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Surfactant enhanced recovery of tetrachloroethylene from a porous medium containing low permeability lenses
1. Experimental studies

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Abstract

A matrix of batch, column and two-dimensional (2-D) box experiments was conducted to investigate the coupled effects of rate-limited solubilization and layering on the entrapment and subsequent recovery of a representative dense NAPL, tetrachloroethylene (PCE), during surfactant flushing. Batch experiments were performed to determine the equilibrium solubilization capacity of the surfactant, polyoxyethylene (20) sorbitan monooleate (Tween 80), and to measure fluid viscosity, density and interfacial tension. Results of one-dimensional column studies indicated that micellar solubilization of residual PCE was rate-limited at Darcy velocities ranging from 0.8 to 8.2 cm/h and during periods of flow interruption. Effluent concentration data were used to develop effective mass transfer coefficient (K_e) expressions that were dependent upon the Darcy velocity and duration of flow interruption. To simulate subsurface heterogeneity, 2-D boxes were packed with layers of F-70 Ottawa sand and Wurtsmith aquifer material within 20–30 mesh Ottawa sand. A 4% Tween 80 solution was then flushed through PCE-contaminated boxes at several flow

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velocities, with periods of flow interruption. Effluent concentration data and visual observations indicated that both rate-limited solubilization and pooling of PCE above the fine layers reduced PCE recovery to levels below those anticipated from batch and column measurements. These experimental results demonstrate the potential impact of both mass transfer limitations and subsurface layering on the recovery of PCE during surfactant enhanced aquifer remediation.
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1. Introduction

The remediation of aquifers contaminated by chlorinated organic solvents, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), is a difficult and costly endeavor. These compounds are typically introduced to the subsurface in neat liquid form as a result of accidental spills and improper waste disposal practices. Upon release, a non-aqueous phase liquid (NAPL) will travel downward through the subsurface as a result of gravitational and capillary forces, with a portion of the NAPL being retained in pore spaces due to capillarity. NAPLs that are more dense than water (DNAPLs) are of special concern because, if a sufficient volume is spilled, the dense liquid will migrate vertically through the saturated zone until the DNAPL is trapped as residual phase and/or forms pools of free product above low permeability lenses or a confining layer. The resulting distribution of contaminant may be extremely complex, depending upon subsurface geological conditions and properties of the infiltrating NAPL (Kueper et al., 1989; Kueper and Frind, 1991).

Traditional pump-and-treat methods have proven to be ineffective for remediating NAPL source zones due to the low aqueous solubilities of most NAPLs, lack of technologies to characterize the subsurface, and heterogeneities associated with formation properties and NAPL entrapment (Mackay and Cherry, 1989; Haley et al., 1991; MacDonald and Kavanaugh, 1994). To improve the performance of pump-and-treat systems, surfactant flushing has been proposed as a means to enhance the recovery of NAPLs. Surfactant enhanced aquifer remediation (SEAR) is based on the ability of surfactants to increase the aqueous solubility of and/or displace NAPLs from porous media. At concentrations exceeding the critical micelle concentration (CMC), surfactant molecules aggregate to form micelles that are able to solubilize organic contaminants. Displacement of NAPLs as free product may also occur if the interfacial tension between the organic liquid and the aqueous phase is reduced to such an extent that viscous and buoyancy forces exceed capillary forces acting on the NAPL. Although the latter recovery process is extremely efficient, displacement of free product may lead to uncontrolled downward migration of DNAPLs and contamination of pristine regions of an aquifer. For these reasons, SEAR treatment of DNAPL source zones has focused on surfactants that function primarily as solubilizing agents.

Although considerable effort has been devoted to surfactant selection and design of SEAR, field trials conducted at DNAPL-contaminated sites have achieved mixed results as evidenced by the following examples. At Canadian Forces Base Borden in Ontario, a mixture of nonylphenol ethoxylate (Alkasurf NP10) and phosphated nonylphenol ethox-

ylate (Rexophos 25/97) was used to remove PCE from a small test cell (Fountain et al., 1990, 1991). The surfactant flood resulted in recovery of 82% (191 l) of the PCE released after flushing with 14 pore volumes of surfactant solution. Upon excavation of the test cell, pooled PCE was observed along the surface of the aquitard and above fine layers within the matrix, indicating that complete removal of PCE would only be achieved after extended treatment time. A field demonstration was conducted at a manufacturing facility in Corpus Cristi, TX to recover carbon tetrachloride using polyoxyethylene (POE) (20) sorbitan monooleate (Witconol 2722) (Fountain et al., 1995). The initial surfactant flood resulted in minimal recovery of the contaminant. Therefore, a second surfactant (Tergitol 15-S-12) was employed, which led to the recovery of approximately 276 l of carbon tetrachloride. The majority of carbon tetrachloride was removed from high permeability regions, while a significant amount of contaminant remained in low permeability regions of the contaminated zone. Another field trial was conducted by University of Texas (Austin), INTERA and Radian researchers within a test cell (6.1×5.4 m) at Hill Air Force Base Operable Unit 2 (OU2) (Brown et al., 1999; AATDF, 1997). OU2 is a closed chemical disposal area contaminated with a mixed DNAPL, consisting primarily of TCE, PCE, and 1,1,1-trichloroethane (TCA). The field demonstration was designed to evaluate the feasibility of DNAPL solubilization using a low interfacial tension reduction surfactant flood. Three delivery and three recovery wells were placed at opposite ends of the test cell. After conducting extensive laboratory investigations, sodium dihexyl sulfosuccinate (4%), isopropyl alcohol (8%), and sodium chloride were selected for the surfactant/cosolvent formulation used in the field demonstration. Overall, 2.5 pore volumes of surfactant formulation were flushed through the contaminated zone. Researchers estimated that 99% of the DNAPL mixture was recovered (Brown et al., 1999; Roote, 1998).

Results of the first two field studies described above illustrate the substantial influence of subsurface heterogeneity on DNAPL entrapment and SEAR performance (Fountain et al., 1991, 1995), whereas the latter example provides evidence of good SEAR performance in a relatively homogeneous system (Brown et al., 1999). Although the available field evidence indicates that subsurface heterogeneity can substantially limit the recovery of DNAPL during surfactant flushing, few laboratory studies have been conducted to assess the effects of macroscopic soil heterogeneities on DNAPL recovery. Walker et al. (1998a,b) reported that surfactant enhanced removal of PCE from a two-dimensional (2-D) sand tank occurred primarily from high permeability zones where PCE existed as residual phase, while PCE existing in pools above low permeability lenses persisted over the course of the study. Such findings mimic results observed for the Borden and Corpus Cristi field trials (Fountain et al., 1991, 1995), and can be attributed to the lower specific interfacial area of DNAPL pools compared to entrapped droplets at residual saturation.

Local mass transfer limitations can also affect DNAPL recovery. Several laboratory studies have demonstrated that micellar solubilization of NAPLs may be rate-limited, even when the NAPL exists as a uniform residual phase (Pennell et al., 1993, 1994; Abriola et al., 1999). Pennell et al. (1993) reported that solubilization of residual dodecane by POE (20) sorbitan monooleate (Witconol 2722) in soil columns was strongly rate-limited, and that flow interruption periods approaching 100 h were required

to reach equilibrium solubility. In a subsequent study, Pennell et al. (1994) demonstrated that solubilization of residual PCE by Witconol 2722 from soil columns was rate-limited, although rates of PCE solubilization under steady-state conditions were approximately four times greater than those of dodecane. More recently, Abriola et al. (1999) reported that solubilization of residual decane by 1% Witconol 2722 deviated from local equilibrium for Darcy velocities ranging from 0.83 to 8.3 cm/h, with effluent concentrations of decane never exceeding 55% of the equilibrium solubility determined in batch tests. Although results of these column experiments clearly demonstrate that non-equilibrium processes may influence NAPL recovery, carefully controlled studies have not been conducted to evaluate the importance of rate-limited solubilization in larger-scale, heterogeneous systems.

The purpose of this study was to investigate the coupled effects of subsurface heterogeneity and rate-limited micellar solubilization on surfactant enhanced recovery of PCE in a two-dimensional (2-D) aquifer cell. A matrix of batch and column experiments was performed to provide independent quantification of 2-D system parameters. A non-ionic surfactant, POE (20) sorbitan monooleate (Tween 80), was selected for use because of its capacity to solubilize PCE and its relatively high interfacial tension with PCE ($\sim$5 dyn/cm), which minimized the potential for PCE displacement (Pennell et al., 1994, 1996). Batch tests were performed to determine the equilibrium solubility of PCE in aqueous surfactant solutions, characterize fluid properties, and to quantify sorption of Tween 80. A series of one-dimensional (1-D) column studies was also conducted to quantify rates of PCE solubilization under flowing and no flow conditions in a uniform porous medium. The coupled effects of low permeability layers and rate-limited solubilization on SEAR performance was then investigated in the 2-D aquifer cells. All experimental results are summarized and discussed herein. Results of batch, column and 2-D box studies are utilized in a companion paper (Rathfelder et al., 2000) to evaluate the ability of a numerical simulator to predict surfactant enhanced PCE solubilization in heterogeneous, 2-D systems, and to explore the relative effects of mass transfer limitations and subsurface heterogeneity on PCE recovery.

