Biosurfactant-enhanced soil remediation
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Chapter 5

Assessment of the Use of Partitioning and Interfacial Tracers to Determine the Content and Removal Rates of Non-Aqueous Phase Liquids

It was assessed whether partitioning and interfacial tracers can be used to determine the content and removal rate of a non-aqueous phase liquid (NAPL) in porous media. Retardation factors for these tracers were determined for five different model matrices contaminated with hexadecane as NAPL. The retardation of the partitioning tracer 2,4-dimethyl-3-pentanol was correlated with the degree of NAPL saturation for four of the five matrices ($r^2=0.86$, $n=7$). The observed retardation factors matched the retardation factors predicted with the independently determined hexadecane-water partitioning constant and the degree of NAPL saturation, indicating that this tracer may be used to estimate the NAPL content of porous media. The removal rate of the NAPL from the columns was determined by measuring the amount of hexadecane in the column effluent during elution with electrolyte solution. The removal rates differed over three orders of magnitude, dependent on the matrix used. The retardation of the interfacial tracer alkylbenzenesulfonate was higher for matrices with higher NAPL removal rates but was not correlated to NAPL content. This indicates that the retardation factors of alkylbenzenesulfonates in NAPL-contaminated media contain information related to the NAPL removal rates.

INTRODUCTION

The determination of the content and removal rates of non-aqueous phase liquids (NAPLs) is essential for soil remediation and risk assessment of sites contaminated with water immiscible components. Recently, the use of partitioning and interfacial tracers for determination of the degree of NAPL saturation and the specific NAPL-water interfacial area has attracted attention (Jin et al., 1995; Wilson, R.D. and Mackay, 1995; Saripalli et al., 1997b; Annable et al., 1998a). An advantage of the use of tracers is that it is non-invasive and yields an average value that refers to the entire flow field. In contrast, traditional ways of soil sampling require analysis of many samples to obtain a representative average value for a site, because of site heterogeneity (Jin et al., 1995).

Compounds that have been used as partitioning tracers for the determination of the NAPL content ($\theta_n$, L NAPL/L porous medium) or degree of NAPL saturation ($S_n$, L NAPL/L pore volume) of contaminated soil include alcohols (Jin et al., 1995; Annable et al., 1998a, b; Jawitz et al., 1998; McCray and Brusseau, 1998), sulfur hexafluoride (Wilson, R.D. and Mackay, 1995; Nelson and Brusseau, 1996), fluorocarbon compounds (Studer, 1997; Deeds et al., 1999) and the naturally occurring isotope $^{222}$Rn (Hunkeler et al., 1997). Partitioning tracers distribute between the NAPL and aqueous phases, causing retardation of these tracers relative to a conservative tracer. The tracers have been applied both in laboratory (Jin et al., 1995; Wilson, R.D. and Mackay, 1995; Hunkeler et al., 1997) and field situations (Nelson and Brusseau, 1996; Hunkeler et al., 1997; Annable et al., 1998b; Jawitz et al., 1998; McCray and Brusseau, 1998) and have been used to determine levels of NAPL saturation $S_n$ between 0.006 and 0.2. The level of NAPL saturation can be calculated from the
retardation factor of a partitioning tracer by using eq 5.1 (Nelson and Brusseau, 1996), provided that the retardation factor is determined solely by the NAPL content $S_n$ and the NAPL-water partitioning constant $K_{nw}$ ($\text{L aqueous phase/ L NAPL}$). Furthermore, the partitioning constant of the tracer must be independent on tracer concentration and the mobile aqueous phase containing the tracers should contact all NAPL present.

$$R = 1 + K_{nw} \frac{S_n}{(1 - S_n)}$$  \hspace{1cm} (5.1)

The $K_{nw}$ values depend on the nature of the tracer and the NAPL. For alcohol tracers, $K_{nw}$ increases with increasing tracer hydrophobicity, and decreases with increasing NAPL hydrophobicity (Dwarakanath and Pope, 1998). Sulfur hexafluoride combines the advantages of having a higher $K_{nw}$ than the commonly used dimethylpentanol tracers and of not sorbing to soil (Wilson, R.D. and Mackay, 1995). The agreement that was generally observed between results obtained with tracer experiments and data from soil core sampling (Hunkeler et al., 1997; Annable et al., 1998b; Jawitz et al., 1998; McCray and Brusseau, 1998; Deeds et al., 1999) suggests that the retardation of partitioning tracers indeed is dependent on $S_n$ and $K_{nw}$. However, a systematic study has not been conducted to determine whether this relation holds for NAPLs present in various porous matrices and at different surface area to volume ratios. Such a more rigorous demonstration would increase the reliability of this promising technique.

