Natural gradient partitioning and interfacial tracer tests for NAPL source zone characterization at a former coal gasification plant

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Abstract A natural gradient partitioning and interfacial tracer test (PITT) at a field site near to a former coal gasification plant was validated in situ for the integrated determination of DNAPL (tar oil) amount and distribution. The efficiency of PITTs was tested in controlled laboratory studies (batch, column, tank) under different flow-velocities (1–5 m day$^{-1}$) and DNAPL distributions (DNAPL coatings, DNAPL blobs, DNAPL pool). The alcohols 4-methyl-2-pentanol, 1-hexanol and 2,4-dimethyl-3-pentanol were used as suitable partitioning tracers to measure the DNAPL saturation, while sodium laurylsulfate, an anionic surfactant, was used as an interfacial tracer to estimate the effective DNAPL–water interfacial area. All PITTs were conducted as pulse-type experiments and the resulting breakthrough curves were analysed by the method of moments.

Key words interfacial area; interfacial tracer; NAPL; partitioning tracer; residual saturation; tar oil; tracer

INTRODUCTION

Contaminant release from residual coal tar, which can typically be found at former coal gasification plants, depends on the composition of the dense non-aqueous phase liquid (DNAPL), the DNAPL volume and the interfacial area between DNAPL and groundwater. The determination of these essential source zone parameters with common sampling methods such as core sampling and groundwater sampling provide only point-scale data at discrete locations.

In the present work, we describe controlled laboratory experiments of in situ partitioning and interfacial tracer tests (PITT), which allow the integrated determination of the DNAPL amount and distribution throughout the subsurface area that is flushed during the experiment.

The PITT methodology employed in this study was initially developed in oil reservoir engineering (Tomich et al., 1973; Sheely, 1978) and adapted to NAPL contaminated field sites by the University of Texas (Jin et al., 1995, 1997). The determination of DNAPL–water interfacial areas via tracer tests is a quite recent development of the University of Florida (Saripalli et al., 1998; Annable et al., 1998). First laboratory experiments with PITTs and a tar oil DNAPL were conducted by Setarge et al. (1999).
THEORETICAL BACKGROUND

Reactive transport

The PITT consists of an injection of a suite of partitioning, interfacial and conservative tracers into a well (column inlet) and the recovery of the tracer solution at an extraction well (column outlet). While the conservative tracers will stay unaffected by the presence of DNAPL, the reactive tracers (partitioning and interfacial tracers) undergo retardation due to their absorption and adsorption behaviour. The result is a chromatographic separation of the tracers, which can be recorded at the extraction well. The higher the affinity to the DNAPL phase the better is the separation of the individual breakthrough curves (BTCs). This effect is quantified by the retardation factor $R$ which is defined as:

$$R_{\text{reactive}} = \frac{\mu_{\text{reactive}}}{\mu_{\text{conservative}}}$$

where $\mu$ is the first normalized temporal moment of the respective tracers at a monitoring location. For a pulse-type experiment this is given by the second term, where $C(t)$ is the monitored tracer concentration (either reactive or conservative) that is normalized by its input concentration $C_0$. $t$ is the experimental time and $t_p$ is the time-correction term for the duration of the tracer-pulse injection.

Retardation of partitioning tracers

The equilibrium-partitioning coefficient $K_{NW}$ [-] is defined as:

$$K_{NW} = \frac{C_N}{C_w}$$

where $C_N$ [g cm$^{-3}$] is the concentration of the tracer in the DNAPL and $C_w$ [g cm$^{-3}$] is the concentration of the tracer in the water phase. Conservative tracers have a partitioning coefficient of zero.

