Laboratory and Field Investigation of Surfactant Sorption Using Single-Well, "Push-Pull" Tests

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Abstract

Sorption to aquifer sediments can limit the effectiveness of surfactants injected to solubilize residual nonaqueous phase liquid contaminants in the subsurface. The objective of this study was to evaluate the ability of the single-well, push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment in situ. Batch sorption isotherms for both surfactants exhibited Langmuir-type sorption behavior with larger apparent sorption maxima for LAS than for DOWFAX. However, numerical transport simulations based on batch sorption isotherms were unable to predict the retardation and chromatographic separation of LAS homologs and conservative transport of DOWFAX observed during laboratory and field push-pull tests, indicating that the single-well, push-pull test method can more accurately describe in situ surfactant sorption and transport behavior than batch sorption isotherms.

Introduction

Nonaqueous phase liquids (NAPLs), which include a variety of common petroleum fuels and chlorinated solvents, are ground water contaminants at many sites. In the subsurface, a portion of the NAPL (called residual NAPL) may become trapped in the pore space by capillary forces. Conventional treatment technologies are typically ineffective in removing residual NAPL because the slow rate of dissolution and low aqueous solubility of many NAPLs limit their removal by extraction pumping. One approach for increasing the effectiveness of NAPL removal is to inject surface-active-agents (surfactants) to enhance NAPL solubilization. Surfactants are complex mixtures of structurally similar homologs or oligomers that are characterized by molecular structures containing both lipophilic and hydrophilic groups (Rosen 1978). In aqueous solution, surfactants form micelles, which are aggregates of surfactant monomers that form spontaneously at a system-specific surfactant concentration called the critical micelle concentration (CMC). Increased NAPL aqueous solubility results from the partitioning of NAPL molecules into the hydrophobic interior of surfactant micelles. The use of injected surfactants to enhance the recovery of residual NAPL from ground water aquifers has been investigated in laboratory (Valsaraj and Thibodeaux 1989; Edwards et al. 1991; West 1992; Jafvert et al. 1994; Pennell et al. 1997) and field experiments (Abdul and Ang 1994; Fountain et al. 1995, 1996; Knox et al. 1997; Sabatini et al. 1997; Smith et al. 1997) and a wide variety of surfactants have been proposed for this purpose (Abdul et al. 1990). However, surfactant selection for this application currently is complicated by the need to balance the physiochemical properties of the surfactant that affect its transport in the aquifer with those that affect its ability to solubilize residual NAPL (West and Harwell 1992). Processes that affect surfactant transport and fate in the subsurface include advection, dispersion, sorption, precipitation, and biodegradation. These processes can decrease the concentration and therefore the solubilization or mobilization activity of an injected surfactant. In particular, the portion of injected surfactant that sorbs to aquifer sediments is unavailable for micelle formation and therefore will be ineffective in solubilizing residual NAPL (Kibbey and Hayes 1997).

Chemical structure can be used to estimate the extent that a particular surfactant will sorb to aquifer sediments. For example, sorption of linear alkylbenzene sulfonates (LAS) increases with increasing alkyl chain length (Hand and Williams 1987) while sorption of polyethoxylated surfactants increases with the number of ethoxy units (Podoll et al. 1987). Also, surfactants with two anionic head groups, such as alkyl diphenyl oxide disulfonates typically sorb less than surfactants with a single anionic head group, such as LAS (Rouse et al. 1993). However, sorption estimates based on chemical structure are largely qualitative and do not provide the quantitative and system-specific information on surfactant sorption required for remedial design. Traditionally, this information has been obtained in small-scale laboratory batch and column experiments performed with sediment samples obtained by coring. However, laboratory-based studies have several disadvantages including (1) the need for core samples, which may be unavailable or costly to obtain, (2) the likelihood that the small sample volumes

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Received June 1998, accepted January 1999.

obtainable by coring are not representative of the heterogeneous subsurface environment, (3) the likelihood that core samples will be disturbed and/or contaminated during collection, and (4) the difficulty in reproducing in situ conditions in the laboratory.

Recently, a novel type of single well test, which we call a "push-pull" test, is proving useful for the quantitative in situ determination of a wide range of aquifer physical, chemical, and biological characteristics (e.g., Istok et al. 1997; Schroth et al. 1998). During the injection phase of a push-pull test, a prepared test solution containing a conservative tracer and one or more additional solutes 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. Water samples collected during the extraction phase are analyzed to prepare breakthrough curves for each solute, which are then interpreted to obtain quantitative information on the transport and/or rate of transformation of injected solutes (e.g., Haggerty et al. 1998).

The objective of this study was to evaluate the utility of push-pull tests for characterizing sorption of injected surfactants to aquifer sediment in situ. Laboratory and field experiments were conducted with two surfactants and natural aquifer sediment collected from a field site. Batch experiments were first conducted to obtain equilibrium sorption isotherms. Laboratory push-pull tests were then conducted in physical aquifer models packed with the same sediment and designed to simulate the radial flow field near an injection/extraction well during field tests. Numerical modeling was used to compare simulated breakthrough curves based on batch sorption isotherms to breakthrough curves from laboratory and field push-pull tests.

Materials and Methods

Aquifer Sediment

Sediment for laboratory experiments was collected from the Building 834 operable unit, Site 300 at Lawrence Livermore National Laboratory (LLNL) in Livermore, California. The shallow, unconfined aquifer at the site was formed in a Pliocene age nonmarine depositional sequence consisting of dense silty sand gradational to silty sandstone with minor gravel (Carpenter et al. 1984). Ground water analyses suggest that residual trichloroethene (TCE) may be present in portions of the aquifer and surfactant-enhanced solubilization of residual TCE is one remediation technology being considered for use at the site. Uncontaminated sediment for laboratory experiments was collected from a surface exposure of the aquifer at a roadcut located approximately 50 m from the monitoring wells used in field push-pull tests at the site (see later description). Sediment for laboratory experiments was collected as 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, 10.9% silt, and 12.1% clay, with a median grain diameter of 0.8 mm, a uniformity coefficient of 2.9, a particle density of 2.65 g/cm3, an organic carbon content of 0.0017, and a pH of 9. All properties were determined using standard methods (Klute 1986).

Surfactants

Two surfactants were used: (1) a 50% active mixture of linear alkylbenzene sulfonate (LAS) (C550 Slurry, Condea Vista Chemical Co., Austin, Texas) consisting of 22% C10, 42% C11, 27% C12, and 9% C13 alkyl chain homologs (Condea Vista); and (2) 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. These surfactants were selected because they are anticipated to have substantially different sorption behavior (based on mixture composition), because LAS is widely distributed in the environment due to its presence in sewage, and because DOWFAX has been used to enhance DNAPL solubilization in recent field trials (Knox et al. 1997).

Batch Sorption Experiments

Batch sorption experiments were conducted using methods similar to those of Rouse et al. (1993). Five grams of air-dried sediment were combined with 25 mL of site ground water containing between 5 and 7000 mg/L LAS or between 39 and 16,600 mg/L DOWFAX. Samples were shaken for 24 hours on a wrist-action shaker, centrifuged, and the supernatant was passed through a 0.45 μm nylon filter and analyzed. Additional experiments indicated that identical sorption behavior occurred when the surfactants were combined with either site ground water or laboratory tap water and, for convenience, tap water was used to prepare test solutions for subsequent laboratory and field push-pull tests. Surfactant precipitation was not observed at any time during these experiments.

