

Reductions in Contaminant Mass Discharge Following Partial Mass Removal from DNAPL Source Zones

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Although *in situ* remediation technologies have been used to aggressively treat dense nonaqueous phase liquid (DNAPL) source zones, complete contaminant removal or destruction is rarely achieved. To evaluate the effects of partial source zone mass removal on dissolved-phase contaminant flux, four experiments were conducted in a two-dimensional aquifer cell that contained a tetrachloroethene (PCE) source zone and down-gradient plume region. Initial source zone PCE saturation distributions, quantified using a light transmission system, were expressed in terms of a ganglia-to-pool ratio (GTP), which ranged from 0.16 (13.8% ganglia) to 1.6 (61.5% ganglia). The cells were flushed sequentially with a 4% (wt.) Tween 80 surfactant solution to achieve incremental PCE mass removal, followed by water flooding until steady-state mass discharge and plume concentrations were established. In all cases, the GTP ratio decreased with increasing mass removal, consistent with the observed preferential dissolution of PCE ganglia and persistence of high-saturation pools. In the ganglia-dominated system (GTP = 1.6), greater than 70% mass removal was required before measurable reductions in plume concentrations and mass discharge were observed. For pool-dominated source zones (GTP < 0.3), substantial reductions (>50%) in mass discharge were realized after only 50% mass removal.

Introduction

Dense nonaqueous phase liquids (DNAPLs) such as tetrachloroethene (PCE) and trichloroethene (TCE) are common groundwater contaminants that have been detected at approximately 60% of National Priority List sites (1). Following the release of DNAPL into an aquifer formation, capillary forces will act to retain discontinuous liquid ganglia or droplets within the porous medium, which are immobile under normal flow regimes. If lower permeability layers or lenses are encountered during downward migration, DNAPL will tend to accumulate and spread laterally along the upper interface of the permeability contrast, forming high-saturation pools (2, 3). The saturation distribution arising from a DNAPL spill will be influenced by a number of factors, including the rate and volume of the DNAPL release, density, viscosity, and interfacial tension, as well as the wettability and permeability distribution of the porous medium (4–8). The complexity of the resulting saturation distribution, which typically includes regions of discontinuous ganglia and high-

saturation pools within a heterogeneous flow field, renders DNAPL site characterization and remediation efforts particularly challenging (9, 10).

A number of *in situ* remediation technologies, including surfactant and/or cosolvent flushing, thermal treatment, air sparging, and chemical oxidation have been employed to aggressively treat DNAPL source zones (11, 12). Although DNAPL mass recoveries of greater than 90% have been reported in some field tests of these technologies (e.g., 13, 14), it is now widely accepted that a fraction of the initial DNAPL mass may persist after treatment (10, 12). In fact, well-controlled field-scale tests of surfactant and cosolvent flushing suggest that typical NAPL recoveries are on the order of 60–70% (15–19). As a consequence, dissolved-phase contaminant concentrations within, and emanating from, treated DNAPL source zones are likely to exceed drinking water standards for considerable periods of time (19, 20). Hence, some scientists and practitioners have questioned the benefits of incomplete or partial mass removal with respect to the protection of human health and the environment (21–23).

Critical assessments of the benefits and limitations of partial mass removal from DNAPL source zones have been based almost exclusively on mathematical predictions of dissolution, often leading to conflicting interpretations (e.g., 24, 25). Sale and McWhorter (20), using analytical solutions for the dissolution of DNAPL ganglia and pools in a uniform aqueous-phase flow field, concluded that almost complete mass removal is required to approach regulatory drinking water standards, and that partial mass reductions will provide only minimal improvements in groundwater quality in the short term. Conversely, Rao and Jawitz (24) reported an 80% reduction in dissolved-phase contaminant mass flux after only 50% DNAPL mass removal based on an analytical “stream tube” model that incorporated uniform DNAPL distributions subject to nonuniform flow. In an extension of this work, Jawitz et al. (26) reported that less mass removal was required to achieve the same reduction in contaminant mass flux as the spatial variability of aquifer properties and DNAPL saturation distributions within the source zone increased. Using a similar stream tube modeling approach, Wood et al. (27) evaluated cosolvent flushing of a mixed-NAPL test cell at Hill Air Force Base, predicting that 60% mass removal would result in an 80% reduction in contaminant mass flux, corresponding to a log reduction in flux-averaged effluent concentrations. Lemke et al. (28) simulated PCE dissolution in a statistically homogeneous, nonuniform sandy aquifer, and found that a two orders-of-magnitude reduction in mass discharge could be realized for mass removals ranging from 60 to 99%. This finding demonstrates the variability in mass removal versus mass flux relationships, even for relatively homogeneous systems, which prompted Lemke et al. (28) to caution that simplified conceptual models of DNAPL source zone dissolution may not accurately capture reductions in contaminant flux resulting from partial mass removal.

