



The impact of composition on the physical properties and evaporative mass transfer of a PCE–diesel immiscible liquid

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ABSTRACT

The impact of immiscible-liquid composition on mass transfer between immiscible liquid and vapor phases was evaluated for a complex mixture of chlorinated solvents and petroleum hydrocarbons. A mixture of tetrachloroethene and diesel was discovered at a site in Tucson, Arizona. Partitioning of tetrachloroethene into a layer of diesel has been observed, with resultant concentrations of tetrachloroethene up to approximately 15% by weight. The density, viscosity, surface tension, and interfacial tension were measured for tetrachloroethene–diesel mixtures with tetrachloroethene fractions ranging from 7% to 32%, and the results indicated that immiscible-liquid composition did impact the physical properties of the tetrachloroethene–diesel mixture. The results of batch phase-partitioning experiments were compared to predictions based on Raoult's Law, and the analysis indicated that immiscible-liquid/vapor and immiscible-liquid/water partitioning were both essentially ideal. Flow-cell experiments were conducted to characterize steady-state tetrachloroethene removal from the tetrachloroethene–diesel mixture via vapor extraction. The effluent concentrations for the experiment conducted with free-phase immiscible liquid were comparable to equilibrium values. Conversely, the effluent concentrations were significantly lower for the experiment wherein a residual saturation of immiscible liquid was distributed within sand. The lower concentrations for the latter experiment were attributed to dilution effects associated with a nonuniform distribution of immiscible liquid within the flow cell.

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1. Introduction

Complex multicomponent immiscible liquids are present at many hazardous waste sites, and significantly complicate contamination characterization and remediation. Previous research evaluating the compositional impacts on multicomponent immiscible liquid evaporation or volatilization has been limited to date [1,2], and has focused on synthetic mixtures of a few similar compounds [3–7]. Additionally, research examining contamination-induced compositional changes that may occur for complex immiscible liquids associated with co-mingled waste (e.g., chlorinated solvents and petroleum distillates), has been limited to date [cf. 2,8]. Compositional changes within an immiscible liquid could affect the density of the mixture, as well as alter other physiochemical properties such as interfacial tension and viscosity, and thus influence displacement processes [e.g. 9,10].

Removal of immiscible-liquid contaminant mass via pump and treat, soil vapor extraction, and related methods is controlled by mass-transfer processes. Mass transfer from immiscible liquid can be nonideal due to mass-transfer rate limitations [7,11–13], accessibility issues associated with heterogeneous source-zone architecture [14,15], and, for multiple-component liquids, compositional issues including mole fraction-associated constraints and nonideal mixture behavior [1,8,16–22]. There have been relatively few investigations of mass transfer between multicomponent immiscible liquid and gas phases in porous media under dynamic conditions [1–7]. Harper et al. [5] compared single-, two-, and four-component immiscible-liquid mixtures, and observed significant variability in mass-transfer rate limitation with immiscible-liquid composition. Abriola et al. [7] observed nonideal and rate-limited volatilization of binary mixtures of toluene and tetrachloroethene during the course of mass removal, and Broholm et al. [1] evaluated the behavior of a complex synthetic fuel during source evolution in the vadose zone. Recently, McColl et al. [2] reported ideal immiscible-liquid/gas partitioning behavior was observed for experiments conducted with a complex multicomponent immiscible liquid obtained from a field site.

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The purpose of this investigation was to evaluate the compositional effects of a complex co-contaminated mixture on physical properties of the immiscible liquid and on mass-transfer behavior under steady-state evaporation. The immiscible liquid evaluated herein was a tetrachloroethene–diesel mixture present at a hazardous waste site in Tucson, Arizona. The impact of tetrachloroethene content on physical properties of the immiscible liquid was investigated. The evaporation behavior of tetrachloroethene was examined with a series of batch and flow-cell experiments.

2. Materials and methods

2.1. Site description

The Park-Euclid Site is a Water Quality Assurance Revolving Fund (or Arizona State Superfund) Site located in Tucson, Arizona [23]. A dual-phase extraction and treatment system is currently being installed to remediate the vadose zone and shallow groundwater, which is contaminated with volatile organic compounds including tetrachloroethene (PCE), trichloroethene (TCE), *cis*-1,2 dichloroethene (DCE), and vinyl chloride. A separate immiscible-liquid phase comprised of diesel fuel is present near the top of the perched water-bearing unit at the site. The partitioning of PCE and other chlorinated compounds into the diesel has formed a complex chlorinated-solvent/hydrocarbon mixture. The presence of elevated PCE concentrations in the immiscible liquid is a concern for remediation efforts.

2.2. Immiscible-liquid mixtures

A sample of the PCE–diesel immiscible liquid present at the Park Euclid site was collected with a Teflon well bailer, and stored at 4°C in amber glass vials (VWR, Brisbane, CA) with Teflon-lined caps. A subsample of the original immiscible-liquid mixture was sent to Transwest Geochem Laboratories (Scottsdale, AZ) for chemical analysis and characterization using gas chromatography–mass spectroscopy (GC–MS) and flame ionization detection (GC–FID). The concentration of PCE in the original immiscible-liquid mixture was determined to be 72,000 mg kg⁻¹, and this was used as the initial (lowest) PCE concentration for the experiments. Four additional subsamples with larger PCE concentrations were then created by adding known amounts of PCE (99% ACS Grade, Acros Chemical Company, New Jersey) to subsamples of the original immiscible-liquid mixture, resulting in PCE compositions ranging from 7.2% to 32% by weight (72,000; 118,206; 169,360; 232,814; and 320,942 mg kg⁻¹ PCE in immiscible liquid). For comparative purposes, a simple two-component immiscible-liquid mixture was created by mixing PCE (15% by weight) and hexadecane (99% ACS Grade, Acros Chemical Company, New Jersey).