A least-squares method was used to fit the Langmuir equation (e.g., Fetter 1993) to batch isotherm data; the Langmuir equation relates the solid (sorbed) phase surfactant concentration S to the aqueous phase concentration C:

$$S = \frac{q_{max} K_L C}{1 + K_L C_0} \tag{1}$$

where q_{max} is the maximum sorption capacity, and K_L is the Langmuir coefficient. For a surfactant, the aqueous phase concentration at which the solid phase concentration reaches q_{max} is equivalent to the CMC (Rosen 1978). CMC values were computed by setting $S = 0.9\ q_{max}$ in Equation 1 and solving for C. Values of the equilibrium sediment-water partition coefficient, K_d, which represents the slope of the Langmuir isotherm at small aqueous phase concentrations (C << CMC) were computed from the fitted Langmuir parameters using

$$K_d = q_{max} K_L \tag{2}$$

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 a monitoring well during a field push-pull test (Figure 1a). The PAMs were constructed of polypropylene (sorption of LAS and DOWFAX to polypropylene was determined to be negligible) with interior dimensions of 5 cm (width at narrow end), 50 cm (width at wide end), 125 cm (length), and 20 cm (height), and a total internal volume of 0.069 m^3 (Figure 1b). Test solutions were injected and extracted using injection/extraction ports located on a vertical plate at the model's narrow end. During the injection phase, flow was directed from the injection/extraction ports toward the model's wide end; during the extraction phase, flow was reversed. A constant head water 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 injected test

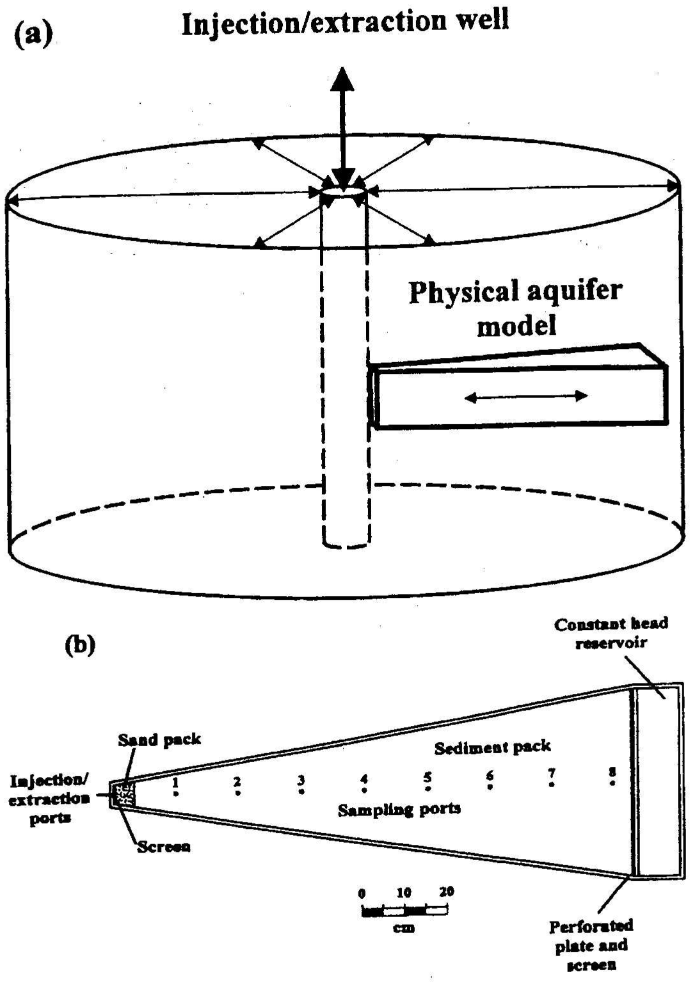

Figure 1. (a) The portion of the flow field near an injection/extraction well represented by a wedge-shaped physical aquifer model, and (b) plan view of physical aquifer model used in laboratory push-pull tests.

solution was selected to insure that no injected test solution left the sediment pack through the constant head water reservoir.

The PAMs were packed using the method of Istok and Humphrey (1995), which involved (1) temporarily dividing the PAM interior into a set of volume elements using thin posterboard partitions, (2) packing dry sediment into each volume element to obtain the same bulk density (1.35 g/cm^3), and (3) carefully removing the partitions. A separate volume element immediately adjacent to the injection/extraction ports was packed with clean silica sand to represent the sand pack present in monitoring wells used in field push-pull tests (Figure 1b). During initial water saturation of the sediment pack, wetting fronts were observed to advance with a uniform and symmetrical shape indicating that the packing method had created an approximately homogeneous sediment pack. New sediment packs were prepared for each laboratory push-pull test.

After the sediment pack was water saturated, the PAMs were sealed by installing a layer of closed cell foam and a lid containing eight sampling ports (Figure 1b). Experiments were performed under confined conditions. Sampling ports were connected to brass "well" screens that fully penetrated the saturated thickness of the sediment pack (Figure 1b). Additional "wells" were connected to manometers to measure hydraulic head. 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.

Injected test solutions consisted of tap water containing 100 mg/L Br$^-$ (prepared from KBr) to serve as a conservative tracer and an initial surfactant concentration, C_o, of either 1924 mg/L LAS or 13,500 mg/L DOWFAX (Table 1). Approximately 9 L of test solution were injected, followed by ~ 0.4 L of a tap water "chaser," which contained no tracer or surfactant, to flush the test solution from the tubing, injection ports, and sand pack prior to the start of the extraction phase. Extraction pumping began within 30 minutes after the end of the chaser injection and continued until ~ 20 L had been extracted. Injection and extraction pumping rates were constant at ~ 15 mL/min. Water samples were collected from the sampling ports during the injection phase by inserting a stainless steel syringe needle 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 during the extraction phase.

Analytical Methods

Bromide concentrations were determined using a Dionex Model DX-120 ion chromatograph equipped with electrical conductivity detector (Sunnyvale, California). Samples were extracted to remove surfactants prior to Br$^-$ analysis by passing samples through a 500 mg C_{18}-bonded phase silica cartridge (Varian, Harbor City, California) prior to analysis. LAS and DOWFAX concentrations were determined using a Waters Alliance Model 2690 high performance liquid chromatograph equipped with photodiode array detector (Milford, Massachusetts). LAS separations were performed on a Supelco ABZ column (4.6 × 150 mm; 5 mm particle size) using a solvent gradient method employing methanol and buffer. DOWFAX 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.

The critical micelle concentration for DOWFAX in tap water was determined from a Gibbs plot (Rosen 1978) constructed by plotting log DOWFAX concentration versus surface tension measured by the spinning drop method (Vista Chemical Co. 1991) using a Model 300 Spinning Drop Interfacial Tensiometer (Vista Chemical, Austin, Texas).

Numerical Simulations

Numerical simulations of tracer and surfactant transport during laboratory push-pull tests were performed using the Subsurface Transport Over Multiple Phases (STOMP) code (White and Oostrom 1997). 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 (Nichols et al. 1997). For these simulations, we assumed that solute (Br$^-$, LAS, or DOWFAX) transport is described by the one-dimensional (radial) form of the advection-dispersion equation:

$$\frac{\partial C}{\partial t} + \frac{\rho b}{n}\frac{\partial S}{\partial t} = \alpha_L |v| \frac{\partial^2 C}{\partial r^2} - v\frac{\partial C}{\partial r} \qquad (3)$$

where t is time; ρb, n, and α_L are the bulk density, effective porosity, and longitudinal dispersivity of the sediment pack; v is the average pore water velocity; and r is radial distance. Equation 3 assumes

Table 1
Experimental Conditions for Laboratory and Field Push-Pull Tests

Exp. No.	Surfactant	C_o [mg/L]	Volume of Injected Test Solution [L]	Duration of Test Solution Injection [h]	Volume of Injected Tap Water Chaser [L]	Duration of Chaser Injection [h]	Extraction Volume [L]	Duration of Extraction Phase [h]
1	LAS[a]	1924	9.6	10.7	0.43	0.50	20.9	23.4
2	DOWFAX[a]	13,500	9.3	10.0	0.49	0.53	21.5	21.0
3	LAS[b]	1924	50	0.8	30	0.5	100	1.7
4	DOWFAX[c]	13,500	50	1.6	0	—	100	2.9

