Mass-flux Reduction and Mass Removal Relationships (MFR-MR) of Pool-dominated Multicomponent DNAPLs in a Heterogeneous Geological System

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GRAPHICAL ABSTRACT
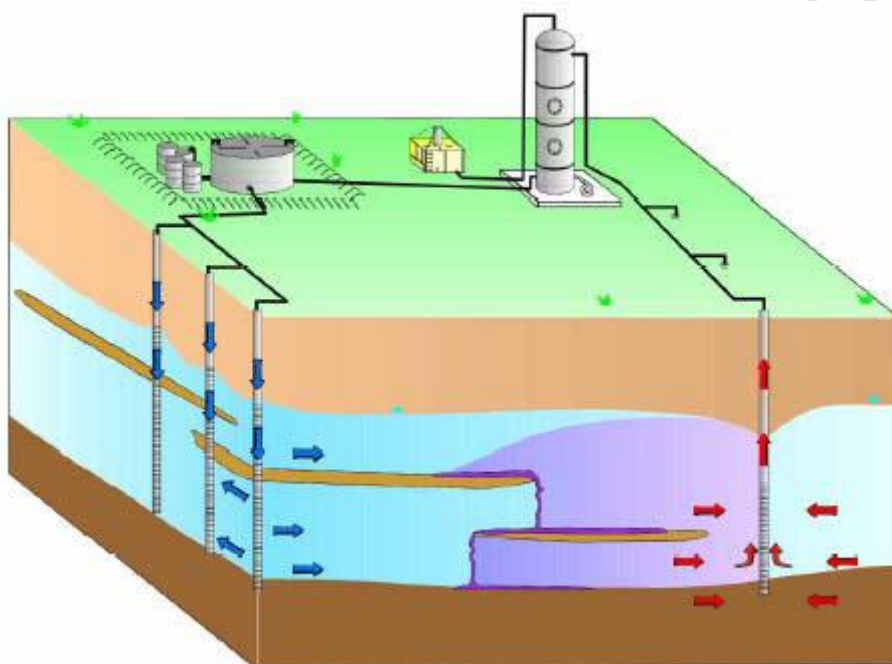
Abstract

Contamination of groundwater by chlorinated solvents such as trichloroethylene (TCE, tetrachloroethylene (PCE), and 1,1-dichloroethylene (1,1DCE) is a widespread problem that can seriously threaten human health and the environment. These compounds are often present as dense nonaqueous phase liquid (DNAPL) mixtures in the subsurface that serve as a long-term groundwater contamination sources. The objective of this study is to test the effectiveness of different in-situ flushing agents (SDS, Tween 80, MCD, and water) for the recovery of DNAPL mixtures (TCE, PCE, 1,1DCE) entrapped in heterogeneous aquifer media. A series of batch tests were first performed to assess the multiphase behavior of water-DNAPL mixture-reagent system. Intermediate scale tank experiments were then performed to compare the performance of the reagent solutions. The flushing breakthrough curves were also used to investigate the impact of solubilization agents on mass-flux reduction/mass-removal behavior relationships. Performance of agents on DNAPL mixture source zone remediation was found

to be in the following order: Tween 80>SDS>MCD>>Water. Individual DNAPL constituents exhibited transient effective solubilities that depend on the reagent contents and DNAPL compositions. Although high fractions of DNAPL source zones in heterogeneous porous media were removed through chemical flushing (SDS, Tween 80, MCD, and water), the heterogeneous system exhibited an extended multi-step concentration behavior. The results emphasized that in the early stage, some portion of the organic liquid is hydraulically accessible (matrix) whereas the later stage of mass removal was controlled by the more poorly accessible mass (pool) associated with higher-saturation zones. Our results also showed that the distribution and the emplacement of organic liquid, flow-field heterogeneity, sorption and desorption, and flushing solution all influenced the DNAPL mixture removal. The results from this study underline the need for understanding the multiphase behaviour of a system, particularly when DNAPL mixtures are present, prior to field-scale remediation implementation.

Keywords: DNAPL, dichloroethylene, trichloroethylene, tetrachloroethylene, surfactants, heterogeneous porous media

1. Introduction

Organic compounds such as chlorinated solvents are widely used in numerous industrial applications. Because of their low solubility, many of these compounds are often present in the environment in the form of non-aqueous phase liquids (NAPLs). Because their density is greater than that of water, chlorinated solvents often accumulate in the subsurface over low permeability barriers as high-saturation pool-dominated DNAPLs. The presence of DNAPL source zones in the subsurface can potentially contaminate large portions of groundwater resources for many decades due to their high toxicity and persistence. The removal of DNAPL source zones from the subsurface is widely considered as one of the toughest remediation challenges.

In-situ chemical flushing (ISCF) has evolved as an effective technology for the enhanced removal of DNAPLs from the subsurface. ISCF typically involve the injection of cosolvents or surfactant solutions (the focus of the current study) to speed up the recovery of the DNAPL from the subsurface (McCray and Brusseau, 1999; Boving and Brusseau, 2000; Tick et al., 2003; Tick and Rincon, 2009; Carroll and Brusseau, 2009; DiFilippo et al., 2010; Harvell, 2012; Akyol et al., 2013; Tick et al., 2015; Aydin-Sarikurt et al., 2016; Akyol and Turkkan, 2018; Akyol, 2018; Mohammed et al., 2019, Demiray et al., 2021, Alazaiza et al., 2022). There

are two general mechanisms by which surfactants can enhance the removal of DNAPLs from aquifers: (i) enhanced solubilization, (ii) mobilization. The design strategy of surfactant enhanced DNAPL solubilization is mainly based on the recovery of a contaminated aqueous phase (Javanbakht and Goual, 2016). The selected surfactant concentrations normally exceed the critical micelle concentration (CMC) which causes surfactant monomers to aggregate forming micelles with a hydrophilic exterior and a hydrophobic interior and allowing for significantly higher DNAPL partitioning (Schramm, 2000; Javanbakht and Goual, 2016). On the other hand, in the DNAPL mobilization mechanism, the interfacial tension (IFT) between DNAPL and the flushing solution is significantly reduced due to the formation of a separate bi-continuous middle-phase micoemulsion, consisting of bilayer vesicles in equilibrium, with aqueous and oil phases stabilized by surfactant molecules (Israelachvili, 2011; Javanbakht and Goual, 2016). As a result, the capillary number is drastically increased and DNAPL mobilization is facilitated. The design strategy, in this case, is based on the recovery of free phase DNAPL (Chevalier, 2003; Javanbakht and Goual, 2016). A primary risk associated with this recovery mechanism is the uncontrolled downward migration of the mobile DNAPL phase, because of its high density relative to that of water, which can lead to the inadvertent contamination of previously clean portions of the aquifer.

The characterization of the multiphase system (DNAPL-water-surfactant) can be evaluated using ternary phase diagrams (TPDs) which describe the solubilization potential of the components within the various phases present in the system (Falta, 1998). TPDs allow all three components (DNAPL-water-surfactant) to be displayed on the same graph which can be used to identify the degree of solubilization (solubility of the organic phase in the aqueous phase) quantitatively. The relationship of TPD along with the interfacial tension (IFT) on surfactant content of the flushing solution can aid in predicting the dominant removal mechanism of DNAPL before actual implementation of the remediation process.

Previous research using enhanced-solubilization agents has primarily focused on the mobilization and solubilization of single-component NAPL with significantly less studies investigating the compositional impacts for the removal of multicomponent NAPL (e.g., Abdul et al., 1990; Edwards et al., 1991; McCray and Brusseau 1998; McCray and Brusseau, 1999; Knox et al., 1999; Khachikian and Harmon, 2000; McCray and Dugan, 2002; Oostrom et al., 2006; Carroll and Brusseau, 2009; McCray et al. 2011; Akgoze Aydin et al., 2011, Agaoglu et al., 2012; Burke, 2012; Tick et al., 2015; Padgett et al., 2017; Mateas et al., 2017). Similarly,

while there has been extensive research solely devoted to examining mass-flux-reduction/mass-removal behavior for single-component NAPL systems (e.g., Boving and Brusseau, 2000; Stroo et al., 2003; Brooks et al., 2004; Lemke et al., 2004; NRC, 2004; Parker and Park, 2004; Phelan et al., 2004; Soga et al., 2004; Falta et al., 2005; Jawitz et al., 2005; Fure et al., 2006; Brusseau et al., 2007, 2008; Basu et al., 2008; DiFilippo and Brusseau, 2008; Marble et al., 2008; Tick and Rincon, 2009; Brusseau et al., 2013; Tick et al., 2015; Akyol et al., 2013; Akyol and Turkkan, 2018), there have been relatively few studies investigating these relationships for multicomponent NAPL systems during both water and enhanced-solubilization flushing conditions (e.g., D'Affonseca et al., 2008; Carroll and Brusseau, 2009; Burke, 2012; Tick et al., 2015; Padgett et al., 2017; Mateas et al., 2017).