2.3. Physical property measurements

Physical property measurements including density, viscosity, and interfacial and surface tensions were conducted for the immiscible-liquid mixture to characterize the effect of PCE. Measurements were also made for the two-component liquid, pure PCE (99% PCE), and pure hexadecane (0% PCE). All fluids were kept in a constant temperature bath, and experiments were performed at 25(±2)°C. Immiscible-liquid volumes were prepared in 5 ml volumetric vials (Kimble-Kontes, Vineland, New Jersey) and masses of the fluids were determined gravimetrically using an analytical balance (Mettler Toledo PG-S, Greifensee, Switzerland). These

measurements were conducted in triplicate, and the density of distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water was also measured to confirm method accuracy. Viscosity measurements were conducted using a Gilmont Instruments Size #1 (0.2 and 10 cP range) Falling Ball Type Viscometer obtained from VWR (Brisbane, CA). The time of descent required for the ball to fall a specified distance imprinted on the viscometer tube was measured with a stop-watch up to five times to examine the experimental variability. The viscosity of NANOpure water and hexadecane were used to calibrate the instrument, and measurements were then made for the various immiscible-liquid mixtures.

The surface and interfacial tension for each of immiscible-liquid mixtures were measured using a Fisher Surface Tensiometer Model 21 (Fisher Scientific International, Inc., Atlanta, GA), following the principles of operation specified by the American Society for Testing Materials in Methods D-971 (interfacial tension of oil against water) and D-1331 (surface and interfacial tensions of detergents). The instrument uses the du Nouy ring-method, which employs a platinum–iridium ring of precisely known dimensions suspended from a counter-balanced lever arm. Clear glass 50 ml beakers (Kimble-Kontes, Vineland, New Jersey) were cleaned with dichloromethane, then acetone, an acid bath, and NANOpure water before oven drying prior to each use. The platinum–iridium ring was cleaned first with dichloromethane and then with acetone, which was allowed to evaporate prior to each measurement. The tensiometer was calibrated before every surface and interfacial tension measurement to the surface tension of NANOpure water to confirm the accuracy of the dial reading. The interfacial tension was measured with immiscible-liquid equilibrated NANOpure water with negligible ionic strength for consistency. Interfacial tensions measured using groundwater with measurable salt concentrations would likely vary somewhat relative to the results reported herein. Interfacial tension measurements were made from the more dense liquid to the less dense liquid by exerting an upward force on the ring, and breaking the interface as the ring is displaced from the lower (denser) liquid to the upper (lighter) liquid.

2.4. Batch experiments

Batch experiments were conducted in triplicate to characterize PCE evaporation and dissolution for each of the PCE–diesel mixtures. The two-phase (immiscible-liquid/water or immiscible-liquid/gas) and three-phase (immiscible-liquid/gas/water) partitioning experiments were conducted at 25(±2)°C with glass vials (VWR Trace-Clean 25 ml vials with open top caps and Teflon-lined septa, Brisbane, CA). NANOpure water was added to the vials, and the mass of the water added was measured with the analytical balance. Immiscible liquid was then injected into the vials with a Gastight Hamilton Company syringe (Reno, Nevada), and the mass of immiscible liquid added was determined with the analytical balance. The vials were placed on an Orbit Model shaker table (Lab-Line Instruments, Inc., Melrose Park, Illinois) set to 200 rpm for 120 h to ensure complete equilibration, which was confirmed from initial testing. The vials were centrifuged (Beckman GP Centrifuge, Palo Alto, CA) at 2000 rpm for 30 min to effect phase separation. Then aqueous and/or gas phase samples were collected from the vials with a Gastight Hamilton Company syringe inserted through the Teflon septa of the vials, which were oriented (e.g., inverted) such that the syringe needle did not contact the immiscible liquid during sampling. The subsamples were analyzed for PCE, and statistical confidence intervals (95% CI) were calculated from the triplicates.

Table 1
Flow cell experimental properties and results

Properties and results	Without porous media	With porous media
Flow-cell dimensions		
Height (cm)	5.3	5.3
Width (cm)	19.9	19.9
Length (cm)	39.7	39.7
Volume (L)	4.2	4.2
Vapor extraction experimental conditions		
Average flow rates (cm ³ min ⁻¹)	40	30
Cross-sectional area (cm ²)	31.2	105.5
Average Darcy velocity (cm h ⁻¹)	77.0	17.1
Average interstitial velocity (cm h ⁻¹)	77.0	53.1
NAPL (L)	0.650	0.075
Water (L)	2.30	0.20
Air (L)	1.24	1.08
Pore volume (L)	1.24	1.08
NAPL saturation (-)	0.16	0.06
Water saturation (-)	0.55	0.15
Air saturation (-)	0.30	0.80
Mass removed through vapor extraction		
PCE mass removed (g)	13.35	0.74
PCE removed (% of initial mass)	31	15
Mass transfer rate-limitation evaluation		
PCE gas phase diffusion coefficient (cm ² h ⁻¹)	316.8	316.8
Lumped mass-transfer rate coefficient (h ⁻¹)	-	0.05
Peclet number (-)	0.38	0.01
Average concentration at steady state (mg L ⁻¹)	7.9 ± 0.8	1.0 ± 0.4
Average equilibrium concentration (mg L ⁻¹)	9.7 ± 1.7	9.7 ± 1.7