[a] Laboraory push-pull test with LLNL Site 300 sediment.
[b] Field push-pull test in monitoring well MW-7 at OSU motor pool.
[c] Field push-pull test in monitoring well D-6 at LLNL Site 300.

that the sediment pack is homogeneous; mechanical dispersion is a linear function of v; and molecular diffusion is negligible (Bear 1979). Note that in a radial flow field the pore water velocity is a function of r:

$$v(r) = Q/(2\pi nb) \tag{4}$$

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

Pumping rates (~ 15 mL/min) were measured for each laboratory push-pull test. The bulk density and thickness of the sediment pack was 1.35 g/cm^3 and 20 cm, respectively. The longitudinal dispersivity (0.3 to 0.5 cm) and effective porosity (0.37) of the sediment were estimated from injection and extraction phase breakthrough curves for Br$^-$ using the method of Gelhar and Collins (1971). Sorption of Br$^-$ was assumed to be negligible ($q_{max} = 0$). Sorption of LAS and DOWFAX was computed using Equation 1 with values of q_{max} and K_L estimated from batch sorption isotherms (Table 2). Equations 1 and 3 are solved in STOMP using a modified Newton-Raphson method. The computational domain consisted of 125 nodes with a uniform node spacing of 1.0 cm. The time step size varied between 0.5 and 20.0 seconds. Initial conditions were C = S = 0 for all solutes. Time-varying third-type (Neumann) boundary conditions at r = 13.9 cm were used to represent pumping at the injection/extraction ports; constant head and zero solute flux boundary conditions at r = 138.9 cm were used to represent the standpipe/overflow system at the wide end of the PAM.

Field Push-Pull Tests

Field push-pull tests were performed at two sites. Due to the anticipated poor recovery of injected LAS, it was not possible to perform push-pull tests with LAS at LLNL. Instead, a test with LAS was performed in monitoring well MW-7 at the Oregon State University (OSU) motor pool. The well is 5 cm in diameter, ~ 4 m deep, and screened over the entire saturated thickness of the aquifer, which consists of a silty sand with some gravel. For this test, 50 L of test solution containing 100 mg/L Br$^-$ and 1924 mg/L LAS were injected at a rate of ~ 1 L/min into the bottom 1 m long portion of the well screen (Table 1). Test solution injection was followed by the injection of a 30 L tap water chaser at 1 L/min. Extraction pumping using a peristaltic pump began immediately after the end of the chaser injection and continued at ~ 1 L/min until 100 L had been extracted. Water samples were collected during the extraction phase and analyzed for Br$^-$ and LAS.

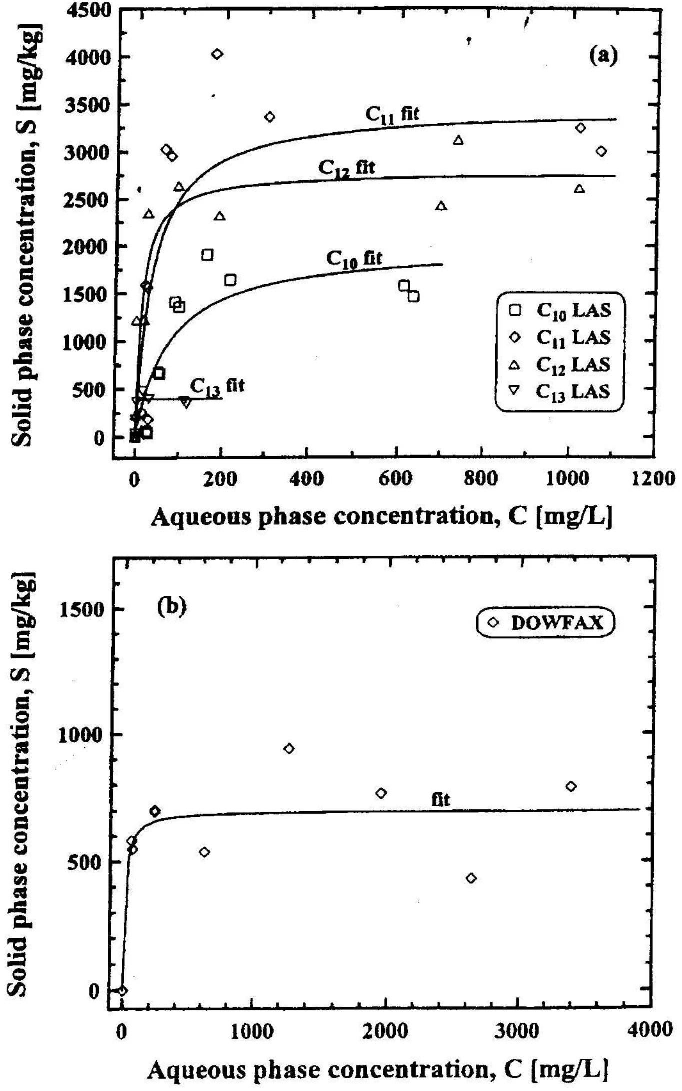

Figure 2. Equilibrium sorption isotherms from batch experiments for (a) LAS homologs, and (b) DOWFAX. Fitted Langmuir isotherms are shown as solid lines.

The field push-pull test with DOWFAX was performed in monitoring well D-6 at the LLNL field site, which is screened in the same aquifer that provided the source of sediment for laboratory experiments (Table 1). The well is 10 cm in diameter and ~ 10 m

Table 2

Estimated Values of Langmuir Sorption Isotherm Parameters (q_{max} and K_L) and Computed Values of Critical Micelle Concentration (CMC) and Sediment Water Distribution Coefficient (K_d) for LAS Homologs and DOWFAX

Component	q_{max} (mg/kg)	K_L (L/mg)	CMC (mg/L)	K_d (L/kg)
C_{10}-LAS	1989	0.013	500	26
C_{11}-LAS	3449	0.027	260	93
C_{12}-LAS	2770	0.076	125	211
C_{13}-LAS	396	5.34	2	2115
DOWFAX	699	0.07	125	49

deep. In this test, 50 L of test solution containing 100 mg/L Br^- and 13,500 mg/L DOWFAX were injected at a rate of ~ 0.5 L/min into the bottom 1 m long portion of the well screen. No tap water chaser was injected. Extraction pumping using a submersible pump began ~ 30 minutes after the end of the test solution injection and continued at ~ 0.3 L/min until 100 L had been extracted. Water samples were collected during the extraction phase and analyzed for Br^- and DOWFAX.

Results and Discussion

Batch Sorption Experiments

Equilibrium sorption isotherms for LAS and individual LAS homologs were characterized by increasing surfactant solid phase concentration with increasing aqueous phase concentration until a maximum solid phase concentration (q_{max}) was reached, which is consistent with the Langmuir-type sorption behavior reported for LAS and other surfactants (e.g., Rouse et al. 1993). Because chromatographic separation of LAS was expected during transport we characterized the sorption of individual LAS homologs (Figure 2a). Fitted values of q_{max} and CMC for individual LAS homologs ranged from 1989 to 396 mg/kg and from 500 to 2 mg/L, respectively (Table 2).

The composition of the LAS mixture in the aqueous and solid phases changed with increasing aqueous phase concentration (data not shown). At aqueous phase concentrations below the CMC, aqueous phase LAS was preferentially depleted in the longer alkyl-chain (i.e., more hydrophobic) homologs while the composition of LAS in the solid phase was enriched in these homologs. At aqueous phase concentrations equal to or larger than the CMC, the compositions of the aqueous and solid phases were identical to that of the commercial mixture. Because q_{max} and CMC for individual oligomers are dependent on the composition of the surfactant mixture (Kibbey and Hayes 1997), estimated values of q_{max} and CMC for LAS homologs in Table 2 would be different if the sorption experiments had been performed with another commercial mixture or with pure homologs. For example, the estimated values of q_{max} for LAS homologs (Table 2) did not decrease with increasing alkyl chain length as would be expected had the experiment been performed with pure homologs (Rosen 1978) (note that pure LAS homolog standards are not commercially available).