2. Experimental methods

2.1. Materials

Polyoxyethylene (20) sorbitan monooleate (Tween 80, Lot 36218) was provided by ICI Surfactants, and was used as received with no further purification. Tween 80 is a biodegradable food-grade additive commonly used in the processing of emulsified food products, and was selected for research because it is likely to be approved by regulatory agencies for field application. The average molecular weight of Tween 80 is 1310 g/mol, the density is 1.07 g/cm^3, the hydrophile–lipophile balance (HLB) is 15, the critical micelle concentration (CMC) is 13 mg/l, and the micelle aggregation number is 110 (Pennell et al., 1997). Tetrachloroethylene was selected as the representative DNAPL for the experimental research. HPLC-grade PCE was obtained from Aldrich Chemical. Tetrachloroethylene has a density of 1.623 g/cm^3, a molecular weight of

165.8 g/mol, and an aqueous solubility of approximately 150 mg/l at 25°C (Verschueren, 1983). The free liquid diffusivity (D_l) of PCE is approximately 8.6×10^{-6} cm^2/s based on the method of Wilke and Chang (1955). Oil-red-O (Fisher Scientific), an organic soluble dye, was used at a concentration of 10^{-4} M to facilitate visual observation of PCE in the column and 2-D box experiments. The influence of this dye addition on interfacial properties was assessed through interfacial tension measurements.

All aqueous solutions were prepared with water that was purified using a Nanopure® Analytical Deionization (Barnstead/Thermolyne) water treatment system. Sodium azide (NaN_3) was used at a concentration of 1 g/l in all solutions to inhibit microbial degradation of PCE and surfactant. Calcium chloride ($CaCl_2$), at a concentration of 0.5 g/l, was employed as background electrolyte for all solutions. The total ionic strength of the background solution ($CaCl_2 + NaN_3$) was 0.0289 mol/l. Potassium iodide (KI) was used as a non-reactive, conservative tracer for the determination of hydrodynamic dispersion coefficients in both column and 2-D box studies.

Ottawa 20–30 mesh sand (0.60–0.85 mm; ASTM), obtained from U.S. Silica, was used as the porous medium for column experiments and as the background medium for box studies. In the 2-D boxes, rectangular layers of low-permeability media were packed within the Ottawa 20–30 mesh sand. The layers consisted of a natural aquifer material obtained from Wurtsmith Air Force Base in Oscoda, MI and F-70 Ottawa sand (40–270 mesh) obtained from U.S. Silica. Table 1 summarizes relevant properties of the porous media.

2.2. Batch experimental methods

A matrix of batch experiments was conducted to measure the density and viscosity of surfactant solutions, the interfacial tension between the surfactant solution and PCE, to quantify surfactant sorption, and to determine the solubilization capacity of Tween 80 for PCE. Density measurements of solutions containing various concentrations of PCE solubilized in 4% (wt.) Tween 80 were performed gravimetrically using 25-ml borosilicate glass pycnometers at 20°C. A Haake® RS 75 RheoStress Rheometer equipped with a double-gap cylinder sensor system was used for viscosity determinations. Viscosity measurements were conducted for 4% Tween 80 solutions at 20°C, with various concentrations of solubilized PCE. The viscosity of water was also measured to allow for comparison with standard reference values.

Table 1
Selected properties and Langmuir sorption coefficients of 20–30 mesh Ottawa sand, F-70 Ottawa sand and Wurtsmith aquifer material

Porous medium	Organic carbon content (%)	Specific surface area (m^2/g)	Intrinsic permeability (m^2)	$S_{m,max}$ (mg/g)	b (l/mg)	Corrected r^2
20–30 mesh Ottawa sand	ND[a]	0.10	3.9×10^{-10}	0.156	0.010	0.939
F-70 Ottawa sand	ND[a]	0.16	8.2×10^{-12}	0.160	0.029	0.846
Wurtsmith aquifer material	0.02	0.51	4.2×10^{-11}	0.194	0.008	0.881

[a] ND = non-detectable (< 0.01% total organic carbon).

Interfacial tension measurements were performed using the drop volume technique described by Hool and Schuchardt (1992). Liquid–liquid interfacial tension was measured between PCE and water and PCE and 4% Tween 80 solutions. Prior to the interfacial tension measurement, the surfactant solutions and PCE were allowed to equilibrate for a minimum of 72 h. Interfacial tension measurements were conducted using both dyed (10^{-4} M Oil-red-O) and undyed PCE at 20°C.

The solubility of PCE in aqueous solutions of Tween 80 was measured in batch reactors at room temperature (20 ± 1°C) following procedures described by Pennell et al. (1994). Thirty-five ml borosilicate glass centrifuge tubes, capped with closed top Teflon®-backed caps, were filled with approximately 2 ml of neat liquid PCE and 30 ml of surfactant solution. Micellar solubilization of PCE was measured in aqueous surfactant solutions ranging in concentration from 5000 to 40,000 mg/l. All surfactant concentrations were prepared in triplicate. The samples were mixed for 7 days on an oscillating shaker (LabQuake®). Macroemulsions that formed during mixing were separated by centrifugation at 2500 rpm for 30 min at 20°C using a Beckman® Avanti J-25 temperature-controlled centrifuge.

Surfactant sorption experiments were conducted with Tween 80 and the three sands used in the 2-D box studies. Thirty-five ml centrifuge tubes capped with Teflon®-backed septa were filled with approximately 30 g of sand and 15 ml of surfactant solution, at concentrations ranging from 100 to 1500 mg/l. The contents of the centrifuge tubes were mixed on an oscillating shaker for 7 days. The solid and aqueous phases were separated at 20°C and 2500 rpm for 1 h using the Beckman® Avanti J-25 temperature-controlled centrifuge.

2.3. Column procedures

The column apparatus, similar to that described by Pennell et al. (1994), consisted of a Kontes® borosilicate glass preparative chromatography column (4.8 cm i.d.) equipped with an adjustable endplate for bed length variation from 1–13 cm. The bottom endplate was fitted with two 40-mesh screens while the top endplate was fitted with two Whatman® No. 42 filters. The columns were then packed with 20–30 mesh Ottawa sand under vibration in 2-cm increments. Layering between sand increments was minimized by mixing the bed surface with a spatula between additions of sand. After packing was complete, the columns were purged with carbon dioxide for 20 min and saturated by flushing with at least 15 pore volumes of Nanopure® water containing 0.5 g/l $CaCl_2$ and 1 g/l NaN_3. For non-reactive tracer tests, a solution containing KI ($\sim$ 450 mg/l) was introduced to the bottom of the column, in up-flow mode, using a Rainin® Model SD-200 high-performance liquid chromatography (HPLC) pump. The first non-reactive tracer test was performed after complete water saturation of the column. Liquid PCE was then introduced from the bottom of the column using a Harvard Apparatus® Model 22 syringe pump at a flow rate of 20 ml/h. When approximately 70% of the pore volume was occupied by PCE, flow was reversed and water was pumped downward from the top of the column. PCE existing as mobile free product was displaced by pumping approximately two pore volumes of water at 1 ml/min, followed by 10 pore volumes of water at 5 ml/min. A second non-reactive tracer test was performed after

the establishment of residual PCE. The final PCE residual saturation was determined gravimetrically and verified based on the results of the second tracer test. The measured tracer breakthrough curves were fit to an analytical solution of the one-dimensional advective–dispersive reaction (ADR) transport equation using CXTFIT (van Genuchten, 1981). An aqueous solution (4% wt.) of Tween 80 was then flushed through columns in a down-flow mode and effluent was collected in 20 ml scintillation vials using an Isco® fraction collector. Scintillation vials were immediately capped and samples were prepared for analysis by gas chromatography (GC). At the end of the solubilization study, the column was drained and the contents of the soil column were washed with isopropanol to extract the remaining PCE from the porous medium. The drained solution and wash solution were then analyzed for PCE. Total mass balance closure of greater than 94% was achieved for all column experiments.

2.4. 2-D box procedures

A schematic diagram of the 2-D box is shown in Fig. 1. The inside dimensions of the 2-D box were 32 cm (height) × 61.7 cm (length) × 1.4 cm (width). Rectangular end chambers, constructed of aluminum alloy, were screened over the entire vertical height of the box. An unscreened section of aluminum served as the bottom of the box and parallel glass plates served as the front and back of the box. Ottawa 20–30 mesh sand was packed under water-saturated conditions in 3-cm increments. Three rectangular layers, consisting of Wurtsmith aquifer material or F-70 Ottawa sand, were packed

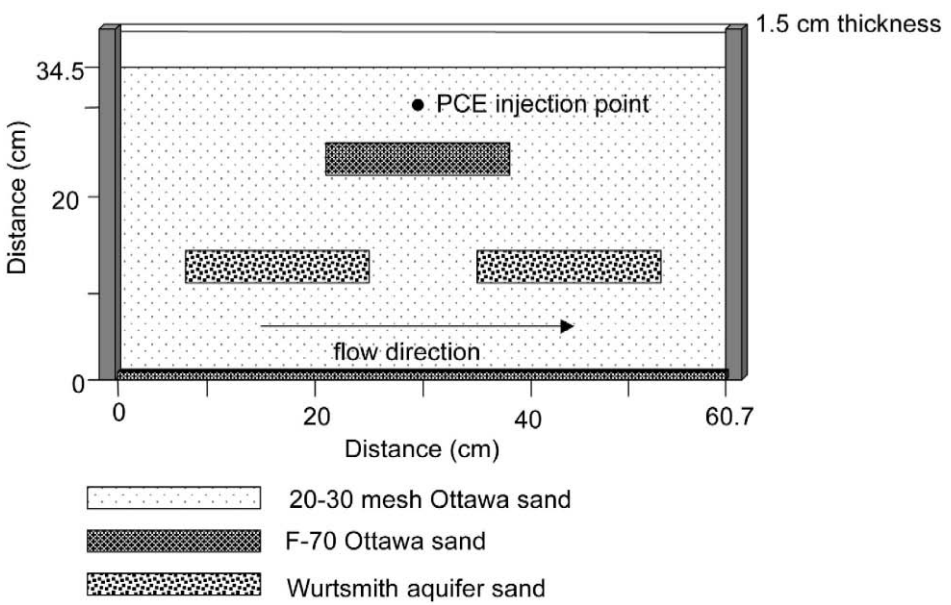

Fig. 1. Schematic diagram of the 2-D boxes packed with 20–30 mesh Ottawa sand, Wurtsmith aquifer material and F-70 Ottawa sand.

