Measurement of NAPL–water interfacial areas and mass transfer rates in two-dimensional flow cell
Muzi Li, Yuanzheng Zhai and Li Wan

ABSTRACT
The nonaqueous-phase liquid (NAPL)–water interfacial area and the mass transfer rate across the NAPL and water interface are often key factors in in situ groundwater pollution treatment. In this study, the NAPL–water interfacial area and residual NAPL saturation were measured using interfacial and partitioning tracer tests in a two-dimensional flow cell. The results were compared with previous column and field experiment results. In addition, the mass transfer rates at various NAPL–water interfacial areas were investigated. Fe$^{2+}$-activated persulfate was used for in situ chemical oxidation remediation to remove NAPL gradually. The results showed that the reduction of NAPL–water interfacial areas as well as NAPL saturation by chemical oxidation caused a linear decrease in the interphase mass transfer rates ($R^2 = 0.97$), revealing the relationship between mass transfer rates and interfacial areas in a two-dimensional system. The NAPL oxidation rates decreased with the reduction of interfacial areas, owing to the control of NAPL mass transfer into the aqueous phase. Key words | chemical remediation, flow cell, interfacial area, mass transfer, NAPL

INTRODUCTION
The nonaqueous-phase liquid (NAPL)–water interfacial area is a key parameter for the remediation of organic contami- nant source zones and risk assessment (Cho et al. 2005; Carroll et al. 2015). Two primary methods are available to measure NAPL–water interfacial areas for natural porous media systems, interfacial partitioning tracer tests (IPTTs) (Brusseau et al. 2010) and synchrotron X-ray microtomogra- phy (Brusseau et al. 2008b, 2009). The IPTT method provides indirect measurements of interfacial area based on the reten- tion behavior of tracers that accumulate at the interface. Previous studies have employed the IPTT to determine NAPL–water interfacial areas in column-scale laboratory experiments (Dobson et al. 2006; Narter & Brusseau 2010). However, multiple-dimensional flow cell experiments, with conditions closer to those in the field, are seldom carried out. It is of particular significance to compare the measure- ment of NAPL–water interfacial areas in different dimensions.

NAPL saturation and NAPL–water interfacial areas are two significant factors to characterize NAPL distribution and source-zone remediation. The partitioning tracer technique has been applied for characterization of residual NAPL saturation in both laboratory (Cho & Annable 2005) and field situations (Hartog et al. 2010). The saturation of NAPL within the tracer-swept region can be quantified by measuring retardation of the partitioning tracers to a conservative tracer. Several alcohols, such as isopropanol, 4-methyl-2-pentanol and 2,4-dimethyl-3-pentanol (24DM3P), have been used as partitioning tracers for the determination of the degree of NAPL saturation (Rhee et al. 2011).

The trapped NAPL is released into the aqueous phase by dissolution, acting as a potential long-term source contribut- ing to groundwater contamination. The mass transfer of NAPL across the NAPL interfacial phase determines both the extent of contamination and the persistence of residual NAPL phases. The determination of mass transfer rate, therefore, plays an important role in NAPL source-zone characterization and NAPL remediation techniques (Jha & Mohan Kumar 2009). It is well-known that interphase mass transfer is closely related to the specific interfacial area. The previous studies of mass transfer with specific interfacial area were mainly conducted in column exper- iments (Cho et al. 2005). There is a need to investigate the effect of interfacial area and NAPL saturation on the mass transfer rate in two-dimensional systems.
Intermediate-scale flow cells have been used to study the behavior of organic liquid in porous media, such as the impact of flow-field heterogeneity on organic liquid migration and distribution, organic liquid dissolution processes, and remediation technologies (Brusseau et al. 2008a; DiFilippo et al. 2010; DiFilippo & Brusseau 2011; Akyol et al. 2013). The objective of this study was to use a flow cell system to measure NAPL–water interfacial areas and residual NAPL saturation employing tracer test techniques, and compare the results with previously published studies. In addition, the impact of NAPL saturation and interfacial area reduction by chemical oxidation on NAPL–water mass transfer rate was also investigated.