Despite the importance of source zone mass flux reductions from both a regulatory and remediation design perspective, only limited data are currently available to validate and refine the mathematical models discussed above (29, 30). Thus, the objective of this study was to quantify the effects of partial source zone mass removal on dissolved-phase contaminant concentrations and mass discharge as a function of the initial PCE-DNAPL saturation distribution. A two-dimensional aquifer cell, containing a source zone and a down-gradient plume region, was employed to allow for

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TABLE 1. Summary of the 2-D Aquifer Cell Experimental Conditions

2-D Cell Parameter	HI-GTP	MID-GTP	MID/LO-GTP	LO-GTP
background porous medium	mixed Accusand ^b	20/30 mesh Accusand	20/30 mesh Accusand	20/30 mesh Accusand
total pore volume (mL)	3630	3950	3950	3820
hydraulic conductivity (cm/min)	2.75	5.83	12.05	33.33
PCE injection rate (mL/min)	1.0	1.0	1.0	0.1
PCE injection volume (mL)	40.9	15.3	25.5	25.1
overall PCE saturation (%)	1.1	0.4	0.6	0.6
initial PCE GTP ^a	1.60	0.40	0.26	0.16
Surfactant Flood 1				
volume injected (mL)	4500	3210	5360	3370
flow rate (mL/min)	5.72 ± 0.50 ^c	5.71 ± 1.84	6.05 ± 0.35	8.59 ± 2.27
pore-water velocity (cm/hr)	14.18	13.07	13.85	20.18
Surfactant Flood 2				
volume injected (mL)	4500	3210	5360	3370
flow rate (mL/min)	5.47 ± 0.21	8.12 ± 1.81	5.52 ± 0.46	7.12 ± 2.50
pore-water velocity (cm/hr)	13.57	18.59	12.64	16.72
Surfactant Flood 3				
volume injected (mL)		4480		3630
flow rate (mL/min)		8.00 ± 2.47		7.38 ± 2.26
pore-water velocity (cm/hr)		18.32		17.34

^a Ganglia to pool ratio. ^b 1:1 mix of 20–30 + 40–50 mesh Accusand. ^c ± standard deviation.

detailed characterization of source zone saturation distributions using a light transmission system. By varying the PCE release and porous medium, four distinct PCE source zone distributions were created. The aquifer cell was flushed sequentially with 4% (wt.) Tween 80 to achieve incremental PCE mass removals ranging from 48 to 92%. Water flushing was performed between surfactant floods to re-establish a steady-state down-gradient plume. Tween 80, a nonionic surfactant, was selected for use because of its relatively large PCE solubilization capacity (0.67 g PCE/g surfactant) and moderate interfacial tension with PCE (~5.0 dyn/cm). These properties allowed for accelerated mass removal via dissolution with minimal risk of mobilizing entrapped PCE under the experimental conditions (31, 32).

Materials and Methods

Materials. High-pressure liquid chromatography (HPLC)-grade PCE (99.9% purity) was purchased from Sigma-Aldrich (Milwaukee, WI). PCE has a density of 1.62 g/mL at 25 °C, a molecular weight of 165.8 g/mol, and an aqueous solubility of approximately 200 mg/L at 25 °C (32). For visualization purposes, the PCE was dyed red with an organic soluble dye, Oil-Red-O (Fisher Scientific, Fair Lawn, NJ) at a concentration of 4×10^{-4} M. Previous research has shown that the presence of Oil-Red-O at this concentration does not significantly alter relevant physical properties of PCE (32). Polyoxyethylene (20) sorbitan monooleate (Tween 80) was obtained from Uniqema (New Castle, DE) and was used without further purification. Tween 80, which has a molecular weight of 1310 g/mol, a liquid density of 1.08 g/cm³, and a critical micelle concentration (CMC) of approximately 13 mg/L, is a food-grade surfactant that can be degraded under both aerobic and anaerobic conditions (33, 34). All aqueous solutions were prepared with water that was purified using a Nanopure Analytical Deionization system (Barnstead/Thermolyne Corp., Dubuque, IA) and contained 500 mg/L CaCl₂ (Fisher Scientific, Fair Lawn, NJ) as a background electrolyte. The aqueous surfactant solution consisted of 4% (wt.) Tween 80, which yielded a dynamic viscosity of 1.31 cP, an equilibrium interfacial tension with dyed PCE was reduced from 43.7 to 4.90 dyn/cm, and an equilibrium PCE solubilization capacity of approximately 27 000 mg/L (32). Accusands (20–30 mesh and 40–50 mesh) and Ottawa F-70 sand (40–270 mesh) were obtained from the Unimin Corp. (New Canaan, CT) and U.S. Silica Co. (Berkeley Springs, WV), respectively. The Accusands were selected for use as the background media because of

their high purity (99.8% SiO₂), absence of organic carbon, and translucent to transparent properties, which renders them well-suited to light transmission analysis (35).