within the background matrix. After each box was packed with sand, flow was established by connecting a 2-l constant head bottle to the influent end chamber and a collection bottle to the effluent end chamber. The height of the constant head bottle and the exit tubing leading to the effluent collection bottle were adjusted to control the rate of water flow through the box. The hydraulic conductivity of the system was determined from the head drop across the box measured at several flow rates. A non-reactive tracer test, consisting of a pulse injection of KI solution, was used to determine the overall hydrodynamic dispersion coefficient. Liquid PCE dyed with Oil-red-O dye (10^{-4} M) was injected at a flow rate of 20 ml/h near the top-center of each box using a Harvard Apparatus® syringe pump. When PCE began to spill over the lower Wurtsmith layers and flow toward the end chambers, PCE injection was terminated. The PCE was allowed to redistribute for approximately 15 h. A second non-reactive tracer test was conducted following PCE injection. A solution of 4% Tween 80 was then flushed through the box at a flow rate of approximately 4 ml/min (box A) and 0.9 ml/min (box B). Aqueous effluent samples were collected over time and analyzed for PCE and Tween 80 using GC and HPLC analysis, respectively. Approximately eight pore volumes (9 l) of surfactant solution were flushed through box A and five pore volumes (5 l) through box B. The effects of rate-limited mass transfer on PCE recovery were assessed through a series of flow interruptions, each lasting for at least 15 h. Tetrachloroethylene remaining in each box after the surfactant flushing procedure was extracted with isopropanol and analyzed by GC. Total mass balance closure of greater than 95% of the PCE was achieved in each of the box studies.

2.5. Analytical methods

Aqueous-phase concentrations of PCE were analyzed using a Hewlett-Packard (HP) Model 6890 GC equipped with an autosampler, a precolumn surfactant trap, an HP5 crosslinked 5% PH Siloxane column, and a flame ionization detector (FID). The precolumn trap was installed to prevent surfactant fouling of the GC inlets, column and detector. Samples were prepared by adding approximately 0.4 ml of the aqueous sample to 1.2 ml of isopropanol in glass autosampler vials. The GC vials were sealed with Teflon-backed aluminum caps to minimize volatilization. A minimum of six PCE standards, prepared using isopropanol and surfactant solution in the same proportions as the analytical samples, were analyzed after every 10 samples. An average of the standards analyzed before and after each sample set was used to produce a standard curve for each sample set. Triplicate injections of each sample were performed.

Analysis of Tween 80 was performed using a Hewlett Packard® 1100 series HPLC equipped with a Sedex® 55 Evaporative Light Scattering Detector (ELSD). The mobile phase consisted of 80% acetonitrile and 20% water at all times. Duplicate injections (5 μl) of each sample were evaluated on the HPLC. Standard curves were obtained after every 10 samples were analyzed. Potassium iodide, used for the 1-D column and 2-D box tracer studies, was analyzed using a continuous flow Isco® V^4 variable UV wavelength absorbance detector equipped with an EZChrom® Chromatography data acquisition system.

3. Results and discussion

3.1. Batch measurements

The density of the 4% Tween 80 solution increased from 1.002 to 1.011 g/cm^3 as the solution-phase concentration of PCE was increased from 0 to 24,000 mg/l. The observed linear relationship between solution density and PCE concentration was consistent with a density correlation reported by Kostarelos et al. (1998) for solutions containing trichloroethylene, ethanol and 4% sodium dihexyl sulfosuccinate (an anionic surfactant). The viscosity of 4% Tween 80 solutions containing 0 to 26,000 mg/l PCE ranged from 1.31 to 1.34 cP at 20°C. Although there appeared to be a slight increase in viscosity with increasing PCE concentration, a statistically significant trend was not obtained between viscosity and the amount of solubilized PCE (i.e., the slope was not significantly different from zero for $P < 0.05$).

The interfacial tension of liquid PCE (undyed) contacted with Nanopure® water at 20°C was found to be 43.71 dyn/cm (± 0.0375) using the drop volume technique. The literature value for the interfacial tension between PCE and water is 47.48 dyn/cm at 20°C (Demond and Lindner, 1993). Despite rigorous cleaning of the instrumentation and repeated calibration checks with other organic–water systems, the interfacial tension between PCE and water remained slightly lower than the reported literature value. The measured interfacial tension between 4% Tween 80 and dyed and undyed PCE was 4.90 (± 0.11) and 5.38 (± 0.04), respectively. The addition of Oil-red-O dye (10^{-4} M) to PCE did not significantly alter the interfacial tension ($P < 0.05$ for $\alpha = 0.05$). Furthermore, the slight change in measured interfacial tension after the addition of Oil-red-O dye did not alter the potential for PCE displacement during surfactant flushing based on a total trapping number analysis (Pennell et al., 1996).

The equilibrium solubility of PCE in aqueous solutions of Tween 80 increased linearly over the surfactant concentration range considered (5000–40,000 mg/l), which is consistent with solubility data reported for other surfactant–organic systems exhibiting Winsor Type I behavior (e.g., Edwards et al., 1991; Pennell et al., 1993). A weight solubilization ratio (WSR) of 0.672 g PCE/g surfactant (corrected $r^2 = 0.999$) was obtained from the slope of the solubility curve above the CMC using a linear regression procedure (SYSTAT®). Based on this relationship, the equilibrium solubility of PCE in 4% Tween 80 was approximately 26,880 mg/l. The solubilization capacity of a surfactant may also be expressed as the molar solubilization ratio (MSR), which is equal to the moles of organic solubilized per mole of surfactant in micellar form (Edwards et al., 1991; Pennell et al., 1993). Using the average molecular weight of Tween 80 and the molecular weight of the PCE, the WSR value reported above was converted to an MSR of 5.41 mol PCE/mol surfactant. This MSR is slightly lower than the value reported by Pennell et al. (1997) for PCE in solutions of Witconol 2722 at 20°C (6.39 mol/mol). Although Witconol 2722 and Tween 80 are both sold as POE (20) sorbitan monooleate, they are produced by different manufacturers. Thus, the observed difference in solubilization capacity between the two surfactants is most likely due to differences in the specific manufacturing process used by each supplier.

The sorption of Tween 80 by 20–30 mesh Ottawa sand, F-70 Ottawa sand, and Wurtsmith aquifer material was measured over a surfactant concentration range of 0–1200 mg/l. Sorption data were expressed as the amount of surfactant sorbed per mass of solid matrix, S_m^s (M/M), versus the aqueous-phase concentration of surfactant, C_a^s (M/L^3). The following form of the Langmuir equation was fit to the measured sorption isotherms using a non-linear regression procedure (SYSTAT®):

$$\frac{S_m^s}{S_{m,max}^s} = \frac{bC_a^s}{1 + bC_a^s} \tag{1}$$

where S_m^s is the amount of surfactant sorbed by the solid matrix (M/M), $S_{m,max}^s$ is the maximum amount of surfactant sorbed (M/M), C_a^s is the aqueous phase concentration of surfactant (M/L^3), and b is a parameter equivalent to the ratio of the adsorption and desorption rates (L^3/M). Fig. 2 provides an example of the sorption isotherm of Tween 80 to 20–30 mesh Ottawa sand. The Langmuir sorption coefficients for Tween 80 and the three sands considered in this study are summarized in Table 1. The values of $S_{m,max}^s$ obtained for Tween 80 ranged from 0.156 to 0.194 mg/g, consistent with data reported for non-ionic surfactant sorption by sandy materials possessing low organic carbon contents and relatively small specific surface areas (e.g., Adeel and Luthy, 1995).