Surfactants such as linear alkylbenzenesulfonate (LAS, also known as sodium dodecylbenzenesulfonate, SDBS) tend to partition between the water-air or water-NAPL interface and bulk water, and can thus be used as interfacial tracers (Kim et al., 1997; Saripalli et al., 1997b, 1998; Annable et al., 1998a). The retardation of these tracers gives information on the NAPL-water (or air-water) interfacial area. Interfacial tracers have also been applied both in laboratory (Kim et al., 1997; Saripalli et al., 1997b, 1998) and field experiments (Annable et al., 1998a). Verification of the relation between tracer retardation and interfacial area is complicated since the interfacial area is difficult to determine independently. The fact that interfacial areas calculated from tracer retardation factors corresponded to values that were calculated based on geometrical or thermodynamic considerations was used as a validation of the method (Saripalli et al., 1997b). The NAPL-water interfacial area is believed to be important for many processes including NAPL dissolution (Powers et al., 1994), removal by transport (Saripalli et al., 1997b; Annable et al., 1998a), and biodegradation (Ortega-Calvo and Alexander, 1994). Therefore, interfacial tracers may be useful for the characterization of NAPL-contaminated sites when their retardation factors would be directly correlated to processes such as NAPL removal rates.

The goal of this work was to investigate how retardation of partitioning tracers is influenced by NAPL present in different porous media and to test the feasibility of interfacial tracers for determination of NAPL removal rates. The term removal rate is used this paper to quantify the elution of NAPL from columns packed with NAPL-contaminated matrices, and includes all physical removal processes such as dissolution, detachment of NAPL microdroplets, or mobilization. Retardation factors for the tracers were determined with column studies in which both NAPL content and NAPL removal rates were varied independently. This was accomplished by using five model matrices with a large variation in particle size, pore size, and specific surface area. These matrices and the procedure for contaminating them with NAPLs were chosen in order to obtain homogeneously contaminated matrices with different specific NAPL-water interfacial areas and surface area to volume ratios, which allowed assessment of the processes that determine tracer retardation.
 MATERIALS AND METHODS

**Chemicals, matrices and solutions.** KBr was obtained from Merck (technical grade, Darmstadt, Germany). The tracers 4-methyl-2-pentanol (99% pure, MMP), 2,4-dimethyl-3-pentanol (99%, DMP), and sodium n-alkylbenzenesulfonate (technical grade, LAS) were obtained from Aldrich (Zwijndrecht, Netherlands). Hexadecane (99%) was obtained from Acros (Geel, Belgium). Pure samples of 5-n-(p-sulfophenyl)-undecane and 5-n-(p-sulfophenyl)-dodecane were kindly provided by Dr. J. Tolls (Tolls et al., 1997). Silica 60 (Merck), sea sand (Merck), controlled pore glass (CPG-10-3000, Electro Nucleonics Inc., Fairfield N.J.), fine glass beads (ABCR, Karlsruhe, Germany) and coarse glass beads (Fisher Scientific, Den Bosch, Netherlands) were used as model matrices (Table 5.1). The buffered electrolyte solution contained 0.53 g/L Na2HPO4·12H2O, 0.14 g/L KH2PO4, 0.1 g/L (NH4)2SO4, 0.02 g/L MgSO4·7H2O, 390 µg/L Ca(NO3)2, 100 µg/L FeSO4·7H2O, 5 µg/L ZnSO4·7H2O, 5 µg/L HBO3, 5 µg/L CoCl2·6H2O, 5 µg/L CuSO4·5H2O, 2 µg/L MnSO4·H2O, 2 µg/L Na2MoO4·2H2O, 1 µg/L NiCl2·6H2O, 1 µg/L Na2WO4·2H2O, and 0.2 g/L NaN3 to prevent biodegradation of the tracers and hexadecane. The pH was adjusted to 7.0. The tracer solution contained 10 mM KBr, 10 mM MMP, 10 mM DMP, and 500 mg/L LAS in electrolyte solution.