The objective of this research is to evaluate the effect of enhanced-solubilization agents (surfactants) on remediation of pool-dominated multicomponent DNAPL (comprising of TCE, PCE, 1,1DCE) distributed within two different heterogeneous geological systems. These compounds were selected because they are widely used in industrial applications and have been often encountered at sites contaminated with DNAPLs (Pankow, 1995; Stroo et al., 2003; NRC, 2004; Tick et al, 2015; Aydin-Sarikurt et al, 2016). The paper will compare the relative behavior of different solubilization agents through a series of batch and 2-D tank experiments. The results of this study will contribute data to the literature in this specific research area, provide insight into the behavior of multicomponent DNAPLs entrapped in porous media, and assist in optimizing field scale remediation studies.

2. Materials and Methods

Batch tests and 2-D tank experiments were conducted to assess different solubilization agents for the removal of multicomponent DNAPL mixture source zones entrapped in two different heterogeneous geological systems. The DNAPL mixture consisted of trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,1 dichloroethylene (1,1DCE) ACS grade (Aldrich) with mole ratio of 1:1:1. Table 1 summarizes some key physicochemical properties of these compounds. Tween 80, Sodium Dodecyl Sulfate (SDS) and Methyl beta-cyclodextrin (MCD), along with water alone, were used as flushing agents for the comparative assessment of remediation efficacy.

Table 1. Physicochemical properties of the DNAPL components

Compound	Chemical formula	Density[1] (g/mL)	Aqueous solubility[2] (mg/L)	Viscosity[2] (cP)	Maximum contaminant level (MCL, μg/L)
PCE	C_2Cl_4	1.6227	150	0.89	5
TCE	C_2HCl_3	1.46	1280	0.532	5
1,1 DCE	$C_2H_2Cl_2$	1.213	2240	0.33	7

[1] at 20 ºC

[2] at 25 ºC

2.1 Batch Tests

The batch experiments were conducted to characterize the DNAPL mixture-water-solubilization reagent system. The measured parameters were solubility, miscibility of the multiphase system (expressed as TPDs), and interfacial tension (IFT) as a function of Tween 80, SDS, and MCD content. The IFTs between the DNAPL mixture and the aqueous phase were measured with a KSV703 Digital Tensiometer using the Du Nouy Ring method. This method involves the immersion of a platinum ring, which is suspended from the tensiometer, and recording the tension generated by the retraction of the ring. The IFT measurements were conducted at 20 °C for Tween 80, SDS, and MCD contents in the aqueous phase ranging from 0 to 0.0093% (100mg/L), 0 to 0.2%, and 0 to 25% by mass, respectively.

Solubility tests were performed to determine the dissolution performance of the DNAPL mixture in aqueous solutions of solubilization agents. The selected agents Tween 80, SDS, and MCD contents in the solubility experiments were 2.5 and 5% by mass. Samples prepared in 40 mL glass tubes were placed in a water bath and allowed to shake at 360 rpm for 48 hours in a horizontal shaker, followed by centrifugation at 4000 rpm for 20 min to provide separation between the DNAPL phase and the aqueous phase of the agents. The dissolved PCE, TCE, and 1,1DCE in the aqueous phase were analyzed using Perkin Elmer Clarus 600 Gas Chromatography equipped with mass detector (GC/MS) and TurboMatrix 40 Trap Headspace sampling (HS) unit. All solubility experiments were performed at 20°C.

TPDs were developed to determine the miscibility of the organic and aqueous phases. A titration procedure was used to determine the turnover points between the one-phase and two-

phase regions which define the location of the miscibility curve on the ternary phase diagrams (Martel et.al., 1998; St-Pierre et.al., 2004; Aydin-Sarikurt et.al., 2016). A mixture of components with known amounts was placed in a glass vial capped with a Teflon mini valve to minimize evaporation. Two components were gradually added to the system using gastight macro syringes. The turning point was observed directly from the change in transparency of the solution. The formed curve expresses the composition of the three reacting components forming one or two phases in terms of the percent mass in the DNAPL mixture-water-solubilizing agent system. All TPD measurements were performed at 20°C.

2.2 Flushing Experiments

The flushing experiments were performed in a rectangular tank made of stainless steel and tempered glass, with dimensions of 40 cm long by 20 cm high by 3 cm wide. The flow cell was equipped with multiple, evenly spaced injection/ extraction ports on each end. In addition, three ports were evenly spaced at the top of the flow cell to allow the injection of organic liquid. Watertight seals were made with silicone sealant. Two silica sand media with different median particle diameters (359 μm (40/50 mesh), and 172 μm (70/100 mesh)) and natural calcareous soil were used for tank experiments. Silica sand materials were purchased from a private company (Santoz). The organic carbon content of silica sand materials is very low (O.C.%=0.05). The calcareous soil has a poorly sorted sandy loam texture representing heterogeneous physical properties. The physical and chemical properties of calcareous soil are given in Table 2.

Table 2. Physical and chemical properties of calcareous soil (from Akyol et al., 2011; Akyol and Yolcubal, 2013)

Sand (%)	Silt (%)	Clay (%)	Texture	Specific Surface area (m²/g)	BulkDensity ρ_b (g/cm³)	TOC (%)	TOM (%)	pH$_{1:1}$	CaCO₃ (%)	SiO₂ (%)
67	30	3	Sandy loam	0.34	1.34	0.97	1.67	8.4	96	2.12

Two heterogeneous porous medium configurations were created for the tank experiments. The first tank configuration consisted of a homogeneous pack of 40/50 sand as the matrix, with a layer of 70/100 sand placed along the bottom boundary (Fig 1). The second configuration

consisted of a matrix of natural calcareous soil with two lenticular lenses of <200 mesh calcareous soil and the bottom boundary was also prepared by <200 mesh calcareous soil (Fig 3). The tank experiments were conducted under saturated and steady-state flow conditions. Once the tank was fully saturated with water, a predetermined amount of DNAPL mixture was injected using the upper middle port and the system was kept for 48 hours (Table 3). After 48 hours, the remedial solution or water was injected at a constant rate, corresponding to an average pore-water velocity of approximately 10 cm/h. This velocity is consistent with the range of velocities commonly considered in flushing activities (e.g., Saba and Illangasekare, 2000; Nambi and Powers, 2003; Yaksi et al., 2021). Eight sets of experiments were conducted for the two physical heterogeneous configurations comprising of the silica sand and natural calcareous soil (Table 3).

Table 3. List of 2-D tank experiments

Experiment Number	Porous Medium	Agent	v (cm/h)	DNAPL mixture form	S_n (%)
1	Silica Sand	5% Tween 80	10.1	Pool	0.04*
2	Silica Sand	5% SDS	10.1	Pool	0.04*
3	Silica Sand	5% MCD	10.1	Pool	0.04*
4	Silica Sand	Water	10.1	Pool	0.04*
		Agent	v (cm/h)	DNAPL mixture form	S_n (%)
1	Calcareous soil	5% Tween 80	9.9	Pool	0.04*
2	Calcareous soil	5% SDS	9.9	Pool	0.04*
3	Calcareous soil	5% MCD	9.9	Pool	0.04*
4	Calcareous soil	Water	9.9	Pool	0.04*

*S_n is defined as the injected volume of the organic liquid divided by the pore volume of the entire system.

Figure 1. Image of DNAPL mixture initial distribution for the first configuration. The matrix was composed of 40/50 mesh sand. The bottom was composed of 70/100 mesh sand (Experiment 1 with 5% Tween 80)

Figure 2. Image of DNAPL mixture initial distribution for the second configuration. The matrix was composed of calcareous soil and the bottom was composed of <200 mesh soil (Experiment 1 with 5% Tween 80)

Tank effluent samples were collected using a 0.5 mL glass syringe and diluted for analysis using the GC/MS. Before analysis, the GC/MS was calibrated with individual DNAPL samples in the range of 0.01-0.5 mg/L to provide a six-point calibration curve. The aqueous samples were diluted if necessary and injection into a 20 mL priorly added 3.5 g of sodium sulfate headspace borosilicate glass vial and crimp sealed with Teflon septa and aluminum caps. Samples were immediately transferred to the GC/MS with headspace unit. The Elite-624 column (Perkin Elmer 30 m, 0.5 mm ID, 3 μm) was used in the GC/MS analyses with helium as the carrier gas. The GC was programmed to increase the oven temperature from an initial value of 40 °C for a 5-minute holding period to a final temperature of 220 °C at a rate of 8 °C per minute (split ratio 1:10).