3.2. Column experiments

To evaluate the solubilization of PCE by 4% Tween 80 in a uniform porous medium, five 1-D column experiments were performed at several flow rates and with periods of

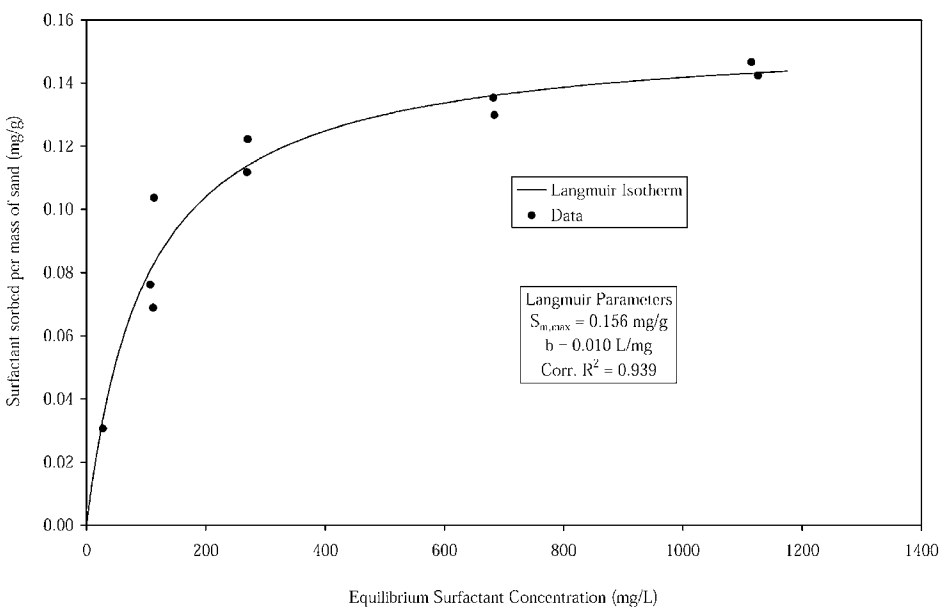

Fig. 2. Equilibrium sorption of Tween 80 by 20–30 mesh Ottawa sand at 20°C.

flow interruption. A summary of the experimental conditions and physical properties of each soil column is presented in Table 2. As anticipated, non-reactive tracer tests conducted before and after PCE entrapment yielded retardation factors of ~ 1.00. However, column dispersivity (α) increased by a factor of 1.4–1.9 following PCE entrapment. These data indicate that hydrodynamic dispersion was enhanced in the presence of residual PCE, most likely due to an increase in local variations in flow velocity and flow path tortuosity. A similar trend was reported for soil columns packed with 20–30 mesh Ottawa sand, although dispersivity values increased by a factor of 2.3–2.5 after the entrapment of residual dodecane (Pennell et al., 1993). The difference in magnitude of this effect is most likely due to the greater residual saturation of dodecane ($s_n = 0.16$–0.20) compared to PCE ($s_n = 0.10$–0.14).

Surfactant flushing of the soil columns was conducted at pore-water velocities (v) ranging from 2.76 to 26.05 cm/h (Darcy velocities (q) of 0.8–8.2 cm/h), and with periods of flow interruption ranging from 8 to 50 h. Effluent concentrations of PCE for a representative experiment (column 2) are shown in Fig. 3 as a function of solution volume displaced. For each column experiment, the initial effluent concentration of PCE was measured at a single flow rate. Although the equilibrium solubility of PCE in 4% Tween 80 was 26,880 mg/l, the initial concentrations of PCE in the effluent did not exceed 12,000 mg/l for any flow rates investigated, which is indicative of rate-limited micellar solubilization. The observed enhancements in effluent PCE concentration after periods of flow interruption provide further evidence that PCE solubilization was rate-limited. Following a 24-h flow interruption, the concentration of PCE approached the equilibrium solubility measured in batch experiments (Fig. 3). These data suggest that the equilibrium solubility of PCE (26,880 mg/l) could be achieved at longer periods of flow interruption. In subsequent column experiments, however, effluent concentrations of PCE after flow interruptions of 50 and 43 h were similar to those obtained after 24 h (21,870 and 22,380 mg/l, respectively). Visual inspection of PCE ganglia trapped in the column revealed that, for flow interruptions exceeding 24 h,

Table 2
Summary of experimental conditions and physical properties of soil columns packed with 20–30 mesh Ottawa sand

Experimental parameter	Column 1	Column 2	Column 3	Column 4	Column 5
Darcy velocity, q (cm/h)	3.250	8.220	0.826	4.075	4.887
Pore-water velocity, v (cm/h)	10.743	26.054	2.762	13.421	15.893
Duration of flow interrupt (h)	14	24	50	43	8
Column length, L (cm)	10.2	9.6	9.9	10.0	10.0
Soil bulk density, ρ_b (g/cm^3)	1.747	1.726	1.732	1.750	1.735
Soil porosity, n (cm^3/cm^3)	0.341	0.349	0.346	0.340	0.345
Pore volume (ml)	71.25	65.91	65.40	68.00	69.05
Dispersivity, α_i (cm)	0.028	0.031	0.029	0.041	0.036
PCE saturation, s_{PCE} (%)	11.28	9.60	13.57	10.70	10.87
Dispersivity, α_n (cm)	0.038	0.057	0.054	0.0642	0.065
Total trapping number (N_T)	1.73e^{-6}	4.35e^{-6}	4.55e^{-7}	2.17e^{-6}	2.59e^{-6}

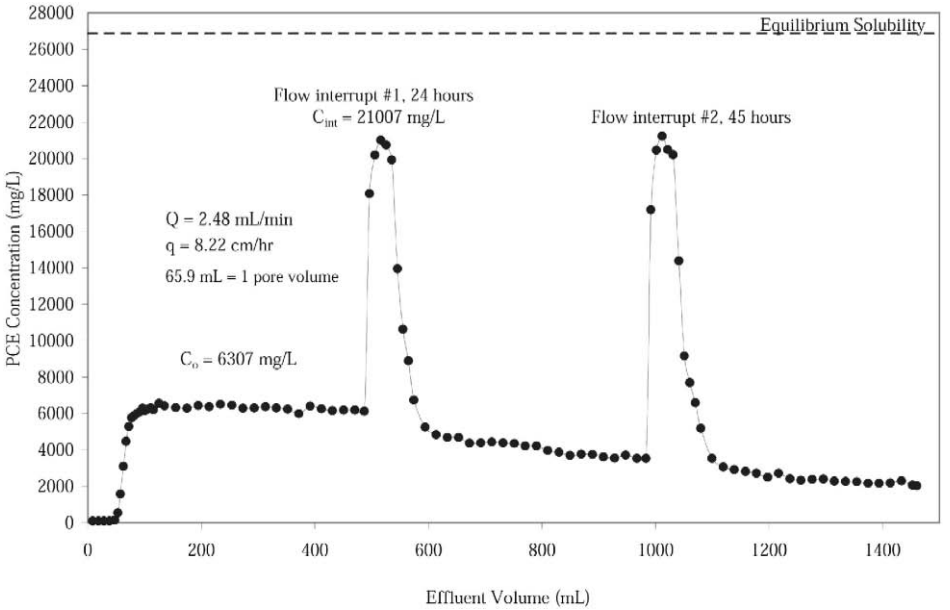

Fig. 3. Measured effluent concentrations of PCE after flushing column 2 with 4% Tween 80.

macroemulsions formed along the surface of the ganglia. It is postulated that this macroemulsion layer inhibited mass transfer of PCE into the aqueous phase under no flow conditions. Macroemulsion formation between PCE and Witconol 2722 has been observed in gently-mixed batch systems, but the volume of the macroemulsion phase was minimized by centrifugation prior to analysis of the aqueous phase (Pennell et al., 1997). More recently, Butler and Hayes (1998) reported substantial macroemulsion formation and partitioning of dodecyl alcohol ethoxylate surfactants into 1,2-dichlorobenzene liquid. Under flowing conditions, however, macroemulsions were not observed within the column or in the effluent samples.

A linear driving force expression, similar to that presented by Powers et al. (1991) and Abriola et al. (1993), was utilized to describe rate-limited micellar solubilization of residual PCE in the columns. Based on this conceptual model, a one-dimensional governing equation can be developed for the aqueous-phase transport of a dissolved organic solute (Abriola et al., 1993):

$$ns_a \frac{\partial C_a^o}{\partial t} + \rho_b \frac{\partial S_m^o}{\partial t} = \frac{\partial}{\partial x}\left(ns_a D_H \frac{\partial C_a^o}{\partial x} \right) - q \frac{\partial C_a^o}{\partial x} + K_e\left(C_{a,sat}^o - C_a^o \right) \tag{2}$$

where n is porosity (L^3/L^3), s_a is the aqueous-phase saturation (L^3/L^3), C_a^o is the concentration of the organic solute in the aqueous phase (M/L^3), ρ_b is the soil bulk density (M/L^3), S_m^o is the sorbed-phase concentration of the organic solute (M/M), D_H is the hydrodynamic dispersion coefficient (L^2/T), x is distance (L), $C_{a,sat}^o$ is the equilibrium concentration of the organic solute in the aqueous phase (M/L^3), and K_e is

the effective mass transfer coefficient (1/t). In this form, the effective mass transfer coefficient (K_e) represents the product of the NAPL interfacial area (a_n, L^2/L^3), and the NAPL-aqueous phase mass transfer coefficient (k_n, 1/t). At early time during the column experiments (less than ~7 pore volumes), the system was assumed to be under pseudo steady-state conditions. That is, the interfacial area of PCE available for mass transfer was assumed to be relatively constant during this time. Under these conditions, the effluent concentrations of PCE should remain relatively constant ($\partial C_o/\partial t \cong 0$), which is consistent with data presented in Fig. 3. Sorption of PCE by the solid phase was considered to be negligible ($S_m^o \cong 0$) relative to the overall mass of PCE in the column. Thus, Eq. (2) can be rewritten as:

$$0 = ns_a D_H \frac{\partial^2 C_a^o}{\partial x^2} - q\frac{\partial C_a^o}{\partial x} + K_e\left(C_{a,sat}^o - C_a^o\right) \tag{3}$$

The analytical solution to Eq. (3) for a semi-infinite medium with first-type boundary conditions may be expressed in dimensionless form as (Powers et al., 1991):

$$C^* = 1 - \exp\left(\frac{1-\sqrt{1+4Da/Pe}}{2/Pe}X\right) \tag{4}$$

where C^* is the normalized concentration ($C_a^o/C_{a,sat}^o$), Da is the Damköhler number ($Da = K_e L/q$), Pe is the Peclet number ($Pe = vL/D_H$), and X is x/L, where x is distance and L is the column length. Based on early-time concentration data obtained in each column experiment, effective mass transfer coefficients (K_e) were determined for each Darcy velocity.

