducted in a TCE-free sediment pack and in a sediment pack initially containing liquid TCE with an initial saturation of ~ 5% of the total pore volume. In an experiment conducted in the absence of DOWFAX, maximum TCE concentrations during the extraction phase were ~ 0.6 g/L. In contrast, in an experiment conducted with 13.5 g/L active DOWFAX, TCE concentrations during the extraction phase increased to ~ 3.2 g/L and TCE mass recovery increased by a factor of ~ 3. Two additional experiments conducted with DOWFAX in the same sediment pack yielded smaller maximum TCE concentrations and mass recoveries. The increased density of injected DOWFAX solutions due to TCE solubilization resulted in significant sinking of injected solutions and an accumulation of DOWFAX and TCE at greater depths in the sediment pack; however, no mobilization or sinking of liquid TCE was observed. The results indicate that push-pull tests can provide useful information on surfactant enhanced solubilization of nonaqueous phase liquids in the subsurface.

Introduction

Pump and treat is typically ineffective for remediating sites contaminated with nonaqueous phase liquids (NAPLs) because the slow rate of dissolution and low aqueous solubility of many NAPLs limit their removal by pumping. One approach for increasing the effectiveness of NAPL removal is to inject surface-active-agents (surfactants) to enhance NAPL aqueous solubility. Increased NAPL solubility in the presence of surfactant micelles results from the partitioning of NAPL molecules into the hydrophobic interior of surfactant micelles, which are aggregates of surfactant monomers that form spontaneously at a system-specific surfactant concentration called the critical micelle concentration (CMC). A surfactant's CMC is known to be a function of a several variables including surfactant chemistry, temperature, ionic strength, and the type and concentration of organic contaminants present (Rosen 1989). The effectiveness of a particular surfactant for enhancing NAPL solubility is typically evaluated in the laboratory using molar (MSR) or weight solubilization (WSR) ratios determined from batch solubilization isotherms (Valsaraj and Thibodeaux 1989; Edwards et al. 1991; Rouse et al. 1993). The magnitude of solubility enhancement can also be quantified using micelle-phase/aqueous-phase partition coefficients that describe the mole or weight fraction of NAPL dissolved in the two phases. For example, the molar micelle-phase/aqueous-phase partition coefficient, Km is defined as

$$K_m = X_m/X_a \quad (1)$$

where X_m and X_a are the NAPL mole fractions in the micellar and aqueous phases, respectively. X_m is calculated as X_m = MSR/(1+MSR), and X_a is calculated as $X_a = (S^*_{CMC}\, Vw)$, where S^*_{CMC} is the solubility of the NAPL at the CMC and V_w is the molar volume of water (0.01805 L/mol) (Edwards et al. 1991).

Many laboratory experiments have been conducted to examine the interactions among surfactant type, composition, and concentration and type and concentration of organic contaminants on enhanced solubility (Valsaraj and Thibodeaux 1989; Abdul et al. 1990; Edwards et al. 1991; West 1992; Rouse et al. 1993; Jafvert et al. 1994; Pennell et al. 1997). Typically, this information is obtained in small-scale batch experiments (e.g., Edwards et al. 1991). Linear relationships between log K_m and log K_{ow} have been reported for a variety of anionic and nonionic surfactants and many chlorinated aliphatic compounds, polycyclic aromatic hydrocarbons, and chlorinated aromatic compounds (Valsaraj and Thibodeaux 1989; Edwards et al. 1991; West 1992; Jafvert et al. 1994). Based on a field investigation of the ability of a diphenyl oxide disulfonate surfactant (Dowfax 8390) to enhance the solubility of residual tetrachloroethene, Knox et al. (1997) concluded that laboratory solubilization experiments should be designed to replicate in situ field conditions as closely as possible in order to provide usable results. However, the utility of batch solubilization experiments for predicting enhanced NAPL solubilization in situ is not clear.

It is also possible that the limited surface area of aqueous-phase/NAPL interfaces in the pore space may reduce the ability of a surfactant to solubilize residual NAPL in situ compared to the batch experiment environment, which typically contains no sediment or only a relatively small volume of highly dispersed sediment particles. Oostrom et al. (1999) demonstrated that residual NAPL is more readily solubilized by injected surfactant than pooled (free liquid) NAPL. In this context, residual NAPL is defined as the NAPL fraction that has become entrapped in the pore space during the imbibition of water into pores prevously occupied by NAPL. Residual NAPL exists as isolated blobs or ganglia and is generally considered immobile. Surfactant composition has been shown to vary during subsurface transport due to differential sorption of the individual

[a]Department of Agricultural Chemistry, Oregon State University, Corvallis, OR 97331; voice mail: (541) 737-2265; fax: (541) 737-0497; E-mail: fieldj@ccmail.orst.edu (first author).

[b]Department of Civil Engineering, Oregon State Univeristy, Corvallis, OR 97731.

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components of commercial surfactant mixtures (Krueger et al. 1998; Istok et al. 1999) and this would be expected to result in spatially varying surfactant CMCs, and hence varying ability of the surfactant to enhance the solubility of residual NAPL.

