



Characterization of a heterogeneous DNAPL source zone in the Borden aquifer using partitioning and interfacial tracers: Residual morphologies and background sorption

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ABSTRACT

A partitioning interwell tracer test (PITT) was performed in the Borden sand aquifer to characterize an aged heterogeneous DNAPL source zone. This zone evolved during 5 years of natural groundwater flow following the infiltration of 50 L chlorinated solvents DNAPL. To assess the lateral variability of remaining DNAPL mass and morphology, four sweepzones were analyzed. The low saturation residual nature of the source zone required correction of tracer breakthrough data for natural background sorption. Corrected estimates of the DNAPL percentage remaining (total 13.2–16.6%), average saturation (0.05–0.18%) and distribution across the sweepzones were in good agreement with previous findings based on detailed transect monitoring, core analyses and ground-penetrating radar reflection. Using a newly defined metric “average spherical radius equivalent (ASRE)”, sweepzone estimates of the average size of DNAPL presence indicated the dominance of single pore DNAPL blobs and suggested the absence of DNAPL pools. Tracer tests indicated that DNAPL presence in the most DNAPL depleted sweepzone was potentially overestimated due to increased sediment sorption by residualized Sudan IV that was added to the DNAPL infiltrate. As hydrophobic compounds are normally present in spent solvent DNAPL, this suggests that additional sorption needs to be considered when using PITTs to characterize aged DNAPL source zones.

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1. Introduction

Accurate assessment of the mass and spatial distribution of dense non-aqueous phase liquids (DNAPLs) in the subsurface is a prerequisite for efficient, cost-effective remediation of these persistent sources of groundwater contamination (Annable et al., 1998a; Divine et al., 2004). Complicating remediation efforts is the generally highly heterogeneous distribution of DNAPL within source zones. This makes assessment of the extent and mass of DNAPL based on interpolation of core-derived data im-

practical due to the large amount of data required for sufficient three-dimensional resolution (Annable et al., 1998b; Meinardus et al., 2002; Jackson and Jin, 2005). During the past decade, the partitioning interwell tracer test (PITT) technique has evolved for the determination of the mass, distribution and morphology of subsurface DNAPL contamination. So far, the ability of partitioning and interfacial tracers to determine DNAPL mass and DNAPL–water interfacial area has only been verified in column-scale lab experiments (Saripalli et al., 1997; Kim et al., 1999; Noordman et al., 2000; Dai et al., 2001). Following the controlled releases of perchloroethylene (PCE) in an aquifer isolated by sheet piling, (Brooks et al., 2002) PITTs were evaluated for characterizing DNAPL in the field. Unfortunately, tracer degradation and remedial fluid interference complicated this evaluation. In recent years, partitioning tracer tests have

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been applied in the field to assess the success of DNAPL remediation efforts in removing contaminant mass (Meinardus et al., 2002; Divine et al., 2004). As PITTs are increasingly used for evaluating remediation performance by comparing the pre- and post-remediation estimates (Cain et al., 2000), careful evaluations of its potential and limitations under conditions of residual DNAPL are needed (Divine et al., 2004).

An intensively studied DNAPL source zone in the aquifer at CFB Borden, Ontario (Fig. 1), provided an excellent opportunity to perform a PITT to evaluate its ability to characterize the highly residual source zone that formed after 50 L of chlorinated solvent DNAPL had been infiltrated 5 years prior. In preparation of site remediation, the PITT was performed to study the nature of the remaining residual DNAPL in terms mass, morphology and spatial heterogeneity. The suspended nature of the residual DNAPL (Fig. 2) and the relatively homogeneous hydraulic properties of the Borden aquifer minimized potential underestimation of DNAPL volume due to tracers bypassing DNAPL in low-K strata or pools (Willson et al., 2000; Wilson et al., 2000; Jalbert et al., 2003). Besides data on the infiltrated DNAPL, ground-penetrating radar data on the reflection of DNAPL surfaces (Hwang et al., 2008) and detailed sampling data from sediment cores (Thomson, 2004) were available. This high level of insight allowed assessment of PITT performance and detailed evaluation of PITT-derived parameters. Our main objectives were to 1) provide a field evaluation of the PITT performance and reliability in characterizing a small, highly residualized source zone 2) to further insight in the potential and limitations of field PITT-derived parameters in assessing residual NAPL saturations and interfacial areas.