Aquifer Cell Studies. Four two-dimensional (2-D) aquifer cell experiments were conducted to quantify the effects of partial mass removal on dissolved-phase PCE concentrations and mass discharge as a function of the initial source zone saturation distribution. The aquifer cell had dimensions of 150 cm (length) × 48 cm (height) × 1.4 cm (thickness), and contained a 58-cm long “source zone” region designed to assess DNAPL mass recovery and saturation distribution, and a 92-cm long “plume region” for monitoring dissolved phase plume development and contaminant mass flux (Supporting Information, Figure S.1). Twenty low-volume, screw-cap sampling ports, constructed from 0.2 mm i.d. glass tubing, were located within the plume region of the front glass plate along four vertical transects. The entire cell was packed under water-saturated conditions with the first (lower) layer consisting of F-70 Ottawa sand, which has an intrinsic permeability (k_i) of approximately 8.2×10^{-12} m². Above this layer, one cell was packed with a 1:1 mixture of 20–30 mesh Accusand ($k_i = 2.5 \times 10^{-10}$ m²) and 40–50 mesh Accusand ($k_i = 9.0 \times 10^{-11}$ m²), while three cells were packed with 20–30 mesh Accusand as the predominant or “background” aquifer material. The upper boundary of the cell was unconfined. Three zones of F-70 Ottawa sand lenses were packed within the source zone region of each cell to represent permeability contrasts that would retain PCE during the initial release event. Dyed PCE (15–41 mL) was introduced into the source zone region aquifer cell at a constant flow rate of 1.0 or 0.1 mL/min using a Harvard Apparatus (Holliston, MA) syringe pump fitted with a 15.2 cm long, 18-gauge stainless steel needle, which was located approximately 5 cm below the sand surface. Liquid PCE was allowed to redistribute for a period of at least 24 h prior to water flushing, yielding overall residual saturations ranging from 0.4 to 1.1% (Table 1).

Aqueous solutions were delivered and extracted from the aquifer cell through two fully screened rectangular chambers, constructed from square (1.27 cm × 1.27 cm) aluminum tubing and milled with 0.203 mm slits on one side, that were located at each end of the cell (Supporting Information, Figure S.1). Flow was controlled by adjusting the height of a constant head reservoir that was connected to the inlet chamber by Teflon tubing. Following PCE injection and redistribution, the overall hydraulic conductivity of the cell was determined

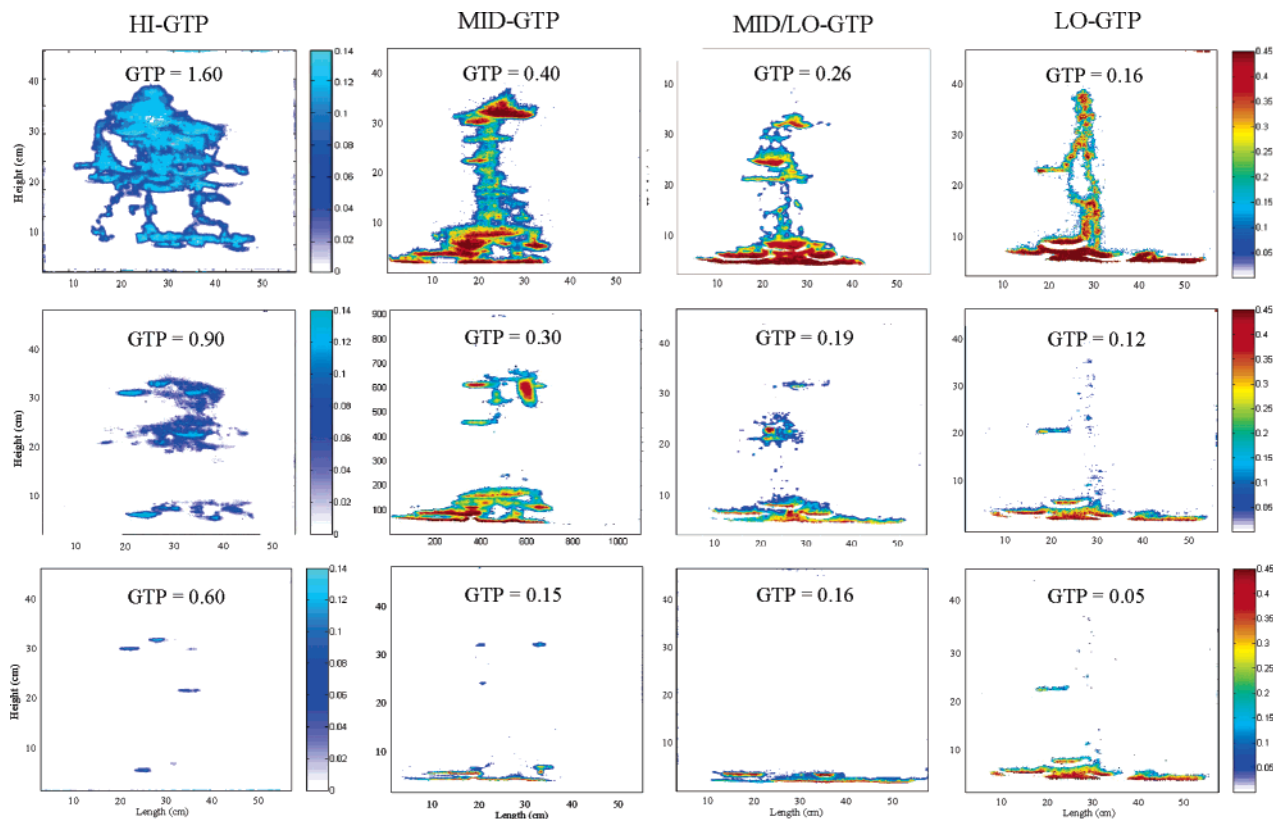


FIGURE 1. PCE saturation distribution profiles for the HI-GTP, MID-GTP, MID/LO GTP, and LO-GTP aquifer cells prior to surfactant flushing (top row), after the first surfactant flood (middle row), and after the final surfactant flood (bottom row).