Under steady-state conditions, the value of K_e decreased from 0.2 to 0.04 1/h for Darcy velocities ranging from 8.2 to 0.8 cm/h. The dependence of the lumped mass transfer coefficient on Darcy velocity may be expressed as $K_e = cq^d$ (linear form: $\ln K = c + d\ln q$), where c and d are fitted coefficients. This functional form was employed by Pfannkuch (1984) to describe the dissolution of a NAPL "pancake" located within the capillary fringe of an aquifer. Conceptually, this relationship represents a diffusion-limited mass transfer process that is enhanced by advective flow of the bulk fluid past the NAPL–water interface. Least squares regression (Microsoft Excel®) was used to obtain the following relationship from the linearized equation (see Fig. 4):

$$K_e = 0.0534\, q^{0.712} \quad \text{corr. } r^2 = 0.997 \tag{5}$$

The magnitude of the "d" coefficient in Eq. (5) ($d = 0.712$) indicates a strong dependence of PCE mass transfer on Darcy velocity. Over the range of Darcy velocities investigated, the value of K_e increased by a factor of 50. When the same relationship ($K_e = cq^d$) was used to describe dodecane solubilization in a similar system, the effective mass transfer coefficient (K_e) was found to be weakly dependent on Darcy velocity, increasing by a factor of 1.4 over the same range of Darcy velocities (Abriola et al., 1993).

To facilitate further comparisons with published data, the effective mass transfer coefficient was expressed in terms of a modified Sherwood number ($Sh' = K_e d_{50}^2/D_l$),

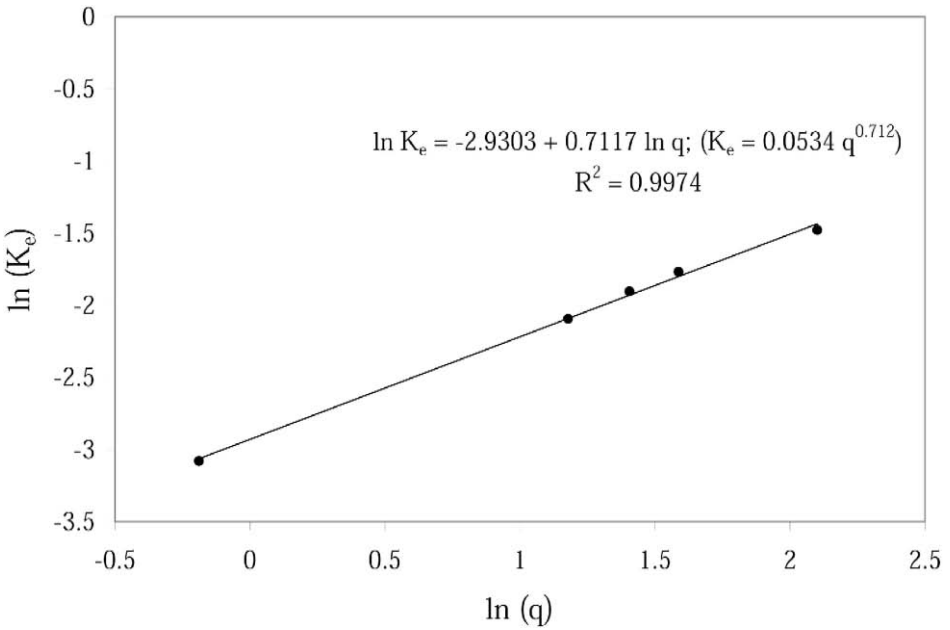

Fig. 4. Regression analysis of effective mass transfer coefficient data (K_e) as a function of Darcy velocity (q) for development of Eq. (5).

where d_{50} is the median grain size (L) and D_l is the free liquid diffusivity of the solute (L^2/t). Based on a phenomenological model presented by Powers et al. (1992) to describe the dissolution of residual styrene in packed columns, the modified Sherwood number was correlated with the Reynolds number ($Re = d_{50}\, q\, \rho_a/\mu_a$) using a least-squares regression procedure (SYSTAT®):

$$Sh' = 0.741\, Re^{0.71} \quad \text{corr. } r^2 = 0.998 \tag{6}$$

The modified Sherwood number correlation is compared to similar correlations developed for the dissolution of residual styrene in water (Powers et al., 1992) and for the micellar solubilization of residual dodecane and decane by 4% Witconol 2722 and 1% Witconol 2722 (Abriola et al. 1993, 1999) in Fig. 5. In previous studies (Powers et al., 1992; Abriola et al., 1999), two additional terms were included in the modified Sherwood number–Reynolds number correlation; the uniformity index of the porous medium (U_i) and a normalized grain size term ($\delta = d_{50}/d_M$), where d_M is the mean grain of a medium sand ($d_M = 0.05$ cm). To allow for direct comparisons with these studies, 20–30 mesh Ottawa sand ($U_i = 1.21$; $d_{50} = 0.071$ cm) was used as the reference porous medium in Fig. 5. In developing these relationships, it was found that the Sherwood number correlation presented by Abriola et al. (1993, Eq. (21)) contained an error; the corrected correlation is as follows: $Sh' = 0.024 Re^{0.91} + 0.003$.

Based on the slope of the modified Sherwood number–Reynolds number correlations shown in Fig. 5, the dependence of PCE mass transfer on the Darcy velocity is similar to that reported for the solubilization of decane in 1% Witconol 2722 and for the

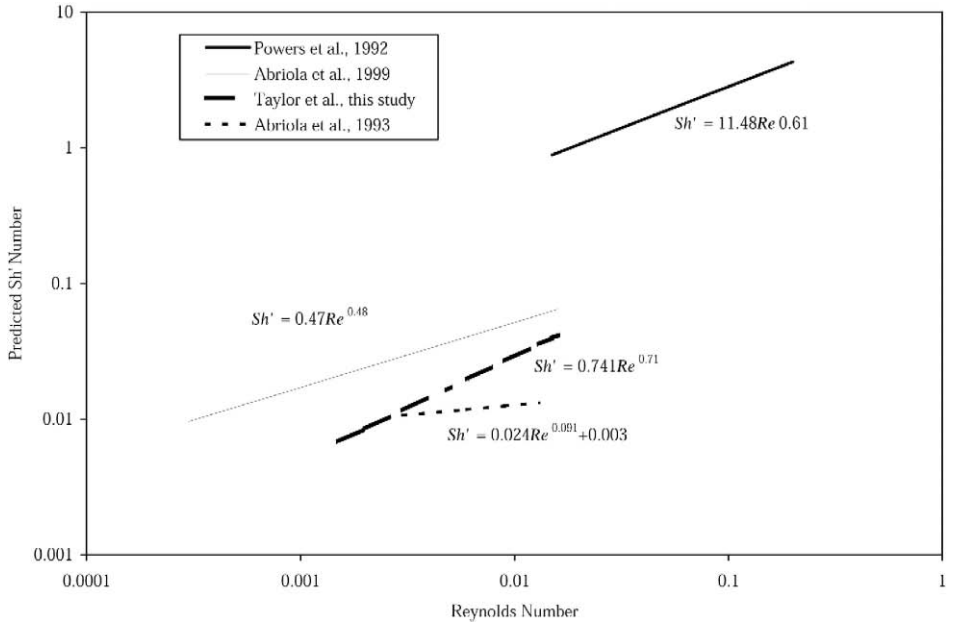

Fig. 5. Comparison of modified Sherwood number (Sh') correlations as a function of Reynolds Number (Re) for 20–30 mesh Ottawa sand.

dissolution of styrene in water. In addition, the rate of NAPL mass transfer (i.e., magnitude of the modified Sherwood number) was greatest for NAPL dissolution into water, and decreased as the surfactant concentration increased. These results suggest that NAPL mass transfer in micellar systems is not controlled solely by diffusion into the aqueous phase (i.e., the non-micellar phase), and that diffusion of micelles to the NAPL–water interface and/or incorporation of NAPL within surfactant micelles may influence the rate of mass transfer. The relationship obtained by Pennell et al. (1993) for dodecane solubilization in 4% Tween 80 shows very little dependence on the Reynolds number (Darcy velocity). This trend may be due, in part, to the extremely hydrophobic nature and large molecular size of dodecane, which could limit the rate of NAPL diffusion into the micelle core.