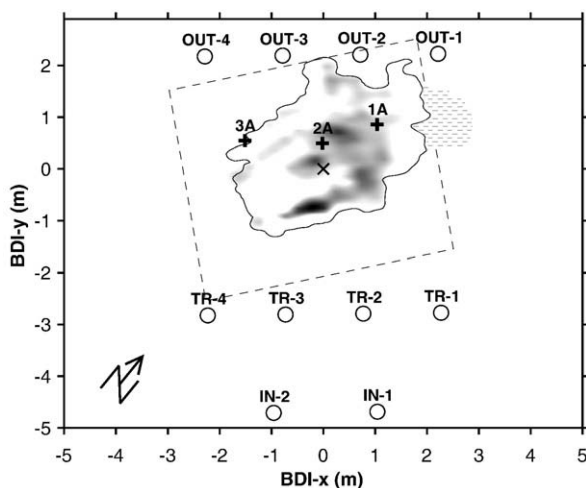


Fig. 1. Plan view of the PITT layout at the Borden DNAPL Infiltration (BDI) site, showing the two hydraulic push wells (IN, 0.8 L/min/well), the four tracer injection wells (TR, 0.25 L/min/well for 4 days) and the 4 pumping wells (OUT, 0.4 L/min/well). Data loggers in the OUT-1 and OUT-4 wells recorded water table elevations. Cross depicts the location where 50 L of DNAPL was infiltrated. The grey shades indicate the DNAPL distribution two years after DNAPL infiltration based on relative reflection from GPR data (Hwang et al., 2008). The surrounding outer line indicates the DNAPL extent two weeks after DNAPL infiltration. The three crosses indicate the locations of cores that were studied in vertical detail for DNAPL distribution (Thomson, 2004). The hatched area marks an area outside the GPR coverage (square) where pure phase was detected in monitoring wells a few weeks after DNAPL infiltration.

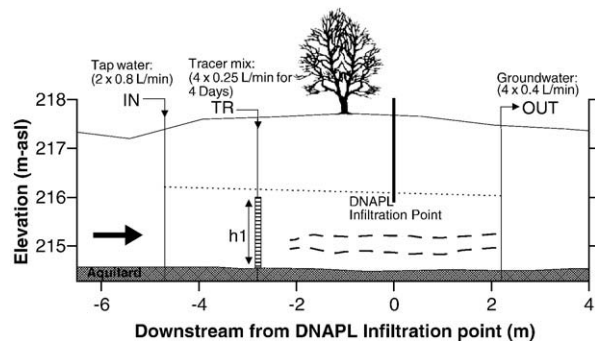


Fig. 2. Cross section of the PITT layout. Dotted line indicates water table elevation 10 days after PITT start. Dashed lines indicate the approximate depths of two DNAPL reflection surfaces distilled from GPR analysis (Hwang et al., 2008). The 4000 L tracer mix was injected over the bottom 1.5 m (h_1 , vertical sweep height) of the aquifer. The hydraulic push and pumping wells were fully penetrating. Natural groundwater flows from left to right.

2. Methods

2.1. Location

The study site is located in the forested area of the Borden research site, close (<25 m) to where previous studies on DNAPL migration and remediation took place in a 9 by 9 sheet pile cell (Brewster et al., 1995; Nelson et al., 2001; Cave et al., 2007). Here, the unconfined aquifer is about 3.2 m thick and is underlain by a regional silt and clay unit. The water table varies seasonally between 0.5 and 1.5 m below ground surface (Fig. 2). Natural groundwater velocity at the site is variable over the year but averages at 15 ± 8 cm/day.

Five years prior to the PITT, a controlled infiltration of a dyed (Sudan IV at 0.94 g/L) DNAPL mixture of PCE (45 vol.%), TCE (45 vol.%) and chloroform (10 vol.%) had created a heterogeneously distributed DNAPL, suspended in the unconsolidated Borden sand aquifer (Laukonen, 2001; Thomson, 2004; Hwang et al., 2008). At the time of the PITT, chlorinated solvent concentrations in groundwater indicated that natural dissolution had fully depleted the more soluble TCE and chloroform components from the original DNAPL mixture, leaving PCE as the only component remaining.