at three steady flow rates using Darcy's law (Table 1). The aqueous flow field was monitored periodically by introducing pulses of aqueous solution containing water-soluble dye, Ergioglaucine A (Fluka Chemical, Milwaukee, WI) at a concentration of 3×10^{-5} M. Water was flushed through the cell at constant rates ranging from 1.0 to 1.5 mL/min to establish steady-state dissolved-phase PCE concentrations in the down-gradient plume region of the cell. A sequence of either two or three surfactant floods was then conducted at flow rates ranging from 5.5 to 8.6 mL/min to remove incremental amounts of PCE from the source zone via dissolution. Following each surfactant flood, several pore volumes of water were introduced into the cell at flow rates from 1.0 to 1.5 mL/min to establish a steady-state dissolved-phase plume. Aqueous samples were collected continuously from the midpoint of the effluent chamber which was connected to a Retriever II fraction collector (Isco Inc., Lincoln, NE) with Teflon tubing, and daily from sampling ports located in the plume region of the cell using a gastight syringe. The experimental conditions of each aquifer cell are summarized in Table 1.

Analytical Methods. Aqueous-phase PCE concentrations were measured using a Hewlett-Packard (HP) model 6890 gas chromatograph (GC) equipped with an HP model 7694 autosampler and a flame ionization detector (FID). Separation was achieved isothermally (45 °C) using a 30 m (length) DB-5 column with a 0.32 mm outside diameter (Agilent Technologies, Palo Alto, CA). Prior to analysis, samples were prepared by $5\times$ dilution in Optima grade 2-propanol (Fisher Scientific, Fair Lawn, NJ). A six-point calibration curve was generated for each sequence run, and calibration check samples were run after every 10 samples. A light transmission (LT) system, based on the design of Tidwell and Glass (36), was used to quantify PCE saturation (S_{PCE}) distributions within the source zone region of the cell. A Nikon Coolpics 900 digital camera was used to image the aquifer cell, which was illuminated

with a Flathead 80 light bank (Kino Flo Inc., Burbank, CA). Local PCE saturations were estimated by comparison of the digital image to previously generated hue–NAPL saturation calibration curves, which were developed using the experimental method of Darnault et al. (37). Thickness-averaged saturation distributions were calculated on a pixel basis (~ 0.3 mm \times 0.3 mm) using MATLAB 6.5 software (MathWorks, Inc., Natick, MA), and summed over the entire source zone region to estimate the total volume of liquid PCE in the source zone (Supporting Information, Figure S.1). The PCE volumes obtained by LT analysis were within 5% of values calculated from the PCE injection flow rate and duration. The resulting PCE saturation distributions were expressed in terms of a ganglia-to-pool (GTP) ratio (28), defined as the ratio of the PCE volume present in the cell at saturations less than residual saturation of the porous media ($S_{PCE} \leq 11\%$ and 13% for 20–30 mesh and mixed Accusand, respectively) to the volume of PCE present in the cell at saturations greater than residual ($S_{PCE} > 11\%$ or 13%). Residual saturation values were obtained from Pennell et al. (31) for the same size fractions of Ottawa sand, and confirmed using the intrinsic permeability–residual saturation correlation developed by Powers (38) for TCE in various sand size fractions.

Results and Discussion

Initial Saturation Distribution. The initial source zone PCE saturation distribution profiles obtained by LT analysis were expressed in terms of the ganglia-to-pool (GTP) volume ratio, yielding values of 1.60 (HI-GTP), 0.40 (MID-GTP), 0.26 (MID/LO-GTP), and 0.16 (LO-GTP) for the four aquifer cells. In the HI-GTP cell, the GTP value of 1.60 indicates that 62% of the PCE volume existed as discrete ganglia or droplets, while the remaining 38% was present in high-saturation ($S_{PCE} > 13\%$) pools (Figure 1, top row). For the two intermediate GTP cells, 20–30 mesh Accusand was used as the background porous media to reduce the amount of PCE entrapped as residual

TABLE 2. Effect of Surfactant Flushing on PCE Mass Removal, Ganglia-to-Pool Ratio, Effluent Concentration, and Mass Discharge