Column effluent data collected following early-time flow interruption were used to evaluate PCE mass transfer under no flow conditions ($q = 0$). If one assumes that PCE sorption is constant over the course of the flow interruption ($\partial S_{\mathrm{m}}^{\mathrm{o}}/\partial t = 0$), and that there is no significant diffusional transport of PCE toward the column inlet ($\partial C_{\mathrm{a}}^{\mathrm{o}}/\partial t \cong 0$), Eq. (2) reduces to:

$$ns_{\mathrm{a}}\frac{\partial C_{\mathrm{a}}^{\mathrm{o}}}{\partial t} = K_{\mathrm{e,int}}\left(C_{\mathrm{a,sat}}^{\mathrm{o}} - C_{\mathrm{a}}^{\mathrm{o}}\right) \tag{7}$$

at the column outlet. Here, $K_{\mathrm{e,int}}$ is the effective mass transfer coefficient under no flow conditions (1/t), $C_{\mathrm{a,sat}}^{\mathrm{o}}$ is the equilibrium concentration of the organic solute in the

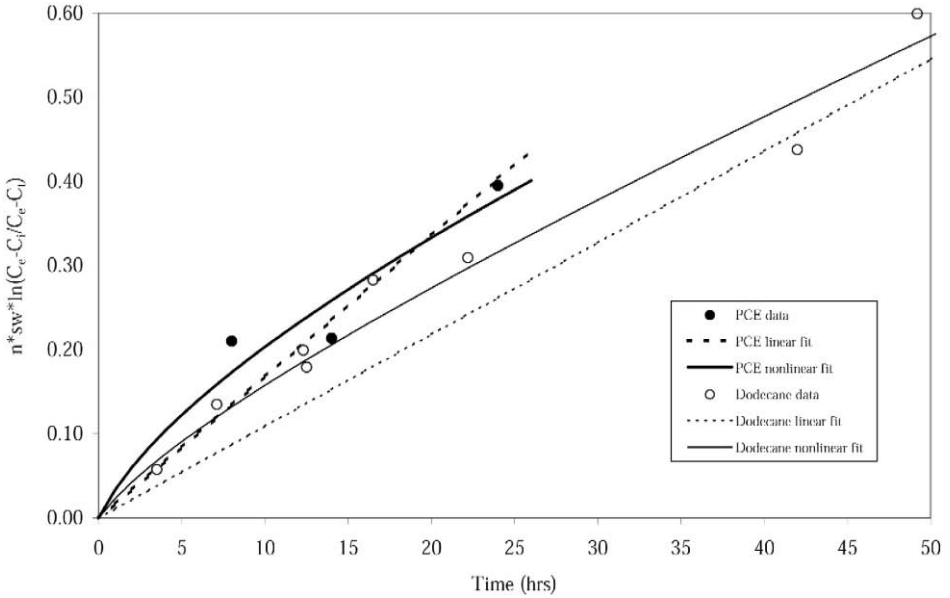

Fig. 6. Linear and nonlinear (time dependent) fits to flow interruption data for PCE (this study) and dodecane (Pennell et al., 1993; Abriola et al., 1993).

aqueous phase (M/L^3), C_a^o is the concentration of the organic solute in the aqueous phase (M/L^3). Eq. (7) may then be integrated to obtain the following relationship:

$$ns_a \ln\left[\frac{C_{a,sat}^o - C_{a(i)}^o}{C_{a,sat}^o - C_{a(t)}^o}\right] = K_{e,int}t \tag{8}$$

where $C_{a(i)}^o$ is the initial effluent concentration of organic solute prior to flow interruption and $C_{a(t)}^o$ is the average peak concentration of organic solute in the column effluent. Plotting the flow interruption data in the form of Eq. (8), $K_{e,int}$ was obtained using a least-squares linear regression procedure with the intercept set to zero (SYSTAT®) (Fig. 6). Experimental data and the fitted $K_{e,int}$ correlation for the dodecane are included in Fig. 6 for comparison purposes (Abriola et al., 1993). The value of $K_{e,int}$ (0.016 1/h, corrected $r^2 = 0.72$) obtained for PCE was slightly larger than the value reported for the solubilization of residual dodecane ($K_{e,int} = 0.011$ 1/h, corrected $r^2 = 0.96$). Based on this analysis, it can be seen that the linear $K_{e,int}$ correlation (Eq. (8)) underpredicted the rate of PCE and dodecane mass transfer at small flow interruption times. Abriola et al. (1993) addressed this problem by developing two mass transfer relationships, one for flow interruption times less than 22 h, and a second for flow interruption times between 22 and 100 h. An alternative approach to capture the rate of mass transfer for short periods of flow interruption is to develop a time-dependent relationship for $K_{e,int}$:

$$K_{e,int}(t) = \left(K_{e,int(i)} - K_{e,int(f)}\right)(1+t)^e + K_{e,int(f)} \tag{9}$$

where $K_{e,int(i)}$ is the initial rate of mass transfer under no flow conditions (1/t), $K_{e,nt(f)}$ is the final rate of mass transfer under no flow conditions (1/t), t is time, and e is an empirical constant. In the limit as time approaches zero or infinity, $K_{e,int}$ reduces to the initial value ($K_{e,int(i)}$) or the final value ($K_{e,int(f)}$), respectively. Substitution of Eq. (9) into Eq. (7), yields the following relationship:

$$ns_a \frac{\partial C_a^o}{\partial t} = \left(\left(K_{e,int(i)} - K_{e,int(f)}\right)(1+t)^e + K_{e,int(f)}\right)\left(C_{a,sat}^o - C_a^o\right) \tag{10}$$

Eq. (10) may be integrated to yield a relationship between effluent concentration and duration of flow interruption:

$$ns_a \ln \frac{\left(C_{a,sat}^o - C_{a(i)}^o\right)}{\left(C_{a,sat}^o - C_{a(t)}^o\right)} = \frac{K_{e,int(i)} - K_{e,int(f)}}{e+1}\left((1+t)^{e+1} - 1\right) + K_{e,int(f)} t \tag{11}$$

Eq. (11) was fit to flow interruption data for both dodecane (Pennell et al., 1993) and PCE (this study) using a non-linear, least-squares regression procedure (SYSTAT®). The fitted values obtained for dodecane were $K_{e,int(i)} = 0.027$ 1/h, $K_{e,int(f)} = 0.007$ and $e = -0.539$, with a corrected r^2 of 0.96. Since only three data points were available for PCE, the dependence of $K_{e,int}$ on time (i.e., value of "e") was considered to be similar to that of dodecane. The resulting fitted values for PCE were: $K_{e,int(i)} = 0.040$ 1/h; $K_{e,int(f)} = 0.005$, with a corrected r^2 of 0.85. A comparison of the fitted correlations for PCE and dodecane are shown in Fig. 6. In both cases it can be seen that a constant mass transfer coefficient provides a poor fit to the solubilization data over the entire range of flow interrupt times. This inadequacy of the linear driving force under static conditions may stem from the fact that the boundary layer becomes poorly defined when flow ceases, extending into the formerly mixed bulk fluid occupying the pore space. Despite this apparent limitation, the linear driving force model has been found to provide reasonable predictions of rate-limited NAPL solubilization in porous media (e.g., Abriola et al., 1993). In a companion paper, the expressions developed for the PCE mass transfer under flowing and no flow conditions are implemented in a numerical simulator and evaluated using results from the column and 2-D box studies (Rathfelder et al., 2000).

3.3. 2-D box experiments

The effect of rate-limited micellar solubilization and subsurface layering on the recovery of PCE by 4% Tween 80 was evaluated in two separate 2-D box studies. The experimental conditions for each box are summarized in Table 3. Box A represented a relatively high overall PCE saturation ($s_{PCE} = 3.49\%$ or 38 ml) compared to box B, which had an overall PCE saturation of 1.02% (10.7 ml). Upon release, the PCE migrated downward through the 20–30 mesh Ottawa sand until a fine layer, consisting of either F-70 Ottawa sand or Wurtsmith aquifer material, was encountered. Regions of high PCE saturation or "pools" formed above each fine layer, and PCE flowed horizontally around the layers. The resulting PCE distribution within each box consisted

Table 3
Summary of experimental conditions and physical properties of the 2-D boxes packed with 20–30 mesh Ottawa sand, Wurtsmith aquifer material and F-70 Ottawa sand

Parameter	Box A	Box B
Darcy velocity, q (cm/h)	4.7	1.1
Bulk density, ρ_b, 20–30 mesh Ottawa (g/cm^3)	1.70	1.72
Bulk density, ρ_b, F-70 Ottawa (g/cm^3)	1.75	1.82
Bulk density, ρ_b, Wurtsmith aquifer (g/cm^3)	1.89	1.77
Pore volume (ml)	1103.6	1041.3
Total trapping number, N_T	2.48e^{-6}	5.80e^{-7}
Total PCE added (ml)	38.05	10.67
Overall PCE saturation, s_{PCE} (%)	3.49	1.02
Volume of surfactant flushed (ml)/(pore volumes)	8717/7.9	4873/4.7
PCE recovered in surfactant flush(ml)	26.52 (69.7%)	8.59 (80.5%)
Total PCE recovered in mass balance (ml)	36.45 (95.8%)	10.31 (96.6%)

of relatively narrow zones (vertical) of residual PCE and regions of high PCE saturation (horizontal) above the fine layers. The pressure heads required for PCE to penetrate the Wurtsmith and Ottawa F-70 layers at 20°C were estimated to be 23 and 44 cm, respectively, using the entry pressure equation of Kueper and McWhorter (1996). The observed PCE heads during the entrapment phase of each box study were less than 5 cm, well below the required entry pressure head. Thus, PCE released into the 2-D boxes resided primarily within the 20–30 mesh Ottawa sand, with no significant amounts of PCE in the fine layers.