2.5. Flow-cell experiments

Two nearly identical two-dimensional (2D) flow cells were used for dynamic vapor-extraction experiments. The inner dimensions of the flow cells were approximately 5.3 cm × 19.9 cm × 39.7 cm (Table 1). The basic construction consisted of a 1/16 in. (0.16 cm) stainless-steel sheet that was cut and welded into a rectangle to the dimensions described above with an approximately 1 in. (2.54 cm) flange lined with a PTFE flange gasket (TEADIT Intl., supplied by McMaster-Carr, Los Angeles, CA) to seal the frame to a 3/8 in. (0.95 cm) tempered glass plate. A 0.2-μm diffusion plate (Mott Metallurgical Corp., Farmington, CT) was welded onto the inside of each of the ends. Four inlet/outlet ports were placed at each end to allow vapor injection and extraction. Sampling ports were installed along a vertical transect in the back side of the flow cell for collection of vapor, immiscible-liquid, and water samples, and consisted of 1/8 in. (0.32 cm) VICI Septum Injector Nuts containing 1/4 in. (0.64 cm) Teflon-lined septa (Valco Instruments Co. Inc., Houston, TX). A Swagelok sampling port (for collection of vapor effluent), a cold trap, a flow meter, a moisture trap, and a carbon filter were connected to the effluent tubing. Subsamples of the original immiscible liquid collected from the site were used in both flow-cell experiments.

One of the experiments was conducted to examine mass transfer for a system containing free-phase immiscible liquid. To simplify the system, this experiment was conducted without porous media packed in the flow cell. Thus, the flow cell contained a layer of water, a layer of immiscible liquid, and a layer of air. After a leak test, 2300 ml of immiscible-liquid equilibrated water were injected into the back port, 650 ml of the PCE-diesel mixture were injected

above the water, and the remainder of the flow-cell volume contained the gas phase (immiscible-liquid equilibrated air). Vapor extraction applied to this flow cell allowed gas to flow through the headspace above the immiscible liquid, and mass transfer occurred between the immobile water and the immobile immiscible liquid and between the immiscible liquid and the mobile gas phase. The system was designed so that samples of each fluid phase could be collected using the ports located at the back of the flow cell.

The other flow-cell experiment was designed to examine mass transfer for a system containing a residual saturation of immiscible liquid. The flow cell was packed with uniform fine-grained sand (0.68 mm median grain size, 20–30 mesh Accusand, Unimin, MN), and also contained water, immiscible liquid, and a mobile gas phase. The sand was wet packed to a bulk density of 1.84 g cm⁻³ and porosity of 0.32, and the flow cell was positioned with the long end in the vertical direction to develop the fluid distribution. The flow cell was saturated with nitrogen-sparged NANOpure water from the bottom (injection port) with a Gilson 305 HPLC piston pump (Gilson Medical Electronics, Middleton, WI) at a flow rate of 0.25 ml min⁻¹ until a constant mass was achieved, which was assumed to indicate complete saturation. The immiscible liquid was introduced into the porous medium-packed flow cell from the top using a gas-tight syringe (SGE Intl. Pty. Ltd., Ringwood, Australia) attached to a syringe pump (Sage Instruments 355 syringe pump, Orion Research Inc., Boston, MA). The ports at the bottom of the flow cell were left open to allow the water in the flow cell to drain freely. Water saturated with the immiscible-liquid components was then pumped into the flow cell at 0.5 ml min⁻¹ for approximately 3 days from the top to distribute the immiscible liquid within the flow cell (none of the immiscible liquid was extracted from the flow cell). The flow cell was then desaturated to trap residual water and immiscible liquid with the injection of immiscible-liquid equilibrated gas. The desaturation mobilized 69.5 ml of the immiscible liquid, which was removed from the lower ports during the process.

A single high performance vacuum pump (RobinAir CoolTech model 15600, 170 L min⁻¹ capacity, RobinAir, SPX Corp., Montpelier, OH) with an in-line flow meter (Gilmont model F1100, Gilmont Instruments, Barrington, IL) was used to simultaneously extract vapor through both flow cells. The pump created a relatively constant flow rate that produced similar discharge from each flow cell (Table 1). Effluent vapor samples (1 ml) were collected periodically for analysis of PCE. In addition, gas, aqueous phase, and PCE-diesel samples were collected for compositional analysis before the start and at the end of the experiment conducted with free-phase immiscible liquid. The gas phase sampling for the compositional analysis involved collection of 50 ml of gas from the port located above the immiscible liquid. The sample was injected into a Tedlar sample bag, which was then sealed, placed on ice, and shipped overnight to Transwest's laboratory for analysis. The PCE-diesel phase was collected from a port on the back of the flow cell using a gas-tight syringe inserted through a Teflon-lined septum nut. The immiscible liquid was injected into a 2 ml amber-glass volatile organic analysis vial (National Scientific Co., Quakertown, PA).