2-D Cell Parameter	HI-GTP	MID-GTP	MID/LO-GTP	LO-GTP
initial GTP ^a [% ganglia]	1.6 [61.5]	0.40 [28.6]	0.26 [20.6]	0.16 [13.8]
initial flux-averaged concn. (mg/L)	95.0 ± 20.0 ^b	101.0 ± 6.0	157.0 ± 10.7	57.0 ± 3.8
initial mass discharge (mg/min)	1.26 ± 0.017	1.54 ± 0.006	3.04 ± 0.014	1.31 ± 0.006
total PCE recovered (mL) [%]	30.7 [75.2]	14.1 [92.2]	21.7 [85.1]	14.4 [57.4]
Post Surfactant Flood 1				
PCE recovered (mL) [cum. %]	20.9 [51.3]	7.8 [51.0]	13.2 [51.8]	12.0 [47.9]
GTP [% ganglia]	0.90 [47.4]	0.30 [23.1]	0.19 [16.0]	0.12 [10.7]
flux-averaged effluent concn. (mg/L)	113.0 ± 12.0	63.6 ± 7.6	76.1 ± 16.3	20.0 ± 2.0
relative effluent concn. (C/C ₀)	1.00 ± 0.12 ^b	0.68 ± 0.06	0.48 ± 0.10	0.35 ± 0.10
effluent mass discharge (mg/min)	0.105 ± 0.011	0.090 ± 0.011	0.112 ± 0.024	0.026 ± 0.003
relative mass discharge (MD/MD ₀)	1.07 ± 0.17	0.77 ± 0.07	0.50 ± 0.12	0.35 ± 0.10
Post Surfactant Flood 2				
PCE recovered (mL) [cum. %]	9.8 [75.2]	3.0 [70.6]	8.5 [85.1]	1.2 [52.5]
GTP [% ganglia]	0.60 [37.5]	0.25 [20.0]	0.16 [13.8]	0.06 [5.7]
flux-averaged effluent concn. (mg/L)	36.7 ± 3.6	59.7 ± 13.8	6.3 ± 1.8	14.8 ± 2.4
relative effluent concn. (C/C ₀)	0.36 ± 0.04	0.59 ± 0.27	0.04 ± 0.04	0.26 ± 0.13
effluent mass discharge (mg/min)	0.033 ± 0.003	0.077 ± 0.022	0.090 ± 0.003	0.018 ± 0.003
relative mass discharge (MD/MD ₀)	0.31 ± 0.02	0.74 ± 0.27	0.04 ± 0.04	0.26 ± 0.13
Post Surfactant Flood 3				
PCE recovered (mL) [cum. %]		3.3 [92.2]		0.3 [53.8]
GTP [% ganglia]		0.15 [13.0]		0.05 [4.7]
flux-averaged effluent concn. (mg/L)		28.9 ± 5.6		12.6 ± 2.2
relative effluent concn. (C/C ₀)		0.27 ± 0.11		0.23 ± 0.15
effluent mass discharge (mg/min)		0.039 ± 0.007		0.016 ± 0.003
relative mass discharge (MD/MD ₀)		0.35 ± 0.11		0.23 ± 0.15

^a Ganglia to pool ratio. ^b ± standard deviation.

ganglia. Approximately 15 mL of PCE was introduced into the MID-GTP aquifer cell, resulting in an overall PCE saturation of 0.4%, and a GTP value of 0.4 (28.6% as ganglia). In the MID/LO-GTP aquifer cell, the volume of PCE released was increased to 25.5 mL, which further reduced the relative amount of residual PCE (GTP = 0.26, 21% as ganglia). The LO-GTP cell was packed with 20–30 mesh Accusand and the PCE injection rate was lowered from 1.0 to 0.1 mL/min to achieve a source zone that was characterized by extensive pooling. Of the 25.1 mL of PCE introduced into the LO-GTP aquifer cell, 86% existed in high-saturation pools (GTP = 0.16), which were primarily located immediately above the lower confining layer of the cell. The initial properties of the four aquifer cell experiments are summarized in Table 1.

Mass Recovery. Two sequential 4% Tween 80 surfactant floods, separated by a water flood, were conducted in the HI-GTP (GTP = 1.60) aquifer cell, resulting in a total PCE recovery of approximately 75% (31 mL). Cumulative PCE mass recovery over the course of the entire experiment is shown in the Supporting Information, Figure S.2a. In the first surfactant flood, 21 mL of PCE was recovered after flushing with 4 500 mL (1.23 pore volumes) of 4% Tween 80 solution, while the second 2.25 pore volume surfactant flood yielded the additional recovery of 10 mL of PCE (Table 2). Both the rate and extent of PCE recovery were greater during the first surfactant flood compared to the second flood, as indicated by the PCE to surfactant recovery efficiency, which declined from 0.12 g/g (i.e., g PCE recovered/g Tween 80 injected) in the first flood to 0.06 g/g in the second flood. This behavior was attributed to the dissolution of high-interfacial area ganglia, which accounted for 62% of the initial PCE volume, followed by less favorable dissolution of PCE from lower-interfacial area pools.