Only a limited number of field studies have been performed to evaluate surfactant-enhanced solubilization of residual NAPLs. Experimental systems have included well-to-well tests with (Fountain et al. 1995, 1996) and without (Smith et al. 1997) sheet-pile enclosures, and vertical recirculation wells (Knox et al. 1997). Although these approaches provide useful pilot-scale information they are typically expensive and logistically complicated. In an attempt to overcome these limitations and those inherent in batch solubilization experiments, an in situ site-characterization technology, called the "push-pull" test, is being developed for use in obtaining site-specific information on surfactant-enhanced solubilization of NAPL. A push-pull test consists of the controlled injection of a prepared test solution into a single monitoring well followed by the recovery of the test solution/ground water mixture from the same well (Istok et al. 1997). The test solution consists of water containing a tracer and one or more reactive solutes; the type, combination, and concentration of these solutes is selected to investigate specific aquifer characteristics. During the injection phase, the prepared test solution is injected ("pushed") into the saturated zone of an aquifer using an existing monitoring well; during the extraction phase, the test solution/ground water mixture is extracted ("pulled") from the same location. Breakthrough curves obtained during the extraction phase are used to obtain quantitative information on transport and transformation of injected solutes.

The objective of this study was to evaluate the utility of the push-pull test for characterizing the ability of an injected surfactant to enhance the aqueous solubility of trichloroethene (TCE) NAPL. Laboratory experiments were performed using TCE, a diphenyl oxide disulfonate surfactant, Dowfax 8390, and sediment from a field site. Batch experiments were first conducted to quantify enhanced TCE solubilization by Dowfax 8390 in aqueous solution. Laboratory push-pull tests were then conducted in physical aquifer models packed with aquifer sediment prepared with and without TCE.

Experimental Methods

Surfactant and Sediment

The surfactant was a 33% active mixture of Dowfax 8390 (DOWFAX) (DOW Chemical Co., Midland, Michigan) consisting of 90% hexadecyl diphenyl oxide disulfonate and 10% dihexadecyl diphenyl oxide disulfonate components. Sediment for laboratory experiments was collected from the Site 300 Building 834 operable unit at Lawrence Livermore National Laboratories (LLNL) in Livermore, California (Carpenter et al. 1984). Sediment was collected from a surface exposure of the aquifer in a single batch, homogenized, sieved (< 5 mm), and air-dried prior to use. The sieved sediment is classified as a sandy loam with 76.9% sand, 21.8% silt, 12.1% clay, a median grain diameter of 0.8 mm, a uniformity coefficient of 2.9, a particle density of 2.65 g/cm^3, an organic carbon content of 0.17 wt %, and a pH of 9, all determined using standard methods (Klute 1986).

Batch Solubilization Experiments

Batch solubilization experiments were conducted using methods similar to those of Rouse et al. (1993). Field site ground water (1.8 mL) containing between 0 and 14 g/L DOWFAX was combined with 200 μL of neat TCE. The samples were shaken for four days on a wrist-action shaker and analyzed. Preliminary experiments indicated that essentially identical solubilization behavior was obtained for site ground water as for tap water; therefore, for convenience tap water was used in subsequent laboratory push-pull tests.

Laboratory Push-Pull Tests

Laboratory push-pull tests were performed in physical aquifer models (PAMs) constructed in a wedge-shape to simulate the radial flow field near an injection/extraction well during a push-pull test (Figure 1a). The PAMs were 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 1b). Air-dried sediment was packed into the PAMs to a uniform bulk density (1.35 g/cm^3) and total porosity (0.49) using the method of Istok et al. (1999). A screen and thin pack of washed silica sand were placed next to the injection/extraction ports to prevent sediment from entering tubing leading to the pump, and a perforated plate and screen were placed at the PAM's wide end to prevent sediment from entering the constant head reservoir (Figure 1b). The sediment packs were saturated with tap water and a lid containing eight sampling ports was installed (Figure 1b). For some experiments, the sediment pack contained a known initial quantity of liquid TCE. This was achieved by first draining the sediment pack and then slowly injecting aliquots of neat TCE at depths from 7 to 10 cm into 53 injection ports located in the model lid between sampling ports 1 and 5 (Figure 1b). A total of 920 g of TCE were injected, which represents a liquid TCE saturation equivalent to ~ 5% of the total pore volume within the treated zone. After TCE injection, the sediment pack was re-saturated with tap water and then flushed for ~ 24 hours with tap water to remove mobile TCE from the injection/extraction ports and to attempt to entrap liquid TCE within the pore space. Less than 40 mL of liquid TCE were removed from the sediment pack during the tap water flush.

Push-pull tests were performed under confined conditions. During the injection phase, flow was directed from the injection/extraction ports at the PAM's narrow end toward the constant head reservoir at the PAM's wide end; during the extraction phase, flow was reversed. Five push-pull tests were conducted. Experiment 1 was conducted in one sediment pack to characterize DOWFAX sorption to LLNL sediment; additional experiments describing the sorption of DOWFAX and a second anionic surfactant to LLNL sediment are described in Istok et al. (1999). Experiment 2 was conducted in a separate sediment pack to quantify TCE recovery in the absence of injected DOWFAX. Experiments 3 through 5 were conducted in the same sediment pack used in experiment 2 to quantify DOWFAX-enhanced TCE solubilization. Bromide (100 mg/L) was used as a conservative tracer in all experiments. DOWFAX was injected at a concentration of 13.5 g/L, which corresponds to a 4 wt % solution of the commercial product or 1.35 wt % of the active (diphenyloxide disulfonate) surfactant, and is similar to concentrations used in recent laboratory sorption experiments (Istok et al. 1999) and field experiments (Knox et al. 1997). At this concentration, DOWFAX forms a single phase Winsor Type I microemulsion (Sabatini et al. 1997).