Fitted values of the Langmuir coefficient, K_L, which indicates the relative affinity of a surfactant for the solid phase, ranged from 0.013 to 5.34 L/mg for LAS homologs and increased with increasing alkyl chain length. Estimated values of K_d for LAS homologs ranged from 26 to 2115 L/kg and increased with increasing alkyl chain length (Table 2). These values are about 10 times larger than those reported for a commercial LAS mixture by Rouse et al. (1993). The $\Delta \log K_d / (\text{-}CH_2\text{-})$ value, which indicates the increase in log K_d with the addition of a single methylene group ($\text{-}CH_2\text{-}$), ranged from 0.35 to 1.0, which is similar to ranges reported for LAS homologs in previous laboratory (Hand and Williams 1987) and field experiments (Krueger et al. 1998).

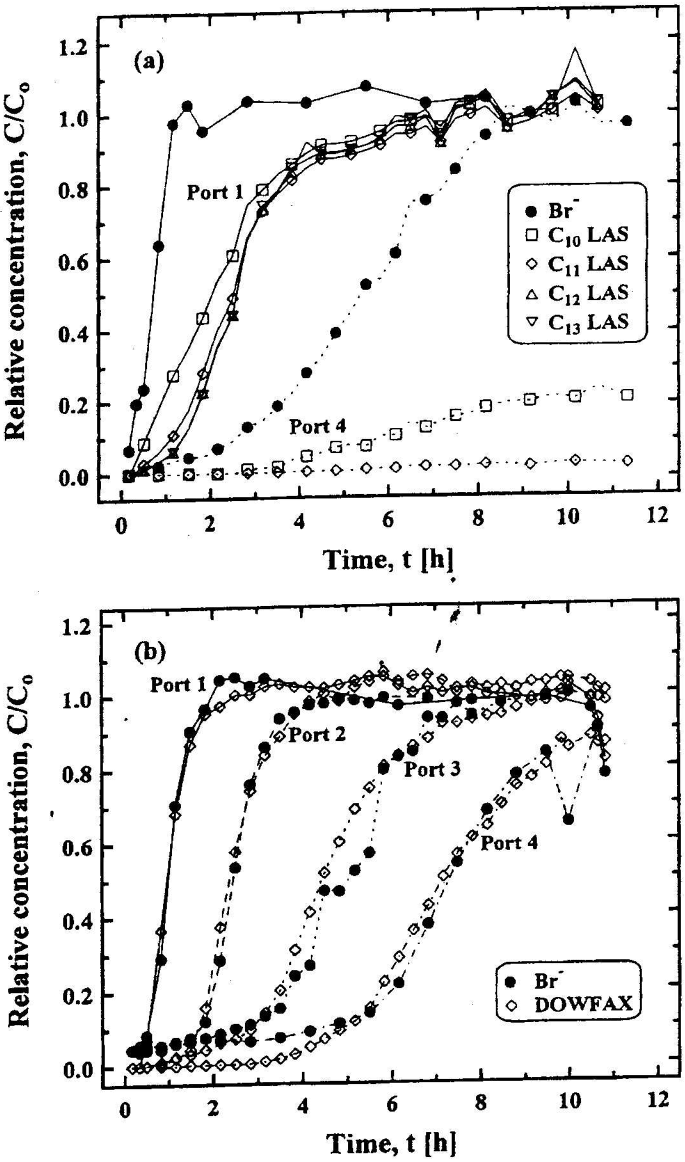

Figure 3. Injection phase breakthrough curves during laboratory push-pull tests for (a) Br^- and LAS homologs, and (b) Br^- and DOWFAX.

Equilibrium sorption isotherms for DOWFAX were also characterized by Langmuir-type behavior (Figure 2b) with fitted values of q_{max} and CMC of 699 mg/kg and 125 mg/L, respectively (Table 2). However, unlike LAS, no differences in aqueous- or solid-phase DOWFAX composition were detected with increasing aqueous surfactant concentration. Because the hexadecyl and dihexadecyl components of DOWFAX showed identical sorption behavior, only total DOWFAX concentrations are reported. Although a CMC of 125 mg/L for DOWFAX is much smaller than the range (2000

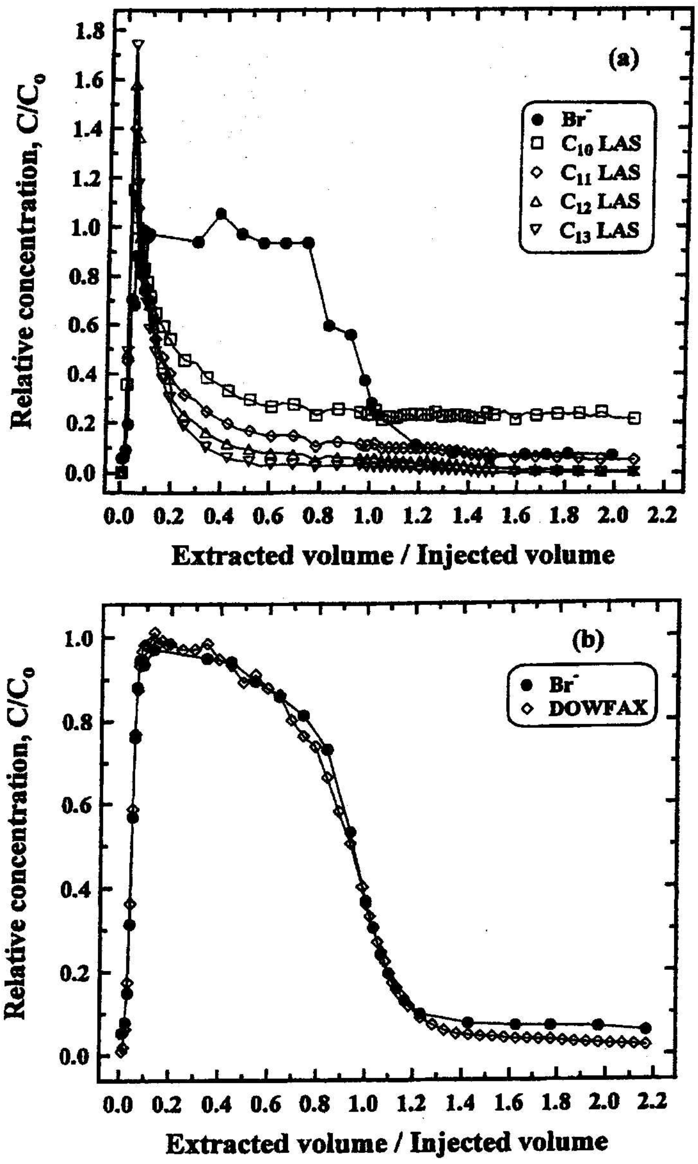

Figure 4. Extraction phase breakthrough curves during laboratory push-pull tests for (a) Br− and LAS homologs, and (b) Br− and DOWFAX.

to 4000 mg/L) of CMC values reported by others (Mukerjee and Mysels 1971; Rouse et al. 1993), it is similar to the CMC value of ~ 320 mg/L reported by Lipe et al. (1996). The CMC value obtained from Figure 2b was confirmed by an independent determination of CMC by the spinning drop method (data not shown). Estimated values of K_L and K_d for DOWFAX (Table 2) were much larger than values for dodecyl diphenyl oxide disulfonate reported by Rouse et al. (1993) for a different sediment with a larger organic carbon fraction than the LLNL sediment.