Following PCE infiltration and entrapment, box A and box B were flushed with a 4% Tween 80 solution at Darcy velocities of 4.7 and 1.1 cm/h, respectively. Fig. 7 shows the position of the surfactant front in box A and box B after flushing with approximately 0.4 and 0.6 pore volumes, respectively, of surfactant solution. For visualization purposes, the aqueous surfactant solution was dyed with Brilliant Blue (Fluka Chemika) and appears as a blue-green solution in Fig. 7. Since the surfactant solution had a slightly greater density than the resident pore water ($\rho_{\text{Surf. Soln}} = 1.002$ g/cm^3 versus $\rho_{H_20} = 0.9983$ g/cm^3), and the injection and extraction end chambers were fully screened, the surfactant solution flowed preferentially along the bottom of the box. This was particularly evident at a Darcy velocity of 1.1 cm/h (box B), where the angle of the advancing surfactant front was approximately 45° from the horizontal axis (downward). The effect of solution density on the angle of the surfactant front was far less evident in box A, which was run at a Darcy velocity of 4.5 cm/h. At the higher flow rate the surfactant front deviated only slightly from piston displacement (90° from the horizontal axis). For contamination scenarios that involve zones of high DNAPL saturation above a confining layer, the use of surfactant solutions that are more dense than the resident aqueous phase may be advantageous due to the tendency for a dense surfactant solution to preferentially flow along the bottom of the contaminated aquifer. If a vertical or piston-displacement surfactant flood is desired, however, the flow rate must be sufficiently high to minimize the density effect. These results indicate that the density contrast between resident aqueous phase and the flushing solution must be given careful consideration

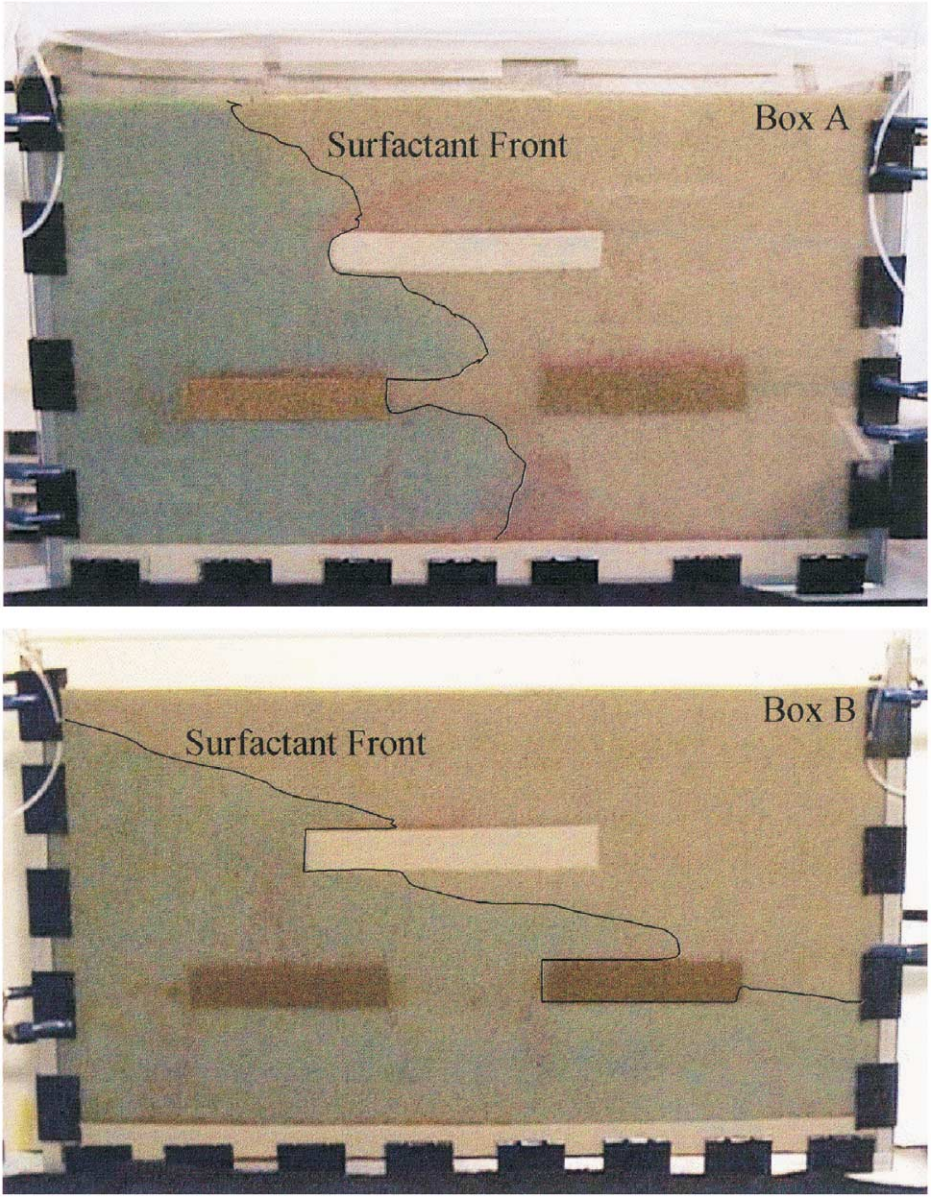

Fig. 7. Position of the surfactant front after flushing (a) box A and (b) box B with 0.4 and 0.6 pore volumes, respectively, of 4% Tween 80.

when designing or modeling SEAR systems. During surfactant flushing no visible mobilization of PCE, existing as residual droplets or in pools above the fine layers, was observed in the boxes. This finding was consistent with the values of the total trapping

number (N_T) calculated for box A and box B (2.48×10^{-6} and 5.80×10^{-7}, respectively), which were well below the critical value of 2.0×10^{-5} required for NAPL displacement in Ottawa sands (Pennell et al., 1996). In box A, approximately 70% of the PCE (38.05 ml) was recovered after flushing with eight pore volumes (8717 ml) of 4% Tween 80. The PCE remaining after the surfactant treatment existed as thin pools above the lower confining layer and above the fine lenses. In box B, approximately 80.5% of the PCE (10.67 ml) was recovered after flushing with five pore volumes (4873 ml) of surfactant solution. The greater recovery efficiency observed in box B can be attributed to the fact that a larger proportion of the PCE mass was entrapped at residual saturation. Excavation and analysis of the boxes following surfactant flushing yielded total mass balance recoveries of greater than 95%. In addition, no PCE liquid was found within the layers of F-70 Ottawa sand and Wurtsmith aquifer material. This indicates that the corresponding entry pressures (5.3 and 2.6 cm, respectively) were not exceeded after the interfacial tension between PCE and the aqueous phase was reduced to 5 dyn/cm during the surfactant flood.

Measured concentrations of PCE and surfactant in the extraction well effluent are shown in Fig. 8. These data are expressed as the concentration of PCE and surfactant versus the cumulative volume of effluent solution collected during each experiment. Based on the surfactant breakthrough curves presented in Fig. 8, sorption losses appeared to have a minimal effect on surfactant transport. Using the batch sorption data reported in Table 1, the maximum amount of Tween 80 that could be sorbed by the solid phase was approximately 750 mg. This represents a loss of 1.75% of the injected mass (40,000 mg/l) over the first pore volume, and only 0.2% of the injected mass for an eight pore volume flood. To further evaluate the potential effects of sorption on surfactant delivery and transport, a dimensionless retardation factor (R_F) was derived based on the Langmuir sorption isotherm (Eq. (1)). Assuming that flow was uniform and one-dimensional in the horizontal direction, Eq. (1) can be differentiated to yield a Langmuir retardation factor:

$$R_{F,\mathrm{Lang}} = \left(1 + \frac{\rho_b S^s_{m,\max} b}{n s_a \left(1 + b C^s_a\right)^2}\right) \tag{12}$$

where ρ_b is the soil bulk density (M/L^3), n is porosity (L^3/L^3), s_a is the aqueous-phase saturation (L^3/L^3), $S^s_{m,\max}$ is the maximum amount of surfactant sorbed (M/M), C^s_a is the aqueous-phase concentration of surfactant (M/L^3), and b is the ratio of the adsorption and desorption rates (L^3/M). For the surfactant concentration used in the box studies (40,000 mg/l), and assuming that flow occurred primarily through Ottawa 20–30 mesh sand, the value of $R_{F,\mathrm{Lang}}$ would be 1.00005. This value is consistent with the surfactant breakthrough curve obtained in box A, for which normalized surfactant concentration ($C^a_s/C^a_{s(i)}$) was approximately equal to 0.5 after one aqueous pore volume (1065 ml) had been displaced through the box (Fig. 8a). This analysis clearly illustrates that for aquifer–surfactant systems exhibiting Langmuir sorption, with relatively small limiting sorption capacities ($S^s_{m,\max}$), loss of surfactant to the solid phase will have little, if any, noticeable impact on surfactant transport in the subsurface. These findings are also consistent with numerical simulations of 1-D surfactant transport through Ottawa sand, which demonstrate that surfactant breakthrough approaches 1.0 pore volume as the