For each experiment, ~ 9 L of test solution was injected, followed by ~ 0.4 L of a tap water "chaser" to flush the test solution from the injection/extraction ports prior to the start of the extraction phase. The volumes of test solution and chaser were selected to insure that no injected test solution left the sediment pack

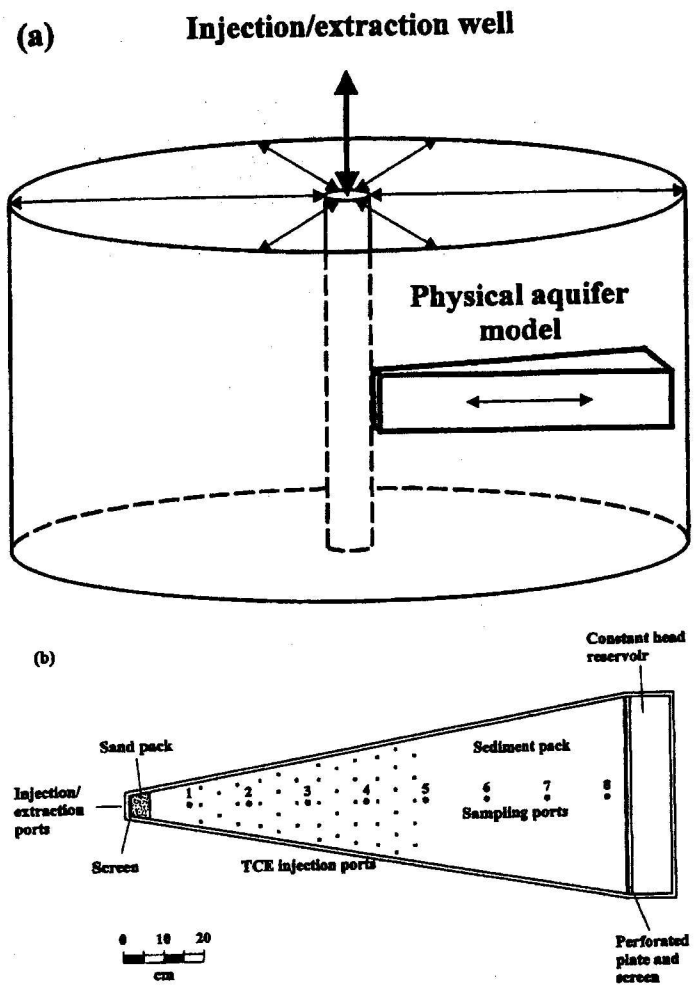

Figure 1. (a) Rationale for physical aquifer model design, (b) plan view of physical aquifer model used in laboratory push-pull tests.

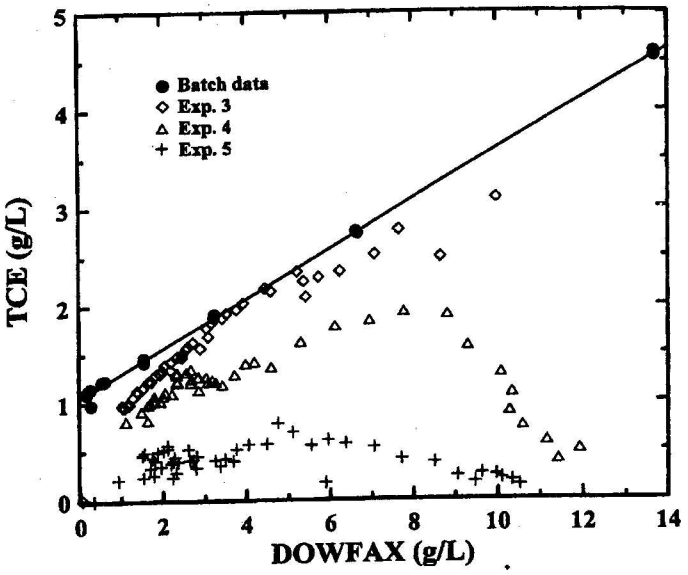

Figure 2. Enhanced solubilization of TCE by DOWFAX in batch experiments and laboratory push-pull tests. Solid line is fitted batch solubilization isotherm.

through the constant head reservoir at the model's wide end. The extraction phase began within 30 minutes after the end of the chaser injection and continued until ~ 22 L had been extracted. Injection and extraction pumping rates were constant at ~ 15 mL/min. Water samples were collected from the sediment pack by inserting a stainless steel syringe needle (through a septum in the sampling port cap) into brass "well" screens that fully penetrated the sediment pack beneath each sampling port. Additional water samples were collected from the injection/extraction ports. After experiment 5, the sediment pack was sampled destructively by collecting cores from 20 locations distributed between ports 1 and 8. To collect cores, the constant head reservoir was drained, the lid was removed, and sections of 5 cm diameter polyvinyl chloride tubing were pressed into the sediment pack to collect core samples at three depths (5 to 6, 12 to 13, and 18 to 19 cm). The cores were then subsampled by transferring ~ 2 g of wet sediment into 10 mL of methanol in a 15 mL glass vial. The vials were shaken, allowed to settle, and the supernatant was diluted with methanol and analyzed for TCE and DOWFAX.

Analytical Methods

Bromide concentrations were determined using a Dionex Model DX-120 ion chromatograph equipped with electrical conductivity detector (Sunnyvale, California). Separations were performed on a 4.6 × 100 mm Star-Ion A300 quaternary amine styrene divinylbenzene column (Phenomenex, Torrance, California). Samples containing surfactants were extracted prior to Br^- analysis by passing samples through a 0.5 g C_{18}-bonded phase silica cartridge (Varian, Harbor City, California). Concentrations of DOWFAX and TCE were determined using a Waters Alliance Model 2690 High Performance Liquid Chromatograph (Milford, Masschusetts) with photodiode array detector. Separations were performed on a Waters C18 Nova-Pak column (3.9 × 150 mm, 4 mm particle size) using a two-step gradient method employing water and acetonitrile. Density measurements were made by placing water samples into 10 mL Gay-Lussac specific gravity vials (Fisher Scientific, Pittsburgh, Pennsylvania) and weighing at 25°C. The interfacial tension between the test solution used in laboratory push-pull tests and TCE was measured by the ring method (Du Noüy 1919) with a CSC Scientific (Fairfax, Virginia) Model 70545 interfacial tensiometer.