In the MID-GTP (GTP = 0.4) experiment, three surfactant floods, separated by two water floods, yielded an overall PCE mass recovery of 92% (Table 2, and Supporting Information Figure S.2b). Of the total PCE recovered (14.1 mL) from the MID-GTP cell, 55.0% was removed during the first 0.81 pore volume surfactant flood, while an additional 3.0 and 3.3 mL of PCE were recovered during the second (0.8 pore volume) and third (1.13 pore volume) surfactant floods, respectively.

Thus, the three sequential surfactant floods yielded PCE to surfactant recovery efficiencies of 0.10, 0.04, and 0.03 g/g, respectively. In the MID/LO-GTP experiment, a total of 21.7 mL (85%) of PCE was recovered after flushing with 1.36 and 2.10 pore volumes of 4% Tween 80 solution (Table 2, and Supporting Information Figure S.2c), which yielded recovery efficiencies of 0.10 and 0.4 g/g, respectively. The similarity in recovery efficiencies obtained for the MID- and MID/LO-GTP experiments, despite differences in the initial PCE volume (15.3 versus 25.5 mL) and number of surfactant floods, indicates that the fraction of PCE mass existing as ganglia, as expressed by the GTP ratio, strongly governs partial mass recovery resulting from a dissolution process such as micellar solubilization.

In the LO-GTP (GTP = 0.16) experiment, which was designed to simulate a source zone dominated by a single DNAPL pool above the lower confining layer, a total of 14.4 mL (57.4%) of PCE was recovered during three sequential surfactant floods (Table 2, and Supporting Information Figure S.2d). The first 0.9 pore volume surfactant flood yielded a PCE to surfactant recovery efficiency of 0.14 g/g, which is similar to the values obtained for the initial 4% Tween 80 floods in the other aquifer cell experiments. The observed consistency in initial mass recovery efficiencies regardless of the GTP ratio is attributed to the dissolution of PCE ganglia, which accounted for at least 14% of the initial PCE volume in all experiments. However, as PCE ganglia were depleted in the LO-GTP experiment, mass recovery efficiencies declined substantially: to 0.014 g/g in the second flood and 0.004 g/g in the third flood. These data suggest that in pool-dominated source zones, where ganglia represent a relatively small fraction (e.g., <25%) of the initial DNAPL mass, remediation strategies based, or dependent upon, dissolution will exhibit reduced mass recovery efficiency over time as the total NAPL interfacial area available for mass transfer decreases. This finding is consistent with cumulative mass recovery data obtained for surfactant and cosolvent flushing of heterogeneous source zones at the laboratory and field scales (e.g., 18, 19, 32).

Change in Saturation Distribution. The changes in GTP ratios as a function of PCE mass removal are shown in Table