The general equation of partitioning tracer retardation ($R_{\text{PART}}$) can be written as:

$$R_{\text{PART}} = \frac{\mu_{\text{PART}}}{\mu_{\text{conservative}}} = 1 + \frac{K_{NW} S_N + \rho_d K_d}{1 - S_N}$$

where $S_N$, $\rho_d$, $K_d$, and $n$ denote the DNAPL residual saturation [-], the bulk density of the aquifer material [g cm$^{-3}$], the solid–water distribution coefficient [cm$^3$ g$^{-1}$] and the porosity [-], respectively. If the tracers are not adsorbed by the aquifer material ($K_d = 0$) the last term equals zero and thus the retardation factor depends only on $S_N$ and $K_{NW}$.

Because the retardation factor for each partitioning tracer is a function of both the partitioning coefficient of the tracer and the average DNAPL residual saturation of the contaminated aquifer, $S_N$ can only be determined by measuring $R_{\text{PART}}$ for tracers with known partitioning coefficient, $K_{NW}$. 

If the average residual saturation is unknown, which is most likely for field tests, a whole suite of partitioning tracers with varying partitioning coefficients should be used to ensure that at least one BTC will have sufficient separation ($1.2 < R_{P, RFT} < 4$) from the conservative tracer BTC, to calculate $S_N$. Additional BTCs with sufficient separation increase the confidence level of the PITT results.

Retardation of interfacial tracers

The DNAPL-water interfacial tension ($\gamma$) was measured as a function of sodium lauryl ethersulphate (SLES) concentration using the drop-weight method (Earnshaw et al., 1996).

The interfacial accumulation of SLES can be described by the Gibbs sorption isotherm (Adamson, 1982):

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{dC} C$$

where $\Gamma$, $\gamma$, $C$, $R$, and $T$ denote the interfacial adsorption [mmol cm$^{-2}$], the surface tension [dynes cm$^{-1}$], the concentration of surfactant [mmol cm$^{-3}$], the universal gas constant [dyne cm/mmol K] and the absolute temperature [K].

The equilibrium interfacial adsorption coefficient, $K_{IFT}$ [cm$^{-1}$], can be determined by:

$$K_{IFT} = -\frac{1}{2RT} \frac{d\gamma}{dC} C_{eq}$$

therefore $K_{IFT}$ can be calculated for a given surfactant concentration ($C_{eq}$) and varies with the slope of the $\gamma$ versus $C$ plot which was obtained by the drop-weight method (Fig. 1 (b)). When pulse input tracer tests are applied, a constant $K_{IFT}$ value can be estimated in a first approximation by using the maximum interfacial tracer concentration of each BTC (Annable et al., 1998). A more elegant solution is an inverse modelling approach proposed by Liedl (personal communication, 2000).

The general equation of interfacial tracer retardation ($R_{IFT}$) can be written as:

$$R_{IFT} = \frac{\mu_{IFT}}{\mu_{conservative}} = 1 + \frac{A_{NW} K_{IFT}}{\theta} + \frac{P_d K_d}{\theta}$$

where $A_{NW}$, $P_d$, $K_d$, and $\theta$ denote the DNAPL–water interfacial area [cm$^2$ cm$^{-3}$], the bulk density of the aquifer material [g cm$^{-3}$], the solid–water distribution coefficient [cm$^3$ g$^{-1}$] and the volumetric water content [–], respectively. If the interfacial tracer adsorption by the aquifer material is negligibly small ($K_d = 0$), the last term equals zero and thus the retardation factor depends only on $A_{NW}$ and $K_{IFT}$.

By measuring the retardation factor of the interfacial tracer, the DNAPL-water interfacial area can be estimated if the adsorption isotherm for the interfacial accumulation is known.

EXPERIMENTAL METHODS AND RESULTS

Materials

The alcohols 4-methyl-2-pentanol (4M2P), 1-hexanol (1HEX) and 2,4-dimethyl-3-pentanol (2,4DM3P) were used as partitioning tracers; they are easily detected by
GC-FID analysis even in the presence of high contaminant concentrations in the water. An anionic surfactant, sodium lauryl-ethersulphate (SLES), was used as an interfacial tracer and was analysed by IC conductivity measurements. Isopropanol (IPA) and sodium chloride (NaCl) were used as conservative tracers. NaCl was quantified by conductivity measurements.