2.6. Chemical analysis

Subsamples of the immiscible liquid collected from the field were analyzed using GC-MS and GC-FID to characterize the immiscible-liquid composition. The analyses, conducted by Transwest Geochem Laboratories (Scottsdale, AZ), consisted of GC-MS following EPA Methods 8260 and 8270 upon extraction with hexadecane, which quantifies volatile and semi-volatile compounds. In addition, GC-FID following method EPA Method 8015 was used to provide combined-total organic compound concentrations for groups of molecules with similar structures and molecular weights

by integration of sections of the chromatogram. These groups represent the molecules of common carbon chain length from 9 to 25, or C₆–C₃₂ range, and chromatogram section integrations were also performed for gasoline, diesel, and oil that is typically reported as C₆–C₁₀, C₁₀–C₂₂, and C₂₂–C₃₂, respectively.

Samples from the batch and flow-cell experiments were analyzed using a GC-17A with FID (Shimadzu, Japan) to determine the concentration of PCE in gas and water samples. Analytical standard solutions were prepared from reagent-grade PCE (99.9% Aldrich), check standard and blank samples were analyzed every five to six samples for quality assurance and control, and the quantifiable detection limit (lowest standard solution concentration standard deviation multiplied by 10) was approximately 0.03 mg L⁻¹. Aqueous-phase samples were prepared by adding 5 ml of the sample to a 21 ml headspace vial (Kimble) sealed with open caps and Teflon-faced septa. The 1 ml gas samples were injected into capped headspace vials that contained 5 ml of NANOpure water. Headspace vials were placed in a Tekmar 7000 Autosampler (Mason, Ohio) connected to the GC. The gas subsamples were injected onto a Supelco capillary column (SPBTM-624, 30-m, 0.53-mm (i.d.), 3 μm film, Sigma–Aldrich) with an initial column temperature of 40 °C, held for 2 min, then heated at 10 °C per minute (to 170 °C).

3. Data analysis

3.1. Partitioning and Raoult's Law

Raoult's Law has been used to predict equilibrium concentrations of compounds in gas or aqueous phases in contact with immiscible-liquid mixtures. For both vapor and aqueous phase systems, the ideality of the partitioning was evaluated by comparing measured concentrations to those predicted with Raoult's Law:

$$S_{Ai} = S_{Ai}^o X_{Ni} \quad (1)$$

where the subscripts A refer to air (vapor phase) or aqueous phase and N refer to immiscible liquid; superscript o signifies the pure phase (single component); S_{Ai} is the equilibrium concentration of the component in gas or water; S_{Ai}^o is the pure compound solubility or equilibrium-vapor concentration; X_{Ni} is the mole fraction of the compound in the immiscible liquid. The mole fractions for specific components of the mixtures were calculated with:

$$X_{Ni} = \frac{C_{Ni}/MW_i}{\sum(C_{Ni}/MW_i)} \quad (2)$$

where C_{Ni} is the mass of an immiscible-liquid component per mass of sample, MW_i is the molecular weight of each component. C_{Ni} values were obtained by chemical analysis of the immiscible-liquid mixture, as described above.

3.2. Mass-transfer kinetics

Evaporation of compounds from immiscible liquid to the gas phase is typically conceptualized as diffusion from the interphase boundary using a linearized form of Fick's law for mass-transfer kinetics:

$$J_i = k_{fi} a_{oi} (S_{Ai} - C_{Ai}) = k_{oi} (S_{Ai} - C_{Ai}) \quad (3)$$

where J_i is the mass-transfer rate per unit volume of immiscible-liquid component between the phases; a_{oi} is the specific interfacial area; k_{fi} is the mass-transfer constant; k_{oi} is the lumped mass-transfer coefficient; S_{Ai} is the concentration of the immiscible-liquid component in the vapor phase at equilibrium with the immiscible liquid; and C_{Ai} is the bulk vapor-phase

concentration of the immiscible-liquid component. The lumped mass-transfer coefficient is generally used due to the difficulties of measuring immiscible-liquid/vapor interfacial areas, and the lumped mass-transfer coefficient may be calculated at quasi-steady-state assuming negligible dispersive flux:

$$k_o = - \left(\frac{q}{L} \right) \ln \left(1 - \frac{C_A}{S_A} \right) \quad (4)$$

where q is the mobile phase Darcy velocity and L is the source length. The above equation was used to calculate the lumped PCE-evaporation rate coefficient based on effluent concentrations from the vapor-extraction experiments.

3.3. Mobilization potential

Immiscible-liquid mobilization potential has generally been evaluated in terms of the capillary and bond numbers. Bond numbers indicate the potential for vertical mobilization due to gravity, and capillary numbers indicate the potential for mobilization of an immobile phase with a mobile phase. The capillary number is the ratio of the viscous force to the capillary force [e.g., 24–27]. The capillary number (N_{Ca}) is:

$$N_{Ca} = \frac{k \rho g \Delta H}{\gamma} = \frac{v \mu}{\gamma} \quad (9)$$

where k is the porous medium intrinsic permeability, g is gravitational acceleration, ΔH is the hydraulic head gradient, v is the groundwater velocity, μ is the aqueous viscosity, and γ is the interfacial tension. Larson et al. [28] measured N_{Ca} values for various flow rates and found that immiscible-liquid displacement began at N_{Ca} of 2×10^{-5} .