Results and Discussion

Batch Solubilization Experiments

Aqueous TCE solubility in batch experiments increased linearly from 1.1 to 4.6 g/L as the DOWFAX concentration increased from 0 to 13.8 g/L (Figure 2). The value of 1.1 g/L is within the range of aqueous TCE solubilities reported by Montgomery (1996) for the temperature of these experiments (25°C). An increase in TCE solubility is expected for surfactant concentrations above the CMC (Rosen 1989) and the CMC for DOWFAX was estimated to be ~ 0.3 g/L from Figure 2. A more refined estimate for the CMC (0.1 to 0.2 g/L) was obtained by the spinning drop method (data not shown), which is consistent with an independent determination of the CMC for DOWFAX (0.13 g/L) obtained from batch sorption isotherms for DOWFAX and LLNL sediment (Istok et al. 1999). However, these values of CMC are much smaller than the range of CMCs for a different DOWFAX series surfactant (2 to 4 g/L) reported by Rouse et al. (1993) but are consistent with the value of 0.32 g/L reported by Lipe et al. (1996).

A fitted solubilization isotherm (Figure 2) yielded computed values of WSR and MSR of 0.26 and 1.25, respectively. The calculated value of log K_m (3.57) in our experiments was similar to the

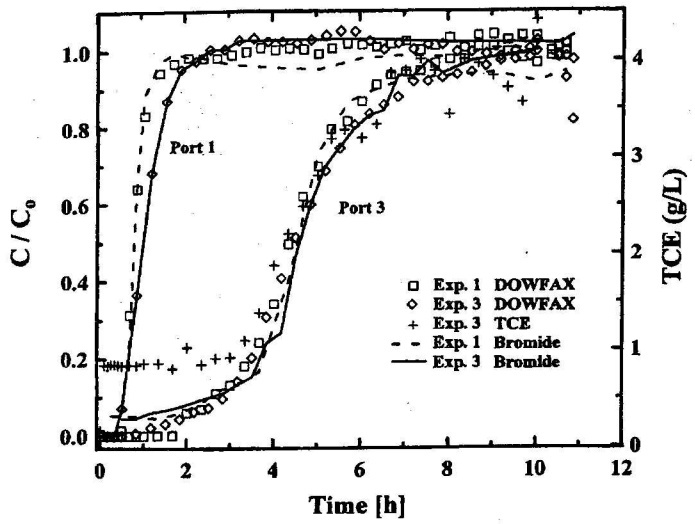

Figure 3.Selected injection phase breakthrough curves for Br⁻, TCE, and DOWFAX during laboratory push-pull tests.

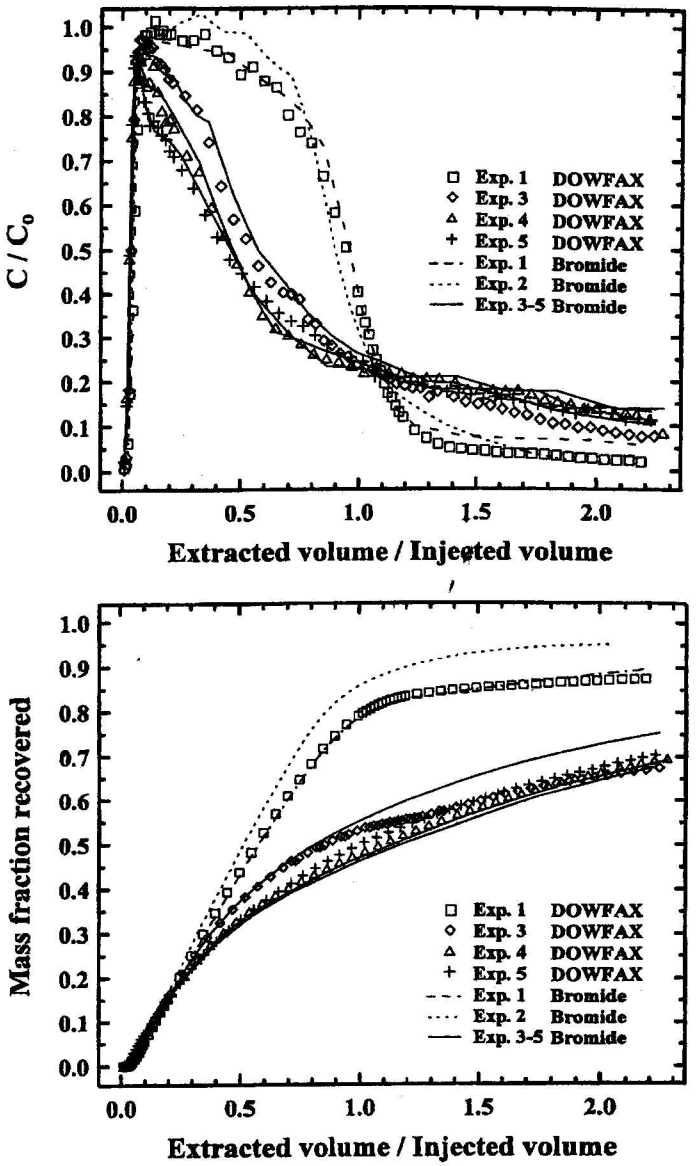

Figure 4. (a) Breakthrough curves and (b) mass recovery plots for Br⁻ and DOWFAX during the extraction phase of laboratory push-pull tests.

range of log K_m values (3.49 to 3.72) reported for a variety of nonionic surfactants by West (1992). Using the empirical relationship reported in Valsaraj and Thibodeaux (1989) and the value of log K_m for DOWFAX, values of log K_{ow} for TCE ranging from 2.93 to 3.06 were calculated that are consistent with published values for TCE (Montgomery 1996).