**Contamination of matrices.** Matrices were contaminated by addition of 90 - 1200 µL hexadecane to 50 g matrix suspended in 100 mL pentane. After incubation for approximately 12 hours, the pentane was gradually removed using a rotary evaporator. Since the volatility of pentane is high (boiling point under ambient pressure 35-36 °C) and reduced pressure was used, it can be assumed that removal of pentane was complete. Columns packed with these materials had degrees of NAPL saturation (Sn) of 0.001 to 0.06 L hexadecane/L aqueous phase (Table 5.2). These saturations were relatively low compared to those used by other investigators, and were chosen to obtain matrices that resembled a residual NAPL. Since Sn could be determined accurately and reproducibly in samples of 100 mg, the method of contamination resulted in homogeneous NAPL distribution over the length of the columns.

**NAPL-water partitioning constants.** The NAPL-water partitioning constants (K_{nw}) of MMP and DMP were determined by extraction of 100 mL aqueous solution containing 1 mM MMP and 1 mM DMP or 10 mM MMP and 10 mM DMP, either with 1 mL or with 10 mL hexadecane. After

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**Table 5.1.** Physical properties of the matrices and parameters associated with column experiments

<table>
<thead>
<tr>
<th>matrix</th>
<th>particle size (µm)</th>
<th>pore size (nm)</th>
<th>specific surface area (m²/g)</th>
<th>bulk density (kg/L)</th>
<th>porosity (-)</th>
<th>pore volume (mL)</th>
<th>interstitial velocity (m/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fine glass beads</td>
<td>40</td>
<td>-</td>
<td>7.3·10⁻²</td>
<td>1.3</td>
<td>0.40</td>
<td>10.6</td>
<td>2.8</td>
</tr>
<tr>
<td>coarse glass beads</td>
<td>1000</td>
<td>2.6·10⁻³</td>
<td>4.1·10⁻¹</td>
<td>1.60</td>
<td>0.40</td>
<td>10.6</td>
<td>2.8</td>
</tr>
<tr>
<td>CPG-10-3000</td>
<td>60-125</td>
<td>300</td>
<td>7.8</td>
<td>0.34</td>
<td>0.76</td>
<td>20.2</td>
<td>1.5</td>
</tr>
<tr>
<td>silica</td>
<td>40-63</td>
<td>6</td>
<td>4.9·10⁻²</td>
<td>0.49</td>
<td>0.70</td>
<td>18.6</td>
<td>1.6</td>
</tr>
<tr>
<td>sea sand</td>
<td>100-300</td>
<td>ND</td>
<td>7.4·10⁻¹</td>
<td>1.40</td>
<td>0.44</td>
<td>11.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

a cm² surface area per cm³ porous medium, derived from specific surface area in m²/g; b value calculated from 4πr² using 0.64 as the fraction of the total volume occupied by the spheres (random close packing); c as given by the manufacturer; d determined by gas-physisorption using nitrogen.
equilibration and centrifugation (3000 rpm, 15 min), the aqueous concentrations of MMP and DMP was determined in triplicate by GC. The partitioning constants for MMP and DMP were 1.4 ± 0.2 and 11 ± 2, respectively. These values are in accordance with literature data (Annable et al., 1998a, b; Dwarakanath and Pope, 1998). The aqueous phase and organic phase concentrations were linearly related in the tested range between 0.5 mM and 9 mM (r²=0.98, n=4).