2.2. Partitioning interwell tracer tests

2.2.1. Field PITT at the Borden DNAPL Infiltration (BDI) site

The tracer solution used during the PITT was created by adding bromide (as NaBr), methanol and 2-methyl-2-propanol (TBA) as conservative tracers, n-hexanol (n-HEX), 2,4-dimethyl-3-pentanol (DMP), 2-octanol (2-OCT), and 3,5,5 trimethyl-1-hexanol (TMH) as partitioning tracers and sodium dodecylbenzenesulfonate (SDBS) as an interfacial tracer to 4000 L of tap water. Tracer concentrations and characteristics are listed in Table 1. Tracers were injected into four wells at 0.4 L/min each for three days. For each injection well the injected solution was distributed equally across three adjoining 0.5 m long screened intervals to ensure homogeneous distribution of the tracers across a sweepheight of 1.5 m. Approximately 5 m down-gradient from each injection well, a fully screened well was pumped at a rate of 0.4 L/min, creating four PITT “sweepzones”

Table 1

Properties of the conservative, partitioning (Brooks et al., 2002) and interfacial (Cho and Annable, 2005) tracers, corrected for groundwater temperature (10 °C). The partitioning coefficients (K_{NW}) and interfacial adsorption coefficient (K_i) are for PCE–water equilibrium.

| Tracer | Tracer input (mg/L) | K_{NW} (–) | K_i (cm) |
|--|---------------------|--------------|------------|
| Bromide (Br) | 321 | 0 | |
| Methanol (MeOH) | 1873 | 0 | |
| 2-Methyl-2-propanol (TBA) | 773 | 0 | |
| n-Hexanol (n-HEX) | 733 | 8 | |
| 2,4-Dimethyl-3-pentanol (DMP) | 498 | 30 | |
| 2-Octanol (2-OCT) | 216 | 110 | |
| 3,5,5-Trimethyl-1-hexanol (TMH) | 77 | 230 | |
| Dodecylbenzenesulfonic acid sodium salt (SDBS) | 176 | | 0.00284 |

(Fig. 1). The pumping wells and two hydraulic “push” wells (0.8 L/min in each well), situated upgradient from the injection wells, were started a week prior to the tracer injection to ensure a stable, steady state flow condition. Water samples from the four pumping wells were obtained several times a week, for 59 days.

2.2.2. Laboratory background PITTs

Column tests were conducted in the laboratory to assess the background sorption for the partitioning and interfacial tracers used in the field PITT. Sediment samples were taken from two different cores in the source zone area, one pristine sediment sample from above the DNAPL infiltration depth (core BDI-1, depth 40–80 cm) that showed non-detects for chlorinated solvents and a sediment sample (core BDI3, depth 160–210 cm) which contained residual Sudan IV but no remaining DNAPL. Sudan IV had been added as a color agent to the originally infiltrated DNAPL mixture.

The sediments were wet-packed in glass columns (L: 15 cm, ID: 4.8 cm) with Teflon end pieces (Kontes Company, Vineland, NJ). Compaction of sediment in the columns was ensured by stirring and vibrating each added sediment layer with a rod before adding the next layer. Before starting the tracer injection, the column was flushed with deionised water until the effluent was clear. Using a syringe pump (Harvard Apparatus, South Natick, MA), 3 ml of tracer solution was injected after which the influent was switched to water. Effluent breakthrough curves (BTCs) were measured under steady water flow (0.5 ml/min), similar to field PITT flow conditions with a tracer pulse-input boundary condition. Effluent samples were collected in 2 mL vials with a 400 µL inserts for analysis.

2.2.3. Analytical methods

Bromide concentrations were determined using a Dionex AI-450 ion chromatograph with a conductivity detector. Alcohol tracers and PCE were analyzed by gas chromatography (Autosystem XL) with a HS 40 headspace sampler (Perkin Elmer, Norwalk, CT) using a flame-ionization detector. SDBS was analyzed using a high performance liquid chromatography (HPLC) system (Perkin Elmer, LC 200, Norwalk, CT) with a UV detector (225 nm). The detection limit for the alcohol tracers and PCE was 10 µg/L and for SDBS 100 µg/L.