Laboratory Push-Pull Tests

Bromide

Representative results for selected sampling ports during LAS and DOWFAX experiments are presented in Figure 3 as breakthrough curves that display relative concentrations (C/C_0) versus time, where C is the measured Br− concentration in a sample and C_0 is the Br− concentration in the injected test solution (100 mg/L). At each port C/C_0 values increased smoothly from zero to one as the injected test solution penetrated further into the sediment pack. Extraction phase breakthrough curves for Br− showed a rapid initial increase in C/C_0 from zero to one (due to the extraction of tap water injected at the end of the injection phase), a plateau with C/C_0 ~ 1, and a gradual decline in C/C_0 from one to zero as tap water entering the PAM from the water reservoir gradually displaced injected test solution from the sediment pack (Figure 4).

LAS

Measured LAS concentrations during the injection phase of laboratory push-pull tests indicated retardation of all LAS homologs relative to Br− for all ports (Figure 3a; note that breakthrough curves for total LAS are not shown because they were nearly identical to those for C_{11}-LAS). Moreover, only C_{10}- and C_{11}-LAS were detected in ports 2 through 4 indicating that chromatographic separation (changing composition due to differential sorption of LAS homologs) occurred during the injection phase. The effect of chromatographic separation on the properties of the surfactant mixture is illustrated by the fact that no micelles, as determined by the pinacyanol chloride test of Rouse et al. (1993), were detected in ports 2 through 4, even though the combined concentration of C_{10}- and C_{11}-LAS was greater than the CMC (200 mg/L) of the injected commercial mixture. This indicates that the C_{10}- and C_{11}-LAS mixture that traveled through ports 2 through 4 has a CMC greater than that of the commercial mixture, which is consistent with the higher CMCs for pure C_{10}- (622 mg/L) and C_{11}-LAS (325 mg/L) homologs reported by Matheson (1995).

Retardation and chromatographic separation of LAS homologs were also apparent in extraction phase breakthrough curves (Figure 4a). Relative concentrations of LAS homologs initially increased rapidly and then declined sharply with prolonged tailing. Anomolously high relative concentrations ($C/C_0 >> 1$) were measured for all homologs in the first few samples extracted from the sediment pack. These samples were cloudy in appearance suggesting the presence of a colloidal phase derived either from the sediment or from surfactant precipitation. Although preliminary experiments indicated that tap water did not cause LAS precipitation, cation exchange between the injected test solution and the sediment in the portion of the sediment pack nearest the injection/extraction ports may have resulted in LAS precipitation.

Retardation and chromatographic separation of LAS homologs was also indicated by the progressive divergence between the extraction phase breakthrough curves for Br− and LAS homologs of increasing alkyl chain length (Figure 4a). The effects of chromatographic separation on LAS recovery during the extraction phase are also apparent in mass recovery plots (Figure 5a), which show the cumulative mass, M, of Br− and LAS homolog recovered with time during the extraction phase as a fraction of the total mass of solute injected, M_0. Although essentially complete recovery of injected Br− was achieved, the mass recovery for LAS homologs decreased progressively with increasing alkyl chain length. Chromatographic separation resulted in a continuous change in LAS homolog composition during the extraction phase (data not shown). In fact, only one sample had a LAS homolog composition similar to the injected commercial mixture.

DOWFAX

In contrast to LAS, injection phase breakthrough curves for Br− and DOWFAX essentially overlapped at all ports (Figure 3b) and no discernible differences between the breakthrough curves for

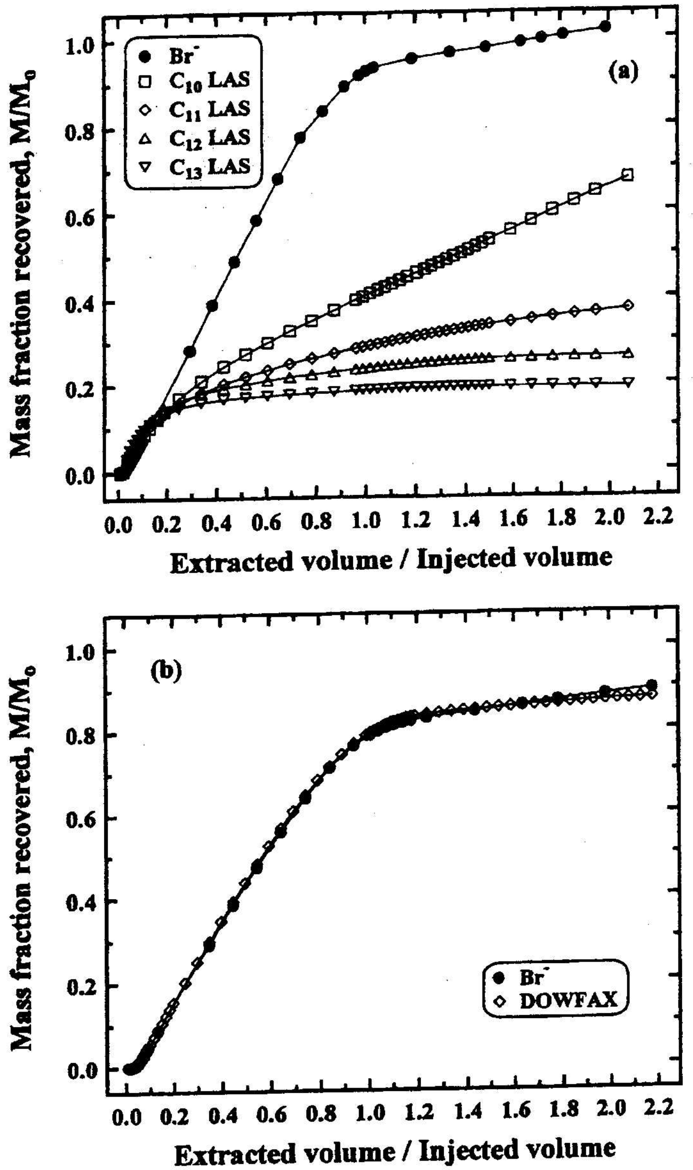

Figure 5. Mass recovery plots during laboratory push-pull tests for (a) Br− and LAS homologs, and (b) Br− and DOWFAX.