Additional TCE solubilization experiments were performed in which calcium chloride was added to DOWFAX solutions. The aqueous-phase solubility of TCE increased with increasing concentrations of calcium up to 2400 mg/L. However, at calcium concentrations greater than 2400 mg/L, the concentration of TCE and DOWFAX in aqueous solution declined, which indicated surfactant partitioning into the TCE phase.

Laboratory Push-Pull Tests

Bromide Transport

Measured Br^- concentrations in all experiments were consistent with conservative transport of a nonreactive tracer in a radial flow field and homogeneous sediment pack. In this and subsequent sections, measured solute (Br^- or DOWFAX) concentrations are presented as breakthrough curves that display relative concentration (C/C_o) vs. time, where during the injection phase C is the solute concentration in samples collected at a sampling port from the mid-depth of the sediment pack, while during the extraction phase C is the solute concentration in water samples from the injection/extraction ports, and C_o is the concentration of the same solute in the injected test solution. At each sampling port, values of C/C_o for Br^- increased smoothly from zero to one as the injected test solution penetrated further into the sediment pack. Injection phase breakthrough curves for Br^- for all ports were essentially identical for experiments conducted with and without DOWFAX in sediment packs prepared with and without TCE; results for two ports and three experiments are representative of those obtained for all experiments (Figure 3). Observed Br^- travel times, defined as the time required for C/C_o to reach 0.5, for each port and experiment were essentially identical to those predicted from the physical model geometry, pumping rate, and an effective sediment pack porosity of 0.37.

Measured Br^- concentrations during the extraction phase of experiments 1 and 2 also were consistent with conservative transport of a nonreactive tracer (Figure 4a). Breakthrough curves indicated a rapid initial increase in C/C_o from zero to one due to the initial extraction of the tap water chaser, a plateau with $C/C_o \approx 1$, and a gradual decline in C/C_o from one to zero as tap water entering the physical model from the constant head reservoir gradually displaced the injected test solution from the sediment pack. The presence of 13.5 g/L DOWFAX in the injected test solution in experiment 1 did not substantially change the shape of the extraction phase breakthrough curve for Br^- compared to that obtained for experiment 2, which was conducted without DOWFAX. The Br^- mass recovery curve, obtained by integrating the extraction phase breakthrough curves in Figure 4a, indicated substantial removal (> 90%) of injected Br^- in experiments 1 and 2 (Figure 4b).

Extraction phase breakthrough curves for Br^- for push-pull tests conducted with DOWFAX in the presence of TCE (experiments 3 through 5) also displayed a rapid initial increase in C/C_o from zero to one; however, C/C_o initially decreased more rapidly and then

decreased more slowly than the extraction phase breakthrough curves for experiment 1 (Figure 4a), which was conducted in a sediment pack containing no TCE. Bromide mass recovery in experiments 3 through 5 decreased relative to that for experiment 1 (Figure 4b). The change in Br^- breakthrough curve shape and the decrease in Br^- mass recovery are attributed to the effects of buoyancy-induced flow (sinking) of injected test solutions in sediment packs containing TCE (Figures 4a and 4b). For example, mass recovery decreased from ~ 95% in experiment 1 where the injected test solution had a measured density of 0.9986 g/cm3 (tap water + 0.1 g/L Br^-) to ~ 90% in experiment 2 where the injected test solution had a measured density of 1.0020 g/cm^3 (tap water + 0.1 g/L Br^- + 13.5 g/L DOWFAX). Mass recoveries were further reduced to ~ 70% in experiments 3 through 5 where the density of injected test solutions was increased during transport due to surfactant enhanced solubilization of TCE. For example, the measured density of a water sample in experiment 3 that contained 100 mg/L Br^-, 13.5 g/L DOWFAX, and 4.5 g/L TCE was 1.0035 g/cm^3. The magnitude of vertical hydraulic gradients due to density differences is comparable to horizontal hydraulic gradients due to injection and extraction pumping. The maximum vertical hydraulic gradient caused by a density difference of (1.0035 to 0.9969)g/cm^3 over the 20 cm deep sediment pack is approximately equal to the maximum horizontal gradient caused by pumping, which occurs within the sediment at the injection/extraction ports. Further away from the injection/extraction ports, horizontal hydraulic gradients are much smaller due to the diverging flow field created by the design of the physical aquifer model. In previous work we have demonstrated that density-driven flow can substantially influence the behavior of injected tracer solutions, even when density differences are smaller than reported here (Istok and Humphrey 1995). Increased density would cause injected test solutions to sink deeper into the sediment pack, decreasing the efficiency of extraction phase pumping and affecting changes in the shapes of extraction phase breakthrough curves.