2.2.4. Calculation of average NAPL saturations and DNAPL–water interfacial areas

The retardation factor (R) of a partitioning tracer was determined directly from the tracer breakthrough curves (BTCs) recorded at each extraction well and is defined relative to the transport of the conservative tracer bromide. Retardation of tracers was calculated with respect to the first moment of bromide breakthrough times (Jin et al., 1995):

$$R_t = \frac{\bar{t}_p}{\bar{t}_c} \quad (1)$$

where \bar{t}_p and \bar{t}_c are the mean travel times for the partitioning and conservative tracers, and first moment of tracer breakthrough is (Jin et al., 1995):

$$\bar{t} = \frac{\int tC(t)dt}{\int C(t)dt} - \frac{t_s}{2} \quad (2)$$

where t_s is the duration of the injection pulse (3 days). For the partitioning tracers, average NAPL saturation (S_n) for each tracer sweep area was calculated using (Annable et al., 1998b):

$$S_n = \frac{R-1}{R + K_{NW}-1} \quad (3)$$

Where, K_{NW} is the NAPL–water partitioning coefficient (Table 1). The retardation factor was corrected for the observed background retardation (R_{BG}) by using (Brooks and Wise, 2005):

$$R_{corr} = R_t - (R_{BG} - 1) \quad (4)$$

Where R_t is the uncorrected retardation factor for tracer breakthrough and R_{BG} is the retardation factor observed in the background tracer lab tests with pristine sediment (Table 2).

2.2.5. Interfacial tracer SDBS

SDBS was used as an interfacial tracer. For interfacial tracers, the NAPL–water interfacial area is calculated as (Saripalli et al., 1997):

$$a_{NW} = \Theta_w \frac{R_{if} - 1}{K_i} \quad (5)$$

where R_{if} is the retardation factor for SDBS and K_i is the interfacial adsorption coefficient, which describes the equilibrium adsorption of the tracer between the interface and the bulk solution, and is the determined water-filled porosity (0.332) of the aquifer (Thomson, 2004). This value was corroborated by the behaviour of the non-reactive tracers in the lab tests.

The adsorption of SDBS in dilute aqueous solutions at the DNAPL–water interface can be described by Gibbs adsorption equation (Saripalli et al., 1997):

$$\Gamma = - \frac{1}{RT} \left(\frac{d\gamma}{dC} \right) C \quad (6)$$

where Γ is the Gibbs surface excess of surfactant (mol/cm²), γ is the interfacial tension between DNAPL and water (J/cm²), C is

Table 2
PITT recovery and retardation results.

| Tracer | Total Recovery | Sweepzone retardation factors ^a | | | | Background retardation factors | | |
|-------------------|----------------|--|------|------|------|---|---|---------------------------------|
| | | 1 | 2 | 3 | 4 | Lab ^b natural sediment | Field ^c natural sediment | Lab ^d Sudan IV |
| Br | 1.08 | | | | | | | |
| MeOH | 1.02 | 1.01 | 1.05 | 1.03 | 1.03 | 1.00 | 1.00 | 1.00 |
| TBA | 1.01 | 1.01 | 1.04 | 1.03 | 1.03 | 1.00 | | 1.00 |
| N-HEX | 0.94 | 1.01 | 1.06 | 0.98 | 1.01 | 1.00 | | 1.01 |
| DMP | 1.15 | 1.03 | 1.07 | 1.05 | 1.04 | 1.01 | 1.00 | 1.02 |
| OCT | 0.97 | 1.08 | 1.18 | 1.09 | 1.08 | 1.04 | 1.02 ^e | 1.08 |
| TMH ^f | 0.87 | 1.29 | 1.41 | 1.19 | 1.13 | 1.07 | 1.04 ^e | 1.13 |
| SDBS ^f | 1.03 | 1.94 | 1.82 | 1.72 | 1.51 | 1.29 | | 1.42 |

^a Calculated retardation factors for the observed BTCs in the sweepzones, uncorrected for background tracer sorption.

^b Background retardation factors determined in the lab on uncontaminated Borden sediment (this study).

^c Derived from a background field PITT at Borden (1996, unpublished data), 50 m down-gradient from the studied DNAPL source zone.

^d Background retardation factors determined in the lab on previously contaminated Borden sediments that contained residual Sudan IV (this study).

^e Calculated based on observed retardation factor for 2-ethyl-1-hexanol of 1.04.

^f Recovery and retardation factors for SDBS and TMH are based on extrapolated BTCs, except for TMH in sweepzone 3 (See text for further details).

the aqueous phase SDBS concentration (mol/cm^3), R is the universal gas constant ($\text{J}/\text{mol}/\text{K}$) and T is temperature (K).

Eq. (6) was used to estimate the distribution coefficient (K_i) at C_{max} at groundwater temperature (10°C) following (Saripalli et al., 1997):

$$K_i = - \left. \frac{1}{RT} \frac{d\gamma}{dC} \right|_{C_{\text{max}}} \quad (7)$$

Since the interfacial sorption isotherm is a function of tracer concentration, a representative K_i value was approximated for each sweepzone based on the maximum SDBS concentration (average $C_{\text{max}} = 0.08 \pm 0.02 \text{ mM}$) observed at the pumping wells (Annable et al., 1998a; Kim et al., 1999, Fig. 3). The R_{fit} was corrected with Eq. (4) using the background retardation by the sediment matrix as determined in the laboratory tracer tests.