**Column studies.** Stainless steel columns (7.0 cm in length, 2.2 cm i.d., Alltech) were dry packed in incremental steps, either with hexadecane-contaminated material or with uncontaminated material. The NAPL distribution and content did not change during packing, since Sn was low and hexadecane was tightly attached to the matrices. Electrolyte solution was delivered to the column in upward flow using an HPLC single piston pump. Stainless steel tubing (0.8 mm i.d.) was used for all connections. After saturating the columns by flushing with 100 mL electrolyte solution at a flow rate of 0.1 mL/min, the amount of hexadecane in the effluent was determined in three 7 mL effluent fractions. The bulk density (ρ, kg/L) and the porosity (θ, -) were determined gravimetrically. Flow rates used during the subsequent tracer experiments were 0.3 mL/min. The resulting interstitial velocities are listed in Table 5.1. An injection loop was used to inject 2.73 mL of tracer solution into the column. The column effluent was directed to a fraction collector and analyzed for bromide, MMP, DMP and LAS for up to 25 pore volumes. Directly afterwards, for each type of matrix at one Sn, the flow was decreased to 0.1 mL/min and the amount of hexadecane was determined in one 7 mL effluent fraction.

**Analytical procedures.** The specific surface area of sea sand was determined by gas-physisorption using nitrogen. The amount of hexadecane in effluent samples and in the matrices were determined by GC-FID after extraction with isooctane. The aqueous bromide concentration was determined using a colorimetric assay (Bergmann and Sanik, 1957). Aqueous MMP and DMP concentrations were analyzed by GC-FID after extraction with pentane. LAS was analyzed using reversed-phase HPLC. Since LAS consists of multiple components that differ in hydrophobicity and interfacial properties, the two major peaks in the chromatogram were integrated. Each peak corresponded to components of uniform hydrophobicity. These components, referred to as LASa and LASb, coeluted with the pure LAS components 5-n-(p-sulfophenyl)-undecane and 5-n-(p-sulfophenyl)-dodecane, respectively. This observation, together with the comparison of our chromatogram with the chromatogram reported by Nakae et al. (1981) (Nakae et al., 1981), suggests that LASa and LASb contain 4-, 5- and 6-n-(p-sulfophenyl)-undecane, and 4-, 5- and 6-n-(p-sulfophenyl)-dodecane, respectively. The HPLC setup consisted of a Spark Basic Marathon autosampler (Spark Holland BV, Emmen, The Netherlands) with an injection volume of 40 µL, a Merck L-6200 pump (Hitachi, Ltd., Tokyo, Japan), a Chromsphere PAH 100 mm column (Chrompack, Bergen op Zoom, The Netherlands), and a Merck L-4200 UV-VIS detector (228 nm, Hitachi). Mobile phase A was a 10 mM aqueous sodium acetate buffer at pH 4.1 and mobile phase B was methanol. Gradient elution was performed by linearly changing the composition of the mobile phase from 66% B to 80% B in 8 min, followed by 8 min at 80% B, using a flow rate of 0.5 mL/min.

**Quantitative analysis.** Retardation factors were calculated from the first central moment corrected for a finite pulse (Das and Kluitenberg, 1996). In all experiments, except for those with silica, the retardation factor for bromide was used to calculate the pore volume. For the silica material, the retardation factor for bromide was less than 1 due to ion exclusion. Therefore, the elution times for the tracers for the columns packed with silica were converted to pore volumes using the porosity. The NAPL removal rates \( v_n \) (g hexadecane/pore volume) were
determined as the product of the amount of hexadecane in the column effluent \((C, \text{g hexadecane/L})\) and the water content of the column \((L/\text{pore volume, Table 5.1})\).

**RESULTS AND DISCUSSION**

**NAPL removal rates.** To determine the removal rate of hexadecane present in the contaminated matrices, the amount of hexadecane in the effluents was measured during continuous flow operation of the columns. The amount of hexadecane in the effluent before the tracer experiment was similar to the amount in the effluent immediately after the tracer experiment for all matrices. For a column packed with contaminated silica \((S_n=0.007)\), the amount of hexadecane in the column effluent remained constant at \((3.9 \pm 0.9) \times 10^{-4} \text{ g/L}\) for 20 pore volumes during continuous elution with electrolyte solution, but temporary increased to \(4 \times 10^{-3} \text{ g/L}\) after an interruption of the flow for 6 h. This behavior is indicative of rate-limited removal (Pennell et al., 1993).