2.3 Mass-flux-reduction/mass-removal relationship

Mass-flux-reduction/mass-removal behavior was simulated based on treating changes in mass-flux as a direct function of the change in contaminant mass (DiFilippo and Brusseau, 2008; Difilippo et al., 2010; Akyol et al., 2013; Tick et al., 2015; Akyol and Turkkan, 2018)

$$MFR = 1 - \frac{J_f}{J_i} = 1 - \frac{Q_f C_f}{Q_i C_i}$$

where J is mass-flux [M/T], C is effluent concentration [M/L^3], Q is flow rate [L^3/T], and the subscripts i and f represent initial and final, respectively. The mass flux reduction mass removal relationship was computed from the effluent concentrations for each DNAPL component separately.

3. Results and Discussion

3.1. Batch experiments- Phase Behavior

The impact of solubilizing agent contents on the IFTs between the DNAPL mixture and the aqueous phase is shown in Figure 3. The IFT of the DNAPL mixture with pure water is about 40 mN/m. The IFT rapid decreases with low Tween 80 contents but exhibits practically no decrease for Tween 80 concentrations greater than 0.005 %wt. This indicates that Tween 80, even at very low contents, is an effective surfactant for chlorinated solvent DNAPL mixtures. However, at higher Tween 80 levels, the IFT is likely not sufficiently depressed to cause DNAPL phase mobility. SDS exhibited similar behavior, however much higher agent contents are needed before the IFT approaches zero. On the other hand, the IFT with MCD did not reach zero. These findings, particularly with Tween 80, are consistent with some studies that have examined the effect of solubilization agents on single phase DNAPLs (Cai and Mohanty, 1997; Boving and Brusseau, 2000; Conrad et al., 2002; Suchomel et al., 2007; Cheng et al., 2016).
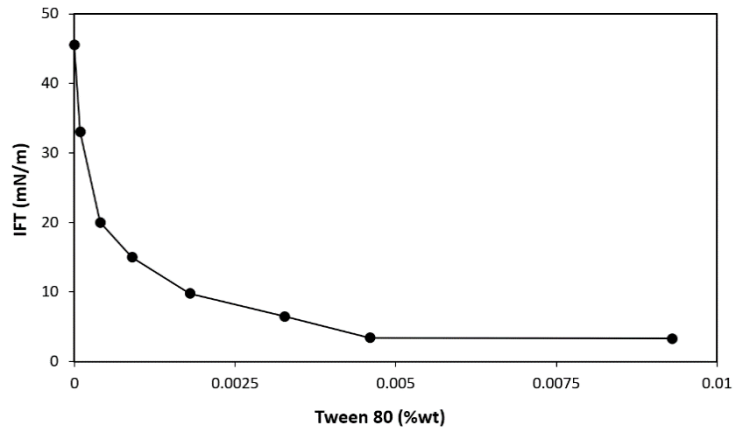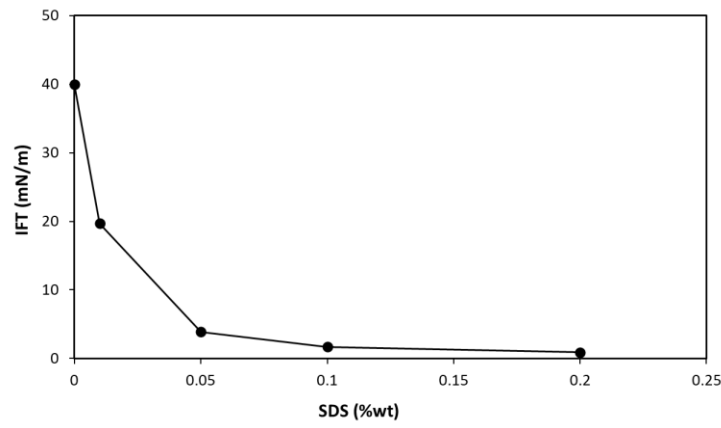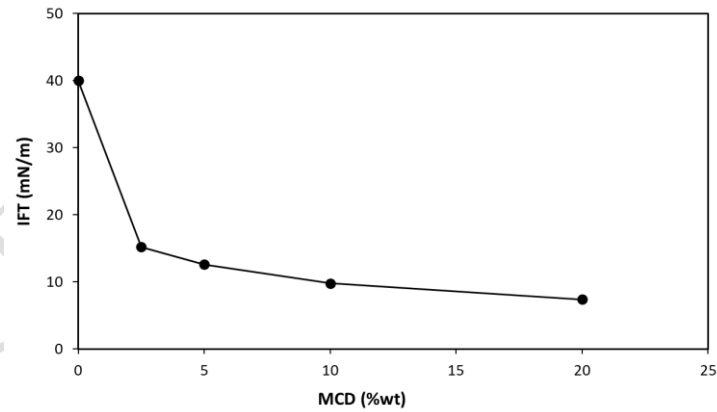
Figure 3. Interfacial tension as a function of (a) Tween 80, (b) SDS, (c) MCD content (% by mass) in the aqueous phase. The DNAPL consisted of TCE, PCE, and 1,1DCE at equal mole fraction

Figure 4 shows the TPDs, expressed on mass basis, of the DNAPL mixture-water-solubilizing agent system. The curves show the miscibility line of the DNAPL-rich phase in the aqueous phase for different solubilization agent contents. Specifically, for compositions above the

miscibility curve, the system is fully miscible. For compositions below the miscibility curve, two phases are present, an aqueous phase and a DNAPL-rich phase. The multiphase system is fully miscible at Tween 80 contents higher than 54 %wt (Figure 4a) with no formation of bilayer vesicles. Due to the high viscosity of pure Tween 80, gels were formed when the aqueous solution exceeded about (10.6; 62.6; 26.8) % by mass. It was observed that with an increase in DNAPL mixture content, the formation of a highly viscous opaque white microemulsion was observed which interfered with the titration procedure. The DNAPL mixture-water-Tween 80 ratio started from (100; 0; 0) to (39; 1; 60) without any physical change. Beyond this ratio, temporary cloudiness was observed with the further addition of water. There was a continuous cloudiness and clearness transition between the two phases with increasing amount of water. At the points at the upper right section of the curve, cloudiness became stable which corresponded to the two-phase region (Figure 4a).