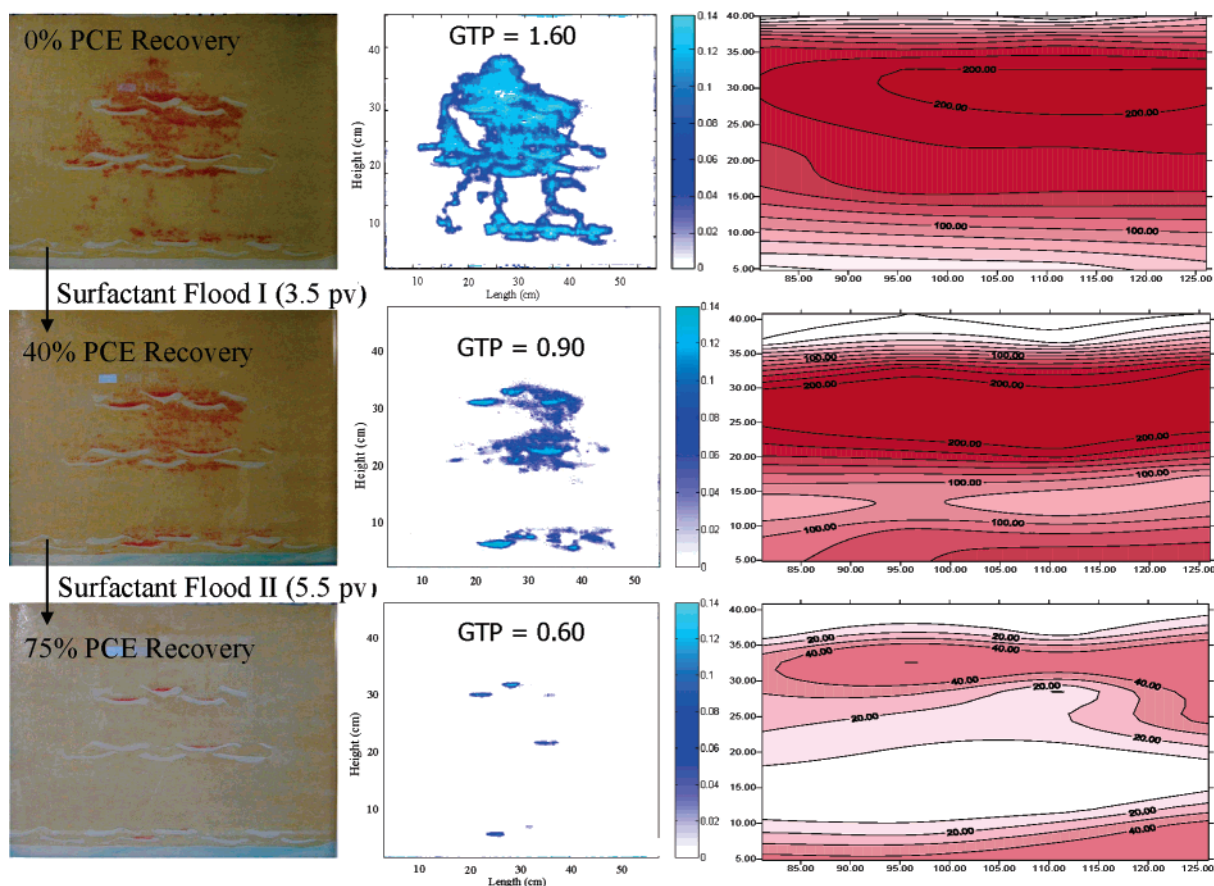


FIGURE 2. Change in source zone saturation distribution and corresponding down-gradient plume concentrations for the HI-GTP aquifer cell prior to surfactant flushing (top row), after the first surfactant flood (middle row), and after the second surfactant flood (bottom row).

2 for each aquifer cell experiment, along with the corresponding percentage of PCE-DNAPL remaining as ganglia (i.e., $S_{PCE} \leq 11\%$ or 13%). In addition, LT images of the PCE saturation distribution profile obtained after the first and final surfactant flood are shown in Figure 1 (middle and bottom rows, respectively) for each aquifer cell experiment. The GTP ratios decreased with increasing PCE recovery in all experiments, providing further evidence that high interfacial area ganglia are readily removed during micellar solubilization surfactant floods. Reductions in the volume of ganglia (Supporting Information Figure S.3) and GTP ratio (Table 2) were most pronounced in the HI-GTP experiment, for which the GTP ratio decreased from an initial value of 1.60 (25.1 mL as ganglia) to a final value of 0.60 (3.8 mL as ganglia). In contrast, for the LO-GTP experiment the GTP ratio decreased from an initial value of 0.16 (3.46 mL as ganglia) to a final value of 0.05 (0.55 mL as ganglia). The sizable decrease in the GTP ratio observed after surfactant flushing of the HI-GTP cell was attributed to dissolution of the relatively large volume of ganglia initially present in the source zone (62%). In contrast, the low GTP ratio (0.05) obtained at the conclusion of the LO-GTP experiment was consistent with the persistent high-saturation pools existing above the lower layer of F70 Ottawa sand (Figure 1).

Plume Concentrations and Mass Discharge. The effects of source zone mass removal on down-gradient plume concentrations and flux-averaged effluent concentrations were monitored after each surfactant flood. Representative dissolved-phase PCE concentrations are shown in Figure 2 for the HI-GTP aquifer cell, along with the corresponding source zone saturation distribution. Following the first surfactant flood of the HI-GTP cell, which achieved 51% mass removal, dissolved-phase concentrations remained near the equilibrium solubility of PCE (200 mg/L) immediately down-

gradient from the most highly contaminated region of the source zone, in which high interfacial area ganglia persisted (Figure 2, middle row). Following the second surfactant flood which resulted in 75% PCE mass removal, however, concentrations of PCE in the plume did not exceed 40 mg/L (Figure 2, bottom row). Corresponding values of mass flux (mass/area·time) within the dissolved-phase plume are shown in Supporting Information Figure S.4 as function of vertical position and PCE mass removal. The highest mass flux values occurred immediately down-gradient from the source zone regions with the greatest contamination since the flow profile was relatively uniform throughout the cell despite the presence of lower-permeability lenses and entrapped PCE.

Relative effluent (flux-averaged) concentrations and mass discharge (mass/time), normalized to the initial condition (i.e., prior to the first surfactant flood) are summarized in Table 2 and plotted as a function of cumulative PCE recovery in Figure 3. For the HI-GTP experiment, relative PCE effluent concentrations and mass discharge remained essentially constant after 50% PCE mass removal, which was attributed to the persistence of PCE ganglia over much of the source zone. However, a 60% reduction in relative mass discharge occurred following the second surfactant flood, at which time 85% of PCE mass initially present as ganglia had been removed (Table 2, and Supporting Information Figure S.3). In the remaining aquifer cell experiments, incremental reductions in relative PCE effluent concentrations and mass discharge occurred after each sequential surfactant flood, with the greatest reductions observed in the LO-GTP cell. This trend was consistent with the fraction of initial PCE mass existing as ganglia, which was reflected in GTP ratio. For example, the observed reduction in relative mass discharge was the greatest in the LO-GTP cell (65% reduction