The amount of hexadecane in the column effluent exceeded its aqueous solubility \((3.6 \times 10^{-6} \text{ g/L}, \text{Schwarzenbach et al., 1993})\) for columns packed with contaminated fine glass beads, coarse glass beads, CPG-10-3000, sea sand, and silica by a factor of 0.6, 0.3, 2 to 15, 42 to 87, and 9 to 120, respectively. Therefore, it must be concluded that mass transfer of NAPL from the matrix to the aqueous phase was not limited by its solubility and that the NAPL was removed from the majority of the columns partly as undissolved microdroplets. However, the removed amounts of NAPL were low since a separate non-aqueous phase was not visible and since the percentage that was removed from the columns was smaller than 0.2% of the amount initially present. This implies that the NAPL was not completely mobile but that individual microdroplets were occasionally detached from the immobile coated NAPL, which also may explain the observed rate-limited removal. The rate of detachment is likely to depend on the NAPL-water interfacial area.

From the amount of hexadecane in the effluent, the NAPL removal rate \((v_n, \text{ g hexadecane eluted/eluted pore volume})\) was calculated (Table 5.2). Since removal was rate-limited and since the residual amounts of hexadecane in the matrix samples taken after the experiment from the top and bottom of the columns were not significantly different from the NAPL content of the mixed column, this removal rate is directly related to the mass transfer rate of hexadecane from the matrix to the mobile phase under the
specified conditions. The NAPL removal rates differed by 3 orders of magnitude, dependent on the matrix used (Table 5.2). No correlation existed between \( v_n \) and \( S_n \) (Fig. 5.1A) or between \( v_n \) and the particle size for the whole data set. However, \( v_n \) increased with increasing specific surface area of the matrices \( a_{\text{mw}/\theta} \) (cm\(^2\) of surface · cm\(^{-3}\) of pore volume, Fig. 5.1B).

The procedure used to contaminate the matrices likely creates thin films of NAPL coated onto the matrices. These films can be characterized by their thickness and interfacial area. When the NAPL does not coat the entire surface area of the matrix, such as in the experiments with silica where the amount of NAPL present was smaller than the amount required to create monolayer coverage, a higher initial \( S_n \) value results in a higher NAPL-water interfacial area and a higher removal rate (Fig. 5.1A). In cases where the NAPL coats the entire matrix, a higher initial \( S_n \) value only results in an increased film thickness which does not affect the removal rate. This was observed for sea sand (Fig. 5.1A). The specific surface area of the matrix represents the maximal \( a_{\text{nw}} \) that can be achieved for a coated NAPL. Therefore, provided that no mobilization occurs, the value for the removal rate \( v_n \) at a NAPL saturation \( S_n \) where the surface is completely covered with NAPL should be related to the surface area of the matrix \( a_{\text{nw}/\theta} \) (Fig. 5.1B).

NAPL dissolution kinetics are frequently characterized by the dimensionless Sherwood number that relates interphase mass transport resistance to molecular mass transport resistance (Powers et al., 1994; Mayer and Miller, 1996). The variation of the Sherwood number \( Sh \) with \( \theta_n \) can be expressed using power law models such as

\[
Sh = \beta_0 \cdot Re^{\beta_1} \cdot \theta_n^{\beta_2}
\]

where \( Re \) is the Reynolds number, and \( \beta_0, \beta_1, \) and \( \beta_2 \) are empirical parameters (Powers et al., 1994; Mayer and Miller, 1996). The value of \( \beta_2 \) that relates the mass transfer constant with initial NAPL content can be derived from the geometric relation between the specific NAPL-water interfacial area and the NAPL volumetric fraction (Powers et al., 1994). For idealized NAPL globules in water-wet media, \( \beta_2 \) ranges from 0.5 to 1.0 (Powers et al., 1994). Based on the expected variation of surface area to volume ratio for the films present in the current columns experiments, the exponent \( \beta_2 \) is expected to vary from 0 for a film where the film thickness changes with changing initial NAPL content (sea sand) to 1 for a film where \( a_{\text{nw}} \) changes with changing initial NAPL content (silica). During the removal of NAPL from the columns, \( \beta_2 \) is expected to be close to 0 because depletion of NAPLs from films reduces film thickness but not \( a_{\text{nw}} \). This analysis of NAPL removal rates in terms of dissolution kinetics confirms that the NAPL removal rates observed in our experiments were constant during the duration of a tracer experiment and explains that the observed dependence of the NAPL removal rates on \( S_n \) was different for the various matrices (Fig. 5.1A).