Unlike Tween 80, clouding and foaming were not observed in the titration for constructing the TPDs of SDS and MCD. The miscibility curve formed closer to the water axis. The total amount of water within the ternary system caused the points to concentrate on one side of the graph (Figure 4b,c). These results suggest that the removal mechanism of the DNAPL mixture is likely to be solubilization since the solubilizing agent concentrations used in tank experiments were substantially below the miscibility curve.
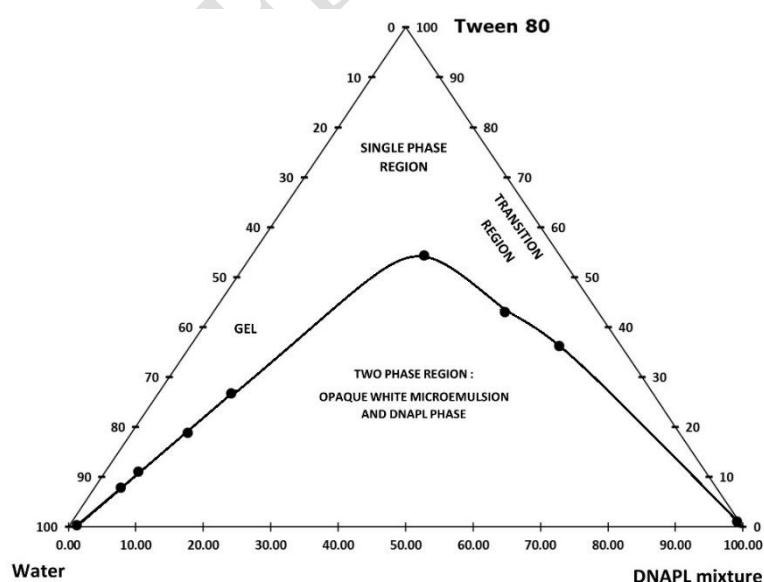
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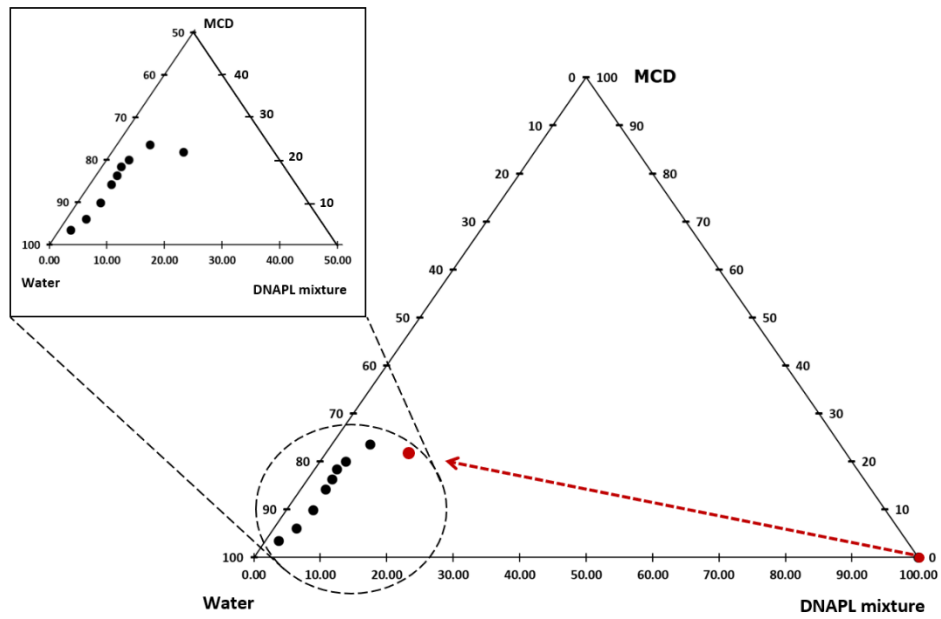
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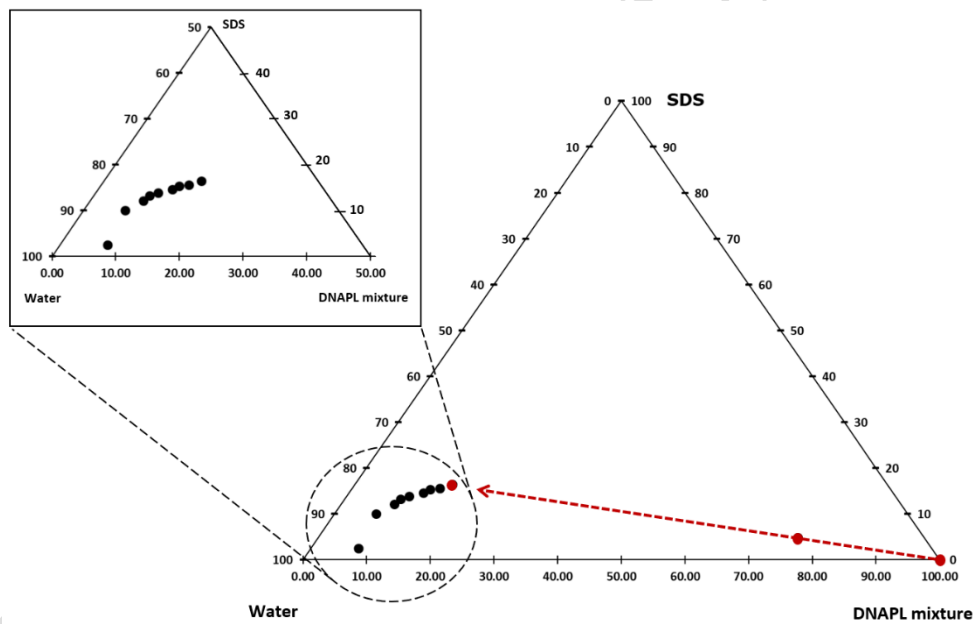
(c)

Figure 4. Ternary phase diagrams for DNAPL mixture-water-solubilizing agent system (mass %) (a) Tween80, (b) MCD, (c) SDS

The measured solubilities of the DNAPL mixture (ratio of 1:1:1 on a mole basis) for solubilizing agent contents of 2.5 and 5 percent by mass are presented in Figure 5. Tween 80 increases the DNAPL component solubilities the most, followed by SDS and finally MCD. The data are also summarized in Table 4.
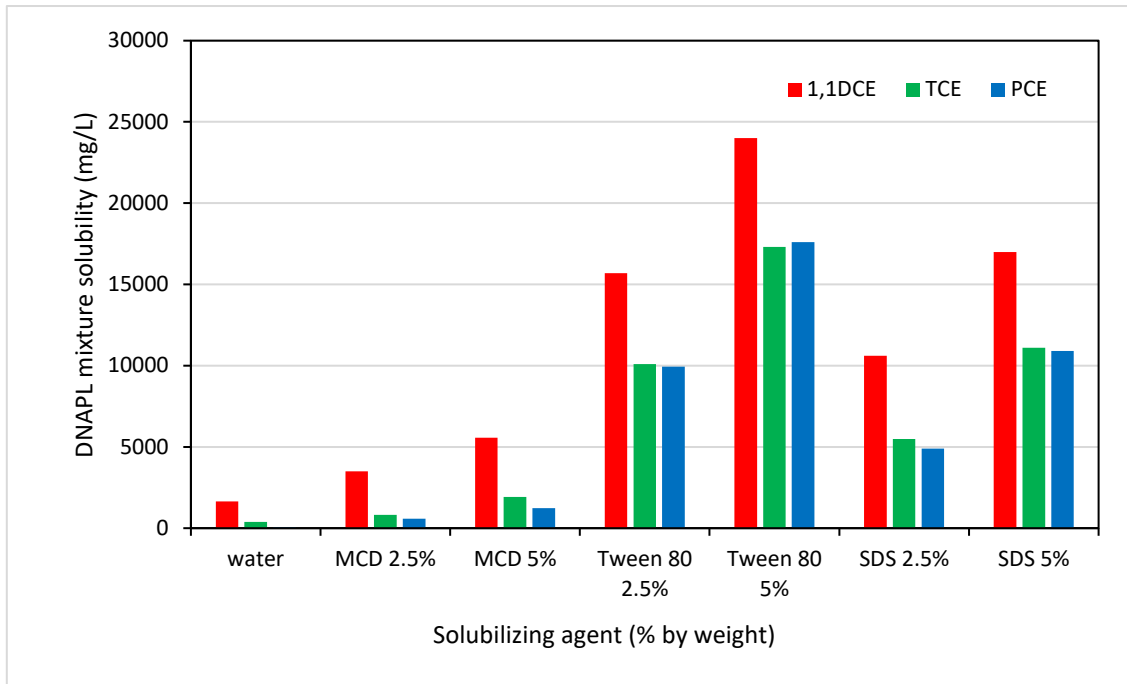
Figure 5. Enhanced-solubility of the DNAPL mixture in Tween80-water, SDS-water, and MCD-water system

Table 4. Comparison of the solubility values of DNAPL mixture components obtained from batch experiments with literature data

DNAPL mixture	Solubilizing agent (%)		This study	Literature		% Error	Reference
				Pure phase DNAPL*	0.33 mol fraction		
1,1 DCE	water	-	1650	3000	990	66.5	Dill et.al., 1980
	MCD	2.5	3500	-	-	-	No data available
		5	5570				
	Tween 80	2.5	15700				
		5	24000				
	SDS	2.5	10600				
		5	17000				
TCE	water	-	390	1200	400	2.2	Horvath et.al., 1999
	MCD	2.5	820	-	-	-	No data available
		5	1920	5500	1800	5.3	Boving and Brusseau, 2000
	Tween 80	2.5	10100	34300	11300	11.0	Huh, 1979
		5	17300	49500	16300	6.0	Zhong et.al., 2003
				85800	28300	38.8	Suchomel et.al., 2007
	SDS	2.5	5480	10000	3300	66.0	Zhong et.al., 2003
		5	11100	23600	7800	43	Zhong et.al., 2003
				30700	10100	9.5	Boving and Brusseau, 2000
PCE	water	-	58	200	66	12	Horvath, 1982

	MCD	2.5	580	-	-	-	No data available
		5	1230				
	Tween 80	2.5	9940	16500	5440	82.5	Taylor et.al., 2004**
		5	17600	33500	11100	59.4	
	SDS	2.5	4900	-	-	-	No data available
		5	10900				

(*) : The values (pure phase DNAPL solubility, $C_{solubility}$, and the solubility enhancement factor, E) obtained from batch experiments were taken into consideration.

(**) : Experimental study (Taylor et al., 2004), up to 4% concentration. The solubility corresponding to the 5% concentration was obtained from the regression equation ($R^2 = 0.999$).

Table 4 also compares the solubility data observed in this study to previously published data. The same data expressed in terms of solubility enhancement factor, E, are presented in Table 5. The enhancement factor E is defined as the solubility of DNAPL with surfactant divided by the solubility of DNAPL in pure water. The data reported from this study were obtained from the batch tests, whereas the data from the literature were obtained from batch tests or flushing experiments, as indicated in Table 5 The ratio of the solubility of each component of DNAPL mixture in 5 %wt solubilizing agent solution (Tween80) to the solubility in pure water is 303.1 for PCE, 44.8 for TCE, and 14.6 for 1,1DCE. 5% SDS content increased the solubility of PCE, TCE and 1,1DCE by factors of 186.7, 28.7 and 10.3, respectively. Finally, for 5% MCD, the solubilities of PCE, TCE and 1,1DCE increases by factors of 21.2, 5 and 3.4 respectively.

Overall, the batch solubility experiments reveal that for the selected solubilization agent contents and DNAPL composition, the performance of the agents followed the corresponding order: Tween80>SDS>MCD>>water. However, greater difficulty was encountered with the Tween 80 solution preparation and titration due to its high viscosity.