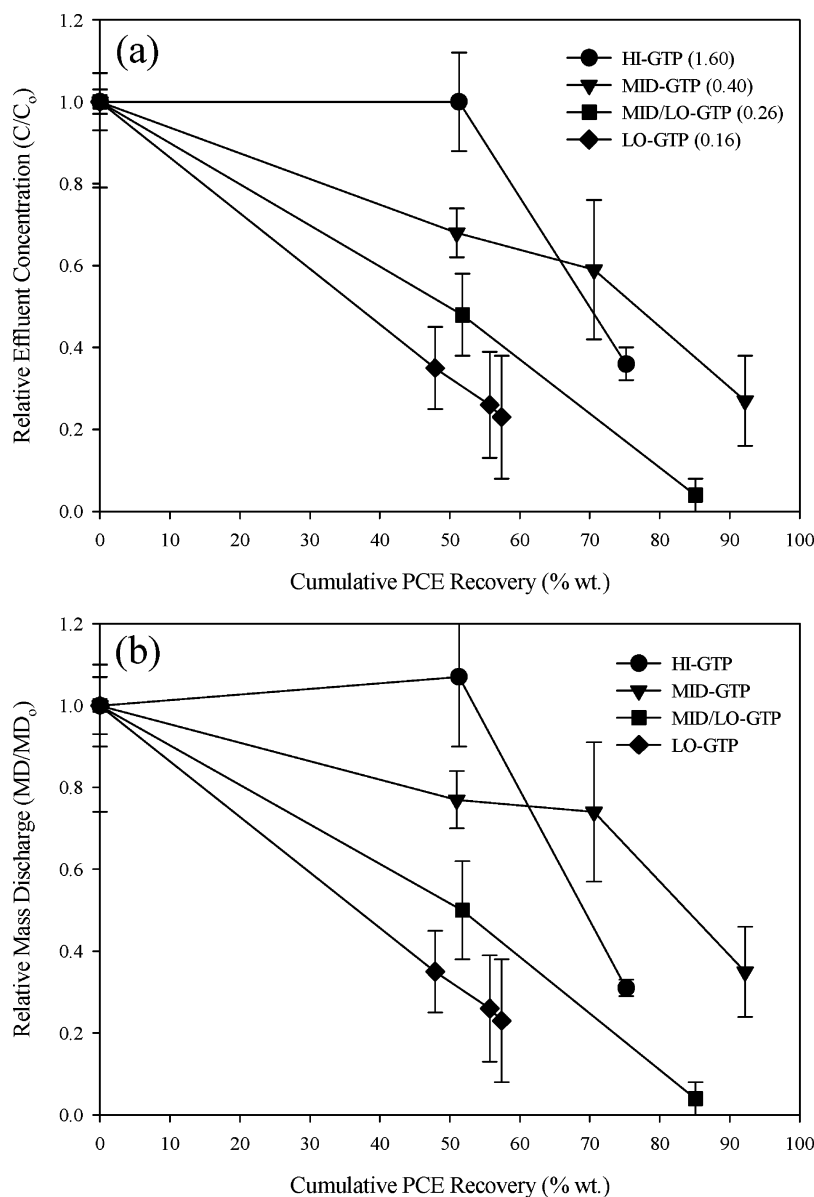


FIGURE 3. Relative flux-averaged effluent concentration (a) and mass discharge (b) as a function of increasing cumulative PCE recovery for the four aquifer cell experiments. Values were normalized to the effluent concentration and mass discharge measured during the initial water flood, prior to surfactant flushing. Error bars represent one standard deviation from mean for 6–10 samples.

after 55% PCE mass removal). However, it should be noted that during the second and third surfactant floods of the LO-GTP cell, when the remaining PCE mass existed in high saturation pools ($GTP < 0.06$), very little additional PCE mass was recovered. Hence, the effectiveness of solubilization-based surfactant flushing is diminished as the source zone became more pool-dominated (GTP decreased), although mass discharge stabilized at a relatively low level (0.016 mg/min) in the LO-GTP case.

Results obtained from the four aquifer cell experiments indicate that flux-averaged effluent concentrations and mass discharge can be expected to decrease substantially (40–96%) following partial (53–85%) source zone mass removal. The relationship between mass removal achieved by enhanced dissolution (i.e., micellar solubilization) and reductions in mass discharge appears to be strongly dependent upon the source zone saturation distribution; specifically, the relative fraction of PCE mass existing as ganglia and pools which can be expressed as the GTP ratio. For ganglia-dominated source zones ($GTP > 1.0$; >50% ganglia), substantial mass removal (>70%) may be required before

meaningful reductions in mass discharge are realized. In contrast, pool-dominated source zones ($GTP < 0.5$, 33% ganglia) may exhibit substantial reductions in mass discharge following relatively modest mass removals (e.g., 50–70%). Further, local plume concentrations and overall mass discharge following partial treatment of low- GTP source zones may be compatible with lower-capital cost, longer-term treatment strategies, or may fall below the attenuation capacity of the down-gradient aquifer formation.

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Supporting Information Available

Configuration of the 2-D aquifer cell (Figure S.1), cumulative PCE mass recoveries (Figure S.2), comparison of PCE volume existing as ganglia and in pools (Figure S.3), and down-gradient mass flux data (Figure S.4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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