Taken together, it can be concluded that the removal of hexadecane was rate-limited and was strongly matrix-dependent. Both the NAPL content and removal rate remained constant during the tracer experiments. Removal of NAPL was dependent on the NAPL-water interfacial area \( a_{\text{nw}} \), which was also observed for residual NAPLs present in water-wet media (Powers et al., 1994). Therefore, this experimental setup was suitable to determine the dependence of tracer retardation on NAPL content and removal rate.

**Tracer studies.** The shapes of breakthrough curves for the conservative tracer potassium bromide were sigmoidal and did not show tailing, indicating that the columns were packed homogeneously and that physical nonequilibrium effects were absent. Preliminary experiments using columns packed with contaminated sea sand showed that transport of the partitioning tracers was independent of the presence of other tracers. Subsequent tracer experiments
Tracers for NAPL characterization

Figure 5.2. Selected breakthrough curves for tracers (A) Breakthrough curves for bromide (O) and DMP (▲, \( S_n = 0 \); ●, \( S_n = 0.027 \); ▼, \( S_n = 0.059 \)) through hexadecane-contaminated sea sand. (B) Breakthrough curves for bromide (O) and LASa (▲, \( S_n = 0 \); ■, \( S_n = 0.0038 \); ◐, \( S_n = 0.017 \)) through hexadecane-contaminated CPG-10-3000. (C) Breakthrough curves for bromide (O, left Y-axis) and LASa (▲, \( S_n = 0 \), left Y-axis; ■, \( S_n = 0.059 \), right Y-axis) through hexadecane-contaminated sea sand.

were performed with a mixture of tracers. Total recovery of the tracers typically was between 80-110%, with a major exception for experiments with contaminated silica, where LAS did not break through during the experiment, and with contaminated sea sand, where due to tailing only 40% of the LAS tracer was recovered within 12 pore volumes after the tracer pulse. Since samples were generally analyzed until the concentration of tracers in the effluent was below \( C/C_0 < 0.001 \), the presence of tailing would always have been noticed. Therefore, the deviations of the mass balances from 100% do not result from a structural missing of the concentrations in the distal portions of the BTC, which would have lead to a structural underestimation of the retardation factors.

**Partitioning tracers.** To determine whether the retardation of the partitioning tracer was determined solely by the NAPL content of a column, breakthrough patterns of the tracers were measured with five matrices contaminated to different degrees of hexadecane saturation \( S_n \) (Fig. 5.2A). The shapes of breakthrough curves for the partitioning tracers through the uncontaminated and contaminated columns did not show tailing, indicating that nonequilibrium effects were absent under the conditions used. This also implies that \( K_{nw} \) was independent of tracer concentration, as was found using the batch partitioning studies. Nonlinear sorption or partitioning would have produced skewed breakthrough curves (Berglund, 1995). The retardation factors for the partitioning tracers with the uncontaminated matrices (except with the silica matrix) were close to unity (Table 5.2), indicating that sorption of these tracers to the matrix was negligible. The retardation factors for MMP with the contaminated matrices were close to unity due to the low \( K_{nw} \). Therefore, this tracer was not useful to determine NAPL content and was omitted from further analysis.

When retardation of partitioning tracers is determined solely by NAPL-water partitioning, the retardation factor \( R \) for the tracers with contaminated matrices is given by eq. 5.1 (Nelson and Brusseau, 1996). At low \( S_n \), as in the experiments described here, this equation reduces to \( R = 1 + K_{nw} S_n \) and thus predicts a linear relation between \( R \) and \( S_n \).

The experimentally determined retardation factors for the partitioning tracer DMP were correlated with \( S_n \) (\( r^2 = 0.86, n=7 \), silica data omitted) and corresponded well to the retardation factor as calculated from the independently determined \( K_{nw} \) and \( S_n \) (Fig. 5.3). This provides convincing evidence that the retardation of DMP is determined by NAPL-water partitioning.