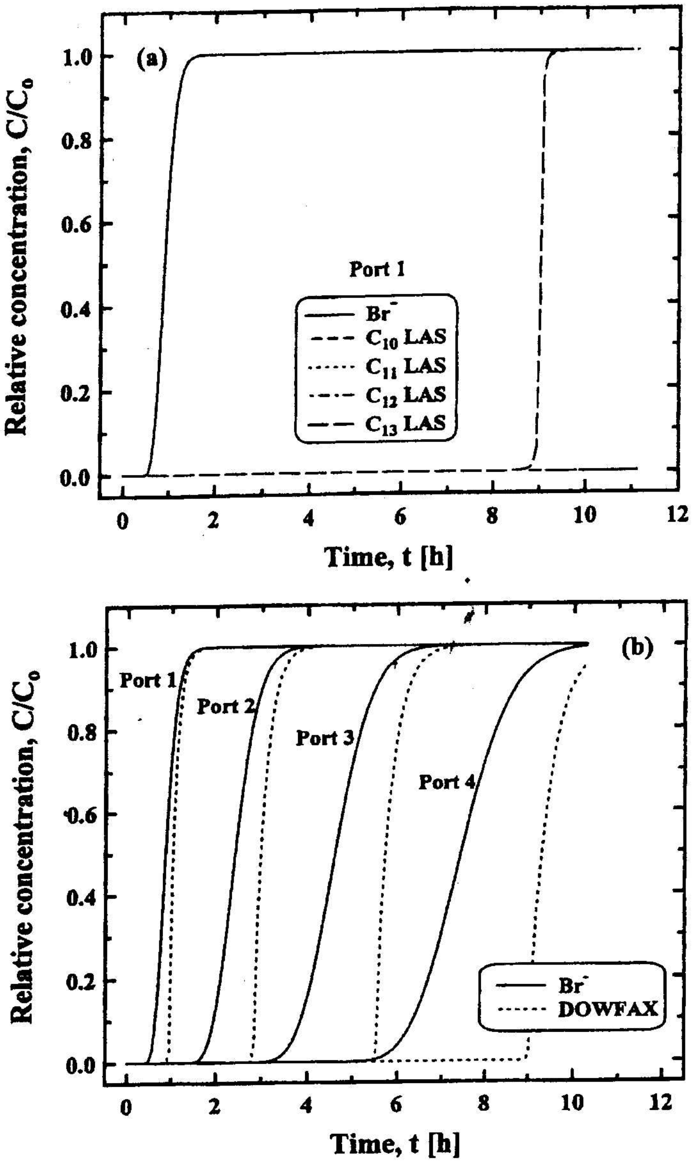

Figure 6. Simulated injection phase breakthrough curves for (a) Br− and LAS homologs, and (b) Br− and DOWFAX.

either the hexadecyl or dihexadecyl DOWFAX components were observed, which is consistent with the identical sorption behavior of these components observed in batch sorption experiments. Extraction phase breakthrough curves also indicated no apparent retardation of DOWFAX relative to Br− (Figure 4b) and mass recovery plots for Br− and DOWFAX were essentially identical (Figure 5b). It is interesting to note that the mass recovery of Br− with DOWFAX was smaller than with LAS, although both experiments were conducted under similar conditions (Table 1). We attribute this to differences in the density of the two injected test solutions. The higher concentration (13,500 mg/L) DOWFAX solution would be expected to be more susceptible to vertical buoyancy-induced flow (sinking) during the injection and extraction phases than the lower concentration (1924 mg/L) LAS solution. Sinking of the injected DOWFAX solution into the sediment pack would decrease the efficiency of mass recovery during the extraction phase. We previously have observed reduced mass recovery in replicate tracer tests conducted in similar sediment packs with tracer solutions having concentration differences as small as ~ 100 mg/L (Istok and Humphrey 1995).

Numerical Simulations

Simulated injection and extraction phase breakthrough curves for Br− approximately matched observed breakthrough curves for both laboratory push-pull tests. For example, compare the simulated breakthrough curves during the injection phase of the LAS and DOWFAX experiments (Figure 6) with the observed breakthrough curves (Figure 3). These results confirm that the PAM geometry, sediment pack properties, and boundary and initial conditions were accurately represented in the simulations.

However, simulated injection phase breakthrough curves for LAS homologs were substantially different from observed breakthrough curves (simulated breakthrough curves for total LAS are not shown because they were nearly identical to those for C_{11}-LAS). For example, the arrival time for C_{13}-LAS at port 1 in the simulations was ~ 9 hours (Figure 6a), while the observed arrival time was

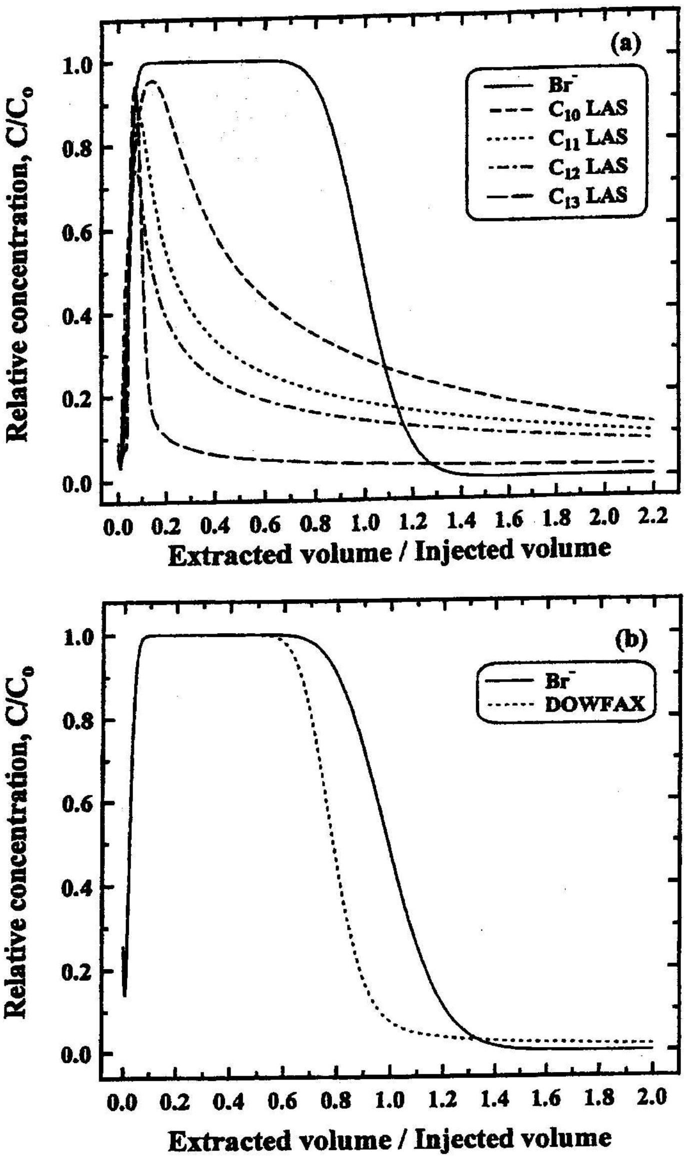

Figure 7. Simulated extraction phase breakthrough curves for (a) Br⁻ and LAS homologs, and (b) Br⁻ and DOWFAX.

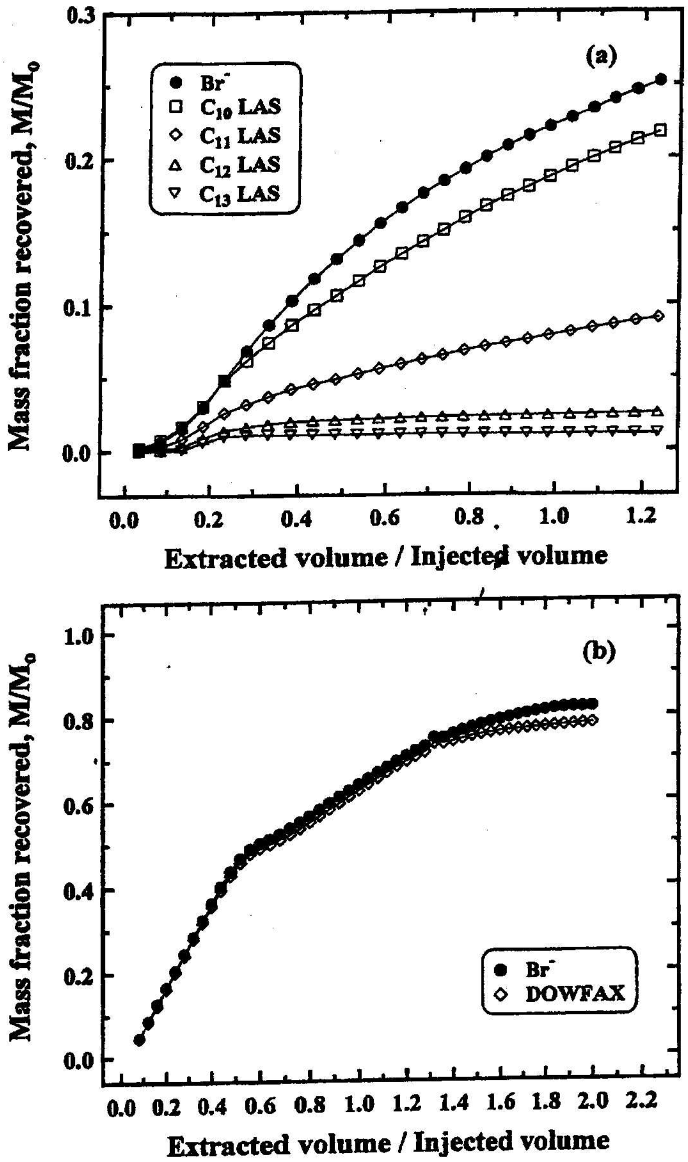

Figure 8. Mass recovry plots during field push-pull tests for (a) Br⁻ and LAS homologs, and (b) Br⁻ and DOWFAX.