This interpretation is supported by analyses performed on water samples collected from the sediment pack as a function of depth immediately after each experiment that indicated increasing DOWFAX and TCE concentrations (discussed further in the next section) with increasing depth at all ports (Figure 5). Although Br^- concentrations were not determined on these samples due to insufficient sample volumes, it is assumed that similar depth-concentration profiles would have been obtained for Br^-. This assumption is consistent with injection and extraction phase breakthrough curves for experiments 1 and 3 through 5 (Figures 3 and 4a), which showed essentially identical transport behavior for Br^- and DOWFAX in all experiments. Based on these results, the changes in extraction phase breakthrough curve shape for Br^- between experiments 1 and 2 and experiments 3 through 5 are attributed to density effects caused by enhanced TCE solubilization by injected DOWFAX. Similar effects were observed by Oostrom et al. (1999) for enhanced TCE solubilization using another surfactant. Because conductivity was essentially constant for all sets of conditions, the viscosity of the bulk pore water was also essentially constant during these tests (recall that hydraulic conductivity can be expressed as $K = \rho g k/\mu$, where ρ and μ are the fluid density and viscosity and k is the intrinsic permeability of the sediment pack). For this reason we conclude that changing viscosity was not responsible for changes in aqueous TCE recovery during these tests

DOWFAX Transport

Apparent conservative transport of DOWFAX in sediment packs prepared with and without TCE was indicated by the essentially identical shape of breakthrough curves for DOWFAX and Br^- for a given experiment during the injection phase (Figure 3) and extraction phase (Figure 4a) of experiments 1 and 3 through 5. In addition, mass recoveries of DOWFAX and Br^- were essentially identical for a given experiment (Figure 4b). This behavior is consistent with both batch sorption and laboratory push-pull tests conducted to characterize DOWFAX sorption to LLNL sediment (Istok et al. 1999) and batch sorption tests conducted with a high purity DOWFAX standard and other sediments by Rouse et al. (1993). Due to the relatively high DOWFAX concentration in the injected test solutions (13.5 g/L) and the weak affinity of DOWFAX for the LLNL sediment, sorption sites were essentially instantaneously saturated during transport without causing any apparent retardation in DOWFAX transport relative to Br^-.

The change in shape of DOWFAX extraction phase breakthrough curves and mass recovery plots in the presence of TCE (experiments 3 through 5) are attributed to buoyancy-induced flow (sinking) of injected test solutions due to increasing density of injected test solutions caused by enhanced TCE solubilization, as discussed in the previous section. The magnitude of the concentration increase with depth was largest in sampling ports 1 through 3, which were within the portion of the sediment pack that both contained TCE and had significant contact with injected DOWFAX (Figure 5). After experiment 3, DOWFAX concentrations near the top of the sediment pack (3 cm depth) were less than 0.5 g/L in all ports but increased with increasing depth in ports 1 through 5 to a maximum of ~ 2 g/L near the bottom of the sediment pack (18 cm depth) in port 1. After experiments 4 and 5, DOWFAX concentrations near the top of the sediment pack remained less than ~ 1 g/L in all ports but continued to increase at all other depths and ports to a maximum value of ~ 9 g/L at a depth of 18 cm in ports 2 and 3 after experiment 5. Sinking of injected test solutions caused the total mass of DOWFAX remaining in the sediment pack to increase after experiments 3 through 5 (Figure 4b).

Another possible explanation for the observed differences in extraction phase breakthrough curves for DOWFAX and Br^- in experiments 3 through 5 compared to those for experiment 1 is that some of the injected surfactant and Br^- partitioned into the TCE phase. In order for DOWFAX to partition into the TCE phase, the divalent cation concentration in the aqueous phase would have to increase sufficiently to cause Winsor Type II behavior, in which the surfactant resides largely in the TCE ("oil") phase as "water-swollen reverse micelles" (West and Harwell 1992). However, partitioning of DOWFAX would result in differences in the extraction phase breakthrough curves for DOWFAX and Br^-, which were not observed.

Enhanced TCE Solubilization

Preliminary batch experiments (data not shown) indicated that sorption of TCE to LLNL sediment was negligible; conservative transport of TCE was also apparent in the breakthrough curve for port 3 during experiment 3 (Figure 3). The maximum TCE concentration observed during the extraction phase of experiment 2 (conducted without DOWFAX) was ~ 0.6 g/L (Figure 6a), which is approximately 60% of the aqueous TCE solubility (1.1 g/L) at the temperature of these experiments (25°C), and reflects the dilution of TCE saturated water (near the emplaced liquid TCE) by TCE-free pore water above and below the zone of TCE emplacement.