An industrial coal tar oil (Ruetgers, Germany), which has a density of 1.2 g cm\(^{-3}\), was employed as the DNAPL in all types of experiment.

Well-graded sand from the River Rhine Quaternary alluvium (1–2 mm diameter) was used in the column and tank experiments.

**Batch experiments**

Batch experiments were performed to determine the equilibrium partitioning coefficients of the alcohols and the tar oil that were used in all following studies. The results are shown in Fig. 1(a) and Table 1.

The drop-weight method was applied to measure DNAPL-water interfacial tension versus interfacial tracer concentration for SLES (Fig. 1(b)). The interfacial tension data obtained were fitted by the following equation (Annable et al., 1998):

\[
\gamma = 1 - \left( \frac{C}{CMC_{FIT}} \right)^{\beta} \left( \gamma_{\text{max}} - \gamma_{\text{min}} \right) + \gamma_{\text{min}}
\]

where \(CMC_{FIT}\) [mmol cm\(^{-3}\)] and \(\beta\) [\(\text{-}\)] are the fitting factors; \(\gamma_{\text{min}}\) and \(\gamma_{\text{max}}\) [dynes cm\(^{-1}\)] are the minimum and maximum interfacial tensions measured. This function was differentiated to estimate the local slope at the desired \(C_{FIT}\) concentration. The introduction of this derivative into equation (6) gives the respective interfacial adsorption coefficient:

\[
K_{FIT} = \frac{\beta \left( \gamma_{\text{max}} - \gamma_{\text{min}} \right)}{2RT(CMC_{FIT})^{\beta}} C_{\text{FIT}}^{\beta-1}
\]

with \(\gamma_{\text{min}} = 10.74\) dynes cm\(^{-1}\), \(\gamma_{\text{max}} = 46.74\) dynes cm\(^{-1}\), \(CMC_{FIT} = 0.0045\) mmol cm\(^{-3}\) and \(\beta = 0.45\), the corresponding \(K_{FIT}\) values for the varying \(C_{FIT}\) values were in the range of \(4.7 \times 10^{-4}\) cm to \(7.6 \times 10^{-4}\) cm (Fig. 1(b), Table 1).

![Partitioning Isotherm](image1.png) ![Interfacial Tension Measurement](image2.png)

**Fig. 1** (a) Partitioning of 4M2P in aqueous and DNAPL phase. (b) Measurement of adsorption characteristics of SLES.
Table 1 Summarized results of the batch, column and tank experiments.

<table>
<thead>
<tr>
<th>Experiment/Tracer</th>
<th>NaCl</th>
<th>IPA</th>
<th>4M2P</th>
<th>1HEX</th>
<th>2,4DM3P</th>
<th>SLES</th>
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<td>$K_{MV}$ [-]</td>
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<td>$K_{MT}$ [cm]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.73 x 10^{-5}</td>
<td>9.24 x 10^{-4}</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Column #8b, SN: 20%, DNAPL blobs, V: 5 m day^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>$R_{d}$ [-] expected</td>
<td>1.11</td>
<td>1.00</td>
<td>1.30</td>
<td>1.79</td>
<td>1.94</td>
<td>1.09</td>
</tr>
<tr>
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<td>1.11</td>
<td>1.00</td>
<td>1.30</td>
<td>1.79</td>
<td>1.94</td>
<td>1.09</td>
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<td>0.0</td>
<td>8.6</td>
<td>7.6</td>
<td>5.5</td>
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<tr>
<td>$A_{SP}$ [cm$^2$ cm$^{-3}$] calculated</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Column #8c, SN: 20%, DNAPL blobs, V: 2.8 m day^{-1}</td>
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<td>1.16</td>
<td>1.00</td>
<td>1.45</td>
<td>2.03</td>
<td>2.59</td>
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<td>1.00</td>
<td>1.45</td>
<td>2.03</td>
<td>2.59</td>
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<td>0.0</td>
<td>12.3</td>
<td>9.7</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>1.08</td>
<td>1.00</td>
<td>1.52</td>
<td>2.69</td>
<td>3.85</td>
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<td>1.00</td>
<td>1.52</td>
<td>2.69</td>
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<td>2.68</td>
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<td>15.0</td>
<td>14.9</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td></td>
</tr>
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<tr>
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<td>1.16</td>
<td>-</td>
<td>-</td>
<td>1.84</td>
<td>n.d.</td>
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<td>1.16</td>
<td>-</td>
<td>-</td>
<td>1.84</td>
<td>n.d.</td>
</tr>
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<td>-</td>
<td>-</td>
<td>0.17</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>24</td>
</tr>
</tbody>
</table>