The bond number represents the ratio of gravitational forces to capillary forces that affect fluid trapping and mobilization [e.g., 29]. The bond number (N_{Bo}) is:

$$N_{Bo} = \frac{\Delta \rho g k}{\gamma} \quad (10)$$

where $\Delta \rho$ is the density difference between the immiscible fluids, g is gravitational acceleration, and k is the intrinsic permeability. Assumptions, including a homogeneous, isotropic hydraulic conductivity of 30.4 ft day⁻¹ based on aquifer test analysis [30], and a uniform hydraulic gradient of 0.008 measured from water level data were used to estimate groundwater velocity and aquifer permeability [23].

4. Results and discussion

4.1. PCE–diesel mixture composition

The results of the chemical analysis of the immiscible-liquid mixture collected from the field are presented in Table 2, along with the calculated mole fractions of the mixture components. The components identified in the immiscible liquid chemical analysis accounted for approximately 89% of the total immiscible-liquid composition. The remaining 11%, representing a combination of analytical error and unidentifiable matrix, was approximated by the average molecular weight of diesel (227 g mol⁻¹) as reported in the literature [19,31,32]. The original PCE–diesel mixture had a PCE composition of approximately 72,000 mg/kg (7% by weight) within the diesel matrix, which confirms that the immiscible liquid was a complex co-contaminated or co-mingled waste. Additionally, the immiscible liquid contained a range of diesel-fraction compounds with a mean carbon chain length of C₁₇ with decreasing concentrations for higher and lower carbon chain lengths, which is typical for diesel fuel devoid of chlorinated solvents. Negligible

Table 2
PCE–diesel mixture composition: initial sample and the post-vapor-extraction sample collected from the experiment without porous media

Chemical ^b	Molecular weight (g mol ⁻¹)	Initial ^a concentration (mg kg ⁻¹)	Initial molality (mol kg ⁻¹)	Initial mole fraction (-)	Final ^a concentration (mg kg ⁻¹)	Final molality (mol kg ⁻¹)	Final mole fraction (-)
PCE	165.83	72,000	0.434	0.099	62,000	0.374	0.083
TCE	131.39	1,300	0.010	0.002	760	0.006	0.001
C ₉	128.25	830	0.006	0.001	890	0.007	0.002
C ₁₀	142.28	2,600	0.018	0.004	3,700	0.026	0.006
C ₁₁	156.31	6,100	0.039	0.009	9,700	0.062	0.014
C ₁₂	170.33	17,000	0.100	0.023	22,000	0.129	0.029
C ₁₃	184.36	49,000	0.266	0.061	65,000	0.353	0.078
C ₁₄	198.38	52,000	0.262	0.060	120,000	0.605	0.134
C ₁₅	212.42	110,000	0.518	0.118	100,000	0.471	0.104
C ₁₆	226.44	100,000	0.442	0.101	130,000	0.574	0.127
C ₁₇	240.47	120,000	0.499	0.114	110,000	0.457	0.101
C ₁₈	254.49	120,000	0.472	0.107	97,000	0.381	0.084
C ₁₉	268.53	88,000	0.328	0.075	67,000	0.250	0.055
C ₂₀	282.55	58,000	0.205	0.047	46,000	0.163	0.036
C ₂₁	296.58	39,000	0.131	0.030	34,000	0.115	0.025
C ₂₂	308.59	25,000	0.081	0.018	16,000	0.052	0.011
C ₂₃	322.62	15,000	0.046	0.011	7,900	0.024	0.005
C ₂₄	338.66	6,900	0.020	0.005	4,000	0.012	0.003
C ₂₅	352.69	2,700	0.008	0.002	1,500	0.004	0.001
Estimated ^c	227.00	114,570	0.505	0.115	102,550	0.452	0.100
Total		1,000,000	4.390	1.000	1,000,000	4.516	1.000

^a Initial concentration refers to the field sample, and final refers to the liquid collected from the flow cell without porous media after 322 pore volumes of vapor extraction.

^b C₉ through C₂₅ refer to molecules with carbon chain lengths of 9 through 25.

^c Estimated or mass not determined from analysis was assumed to be composed of the average molecular weight of 227 g mol⁻¹.

concentrations were measured for the gasoline and oil fractions below C₁₀ and above C₂₂. The composition and mole fractions determined after subjecting the immiscible liquid to vapor extraction are also presented in Table 2. The unidentified fraction of the mixture was approximately 10% by weight after the vapor-extraction experiment, similar to the initial percentage.

4.2. Immiscible liquid physical properties

The measured densities and viscosities for the PCE–diesel mixtures are presented in Fig. 1a. As expected, the immiscible-liquid mixture density increased with increasing PCE concentration. The measured densities of PCE (1.6 g cm⁻³) and hexadecane (0.773 g cm⁻³) were comparable to published values [33]. The immiscible liquid transitioned from being less dense than water to denser than water when PCE concentrations exceeded approximately 26% by weight (Fig. 1a). The immiscible-liquid mixture viscosity decreased with increasing PCE concentrations, which was also expected. The change in both density and viscosity were linear functions of PCE concentration. Both of the trends for density and viscosity suggest that immiscible-liquid mobility potential increased with PCE concentration.

The surface and interfacial tension measurement results are shown in Fig. 1b. The immiscible-liquid surface tension remained relatively constant over the measured PCE composition range for both the PCE–diesel mixtures and the two-component immiscible-liquid mixture. The measured surface tension of hexadecane (27 dyn cm⁻¹) was comparable to published values [33]. The PCE–diesel mixture interfacial tensions are within the previously reported range for weathered diesel fuels [34]. The interfacial tension values followed a linear trend of decreasing tension with increasing PCE concentration for the PCE–diesel mixture. The observed decrease in interfacial tension with increased PCE concentration is another factor that may potentially influence immiscible-liquid configuration (and thus impact mass transfer) and mobility.