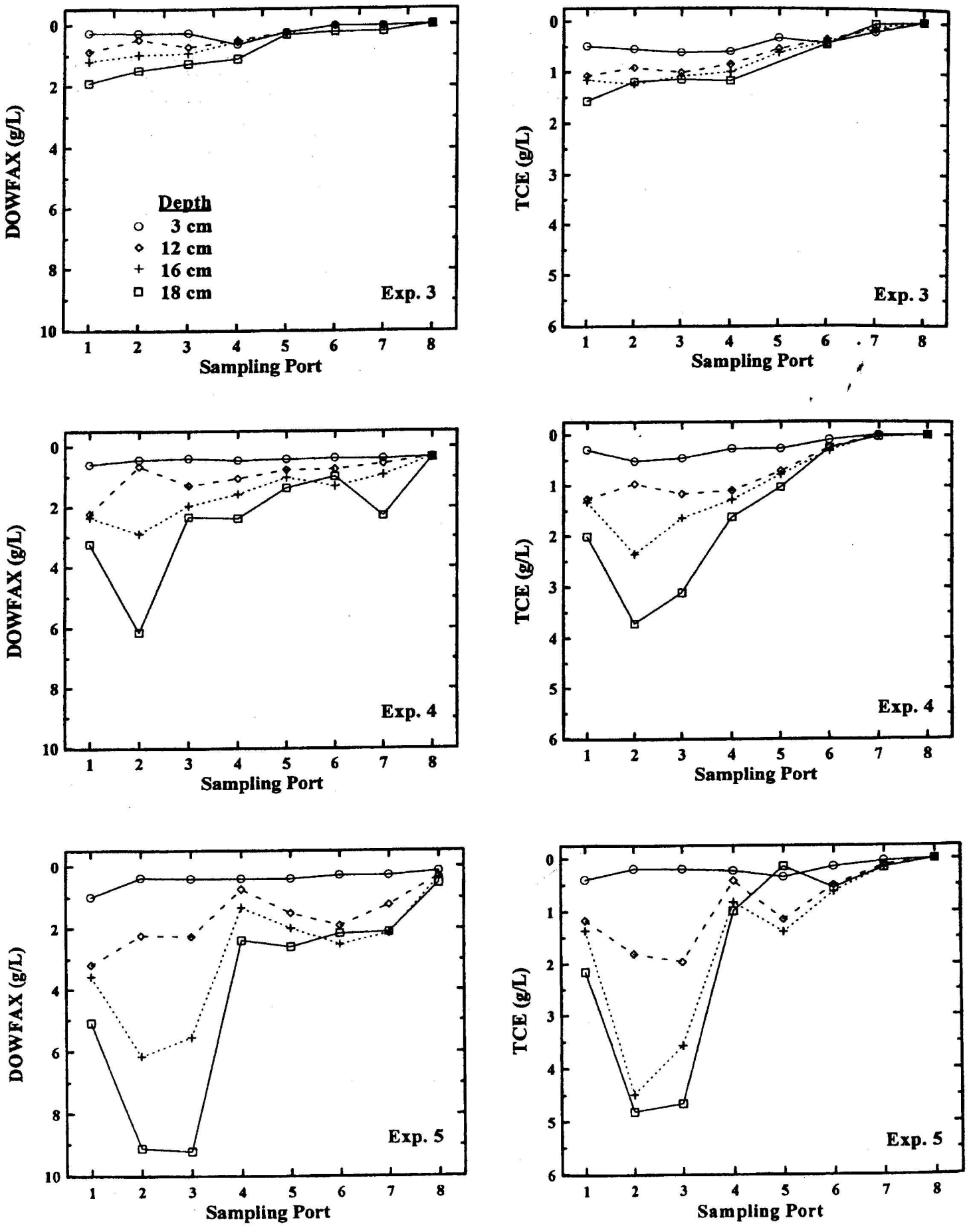

Figure 5. Variation of DOWFAX and TCE concentrations with depth at the end of (a,b) experiment 4; (c,d) experiment 5; and (e,f) experiment 6.

TCE mass recovery during this test (12 g; Figure 6b) represents ~ 1% of the initial TCE mass emplaced.

The maximum TCE concentration observed during the extraction phase of experiment 3 (the first push-pull test conducted with DOWFAX) was ~3.2 g/L (Figure 6a) with a corresponding TCE mass recovery of ~35 g (Figure 6b). During the extraction phase of experiments 4 and 5 the maximum TCE concentration decreased to ~1.9 and ~ 0.6 g/L, respectively (Figure 6a). TCE mass recovery also decreased to ~25 g in experiment 4 and to ~ 8 g in experiment 5, which is less than the 12 g of TCE recovered in experiment 2 performed with no DOWFAX (Figure 6b). Buoyancy-induced flow of injected test solutions described for Br^- and DOWFAX was also apparent in vertical variations in TCE concentration observed in the sampling ports following experiments 3 through 5 (Figure 5). After experiment 3, TCE concentrations near the top of the sediment pack (3 cm depth) were generally uniform at ~ 0.5 g/L in ports 1 through 6 but increased to a maximum of 1.5 g/L at a depth of 18.3 cm at port 1. However, after experiments 4 and 5, TCE concentrations increased at all depths > 3 cm in ports 1 through 5, to a maximum value of ~ 5 g/L in port 2 after experiment 5. Reduced TCE concentrations in some extraction phase samples compared to batch isotherms may be attributed to the smaller contact time for injected DOWFAX (10 to 30 hours) compared to batch (96 hours).

The decreasing effectiveness of sequential DOWFAX injections in enhancing TCE solubilization is perhaps most clearly seen by plotting pairs of measured TCE and DOWFAX concentrations during the extraction phase of experiments 3 through 5 on the batch solubilization isotherm in Figure 2. To prepare these plots, only a portion of the extraction phase data was used. Samples collected for values of (extracted volume)/(injected volume) less than 0.2 were excluded because these represent the tap water flush (containing no DOWFAX) injected after the test solution; samples with a DOWFAX concentration less than the CMC (0.13 g/L) were also excluded because enhanced TCE solubilization will not occur for DOWFAX concentrations below the CMC. Measured DOWFAX and TCE concentrations during the extraction phase of experiment 3 were in general agreement with batch data and had a similar WSR and MSR as the batch solubilization isotherm (Figure 2). Evidence of enhanced TCE solubilization was also apparent during the extraction phase of experiment 4 but resulted in slightly smaller values of WSR and MSR. No evidence of enhanced TCE solubilization was apparent in the data from experiment 5, as no samples had TCE concentrations above the aqueous solubility (1.1 g/L), although DOWFAX concentrations were above the CMC in every sample.

Reduced mass recovery of TCE in experiments 4 and 5 cannot be attributed to sinking of liquid TCE to greater depths within the sediment pack. Sediment cores were obtained and analyzed after experiment 5 in order to determine the distribution of TCE within the sediment pack. Concentrations of TCE that exceeded that predicted from the solubilization isotherm by a factor of 2 were used to infer the presence of liquid TCE in sediment cores. The distribution of TCE as determined from sediment cores (data not shown) indicated no evidence of the vertical redistribution of liquid TCE within the sediment pack; essentially all of the remaining TCE was located where it was emplaced (depths of 7 to 10 cm between ports 1 and 5). Moreover, measurements using the ring method indicated that interfacial tensions for aqueous DOWFAX and liquid TCE were not reduced to sufficiently small values to allow remobilization of residual TCE to occur. For example, the minimum measured water-TCE interfacial tension (obtained for a DOWFAX concentrations of 13.5 g/L) was ~ 18 mN/m. Using this value and values for the pore water velocity (which is a function of radial distance from the injection/extraction ports) and hydraulic conductivity of the sediment pack, the maximum value of the total trapping number for the sediment pack during experiments 3 through 5 was calculated to be 3×10^{-6}, which should be insufficient to remobilize liquid TCE (Pennell et al. 1996).