MATERIALS AND METHODS

Flow cell materials

Commercially available well-sorted natural silica sands (Accusand, Unimin Inc.), with a median grain diameter of 0.359 mm (40/50 mesh), were used for the study. Trichloroethylene (TCE, Sigma, >99.5%) was used as the model immiscible liquid. The organic liquid was dyed with Sudan IV (Aldrich) at a concentration of 100 mg L\(^{-1}\), which has been shown to have minimal impact on fluid properties and behavior. Sodium dodecyl benzene sulfonate (SDBS, TCI, >98%) (35 mg L\(^{-1}\)) and Br\(^{-}\) (in the form of CaBr\(_2\), Aldrich, 98%) (200 mg L\(^{-1}\)) were utilized as the interfacial tracer and nonreactive tracer, respectively. Alcohol, 24DM3P (Aldrich, 99%) (100 mg L\(^{-1}\)) was used as partitioning tracer. The solutions were prepared with deionized water saturated with the organic compound. Fe\(^{2+}\)-activated persulfate (5 mM sodium persulfate (Na\(_2\)S\(_2\)O\(_8\)) and 0.8 mM ferrous sulfate (FeSO\(_4\)) was used for in situ chemical oxidation (ISCO) to remove NAPL gradually. SO\(_4^{2-}\) (standard electrode potential \(E_0 = 2.5–3.1\) V) and sulfate are generated as oxidant by Fe(II) activated persulfate, as depicted by Equation (1).

\[
\text{S}_2\text{O}_8^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (1)
\]

Figure 1 illustrates the experimental setup. The flow cell was constructed of stainless steel, with dimensions of 43.5 cm long by 25.5 cm high by 2.7 cm wide. A board of tempered glass was attached to the front of the flow cell, while the stainless steel board was attached to the back. The flow cell possessed three evenly spaced injection ports and three outflow ports on each end. In addition, five ports were evenly spaced on the top of the flow cell to allow injection of organic liquid. The porosity (equal to the saturated water contents) and the pore volume were determined based on the mass of water used for packing and the inside volume of the flow cell. A high-performance liquid chromatography pump with single-piston precision-flow was used to provide constant flow rate, equivalent to an average pore-water velocity of approximately 9 cm/h (DiFilippo et al. 2010; DiFilippo & Brusseau 2011).

Organic-liquid injection

Organic liquid was injected in the water-saturated flow cell through the top injection ports using a gas-tight syringe and needle. A total of 8 mL of TCE organic liquid was injected in 1 mL increments at a rate of 1 mL min\(^{-1}\). After completion of TCE injection, the flow cell remained undisturbed for 48 h to attain a stable non-wetting fluid distribution. TCE-saturated water was then pumped into...
the flow cell to displace mobile immiscible liquid and thus establish a local residual form in the flow cell.

Tracer test methods

Before injection of the NAPL, tracer tests were conducted under water-saturated conditions (no immiscible liquid) to measure background adsorption of SDBS by the porous media. After emplacement of the organic liquid, a total of three sets of interfacial and partitioning tracer tests were performed using a single flow cell to measure NAPL–water interfacial areas and NAPL saturation in a residual form. The results of the three sets of tracer tests will be validated against each other to get relatively reliable results. Retardation factors for SDBS were obtained by moment analysis of the breakthrough curves. The specific organic–liquid–water interfacial area (A_{int}, cm^{-1}), which represents area of interface normalized by the porous medium volume, was obtained from the following equation:

$$R_{pf} = 1 + \frac{A_{int} K_i}{\theta_w} + \frac{\rho_b K_d}{\theta_w}$$

(2)

where $R_{pf}$ is the retardation factor of interfacial tracer; $K_i$ is the equilibrium sorption coefficient (mL g^{-1}); $\rho_b$ is the matrix bulk density (g cm^{-3}); $\theta_w$ is the volumetric water content; and $K_i$ is the interfacial partition coefficient (cm). In this study, equilibrium sorption coefficient of 0.07 mL g^{-1} was determined for the sand media. $K_i$ at an SDBS concentration of 35 mg L^{-1} was measured to be 7.04 × 10^{-4} cm.

Partitioning tracer tests in the presence of NAPL (TCE) were conducted to measure NAPL saturation. The retardation factor of partitioning tracer (alcohol) was determined by moment analysis of the breakthrough curves. The NAPL saturation ($S_n$), which represents average NAPL saturation for each tracer sweep area, was obtained from the following equation:

$$R_{pt} = 1 + \frac{\rho_b K_d}{\theta_w} + \frac{K_{mw} S_n}{1 - S_n}$$

(3)

where $R_{pt}$ is the retardation factor of partitioning tracer; $K_{mw}$ is the partitioning coefficient between NAPL and water, which was determined by the slope of the regressed curve between partitioning tracer concentrations in NAPL and water phases. In this study, the sorption of partitioning tracer to the background media was negligible ($K_d = 0$). Based on the previous studies, $K_{mw}$ value was determined to be 38.2 (Young et al. 1999).

The flow cell, saturated with residual NAPL from the third set of the tracer test experiments, was continuously used to investigate mass transfer with varied interfacial area and NAPL saturation. Fe^{2+}-activated persulfate was used for ISCO remediation to remove NAPL gradually by increased pore volumes (PV) of persulfate. Fe^{2+}-activated persulfate was selected because of good oxidation capacity with minimal mobilization (Liang et al. 2004; Anotai et al. 2011). Interfacial transfer within the cell was evaluated immediately after initial saturation and again after each of four successive flushes of 3 PV of persulfate.