**Column experiments**

All pulse type PITTs were conducted in glass columns (6 cm diameter, 15 cm length) filled with sand containing a tar oil residual saturation ($S_N$) of exactly 20%. The linear flow-velocity was varied between 1 m day$^{-1}$ and 5 m day$^{-1}$ to evaluate the influence of non-equilibrium transport (Table 1). A further series of columns contained DNAPL as grain-coatings, as blobs, and as pools/ganglia at the same residual DNAPL saturation,
in order to study the influence on the BTCs (kinetics). The varying DNAPL–water interfacial area of these experimental set-ups was used to get a first validation of interfacial tracer data (Fig. 2(a and b) and Table. 1).

**Large-scale tank experiment**

Additional pulse type PITTs were conducted in a large-scale tank (8 m × 3 m × 1 m), filled with sand (1–2 mm), by continuous injection/pumping to create a forced gradient flow field. The withdrawal rate was 1.6 times the injection rate. The injection and extraction wells were only partially penetrating, separated by 0.6 m and aligned in the direction of the tank-gradient flow field (5 m day⁻¹). The wells were located just at the edge of a tar oil blob zone (0.5 m × 1 m × 1 m, Sₚ: 5%). See Table 1 for the results.

**CONCLUSIONS**

The results of the PITTs are in general agreement with the current understanding of partitioning and interfacial tracer behaviour.

Suitability of the PITT was proven for the complex multi-component mixtures (tar oil) which can be found at former coal gasification plants.

The combination of interfacial and partitioning tracers during a PITT not only determines the DNAPL saturation, it also enables the user to distinguish between different DNAPL distribution geometries, which are an important prerequisite for the prediction of the long-time behaviour of the source zone.

However, the PITT-determined tar oil residual saturation of each experiment conducted during this study was smaller than the actual DNAPL-volume. This is believed to be a coupled effect of non-equilibrium tracer transport (resulting in strong asymmetric BTCs) and the interpretation of pulse-type tests using the trapezoidal rule and the method of temporal moments. The generally used formulation does not consider transport under non-equilibrium conditions. It should be noted that all column experiments conducted in this study showed clear mass transfer limitations of partitioning tracers in coal tar. As a consequence of slow kinetics, a reduced tracer retardation, and consequently a smaller saturation compared to the actual one, may result from the unavoidable truncation of the BTC tailing (mass recovery was between 76% and 101%) by the detection limit of the tracer substances, which was 3 to 4 orders of magnitude less than the injected concentration.

These effects may cause limitations of the applicability of PITTs at field scale. Under the given settings (see results of the large scale tank experiment, Table 1) residual tar oil saturation should exceed 5% to obtain significant retardation of the tracers. The approximate location and extension of the zone of residual DNAPL saturation should be known in advance, and the flow velocity has to be smaller than 5 m day⁻¹ to approach equilibrium conditions. Also, improved evaluation approaches, based for example on the fitting of solutions from process-based formulations of the reactive tracer transport, should be developed to account for the truncation of the BTCs.
Acknowledgements This work was funded by Deutsche Forschungsgemeinschaft, Priority programme 546: “Geochemical processes with long-term effects in anthropogenically-affected seepage- and groundwater”.

REFERENCES