**Interfacial tracers.** The shapes of the breakthrough curves for the interfacial tracers through the uncontaminated matrices did not show tailing, indicating that transport was not influenced by nonlinear sorption.
Chapter 5

Figure 5.3. Dependence of retardation factors for the partitioning tracers on the degree of NAPL saturation of the matrix. Fine glass beads (■), coarse glass beads (△), CPG-10-3000 (Δ), and sea sand (●) were used as matrices. The solid line gives predicted retardation factors for DMP using the experimentally determined $K_{nw}$ and $S_n$, the dotted lines give ± 1 standard deviation.

breakthrough curves for LAS through most of the contaminated matrices also did not show tailing (Fig. 5.3B). However, significant tailing was observed for experiments using contaminated sea sand, reflecting the nonlinear nature of the interfacial NAPL-water adsorption isotherm (Fig. 5.3C). The retardation factors for the more hydrophobic LASb were higher than for LASa, indicating that NAPL-water interfacial adsorption increased with increasing tracer hydrophobicity. This also indicated that it is appropriate to determine breakthrough of LAS components instead of LAS as total surfactant (Field and Istok, 1998).

The retardation factor for the LAS tracers varied from 1.06 to >20 for the four model matrices at a similar degree of NAPL saturation $S_n$ of approximately $2 \times 10^{-2}$, indicating that retardation of these tracers was not determined by NAPL-water partitioning. The retardation factors for the interfacial tracers, especially for those obtained with the contaminated sea sand and silica, were relatively high compared to those found in a field study (Annable et al., 1998a), even though the $S_n$ values in the field study were somewhat higher than in the present study. This indicated that the surface area to volume ratios for the NAPLs in the present study were relatively high, as is expected for NAPLs that are coated to matrices as thin films. We could not derive specific NAPL-water interfacial areas $a_{nw}$ from the

<p>| Table 5.2. Residual saturations $S_n$, removal rates of hexadecane $v_n$, and retardation factors for tracers |
|----------------------------------|-----------------|------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>matrix</th>
<th>$S_n$ (L/L)</th>
<th>$v_n$ (g/pore volume)</th>
<th>retardation factors</th>
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<tr>
<td>glass beads fine</td>
<td>0</td>
<td>$2.2 \times 10^{-2}$</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>$2.2 \times 10^{-2}$</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>glass beads coarse</td>
<td>0</td>
<td>$2.2 \times 10^{-8}$</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>$1.2 \times 10^{-8}$</td>
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<td></td>
</tr>
<tr>
<td>CPG-10-3000</td>
<td>0</td>
<td>$3.8 \times 10^{-3}$</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$1.6 \times 10^{-7}$</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>silica</td>
<td>0</td>
<td>$1.7 \times 10^{-2}$</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{-6}$</td>
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<td></td>
</tr>
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<td>sea sand</td>
<td>0</td>
<td>$9.8 \times 10^{-4}$</td>
<td>2.96</td>
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<tr>
<td></td>
<td>$5.9 \times 10^{-7}$</td>
<td>2.96</td>
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<tr>
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<td>$5.3 \times 10^{-7}$</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{-6}$</td>
<td>2.96</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ not measurable. As LAS caused clogging of the column, the tracer was omitted in this experiment; $^b$ not determined; $^c$ no breakthrough within 20 pore volumes
Tracers for NAPL characterization

63

retardation factors for LAS, because this would require detailed knowledge of the interfacial adsorption isotherm (Annable et al., 1998a). Furthermore, the derived values could not be verified because \( a_{nw} \) values were not determined independently.

A positive correlation was observed between retardation of the interfacial tracers and the independently determined NAPL removal rate \( v_n \) (Table 5.2, Fig. 5.1C). For instance, the retardation factors for LASa and LASb were low for the experiments with the matrices with low \( v_n \) (coarse glass beads and CPG-10-3000), and high for the matrices with high \( v_n \) (sea sand and silica). A correlation between retardation of LAS and NAPL removal rate was expected since both the retardation of LAS (Saripalli et al., 1997b) and the NAPL dissolution rate (Abriola et al., 1993; Powers et al., 1994; Annable et al., 1998a) depend on the specific NAPL-water interfacial area (\( a_{lw} \), cm² interface cm⁻³ unit column volume). However, several factors may disturb the correlation between \( v_n \) and \( R \). For instance, the nonlinearity of the NAPL-water interfacial isotherm may have caused LAS retardation to be non-proportional to \( a_{nw} \) (Annable et al., 1998a). Also, the viscosity, buoyancy, and capillary forces that determine whether removal of NAPL occurs by mobilization (Pennell et al., 1996) are not strictly related to \( a_{lw} \).