After each set of oxidation tests in the five sets, the flow cell was flushed with 2 PV of deionized, de-aired water to investigate the mass transfer rate between NAPL and water, as a dissolution test. The effluent TCE concentration was tested at 2 h intervals to calculate the mass of NAPL transfer. Interfacial and partitioning tracer tests were next conducted sequentially to measure varied interfacial area and NAPL saturation.

Analytical methods

All of the tracer test experiment samples were taken at 1 h intervals (sampling frequency of approximately five data points per pore volume) with a glass syringe. SDBS was analyzed using UV-Vis spectrophotometry (Shimadzu, model 5100) at a wavelength of 223 nm. Concentrations of Br^- were analyzed using a Dionex AI-450 ion chromatograph with a conductivity detector. Alcohol and TCE concentrations were analyzed by gas chromatography (GC, Shimadzu 14A) equipped with a flame-ionization detector. The GC column was set at 45 °C for 3 min, and then it was gradually increased to 160 °C at a rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Measurement of interfacial areas and residual NAPL saturation

Three sets of interfacial and partitioning tracer tests were performed using a single flow cell to measure NAPL–water interfacial areas and NAPL saturation in a residual form. The results are shown in Table 1. The NAPL–water interfacial areas of 215, 181, and 206 cm^{-1} were obtained in the three sets of interfacial tracer tests, respectively. The measured interfacial areas have a fair degree of uncertainty, with coefficients of variation of approximately 9%. Residual NAPL saturations of 1.31%, 1.23%, and 1.54% were
obtained in the three sets of partitioning tracer tests respectively, with coefficients of variation of approximately 4%.

Several IPTT studies have been reported in the literature, and these studies have typically employed glass beads, soil or silica sands. The values of interfacial area obtained from flow cell experiments are significantly larger than values reported in prior tracer test studies employing sands in column experiments, which range from approximately 30 cm$^{-1}$ to 100 cm$^{-1}$ under residual-saturation conditions (Saripalli et al. 1998; Cho & Annable 2005; Dobson et al. 2006; Brusseau et al. 2008b). The difference in experiment dimensions caused the diversity of measured interfacial area values. In the flow cell, the measured interfacial area could be influenced by the vertical variation of the flow field after DNAPL injection, which could cause the difference in the interfacial area values by one-dimensional column experiments.

The maximum specific interfacial area ($A_m$), which is equivalent to interfacial area normalized by non-wetting fluid volume (defined as $A_m = A_{nw}/S_n$), represents the specific interfacial area at a non-wetting fluid saturation of 100% (water saturation of 0). The $A_m$ serves as an index for a given system, indicative of the magnitude of interfacial area associated with that system (Brusseau et al. 2009; Narter & Brusseau 2010). The calculated $A_m$ values were about 16,400, 14,700, and 15,500 cm$^{-1}$ in flow cell experiments, illustrating the magnitude of the interfacial area associated with a two-dimensional system in homogeneous sand medium. The $A_m$ values obtained from previous one-dimensional column experiments using tracer test method range from approximately 100 cm$^{-1}$ to 1,000 cm$^{-1}$ (Saripalli et al. 1998; Cho & Annable 2005; Dobson et al. 2006; Brusseau et al. 2008b), while the $A_m$ values from previous filed experiments range from approximately $1 \times 10^4$ to $1 \times 10^5$ cm$^{-1}$ (Annable et al. 1998; Hartog et al. 2010), two orders of magnitude larger than the values from column experiments. Compared with the values from one-dimensional column experiments, the measured $A_m$ values in this flow cell were closer to the values obtained in field study, which is essential for the study of interfacial area in different experiment systems.

Gradual decrease of interfacial areas and NAPL saturation

After the measurement of interfacial area and NAPL saturation in residual NAPL form, five sets of dissolution tests were conducted to investigate mass transfer rates at varied interfacial area and NAPL saturation. The flow cell was prepared by four successive flushes of 3 PV of persulfate. The breakthrough curves for the five sets of interfacial and partitioning tracer tests are presented in Figures 2 and 3. Figure 2 shows that the rate of SDBS breakthrough curves reaching $C/C_0 = 1$ became faster with increased pore volumes of persulfate, which demonstrated the decrease of retardation of SDBS caused by the interfacial area adsorption. A similar phenomenon was observed for alcohol breakthrough curves (Figure 3). Table 2 shows that the NAPL–water interfacial area and NAPL saturation decreased with increased pore volumes of persulfate. Moreover, there was a linear relationship between interfacial area with NAPL saturation, which was also observed in previous literature (Cho & Annable 2005; Brusseau et al. 2009; Narter & Brusseau 2010). The relationship can be used as basis for a simple method for estimating interfacial area as a function of NAPL saturation in a two-dimensional system.