The calculated capillary and bond numbers for the PCE–diesel immiscible-liquid mixtures are shown in Fig. 1c. The bond num-

ber increased with increasing PCE concentration due to an increase in the gravitational force and a decrease in the capillary force. The sample with the highest PCE concentration became a dense immiscible liquid, and the bond number became positive. Capillary numbers also increased with increasing PCE concentrations, due to the decreased capillary force. However, all of the calculated capillary numbers were orders of magnitude below the range of values that have been previously reported for immiscible-liquid mobilization [28]. These results indicate that immiscible-liquid compositional changes did not impact the physical properties sufficiently to mobilize immiscible liquid with groundwater flow.

4.3. Phase partitioning

The results of the batch immiscible-liquid/water and immiscible-liquid/gas partitioning experiments are presented in Fig. 2a. The expected linear partitioning is observed for both aqueous and gas phases, and the behavior is similar for both two- and three-phase systems. The PCE concentrations predicted with Raoult's Law are compared to the measured concentrations in Fig. 2b. Deviations from the one-to-one line (representing ideal behavior) are within the bounds of uncertainty associated with experimental and prediction error as represented by the plotted error bars. Similar behavior has been observed for PCE, TCE, and DCE in groundwater samples collected from the site [21]. These results suggest that this PCE–diesel mixture is ideal and can be evaluated using Raoult's Law, which was also the conclusion of a recent investigation of another co-contaminated mixed waste [8].

4.4. Vapor-extraction results

The results of the dynamic vapor-extraction experiments are presented in Fig. 3. The effluent PCE vapor concentrations remained relatively constant at an average of 7.9 mg L⁻¹ throughout the approximately 300 pore volumes of vapor extraction for the flow cell containing no porous medium (Fig. 3a). Vapor concentrations measured for samples collected within the flow cell were similar to the effluent samples. The initial effluent vapor concentration

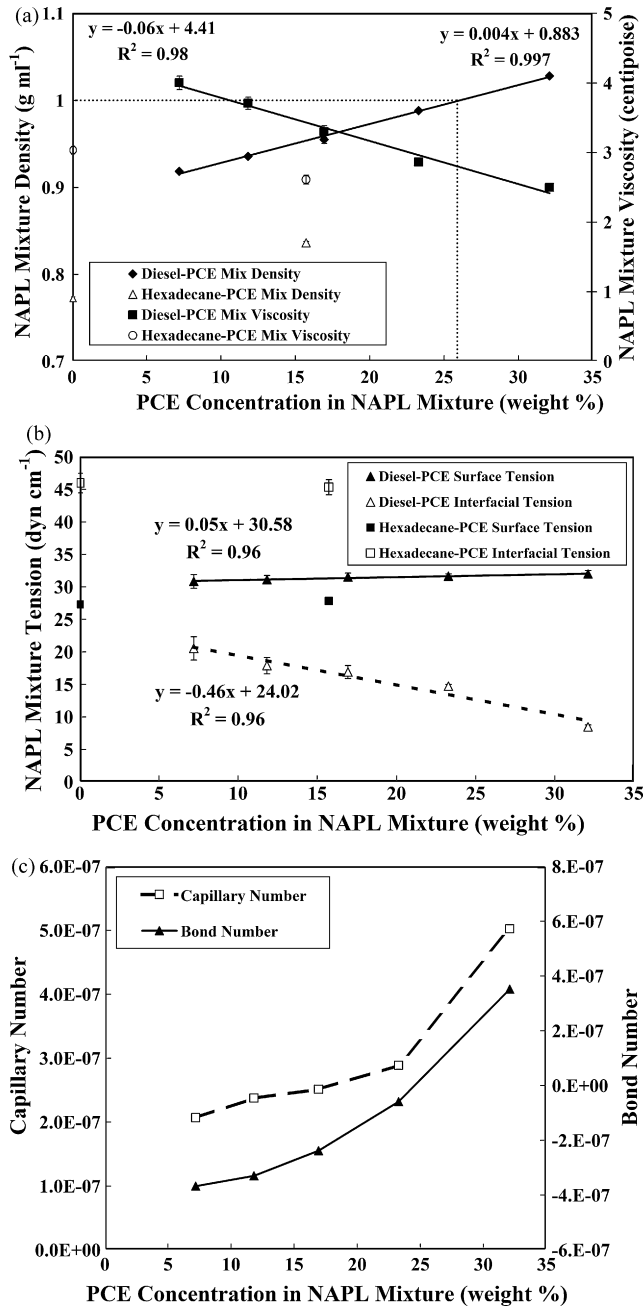


Fig. 1. (a) Density and viscosity of the PCE–diesel and synthetic immiscible-liquid mixtures; error bars calculated from the 95% confidence interval (CI). (b) Surface and interfacial tension of the PCE–diesel and synthetic immiscible-liquid mixtures; error bars calculated from the 95% CI. (c) Capillary and bond numbers of the PCE–diesel immiscible-liquid mixture.

of PCE for the flow cell with porous media was similar to that of the other flow cell. However, the effluent concentrations decreased (Fig. 3b) after the first pore volume to a relatively constant mean concentration (1.0 mg L^{-1}) that was significantly lower than that observed for the flow cell without porous media. The flow rates used for both flow cells were similar (average of $40\text{--}30 \text{ ml min}^{-1}$), and the interstitial velocities were 77 and 53 cm h^{-1} for the flow cells without and with porous media, respectively (Table 1).