Table 5. Comparison of the enhancement factors from this study to available literature values

Study	Experimental Conditions		Surfactant (%)	Compound	Solubility Enhancement Factor (E)
Slavic, 2014		Flow-cell/multiple-component	5% SDS	PCE	60
			5% SDS	TCE	16.5
			5% MCD	PCE	15
			5% MCD	TCE	7.7
		Column/single-component	5% MCD	TCE	4.6

Reference	Port	Method/Component	Surfactant	Compound	Value
Boving & Brusseau, 2000			5% SDS	TCE	25.6
Tick & Rincon, 2009		Column/single-component	5% SDS	TCE	20
Akyol et. al., 2013		Column/single-component	5% SDS	TCE	37
		Flow-cell/single-component	5% SDS	TCE	~5-9
Tick et. al., 2015	Extraction port	Flow-cell/multiple-component	5% SDS	cisDCE	5.5
	Extraction port		5% SDS	TCE	18.6
	Extraction port		5% SDS	PCE	58.5
	Source-zone port		5% SDS	cisDCE	3.4
	Source-zone port		5% SDS	TCE	5.3
	Source-zone port		5% SDS	PCE	12.7
Zhong et. al., 2003		Batch/single-component	5% SDS	TCE	19.6
			5% Tween80	TCE	41.25
Suchomel et. al., 2007		Batch/single-component	5% Tween80	TCE	71.5
			4% Tween80	TCE	52.9
Taylor et. al., 2004		Batch/single-component	4% Tween80	PCE	137.5
This study		Batch/single-component	5% Tween80	PCE	106.6
		Batch/multiple-component	5% SDS	PCE	186.7
		Batch/multiple-component	5% MCD	PCE	21.2
		Batch/multiple-component	5% Tween80	PCE	303.1
		Batch/multiple-component	5% SDS	TCE	28.7
		Batch/multiple-component	5% MCD	TCE	5.0
		Batch/multiple-component	5% Tween80	TCE	44.8
		Batch/multiple-component	5% SDS	1,1DCE	10.3
		Batch/multiple-component	5% MCD	1,1DCE	3.4
		Batch/multiple-component	5% Tween80	1,1DCE	14.6

3.2. Tank Experiments

3.2.1. Contaminant Elution Behavior

The contaminant elution curves obtained from the tank experiments are presented in Figures 6 (a-d) and Figures 7 (a-c) for silica sand and natural calcareous soil configurations, respectively. The observed effluent data are used to evaluate the remediation performance of the different solubilization agent (Tween 80, SDS, MCD, and water flood) and their effects on mass-flux-reduction/mass-removal behavior for pool-dominated multicomponent DNAPL source zones.

For the first physical heterogeneous configuration using silica sand, four tank experiments were conducted. In the first experiment, the DNAPL mixture was injected followed by the flushing of a 5% Tween 80 solution (Fig. 6a). Upon flushing, TCE effluent concentrations reached a maximum of 705 mg/L in 1.4 PVs and decreased to 40-45 mg/L gradually followed by a steady TCE concentration for 2 PVs (Fig. 6a). After a total of 8.8 PVs of Tween 80 flushing, TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 504 mg/L in 2.3 PVs and decreased to 20-25 mg/L gradually followed by a steady PCE concentration for 2 PVs of Tween 80 flushing (Fig. 6a). After a total of 9 PVs of Tween 80 flushing, PCE effluent concentration dropped below 1 mg/L. 1,1DCE concentrations reached a maximum of 1601 mg/L in 1.3 PVs and decreased to 30 mg/L gradually followed by a steady 1,1DCE concentration for 0.83 PV of Tween 80 flushing (Fig. 6a). After a total of 4.1 PVs of Tween 80 flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculations carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 98.1%, 97.5%, and 97.3% for TCE, PCE, and 1,1DCE, respectively.

In the second experiment, the DNAPL mixture was injected followed by the flushing of a 5% SDS solution (Fig. 6b). Upon flushing, TCE effluent concentrations reached a maximum of 684 mg/L in 1.7 PVs and decreased to 35-40 mg/L gradually followed by a steady TCE concentration for 1.9 PVs of SDS flushing (Fig. 6b). After a total of 9.6 PVs of SDS flushing, TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 133 mg/L in 2.3 PVs and decreased to 20-25 mg/L gradually followed by a steady of PCE concentration for 2 PVs of SDS flushing (Fig. 6b). After a total of 10 PVs of SDS flushing, the PCE effluent concentration dropped below 1 mg/L. 1,1DCE concentrations reached a maximum

of 1410 mg/L in 1.4 PVs and decreased to 30 mg/L gradually followed by a steady 1,1DCE concentration for 0.6 PV of SDS flushing (Fig. 6b). After a total of 4.6 PVs of SDS flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculations carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 97.4%, 99.2% and 98.4% for TCE, PCE, and 1,1DCE, respectively.

In the third experiment, the DNAPL mixture was injected followed by the flushing of a 5% MCD solution (Fig. 6c). Upon flushing, TCE effluent concentrations reached a maximum of 493 mg/L in 1.7 PVs and decreased to 30-40 mg/L gradually followed by a steady TCE concentration for 2 PVs of MCD flushing (Fig. 6c). After a total of 10.4 PVs of MCD flushing, TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 101 mg/L in 2.3 PVs and decreased to 15-20 mg/L gradually followed by a steady of PCE concentration for 4.2 PVs of MCD flushing (Fig. 6c). After a total of 10.8 PVs of MCD flushing, PCE effluent concentration dropped below 1 mg/L. 1,1DCE concentrations reached a maximum of 1150 mg/L in 1.4 PVs and decreased to 30 mg/L gradually followed by a steady of 1,1DCE concentration for 0.83 PVs of MCD flushing (Fig. 6c). After a total of 5.4 PVs of SDS flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculations carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 96.8%, 96.5% and 97.9% for TCE, PCE, and 1,1DCE, respectively.
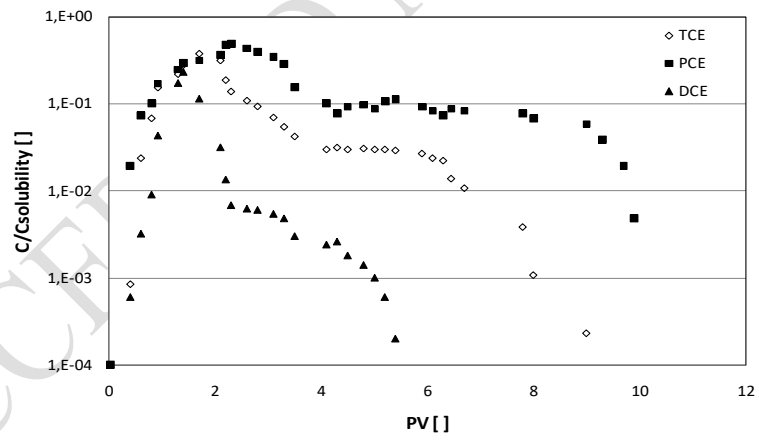
In the fourth experiment, the DNAPL mixture was injected followed by water flooding (Fig. 6d). Upon flushing, TCE effluent concentrations reached a maximum of 210 mg/L in 1.7 PVs and decreased to 30-40 mg/L gradually followed by a steady TCE concentration for the remainder of water flooding time period (Fig. 6d). PCE concentrations reached a maximum of 58 mg/L in 2.3 PVs and decreased to 15-20 mg/L gradually followed by a steady PCE concentration during water flooding (Fig. 6d). 1,1DCE concentrations reached a maximum of 1421 mg/L in 1.4 PVs and decreased to 10-15 mg/L gradually followed by a steady of PCE concentration for the remainder of water flooding experiment (Fig. 6d). Mass balance calculations carried out on the TCE/PCE and 1,1 DCE data showed that mass recoveries are below 50% for TCE, PCE, and 1,1DCE, respectively.
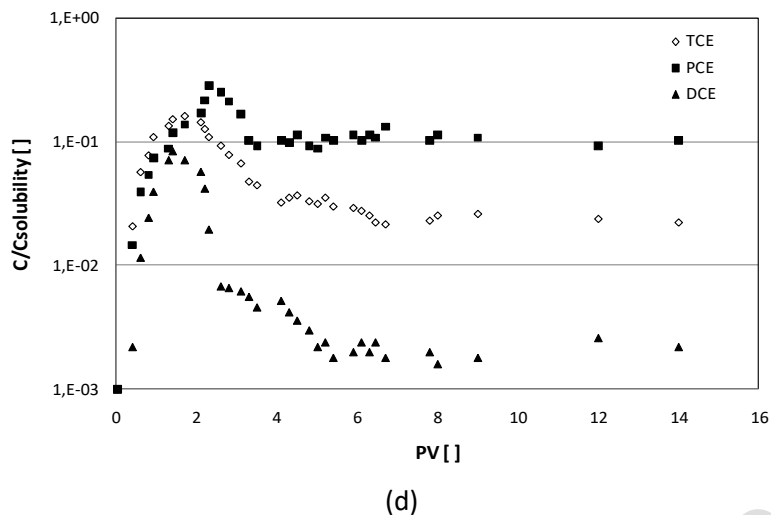
(a)