The results show that retardation factors for LAS tracers can provide qualitative information about NAPL removal rates under the conditions employed in this work. Further work is needed to establish whether retardation of interfacial tracers is related to NAPL removal rates in situations where the NAPL-contamination is created by addition of NAPL to a water-wet matrix, in situations where the NAPL is a multicomponent mixture, and under conditions where the NAPL is mobile. Saripalli et al. have shown that LAS retardation increases following NAPL mobilization (Saripalli et al., 1997b). This probably occurs due to an increase in \( a_{nw} \) that accompanies the formation of emulsions during the conditions that cause NAPL mobilization.

Silica. With the contaminated silica matrix, the retardation factors for both the partitioning tracer and the interfacial tracers were considerably larger than with all other matrices at similar \( S_n \) (Table 5.2). This strong retardation was likely to be caused by the surface area to volume ratio of the NAPL film which was expected to be exceptionally large due to the large specific surface area of silica (Table 5.1). The strong retardation of DMP suggested that this tracer behaved to some extent as an interfacial tracer. This is well possible, since amphiphilic alcohols are frequently used as cosurfactants, and air-water interfacial adsorption of alcohols (\( n \)-hexanol to \( n \)-nonanol) caused significant retardation in unsaturated porous media (Kim et al., 1998). Since the specific surface area of silica is much larger than the surface areas of soil or aquifer material, interfacial adsorption of DMP is not expected to influence its retardation under practical conditions.

Implications for practical application. Although the NAPLs employed in this study may not always be representative of NAPLs present in practical situations, their use gave insight into the physical processes that determine tracer retardation. These processes will also determine tracer retardation in practical situations. Therefore, the present study corroborates the possibility to use partitioning tracers to determine the NAPL content by demonstrating the convincing dependence of their retardation factors on \( K_{nw} \) and \( S_n \). The retardation of the partitioning tracers was largely independent on the type and porosity of the matrices and on the surface area to volume ratios of the NAPL. The experimental data show that strong retardation of interfacial tracers is correlated with high NAPL removal rates. For application in the field, it must be ensured that tracers do not precipitate (LAS precipitates in the presence of 2 mM Ca\(^{2+}\)) and are not biodegraded during the course of the experiment. Sorption of the tracers to soil can be compensated for by determination of
tracer sorption to uncontaminated soil as was done in the current work. However, compensating for tracer sorption may be complicated when sorption of the tracers is nonlinear. In this case, the contributions of sorption and NAPL-water (interfacial) partitioning to the observed retardation factor are not independent.

NOTATION

\( a_{nw} \) specific NAPL-water interfacial area, \( \text{cm}^2 \text{ interface} / \text{cm}^3 \text{ unit column volume} \)
\( a_{mw} \) specific surface area for a matrix, \( \text{cm}^2 \text{ interface} / \text{cm}^3 \text{ unit column volume} \)
\( C \) concentration of tracers or hexadecane in the effluent, \( \text{g} / \text{L aqueous phase} \)
\( C_0 \) concentration of tracer in the influent, \( \text{g tracer} / \text{L aqueous phase} \)
\( K_{nw} \) NAPL-water partitioning constant, \( \text{L aqueous phase} / \text{L NAPL} \)
\( R \) retardation factor for a tracer with the contaminated matrix
\( R_0 \) retardation factor for a tracer with the uncontaminated matrix
\( Re \) dimensionless Reynolds number
\( Sh \) dimensionless Sherwood number
\( S_n \) degree of NAPL saturation, \( \text{L NAPL} / \text{L pore volume} \)
\( v_n \) removal rate, \( \text{g hexadecane removed} / \text{pore volume} \)
\( \beta_i \) empirical parameters
\( \rho \) bulk density, \( \text{kg matrix} / \text{L column volume} \)
\( \theta \) porosity, \( \text{L pore volume} / \text{L column volume} \)
\( \theta_n \) NAPL content, \( \text{L NAPL} / \text{L column volume} \)