The mass of PCE removed during vapor extraction was estimated using the average flow rate and the effluent concentrations. After approximately 33 days, 15% (0.74 g) of the initial PCE mass

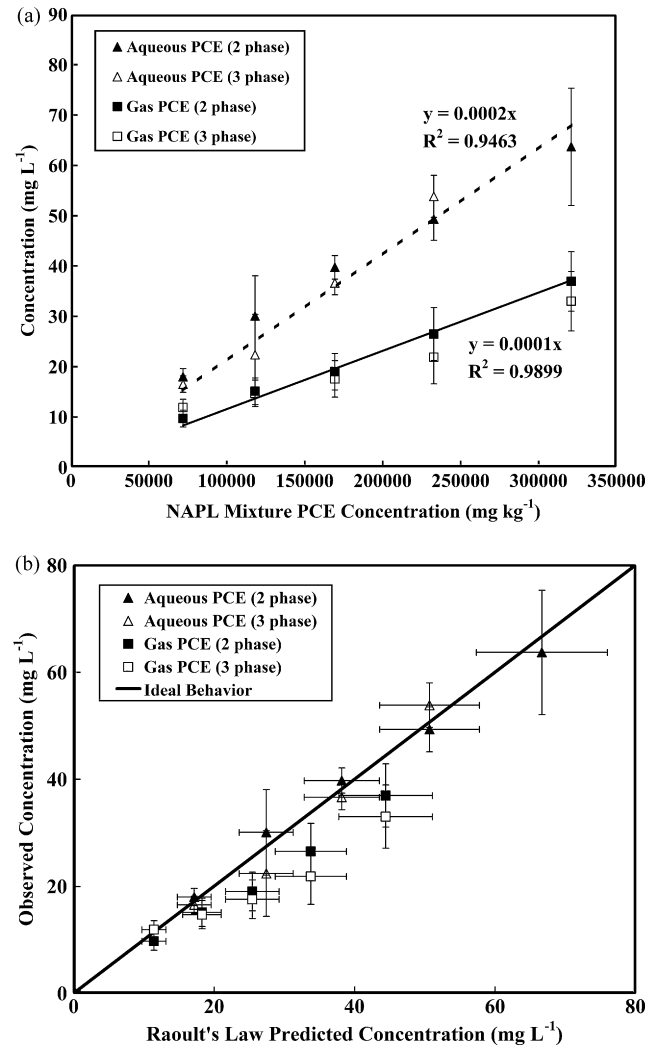


Fig. 2. (a) Equilibrium PCE partitioning behavior of the PCE–diesel immiscible-liquid mixture; error bars calculated from the 95% CI. (b) Raoult's Law prediction and observed PCE partitioning from the immiscible-liquid mixture; error bars represent the uncertainty based on the observed data replicates, and the prediction uncertainty from the error associated with the two variables in Eq. (1).

was removed from the flow cell with porous media. The experiment conducted with the flow cell containing no porous medium extended for approximately 29 days, and 31% (13 g) of the initial PCE mass was removed (Table 2). This value is similar to the mass removal (37%) calculated from the immiscible liquid compositional analysis conducted before and after vapor extraction. The larger mass removal for the flow cell without porous media is a result of the higher vapor concentrations, as mentioned above.

The results from the PCE–diesel mixture chemical analysis for different carbon chain length ranges ($C_6\text{--}C_{10}$, $C_{10}\text{--}C_{22}$, and $C_{22}\text{--}C_{32}$) for the initial sample and samples collected over time are presented in Table 3. These data suggest that there was a relatively minor change in composition during the experiment. The relatively constant effluent concentrations observed throughout the course of the experiments, in conjunction with the limited mass removal, suggests that the experiments remained under steady-state conditions. Greater changes in composition would be expected after longer time periods of vapor extraction and corresponding greater fractions of mass removal.