It is hypothesized that the reduction in enhanced TCE solubilization by DOWFAX from experiment 3 to experiments 4 and 5 is due to differences in the relative effectiveness of DOWFAX in solubilizing residual TCE and TCE existing as a free liquid. It is unlikely that the method of TCE emplacement was able to entrap 100% of emplaced TCE. In fact, 40 g of the initial 920 g of injected TCE were removed during initial resaturation and tap water flushing of the sediment pack indicating that some of the injected TCE existed as free liquid. Although the total mass of liquid TCE within the sediment pack was essentially constant during experiments 3 through 5 (because the quantity of TCE recovered during each experiment was relatively small), it is possible that residual TCE was being preferentially removed from the sediment pack and was essentially all removed by the end of experiment 4. For example, Oostrom et al. (1999) reported the preferential removal of residual

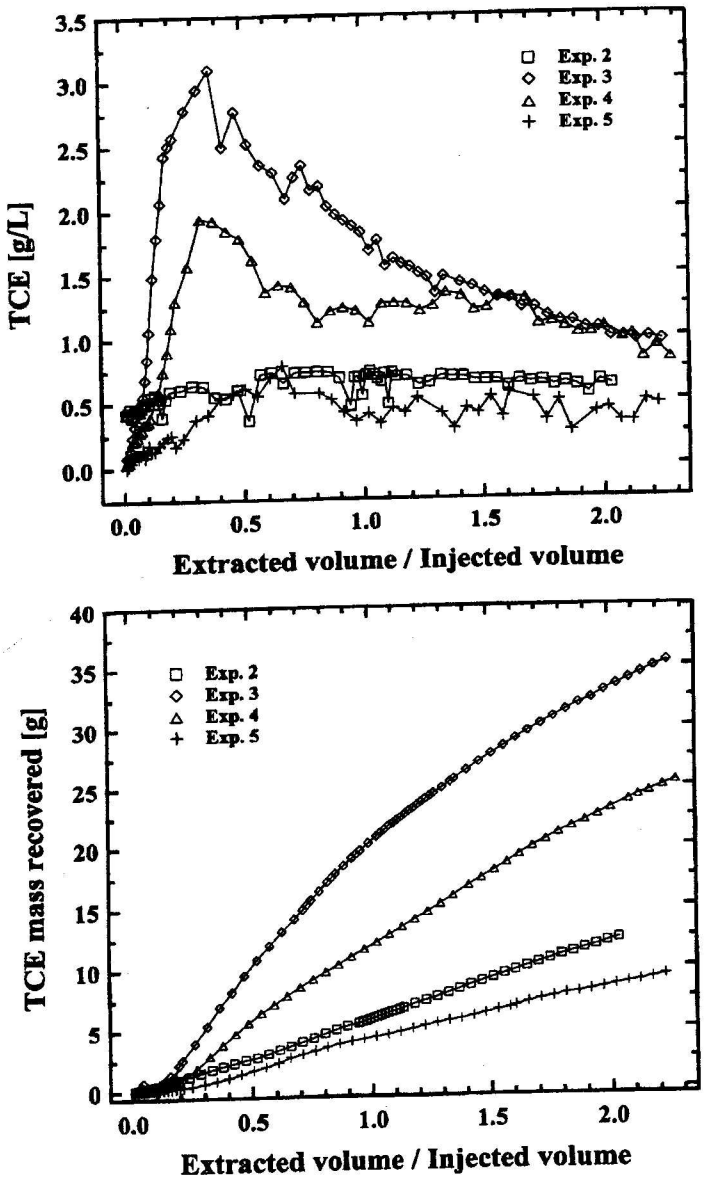

Figure 6. (a) Breakthrough curves and (b) mass recovery plots for Br^- and TCE during the extraction phase of laboratory push-pull tests.

TCE compared to free liquid during surfactant solubilization experiments in a layered sand system. Apparently the larger surface area of TCE within the small blobs and ganglia of entrapped TCE that forms the residual saturation is more accessible to solubilization by injected surfactants than free TCE liquid (which has a smaller surface area to volume ratio than residual TCE). If essentially all residual TCE had been removed by the end of experiment 4, an estimate for the residual saturation of TCE in this system is given by the total mass of TCE recovered during experiments 3 and 4, 35 + 25 = 60 g (or 41 cm^3).

It is also possible that the reduction in TCE solubilization could be due to changing flow patterns within the sediment pack caused by the increasing concentrations of DOWFAX and aqueous TCE at depth within the sediment pack (Figure 5). The increasing concentrations and density of pore water at the bottom of the sediment pack may have created upward buoyancy forces on injected DOWFAX solutions, causing some flow to bypass portions of the sediment pack containing liquid TCE.

Conclusions

The results of intermediate-scale laboratory experiments indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing liquid TCE solubilization in natural aquifer sediments. Push-pull test extraction phase breakthrough curves can be used (1) to examine surfactant transport behavior relative to that of a coinjected tracer, (2) to determine the recovery efficiency of an injected surfactant, and (3) to quantify the increase in aqueous TCE solubility due to injected surfactant.

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