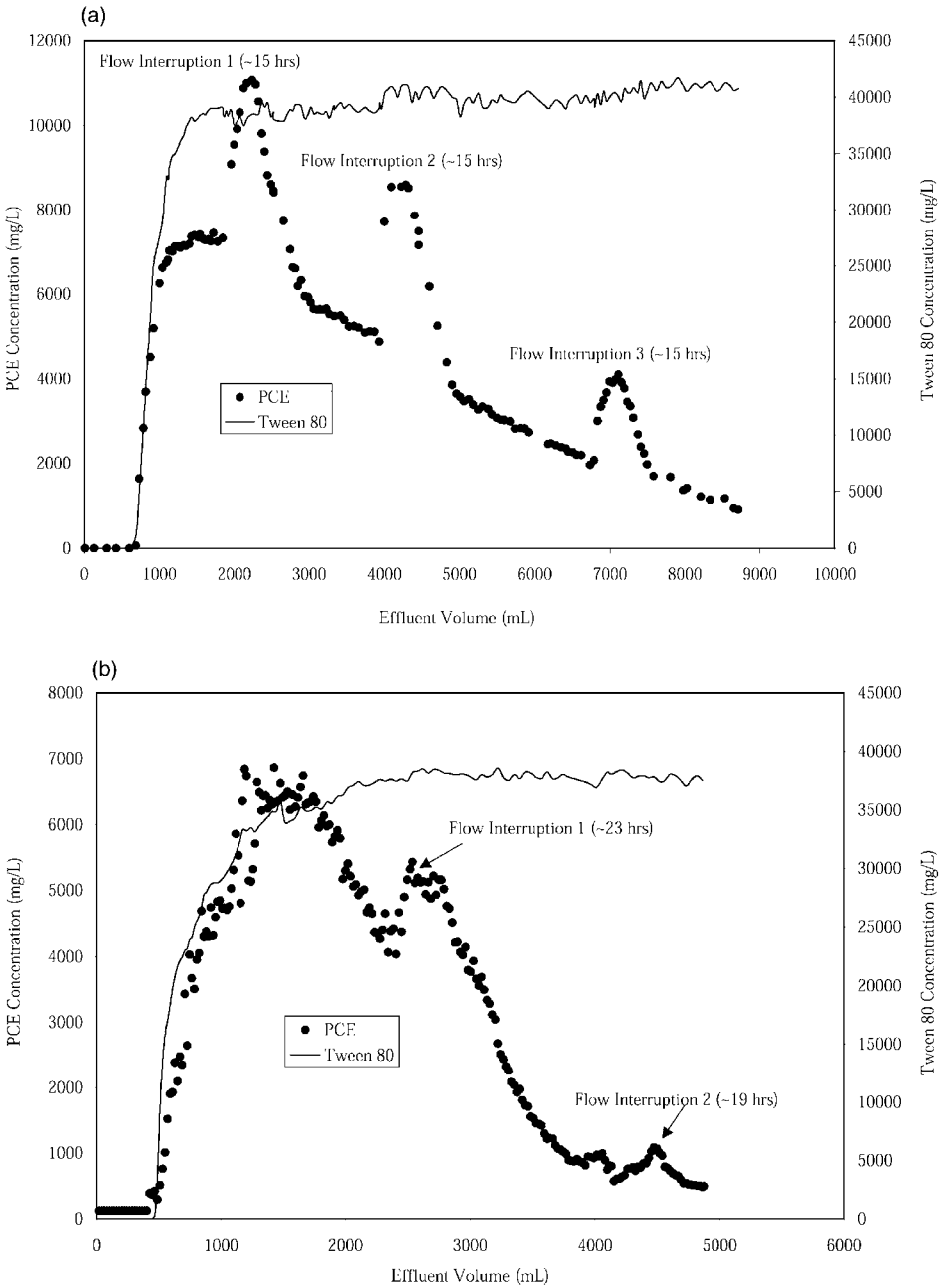

Fig. 8. Effluent concentrations of PCE and Tween 80 measured in (a) box A and (b) box B during surfactant flushing.

influent concentration of surfactant increases above the CMC (Weber et al., 1996). For box B, the normalized surfactant concentration ($C_s^a/C_{s(i)}^a$) approached a value of 0.5 after only 0.5 pore volumes of surfactant were injected, and exhibited a more gradual rise to the applied surfactant concentration (40,000 mg/l) (Fig. 8b). This behavior was attributed to the non-uniform flow of the surfactant solution (Fig. 7b), which resulted in early breakthrough of the surfactant solution and dilution effects. As discussed above, this effect was more pronounced in box B because the surfactant solution was applied at a Darcy velocity of only 1.1 cm/h.

As anticipated from the batch solubilization results, a sharp rise in effluent PCE concentration coincided with surfactant breakthrough (Fig. 8). In box A, the initial PCE concentration reached a maximum value of approximately 7200 mg/l. This value is similar to the initial steady-state effluent concentration of PCE measured in column 5 (7900 mg/l), which was conducted at a similar Darcy velocity. The greater overall PCE saturation of the column systems (10.87%) allowed the steady-state value to be maintained for nearly seven pore volumes, whereas in the box experiment the effluent PCE concentration under flowing conditions began to decline after flushing with less than two pore volumes of 4% Tween 80. In the second experiment (box B), the effluent concentration reached a maximum value of approximately 6900 mg/l and immediately began to decline as more solution was flushed through the system. Based on the column results, the effluent PCE concentration should have been approximately 10,000 mg/l if rate-limited micellar solubilization was the only factor influencing PCE recovery. The discrepancy in the measured value was attributed to the relatively low PCE saturation (1.02%), dilution and by-passing effects, and the non-uniform flow field resulting from density stratification.

Following the initial rise in PCE concentration and brief period of pseudo steady-state conditions, effluent PCE concentrations declined sharply as more surfactant solution was displaced through each box. This behavior is characteristic of transient NAPL dissolution or solubilization, in which the interfacial area of NAPL available for mass transfer is reduced (e.g., Powers et al., 1992; Pennell et al., 1994). In the 2-D box studies, PCE existing at residual saturation (small droplets or ganglia) was rapidly removed from the system. The PCE remaining at later time existed as pools above the fine layers. The pools of PCE, which possessed relatively small specific interfacial area, persisted throughout the course of the experiments. These findings are consistent with the results of a surfactant field trial conducted at Canadian Forces Base Borden, in which PCE was observed above the aquitard and fine layers after a surfactant flood (Fountain et al., 1991).

The effect of flow interruption, ranging in duration from 15 to 23 h, on effluent PCE concentrations was also evaluated in the box experiments. The observed increase in PCE concentrations after flow stoppage demonstrated the influence of rate-limited solubilization on PCE recovery. Although these results cannot be directly compared to those obtained in the column studies, the magnitude of the PCE increase following flow interruption was substantially less (1000–5000 mg/l) than that observed under uniform conditions (16,000–18,000 mg/l). These results demonstrate that although rate-limited mass transfer influenced PCE recovery, subsurface layering and dilution effects were primarily responsible for the observed reduction in PCE recovery.

4. Conclusions

In this study a matrix of batch, column and 2-D box experiments was performed to investigate the coupled effects of mass transfer limitations and subsurface layering on PCE recovery during surfactant flushing. Results obtained from the 1-D column experiments demonstrated that PCE solubilization was rate-limited under flowing and no flow conditions. Effective mass transfer coefficients derived from effluent concentration data indicated that the rate of PCE mass transfer was strongly dependent upon Darcy velocity. Comparisons with published modified Sherwood number–Reynolds number correlations revealed that the slope of the PCE–4% Tween 80 correlation was similar to that obtained for styrene dissolution into water and decane solubilization by 1% Witconol 2722. Under no flow conditions, the rate of mass transfer was found to depend on the duration of flow interruption. A functional form was developed to describe this time dependence, which fit the greater rate of PCE mass transfer observed for short periods of flow interruption.

Results of the box studies demonstrated that both rate-limited solubilization and subsurface layering influenced the recovery of PCE from the 2-D system. The presence of fine layers within the 2-D box resulted in a bimodal PCE distribution that consisted of high saturation zones or pools above fine layers and regions of residual PCE existing as entrapped droplets or ganglia. Upon flushing with 4% Tween 80, entrapped PCE droplets were readily solubilized, whereas pools of PCE above fine layers, which possessed a much lower interfacial area, persisted throughout the surfactant flood. Effluent concentrations of PCE and Tween 80 indicated that both mass transfer limitations and the presence of low-permeability lenses strongly influenced PCE recovery, and that sorption processes had no discernable effect on surfactant delivery and PCE solubilization. Effluent concentration data are utilized in a companion paper (Rathfelder et al., 2000) to evaluate the coupled effects of solution density, rate-limited solubilization and subsurface layering on PCE recovery during surfactant flushing.

Notation

a	specific interfacial area (L^2/L^3)
b	Langmuir sorption constant (L^3/M)
c	fitting parameter, K_e relationship
d	fitting parameter, K_e relationship
e	fitting parameter, $K_{e,int}$ relationship
C	mass concentration (M/L^3)
$C_{a,sat}$	saturated aqueous-phase concentration (M/L^3)
C^*	normalized concentration, $C/C_{(i)}$ (dimensionless)
d_{50}	mean grain size (L)
d_M	mean grain size of a medium sand ($L = 0.05$ cm)
Da	Damköhler number, $K_e L/q$ (dimensionless)
D_H	hydrodynamic dispersion (L^2/t)
D_l	free liquid diffusivity (L^2/t)
k	intrinsic permeability (L^2)
k_n	NAPL-aqueous phase mass transfer coefficient (L/t)

K_e	effective mass transfer coefficient, $k_n a_n$ (1/t)
$K_{e,int}$	effective mass transfer coefficient during flow interruption (1/t)
L	column length (L)
n	porosity (L^3/L^3)
N_T	total trapping number (dimensionless)
Pe	Peclet number, vL/D_H (dimensionless)
q	Darcy or superficial velocity (L/t)
Re	Reynolds number, $d_{50} q \rho_a/\mu_a$ (dimensionless)
$R_{F,Lang}$	Langmuir retardation factor (dimensionless)
s	fluid saturation (L^3/L^3)
S	sorbed-phase concentration (M/M)
Sh'	modified Sherwood number, $K_e d_{50}^2/D_l$ (dimensionless)
$S_{m,max}$	Langmuir maximum sorption capacity (M/M)
t	time (t)
U_i	grain size uniformity index (dimensionless)
v	pore-water or interstitial velocity (L/t)
x	distance (L)
X	normalized distance, x/L (dimensionless)

Greek Symbols

α	dispersivity, D_H/v (dimensionless)
ρ	mass density (M/L^3)
ρ_b	soil matrix bulk density (M/L^3)
δ	normalized grain size, d_{50}/d_M (dimensionless)
μ	dynamic viscosity (M/L t)

Subscripts and Superscripts

a	aqueous phase
(i)	initial time
(f)	final time
m	solid matrix
n	organic liquid phase (NAPL)
o	organic species
s	surfactant species

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