### Table 1 | Results of tracer tests at residual NAPL saturation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\theta_w$ (g cm$^{-3}$)</th>
<th>$\rho_b$ (g cm$^{-3}$)</th>
<th>$R_n$</th>
<th>$A_{nw}$ (cm$^{-1}$)</th>
<th>$R_p$</th>
<th>$S_n$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.289</td>
<td>1.875</td>
<td>2.04</td>
<td>215</td>
<td>1.51</td>
<td>1.31</td>
</tr>
<tr>
<td>3</td>
<td>0.291</td>
<td>1.871</td>
<td>1.91</td>
<td>181</td>
<td>1.48</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>0.291</td>
<td>1.871</td>
<td>1.95</td>
<td>206</td>
<td>1.52</td>
<td>1.34</td>
</tr>
<tr>
<td>CV (%)</td>
<td></td>
<td></td>
<td></td>
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<td>–</td>
<td>– 4</td>
</tr>
</tbody>
</table>

$\theta_w$ is the water content; $\rho_b$ is the bulk density; $R_n$ is the retardation factor of interfacial partitioning tracer; $R_p$ is the retardation factor of bulk partitioning tracer; $A_{nw}$ is the specific NAPL–water interfacial area; $S_n$ is the mean immiscible liquid saturation for the tracer sweep area; CV is the coefficient of variation.
Interphase mass transfer rates

Normalized effluent TCE concentrations of the flow cell at different NAPL saturation as a function of pore volumes of de-aired water are shown in Figure 4. The normalized effluent TCE concentrations at certain NAPL saturation are in steady-state with the constant water flow rate (2.84 mL min⁻¹), except for the first point at each saturation in Figure 4. The observed effluent TCE concentration decreased with NAPL saturation reduction by chemical oxidation.

The concentration of effluent contaminant is controlled by the mass transfer rates between NAPL and water. In Figure 4, higher normalized effluent concentration indicates higher mass transfer rate. The mass transfer rates (g of TCE removed/PV) were determined by the effluent TCE concentration (C, mg L⁻¹) and the water content of the flow cell (L/PV). Prior studies imply that the specific interfacial area is a primary factor controlling mass transfer at the NAPL–water interface (Cho et al. 2005). In this study, the results of mass transfer rates as a function of interfacial area (or NAPL saturation) reduction by chemical oxidation are shown in Figure 5, revealing the linear relationship between mass transfer rate and interfacial area (R² = 0.97). However, previous column experiment results showed that, below a critical velocity, the mass transfer rate was nearly independent of the magnitude of specific interfacial area (Cho et al. 2005). Further work is needed to investigate the correlation of mass transfer rate and interfacial area of different pore-water velocity and different porous media in flow cell experiments.
Additionally, it is also observed in Figures 4 and 5 that the decrease in NAPL saturation and interfacial area became less with each successive flush of persulfate, indicating that the NAPL mass removal rate by chemical oxidation (NAPL oxidation rates) decreased during the chemical oxidation process in the experiment range. This observation corresponds to the previous findings regarding NAPL oxidation using persulfate (Liang et al. 2004, 2008; Schaefer et al. 2012). Several laboratory studies applying permanganate have shown that NAPL mass removal rates quickly diminish long before NAPL is completely removed owing to the control of mass transfer into the aqueous phase (Heiderscheidt et al. 2008). In this study, the reduction of interfacial area, indicating the mass transfer became substantially diminished during treatment, resulted in the decrease in the NAPL oxidation rates (from 1.4 g/PV to 0.19 g/PV). The results suggest that the interfacial area is an important controlling factor for the NAPL oxidation rate in a two-dimensional system.

CONCLUSIONS

In the present study, NAPL–water interfacial areas and residual NAPL saturation were measured using interfacial and partitioning tracer tests in the flow cell. The results showed that compared with the values from one-dimensional column study, the measured maximum specific interfacial area value (indicating the magnitude of interfacial area) in the flow cell was closer to the values obtained from previous field experiments employing the tracer test method. A linear relationship was observed between interphase mass transfer rates with NAPL–water interfacial areas ($R^2 = 0.97$). The NAPL oxidation rates decreased from 1.4 g/PV to 0.19 g/PV with the reduction of NAPL–water interfacial areas, owing to the control of NAPL mass transfer into the aqueous phase. This study revealed the relationship between mass transfer rates and interfacial areas during chemical oxidation, and provided useful information for NAPL remediation technology in multiple dimensions.

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