only ~ 2 hours (Figure 3a). Similarly, simulated values of C/C_o in port 1 remained less than 0.01 for C_{10}-, C_{11}-, and C_{12}-LAS homologs throughout the injection phase (Figure 6a), while observed values in port 1 approached C/C_o ~ 1 for all homologs (Figure 3a). Surprisingly, simulated extraction phase breakthrough curves for LAS homologs (Figure 7a) indicated much better agreement with the experimental breakthrough curves (Figure 4a). However, simulated breakthrough curves declined more quickly and had less extensive tailing than observed breakthrough curves. Differences between simulated and observed breakthrough curves are not unexpected given the artificial and unrepresentative conditions of the batch environment, which include dispersion of sediment particles by shaking and high sediment to aqueous phase volume ratios (Fortin et al. 1997). It may also be possible that sorption of LAS homologs may be kinetically limited (e.g., limited by the time required for surfactant to diffuse from the bulk aqueous phase to the sediment surface). Numerical simulations were performed assuming equilibrium between aqueous and solid phase surfactant concentrations although equilibrium sorption required ~ 24 hours in the batch experiments. Because pore water velocity is highest (and contact times are smallest) nearest the injection/extraction well in the radial flow field of a push-pull test and decreases with increasing radial distance from the well (see Equation 2) (Valocchi 1986), kinetic effects are expected to be more pronounced in laboratory push-pull tests than in batch sorption experiments.

Simulated injection phase breakthrough curves agreed more closely with observed breakthrough curves for DOWFAX than for LAS. For example, simulations accurately predicted values of C/C_o ~ 1 for DOWFAX in ports 1 through 4 (compare Figures 6b and 3b). However, while observed breakthrough curves for Br⁻ and DOWFAX were essentially identical for all ports, simulated breakthrough curves for DOWFAX were slightly retarded relative to breakthrough curves for Br⁻. Moreover, the separation between simulated Br⁻ and DOWFAX breakthrough curves increased with increasing radial distance from the injection/extraction ports, which was not observed in laboratory push-pull tests. Because the simulations were performed assuming equilibrium sorption, it is possible that that kinetically limited sorption of DOWFAX also may be occurring during laboratory push-pull tests. Slight differences between simulated and observed extraction phase breakthrough curves for DOWFAX may also be due to kinetically limited sorption (compare Figures 7b and 4b). Due to the relatively high surfactant concentration in the injected test solution (13,500 mg/L) and the weak affinity of DOWFAX for the solid phase, sorption sites may have been essentially instantaneously saturated during transport without causing a significant local decrease in aqueous phase concentrations. Unfortunately, it was not possible to simulate kinetically limited sorption with Langmuir isotherms using STOMP. Simulated breakthrough curves assuming kinetically limited sorption and a linear isotherm with the estimated value of K_d for DOWFAX (Table 2) also did not agree with observed breakthrough curves (simulations not shown).

Field Push-Pull Tests

Due to the low observed recovery of LAS in laboratory push-pull tests, low recovery of injected LAS was anticipated in field push-pull tests. For this reason, field push-pull tests with LAS were not performed at LLNL and instead were performed at the OSU motor pool site. Although no sediment from the aquifer at this site was available, extraction phase breakthrough curves and mass recovery plots for Br^- and LAS homologs were similar to those obtained during laboratory push-pull tests performed with LLNL sediment. For example, mass recovery plots for field push-pull tests clearly show the effects of chromatographic separation on the transport of LAS homologs (Figure 8a). In sharp contrast, mass recovery plots for Br^- and DOWFAX during field push-pull tests were essentially identical (Figure 8b), which is consistent with the conservative transport behavior of DOWFAX observed in laboratory push-pull tests performed with LLNL sediment (Figure 5b).

Conclusions

The results have demonstrated the ability of the single-well, push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment under laboratory and in situ field conditions. Increased retardation and chromatographic separation of LAS homologs relative to Br^- observed during laboratory push-pull tests could not be accurately described by numerical transport simulations based on fitted sorption isotherms obtained from batch sorption experiments. Better agreement was obtained between simulated and observed breakthrough curves for DOWFAX; however, simulations predicted slight retardation for DOWFAX that was not observed in either laboratory or field push-pull tests. We attribute these differences to the inability of batch sorption isotherms to accurately represent in situ conditions. In particular, simulations based on batch sorption isotherms produced for a commercial surfactant mixture cannot accurately describe surfactant transport when the composition of the surfactant mixture changes (e.g., due to chromatographic separation) during transport. Moreover, equilibrium sorption isotherms produced in batch experiments cannot describe the kinetically limited sorption of a surfactant that potentially occurs during transport in the highly nonuniform pore water velocity field around an injection well.

However, generally close agreement was observed for extraction phase breakthrough curves for LAS and DOWFAX in laboratory and field push-pull tests. Retardation and chromatographic separation of LAS homologs observed in breakthrough curves and mass recovery plots from laboratory push-pull tests were clearly visible in breakthrough curves and mass recovery plots for field push-pull tests conducted in situ. Based on the results of this study, the single-well, push-pull test appears to be a useful method for obtaining site-specific information on the sorption behavior of injected surfactants (or other solutes). The method can be applied in existing monitoring wells without the need for sediment cores and appears to provide results that are more representative of in situ conditions than laboratory batch sorption experiments. It should also be noted that the laboratory and field push-pull tests confirmed that information on sorption characteristics of an injected solute can be obtained from only the extraction phase breakthrough curves, without the need for observations at additional monitoring wells. The method should be particularly useful for selecting and evaluating surfactants as part of a feasibility assessment. In addition, the method can be used to perform small-scale pilot tests because the test conditions closely approximate those occurring in the vicinity of injection wells that will be used in full-scale surfactant-enhanced NAPL recovery systems. The method also provides a simple and rapid method for characterizing the in situ transport behavior of any solute without the need for sediment cores. In future manuscripts we will present applications of this method for quantifying the effects of cation-exchange on metal transport, the effects of sorption on organic contaminant transport, and the effects of diffusion and partitioning on dissolved gas transport.

Acknowledgments

This work was funded by the Department of Energy Environmental Management Science Program Grant No. DE-FG07-96ER14721. Special thanks to Richard Landgraf, Paul Daley, Marvin Lima, and Eric Walters of Lawrence Livermore National Laboratory. We also thank Dow Chemical Co., Pilot Chemical Co., and Condea Vista Chemical Co. for supplying surfactant standards and commercial mixtures, and Mart Oostrom and Mark White at Pacific Northwest National Laboratory for providing technical assistance with STOMP.

References

Abdul, A.S., and C.C. Ang. 1994. In situ surfactant washing of polychlorinated biphenyls and oils from a contaminated field site: Phase II study. *Ground Water* 32, no. 5: 727–734.

Abdul, A.S., T.L. Gibson, and D.N. Rai. 1990. Selection of surfactants for the removal of petroleum products from shallow sandy aquifers. *Ground Water* 28, no. 6: 920–926.