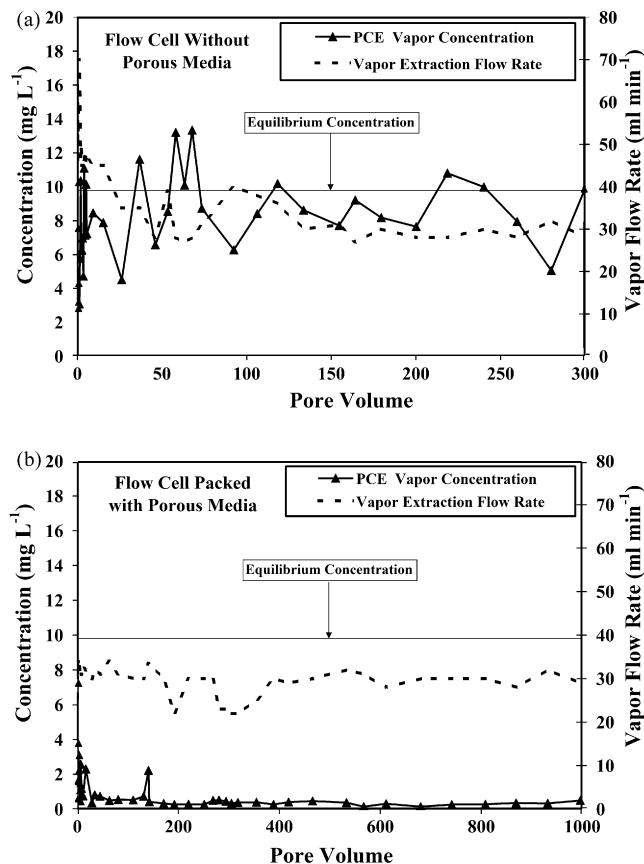


Fig. 3. (a) Effluent PCE vapor concentrations, equilibrium PCE vapor concentration, and vapor flow rate comparison for the flow cell conducted without porous media (free-phase immiscible liquid). (b) Effluent PCE vapor concentrations, equilibrium PCE vapor concentration, and vapor flow rate comparison for the flow cell packed with porous media (residual-phase immiscible liquid).

4.5. Vapor extraction mass-transfer behavior

The effluent concentrations measured during the flow-cell experiments were compared to equilibrium values measured for the batch experiments to evaluate potential mass-transfer rate limitations (Table 1 and Fig. 3). The gas-phase concentrations observed for the flow cell containing no porous medium (Fig. 3a), which averaged $7.9 \pm 0.8 \text{ mg L}^{-1}$, were not statistically different from the batch equilibrium mean concentration ($9.7 \pm 1.7 \text{ mg L}^{-1}$). This indicates that partitioning between the gas and immiscible liquid was essentially at equilibrium, suggesting negligible mass-transfer rate limitation for the flow cell without porous media. This also indicates that partitioning under dynamic flow conditions remained ideal with respect to Raoult's

Law. The effluent concentrations were significantly lower than vapor concentrations at equilibrium with pure PCE, which is 104 mg L^{-1} as determined from batch experiments, as would be expected.

Initial effluent concentrations for the flow cell packed with porous media were similar to the batch results due to the equilibration of phases prior to vapor extraction. As mentioned above, the vapor concentrations decreased after the initiation of vapor extraction, and the resulting mean vapor concentration was significantly lower than the batch results (Fig. 3b). These lower concentrations suggest the existence of apparent mass-transfer rate limitations between the immiscible liquid and the gas phase that could be the result of inter- or intraphase mass-transfer kinetics, flow bypass around (as opposed to through) the immiscible liquid, or dilution due to nonuniform immiscible-liquid distribution. The apparent mass-transfer rate limitations are not likely to have resulted from inter- or intraphase mass-transfer constraints, because such behavior would also have been observed for the flow cell without porous media, for which mass transfer was at or very near equilibrium. For the flow cell with porous media, immiscible liquid was injected (as opposed to mixed into the porous media prior to packing), and the limited volume injected was not sufficient to create a uniform distribution. Thus, it is likely that dilution effects associated with the nonuniform immiscible-liquid distribution were primarily responsible for the observed apparent mass-transfer rate limitation. Liang and Udell [4] observed similar behavior in vapor-extraction experiments with nonuniform immiscible-liquid distributions where vapor transport occurred adjacent to, but not through, the immiscible-liquid source zone.

Eq. (4) was used to determine k_0 for the porous media flow-cell experiment (Table 1). The resultant value presented in Table 1 was compared to the values presented in the literature for column experiments [5,11]. The value of 0.05 h^{-1} was lower than the values presented in Wilkins et al. [11] for single-component immiscible liquids and within the range presented in Harper et al. [5], which was $0.03\text{--}2.6 \text{ h}^{-1}$ for an immiscible-liquid mixture containing four compounds. The rate coefficients were not evaluated for the flow cell without porous media, which was determined to be at or very near equilibrium based on the above discussion.

5. Conclusion

This investigation examined the impact of co-contamination-induced composition effects on immiscible liquid behavior. The results showed that increasing the PCE content within the PCE-diesel immiscible-liquid mixture did affect the physical properties and the phase-partitioning behavior of the mixture. The phase partitioning evaluated herein was relatively ideal, which suggests that Raoult's Law can be used to adequately predict partitioning behavior for this complex mixture that was obtained from a hazardous waste site.

The equilibrium partitioning was also compared to steady-state vapor-extraction experiments to evaluate the effect of remediation on immiscible-liquid composition. The results suggest that PCE evaporation concentrations were lower than equilibrium values, signifying apparent rate limitation, for the experiment conducted in the flow cell packed with porous media, whereas equilibrium was observed for the flow cell without porous media. The decreased steady-state concentrations and apparent rate limitation behavior were attributed to a nonuniform immiscible-liquid distribution and dilution effects. The results of this research illustrate the benefits associated with characterization of multicomponent immiscible-liquid composition for understanding contaminant distribution and mobility, phase partitioning, and remediation feasibility.

Table 3

PCE-diesel mixture composition (mg kg^{-1}) over time during the vapor-extraction experiment without porous media

Sample event ^a	C ₆ –C ₁₀	C ₁₀ –C ₂₂	C ₂₂ –C ₃₂	C ₁₀ –C ₃₂
1	<40,000	830,000	<200,000	830,000
2	45,000	770,000	<200,000	770,000
3	46,000	910,000	<200,000	910,000
4	51,000	900,000	<200,000	900,000
5	45,000	770,000	<200,000	770,000
6	<40,000	890,000	<200,000	890,000

^a The #1 and #6 results are the immiscible-liquid samples reported as initial and final in Table 2, respectively.

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