(b)

(c)

(d)
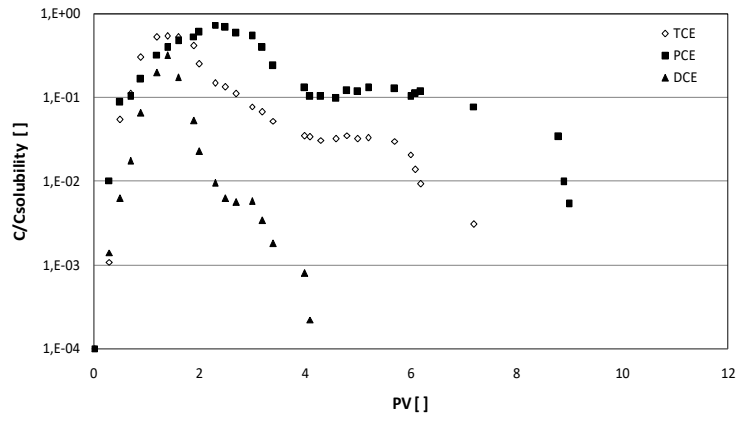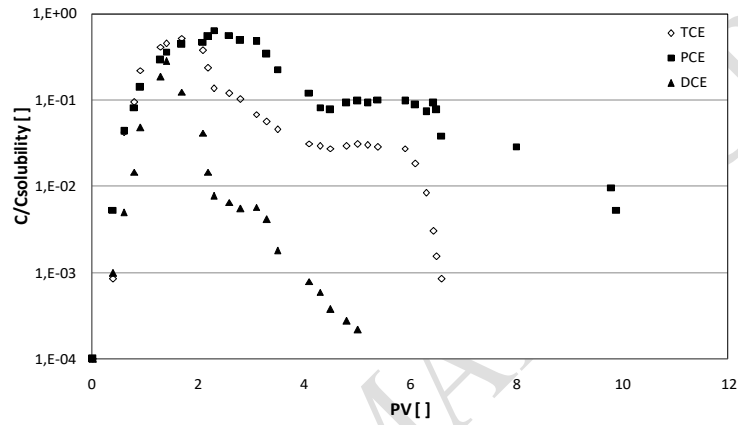
Figure 6. Effluent TCE, PCE, and 1,1DCE concentrations versus pore volume (PV) for the silica sand dissolution experiments with a) Tween 80, b) SDS, c) MCD, d) Water. (1 PV= 2.4 hours)
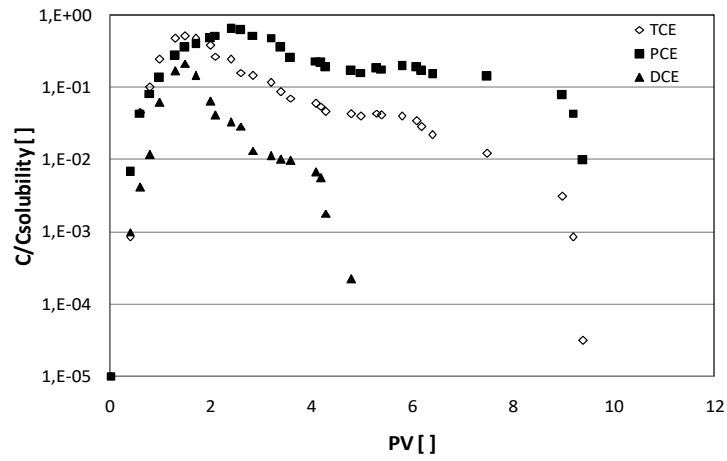
The second set of experiments was conducted within physically heterogeneous porous media configurations using calcareous soil. The same amount of DNAPL mixture source zone was added into the second configuration. In the first experiment, the DNAPL mixture was injected followed by flushing with a 5% Tween 80 solution (Fig. 7a). Upon flushing, TCE effluent concentrations reached a maximum of 672 mg/L in 1.4 PVs and decreased to 40-45 mg/L gradually followed by a steady TCE concentration for 2 PVs of Tween 80 flushing (Fig. 7a). After a total of 9.6 PVs of Tween 80 flushing, TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 132 mg/L in 2.4 PVs and decreased to 30-35 mg/L gradually followed by a steady PCE concentration for 2.8 PVs of Tween 80 flushing (Fig. 7a). After a total of 10.4 PVs of Tween 80 flushing, PCE effluent concentration dropped below 1 mg/L. 1,1 DCE concentrations reached a maximum of 1087 mg/L in 1.5 PVs and decreased to 45-55 mg/L gradually followed by a steady of 1,1DCE concentration for 0.8 PV of Tween 80 flushing (Fig. 7a). After a total of 4.7 PVs of Tween 80 flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculation carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 95.7%, 97.7%, and 96.2% for TCE, PCE, and 1,1DCE, respectively.

In the second experiment, the DNAPL mixture was injected followed by the flushing of a 5% SDS solution (Fig. 7b). Upon flushing, TCE effluent concentrations reached a maximum of 458 mg/L in 1.3 PVs and decreased to 45-60 mg/L gradually followed by a steady TCE concentration for 2 PVs of SDS flushing (Fig. 7b). After a total of 10 PVs of SDS flushing,
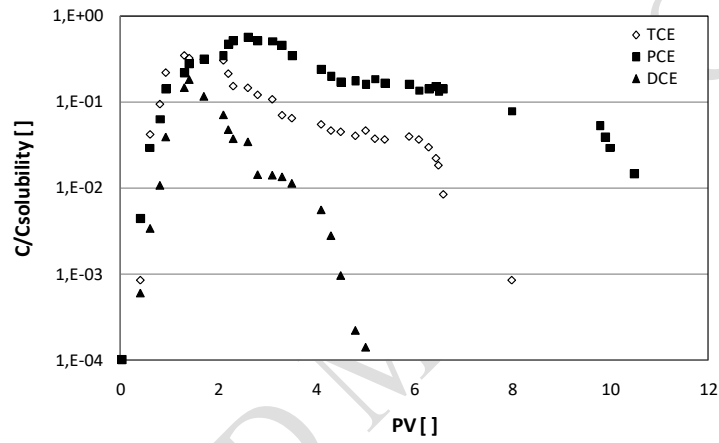
TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 117 mg/L in 2.5 PVs and decreased to 30-40 mg/L gradually followed by a steady PCE concentration for 2 PVs of SDS flushing (Fig. 7b). After a total of 10.8 PVs of SDS flushing, PCE effluent concentration dropped below 1 mg/L. 1,1DCE concentrations reached a maximum of 924 mg/L in 1.4 PVs and decreased to 55-60 mg/L gradually followed by a steady 1,1DCE concentration for 0.8 PV of SDS flushing (Fig. 7b). After a total of 4.9 PVs of SDS flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculations carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 96.4%, 98.6%, and 97.9% for TCE, PCE, and 1,1DCE, respectively.