Bear, J. 1979. *Hydraulics of Groundwater*. New York: McGraw-Hill.

Carpenter, D.W., J.J. Sweeney, P.W. Kasameyer, N.R. Burkhard, K.G. Knauss, and R.J. Shlemon. 1984. *Geology of the Lawrence Livermore National Laboratory*. UCRL-53316. Livermore, California: Lawrence Livermore National Laboratory.

Edwards, D.A., R.G. Luthy, and Z. Liu. 1991. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. *Environ. Sci. Technol*. 25, no. 1: 127–133.

Fetter, C.W. 1993. *Contaminant Hydrogeology*. New York: Macmillan Publishing Co.

Fortin, J., W.A. Jury, and M.A. Anderson. 1997. Enhanced removal of trapped non-aqueous phase liquids from saturated soil using surfactant solutions. *J. Contamin. Hydrol*. 24, no. 3/4: 247–267.

Fountain, J.C., C. Waddell-Sheets, A. Lagowski, C. Taylor, D. Frazier, and M. Byrne. 1995. Enhanced removal of dense nonaqueous-phase liquids using surfactants: Capabiliites and limitations from field trials. In *Surfactant-Enhanced Subsurface Remediation: Emerging Technologies*, ed. D.A. Sabatini, R.C. Knox, and J. H. Harwell, 594: 177–190. Washington D.C.: American Chemical Society.

Fountain, J.C., R.C. Starr, T. Middleton, M. Beikirch, C. Taylor, and D. Hodge. 1996. A controlled field test of surfactant-enhance aquifer remediation. *Ground Water* 34, no. 5: 910–916.

Gelhar, L.W., and M.A. Collins. 1971. General analysis of longitudinal dispersion in nonuniform flow. *Water Resour. Res.* 15, no. 6: 1511–1521.

Haggerty, R., M.H. Schroth, and J.D. Istok. 1998. Simplified method of "push-pull" test data analysis for determining in situ reaction rate coefficients. *Ground Water* 36, no. 2: 314–324.

Hand, V.C., and G.K. Williams. 1987. Structure-activity relationships for sorption of linear alkylbenzenesulfonates. *Environ. Sci. Technol.* 21, no. 4: 370–373.

Istok, J.D., and M.D. Humphrey. 1995. Laboratory investigation of buoyancy-induced flow (plume sinking) during two-well tracer tests. *Ground Water* 33, no. 4: 597–604.

Istok, J.D., M.D. Humphrey, M.H. Schroth, M.R. Hyman, and K.T. O'Reilly. 1997. Single-well, "push-pull" test method for in situ determination of microbial metabolic activities. *Ground Water* 35, no. 4: 619–631.

Jafvert, C.T., P.L.V. Hoof, and J.K. Heath. 1994. Solubilization of non-polar compounds by non-ionic surfactant micelles. *Water Res.* 28, no. 5: 1009–1017.

Kibbey, T.C.G., and K.F. Hayes. 1987. A multicomponent analysis of the sorption of polydisperse ethoxylated nonionic surfactants to aquifer materials: Equilibrium sorption behavior. *Environ. Sci. Technol.* 31, no. 4: 1171–1177.

Klute, A., ed. 1986. *Methods of Soil Analysis: Part 1–Physical and Mineralogical Methods.* Madison, Wisconsin: American Society of Agronomy.

Knox, R.C., D.A.Sabatini, J.H. Harwell, R.E. Brown, C.C. West, F. Blaha, and C. Griffin. 1997. Surfactant remediation field demonstration using a vertical circulation well. *Ground Water* 35, no. 6: 948-953.

Krueger, C.J., L.B. Barber, D.W. Metge, and J.A. Field. 1998. Fate and transport of linear alkylbenzene sulfonate in a sewage-contaminated aquifer: A comparison of natural-gradient pulsed tracer tests. *Environ. Sci. Technol.* 32, no. 8: 1134–1142.

Lipe, M.K., D.A. Sabatini, M.A. Hasegawa, and J.H. Harwell. 1996. Micellar-enhanced ultrafiltration and air stripping for surfactant-contaminant separation and surfactant reuse. *Ground Water Monitoring and Remediation* 16, no. 1: 85–92.

Matheson, K.L. 1995. Physical properties and behavior of linear alkylbenzenesulfonates in mixtures with other surfactants in household detergent products. In *Anionic Surfactants*, ed. H.W. Stache, 109–142. New York: Marcel Dekker.

Mukerjee, P., and K.J. Mysels. 1971. Critical micelle concentration of aqueous surfactant systems. NSR DS-NBS 36. Washington, D.C.: U.S. Dept. of Commerce.

Nichols, W.E., N.J. Aimo, M. Oostrom, and M.D. White. 1997. *STOMP: Subsurface Transport Over Multiple Phases. Application Guide.* PNNL-11216. Richland, Washington: Pacific Northwest National Laboratory.

Pennell, K.D., A.M. Adinolfi, L.M. Abriola, and M.S. Diallo. 1997. Solubilization of dodecane, tetrachloroethylene, and 1,2-dichlorobenzene in micellar solutions of ethoxylated nonionic surfactants. *Environ. Sci. Technol.* 31, no. 5: 1382–1389.

Podoll, R.T., K.C. Irwin, and S. Brendlinger. 1987. Sorption of water-soluble oligomers on sediments. *Environ. Sci. Technol.* 21, no. 3: 562–568.

Rosen, M. 1978. *Surfactants and Interfacial Phenomena.* New York: John Wiley and Sons Inc.

Rouse, J.D., D.A. Sabatini, and J.H. Harwell. 1993. Minimizing surfactant losses using twin-head anionic surfactants in subsurface remediation. *Environ. Sci. Technol.* 27, no. 10: 2072–2078.

Sabatini, D.A., R.C. Knox, J.H. Harwell, T. Soerens, L. Chen, R.E. Brown, and C.C. West. 1997. Design of a surfactant remediation field demonstration based on laboratory and modeling studies. *Ground Water* 35, no.6: 954–963.

Schroth, M.H., J.D. Istok, G.T. Conner, M.R. Hyman, R. Haggerty, and K.T. O'Reilly. 1998. Spatial variability in in situ aerobic respiration and denitrification rates in a petroleum contaminated aquifer. *Ground Water* 36, no. 6: 924–937.

Smith, J.A., D. Sahoo, H.M. McLellan, and T.E. Imbrigiotta. 1997. Surfactant-enhanced remediation of a trichloroethene-contaminated aquifer. 1. Transport of Triton X-100. *Environ. Sci. Technol.* 31, no. 12: 3565–3572.

Valocchi, A.J. 1986. Effect of radial flow on deviations from local equilibrium during sorbing solute transport through homogeneous soils. *Water Resour. Res.* 22, no. 12: 1693–1701.

Valsaraj, K.T., and L.J. Thibodeaux. 1989. Relationships between micell-water and octanol-water partition constants for hydrophobic organics of environmental interest. *Water Research* 23, no. 2: 183–189.

Vista Chemical Co. 1991. Procedure for running surface tension/interfacial tension. Lab Method 350–91. Austin, Texas: Vista Chemical Co.

West, C.C. 1992. Surfactant-enhanced solubilization of tetrachloroethylene and degradation products in pump and treat remediation. In *Transport and Remediation of Subsurface Contaminants*, ed. D.A. Sabatini and R.C. Knox, 491: 149–158. Washington, D.C.: American Chemical Society.

West, C.C., and J.H. Harwell. 1992. Surfactants and subsurface remediation. *Environ. Sci. Technol.* 26, no. 12: 2324–2330.

White, M.D., and M. Oostrom. 1997. *STOMP: Subsurface Transport Over Multiple Phases. User's Guide.* PNNL-11218. Richland, Washington: Pacific Northwest National Laboratory.