In the third experiment, the DNAPL mixture was injected followed by the flushing of a 5% MCD solution (Fig. 7c). Upon flushing, TCE effluent concentrations reached a maximum of 365 mg/L in 1.6 PVs and decreased to 50-60 mg/L gradually followed by a steady TCE concentration for 2 PVs of MCD flushing (Fig. 7c). After a total of 10.8 PVs of MCD flushing, TCE effluent concentration dropped below 1 mg/L. PCE concentrations reached a maximum of 97.1 mg/L in 2.2 PVs and decreased to 30-35 mg/L gradually followed by a steady PCE concentration for 4 PVs of MCD flushing (Fig. 7c). After a total of 11.2 PVs of MCD flushing, PCE effluent concentration dropped below 1 mg/L. 1,1DCE concentrations reached a maximum of 842 mg/L in 1.4 PVs and decreased to 30-40 mg/L gradually followed by a steady 1,1DCE concentration for 2 PVs of MCD flushing (Fig. 7c). After a total of 6 PVs of SDS flushing, 1,1DCE effluent concentration dropped below 1 mg/L. Mass balance calculations carried out for the TCE/PCE and 1,1DCE data showed that mass recoveries are 96.8%, 97.2%, and 95.8% for TCE, PCE, and 1,1DCE, respectively.
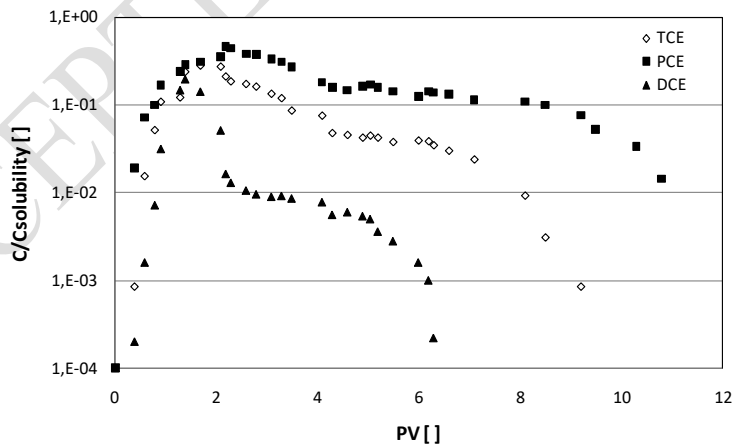
In the fourth experiment, DNAPL mixture was injected followed by water flooding (Fig. 7d). Upon flushing, TCE effluent concentrations reached a maximum of 183 mg/L in 2 PVs and decreased to 40-50 mg/L gradually followed by a steady TCE concentration for the remainder of water flooding time period (Fig. 7d). PCE concentrations reached a maximum of 48 mg/L in 2.4 PVs and decreased to 25-30 mg/L gradually followed by a steady PCE concentration of water flooding (Fig. 7d). 1,1DCE concentrations reached a maximum of 356 mg/L in 1.2 PVs and decreased to 15-20 mg/L gradually followed by a steady of 1,1DCE concentration for the remainder of water flooding experiment (Fig. 7d). Mass balance calculations carried out for the TCE/PCE, and 1,1DCE data showed that mass recoveries are below 50% for TCE, PCE, and 1,1DCE, respectively.

(a)

C/Csolubility [ ]

PV [ ]

◇ TCE
■ PCE
▲ DCE

(b)

C/Csolubility [ ]

PV [ ]

◇ TCE
■ PCE
▲ DCE

(c)

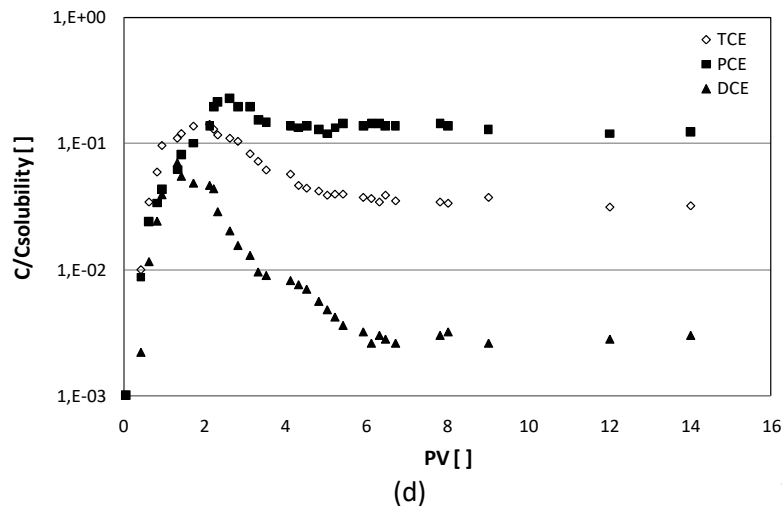C/Csolubility [ ]

PV [ ]

◇ TCE
■ PCE
▲ DCE

Figure 7. Effluent TCE, PCE, and 1,1DCE concentrations vs pore volume (PV) for the natural calcareous soil flushing experiments with a) Tween 80, b) SDS, c) MCD, d) Water. (1 PV= 2.5 hours)

Table 6. Summary results of the 2-D tank experiments

Experiment Number	Porous Medium	Agent	TCE, PCE, DCE Max Conc. (mg/L)	TCE, PCE, DCE Time to reach 1 mg/L [ ]*	TCE, PCE, DCE Time to max Conc. [ ]*	TCE/PCE/1,1DCE Recoveries (%)
1	Silica Sand	5% Tween 80	705, 151, 1601	8.8, 9.0, 4.1	1.4, 2.3, 1.3	97.1
2	Silica Sand	5% SDS	684, 133, 1410	9.6, 10.0, 4.6	1.7, 2.3, 1.4	99.5
3	Silica Sand	5% MCD	493, 101, 1150	10.4, 10.8, 5.4	1.7, 2.3, 1.4	98.7
4	Silica Sand	Water	210, 58, 421	-	1.7, 2.3, 1.4	73.8
1	Calcareous soil	5% Tween 80	672, 132, 1087	9.6, 10.4, 4.7	1.4, 2.4, 1.5	97.5
2	Calcareous soil	5% SDS	458, 117, 924	10.0, 10.8, 4.9	1.3, 2.5, 1.4	98.2
3	Calcareous soil	5% MCD	374, 98, 987	10.8, 11.2, 6.0	1.6, 2.2,1.4	98.9
4	Calcareous soil	Water	187, 48, 356	-	2.0, 2.4, 1.2	62.7

*Denotes dimensionless time as Pore Volume [-]. For the water flood, the concentration did not reach 1 mg/L at the end of the experiment

Table 6 summarizes some key parameters obtained from the different flushing experiments. These values help in comparing the impact of the different flushing solutions on the DNAPL mixture recovery ("remediation"). The evaluation of the complete combination of flow tank results showed that the performance of the agents on DNAPL mixture source zone remediation was found to be in the following order: Tween80>SDS>MCD>>Water. Although high fractions of DNAPL source zones in heterogeneous porous media were removed by chemical flushing (SDS, Tween 80, MCD, and water) for DNAPL mixtures, the heterogeneous system exhibited an extended multi-step elution concentration behavior. (Figs 6 and 7). The presence of less-

hydraulically accessible NAPL (i.e., pooled DNAPL) zones may explain the observed multi-step (decline/steady-state/decline) TCE, PCE, and 1,1DCE elution concentration behavior. The elution curves for the enhanced dissolution experiments exhibited relatively long decline/tailing periods (extending over more than 10 PV) wherein the TCE/PCE/1,1DCE concentrations increased to a maximum value and decreased gradually before reaching long-term steady-state concentration condition and finally a relatively rapid decrease in concentration to below 1 mg/L. This behavior is also consistent with observed non-ideal chlorinated solvent dissolution behavior under water and enhanced agent flooding experiments (Russo et al., 2009; Difilippo et al. 2010; Mahal et al. 2010; Akyol et al. 2013; Agaoglu et al., 2015; Akyol and Turkkan, 2018). It is hypothesized that the pore-scale configuration of the organic liquid and the flow pattern configuration is quite complex for both the silica sand and natural porous media which leads to the observed non-ideal dissolution and corresponding elution behavior. Results also imply that the performance of such flushing-based technologies depends upon the site characteristics which are essential for evaluating the efficacy of DNAPL remediation strategies of contaminated sites.

3.2.2. Mass Flux Reduction-Mass Removal

The flushing experiments were also examined in terms of the relation between the Mass-flux and mass removal (MF/MR). Such relationships are useful to assess the DNAPL removal efficiency of the different solubilization agents. A linear relationship would indicate that the mass flux decreases gradually as remaining DNAPL mass diminishes. On the other hand, a nonlinear relationship would indicate that less efficient DNAPL mass recovery or a more efficient mass recovery depending on whether the mass recovery is delayed or not (Tick and Rincon, 2009). Non-ideal behavior would mean that the recovery is likely influenced by other system properties such as non-uniform porous media properties and DNAPL mass distribution.

Figures 8 and 9 show the MFR plotted against the fraction of mass removed. Separate plots are made for each DNAPL component and each solubilizing agent. Although differences between the various MF/MR curves can be observed, all curves generally exhibit a multi-step behavior, consisting of two distinct stages. In the first stage, which corresponds to a mass removal of about 20-30%, significant reductions of contaminant mass flux occurred. The mass-flux reduction/mass-removal was linear until approximately 60-80% of the DNAPL mass was removed for the enhanced-dissolution experiments using silica sand and natural calcareous soil.

This multi-step behavior is observed from the contaminant elution curves obtained, wherein concentrations increased to a maximum level and started decreasing gradually until reaching steady-state concentration for the majority of agent flooding. The mass-flux reduction/mass-removal relationship observed for the silica sand, in the absence of an enhanced-solubilization agent, exhibited more non-ideal behavior, indicating rate-limited dissolution due to the trapping, distribution, and relatively low solubility of organic liquid in the pores and the resulting slow dissolution process (Fig 8). The mass-flux reduction/mass-removal behavior observed for the natural calcareous soil during agent flooding exhibited more non-ideal compared to silica sand configuration experiment. The second stage of mass-flux reduction/mass-removal reflects the limited removal of poorly accessible organic liquid mass from the entrapped pool at the top of the low-K zone.

Among the different flushing solutions, the least ideal behavior is observed for the water flooding whereby the mass flux rapidly decreases even though a significant portion of the DNAPL mass still remained within the porous medium.. Similar mass flux behavior is observed for both physical media, the silica sand and the calcareous soil, suggesting that the water flood is least effective for the removal of DNAPL mass that is trapped in the less accessible portions of the medium.

Comparison of the different flushing experiments suggest that the removal efficiency (MF/MR perspective) of Tween 80 is slightly greater than the other two agents (SDS and MCD). This may be due to the higher viscosity of the Tween 80 flushing solution, as discussed in Section 3.1. Under such conditions an enhanced sweep efficiency of the DNAPL may result compared to the other two less viscous agents (SDS and MCD). Moreover, the efficiency of the PCE removal (MF/MR analysis) appears to be slightly higher than the other two DNAPL components (TCE and 1,1DCE), indicating that the solubilization agents have greater impact on the efficiency removal of the less soluble components in the system.
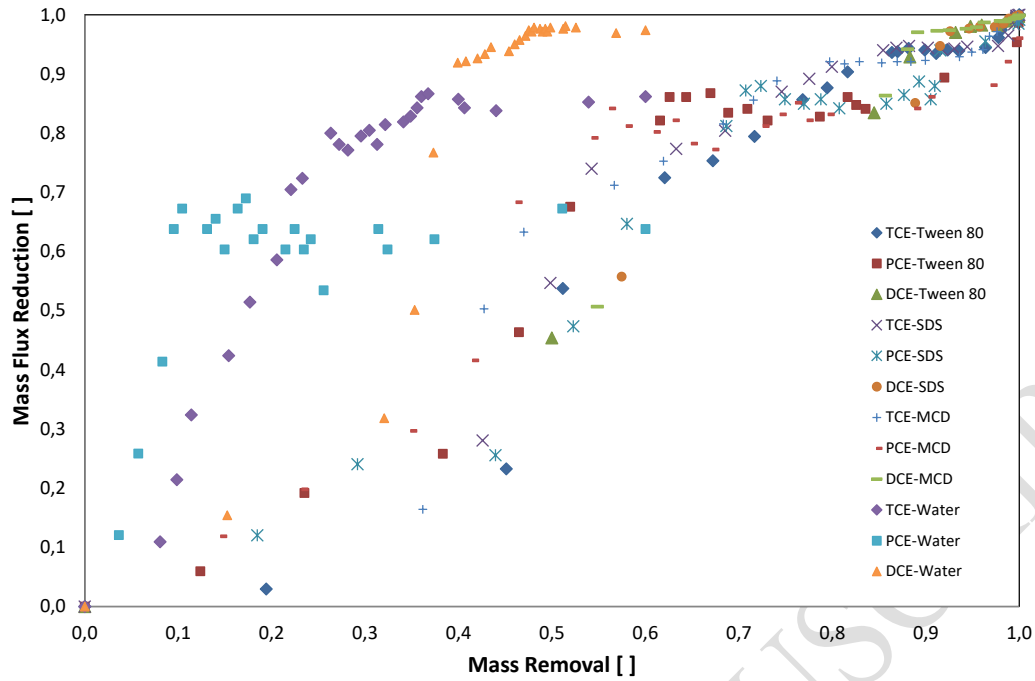
Figure 8. Mass-flux reduction versus mass removal relationships for Tween 80, SDS, MCD and water flushing tank experiments with sand (First configuration)
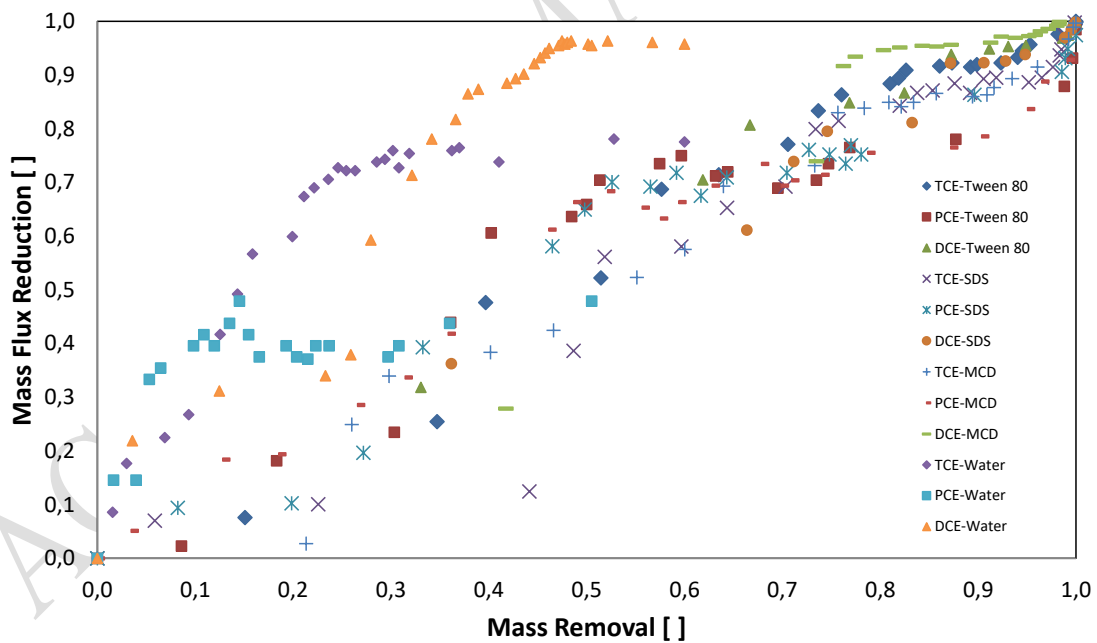

Figure 9. Mass-flux reduction versus mass removal relationships for Tween 80, SDS, MCD, and water flushing tank experiments with calcareous soil (Second configuration)

4. Conclusion

Field data often show that DNAPL encountered in the subsurface are more often found in the form of mixtures rather than single components. In this study, a series of batch and 2-D tank experiments were conducted to investigate the effect of different solubilization agents on the removal efficiency of multicomponent DNAPL mixtures (TCE, PCE, and 1,1DCE) and for the comparison of enhanced-solubilization agents on the relationship between source-zone mass removal and mass flux reduction. The flushing agents considered in this study included 5% Tween 80, 5% SDS, 5% MCD solutions, as well as water flooding (flushing agent). Based on the batch tests, selected flushing agent solutions caused the solubilities of DNAPL compounds to increase by a factor of 10 to 300 for the surfactant agents and 3 to 20 for MCD. However, experiments confirmed that the IFT was not significantly lowered to cause DNAPL mobility, indicating that enhanced solubilization would be the dominant recovery mechanism for these systems. This was also confirmed by the flushing experiments which did not show any DNAPL mobility. The ternary phase diagrams also showed that, at the selected solubilization contents, a multiple phase system will be present. Moreover, the titration method used in the construction of the TPD curves revealed that the Tween 80 solution, in particular, had a much higher viscosity than the other 2 flushing agent solutions.

The flushing agent experiments were performed in a 2D tank with the DNAPL mixture emplaced predominantly as a pooled form, over a low permeability barrier. According to the flushing experiments, the performance of agents on pool-dominated DNAPL source zone remediation (source removal) was found to be in the following order: Tween 80> SDS>MCD>>Water. Results showed that the flow-field heterogeneity, type of agent, and the type of porous media significantly influenced the mass flux reduction/mass-removal behavior for the heterogeneous systems using silica sand and natural calcareous soil wherein a multi-step mass-flux reduction/mass-removal process occurred. This non-ideal MF/MR behavior was observed most significantly for the water-flood but also, to a lesser degree, for the enhanced-solubilization agent flushing experiments.

The effect of enhanced-solubilization agents, compared to water flushing, exhibited a lower degree of multi-step mass-flux reduction/mass-removal behavior which demonstrates a more ideal removal process for the systems investigated. For both the water flood as well as the enhanced dissolution experiments, the results demonstrate that during the early stages of flushing and DNAPL removal, some predominant portion of the organic liquid is hydraulically accessible, whereas during later stages of flushing mass removal is controlled by the more

poorly accessible NAPL mass associated with higher-saturation zones. Moreover, the impact of the solubilization agents initiated a relatively greater solubility enhancement for PCE, the least soluble component of the 3-component DNAPL source system.

Overall, the results of this study show that the presence of multicomponent DNAPL mixtures complicates the performance of the remedial activity particularly when enhanced solubilization agents are used. There is a clear remediation (mass removal) benefit to using solubilization agents; however, the enhanced removal performance also depends on the flushing agent as well as the individual components of the DNAPL mixture. Understanding the dissolution and mass-flux behavior associated with organic liquid mixtures should be taken into account, particularly in the design and evaluation of enhanced solubilization activities in the field.

Data Availability

Data will be provided by corresponding author upon request.

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