During the course of the PITT measured pH values at the pumping wells remained stable (7.4 ± 0.1). Ionic strength remained at the dilute average groundwater background of 6.7 meq/L with a maximum of 10 meq/L during bromide tracer breakthrough, so ionic strength effects on the interfacial tracer behaviour in the sweepzones were expected to be negligible (Rosen, 2004).

3. Results and discussion

3.1. Tracer recovery

Recovery for all tracers was good to excellent, ranging from 0.87 for the TMH to 1.15 for the DMP partitioning tracers, with 2-OCT showing best recovery of the partitioning tracers at 0.97. Though particularly the straight chain alcohols tracers could be susceptible to biodegradation (Brooks and Wise, 2005), recovery data and BTCs show no indications that this affected tracer behaviour significantly during this PITT. Based on the

average breakthrough of the conservative tracers, average groundwater flow velocities during the PITT ($31.6 \pm 5.5 \text{ cm}/\text{day}$) were a bit higher than the maximum natural groundwater velocity ($23 \text{ cm}/\text{day}$) estimated for this site. However, both the BTCs from the lab and from the field test (Fig. 3) did not show the extensive tailing expected for rate-limitations in the partitioning processes, nor did the conservative tracer breakthrough curves indicate physical limitations on tracer transport.

3.2. NAPL saturation estimates

The relatively small partitioning coefficient for n-hexanol (Table 1) resulted in insufficient retardation with respect to

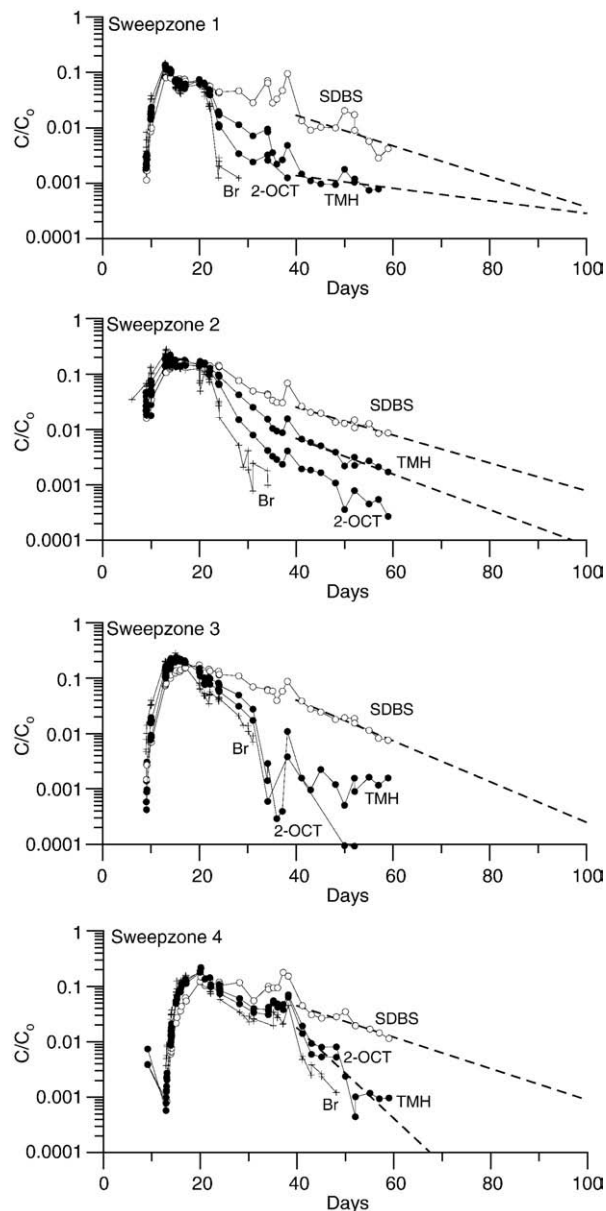


Fig. 3. Breakthrough of conservative (Br), partitioning and interfacial tracers for sweepzones 1–4. Dashed line indicates the extrapolation (data >40 days) using an exponential decay function obtained by least squares approximation.

the conservative tracers to allow calculations of NAPL saturation (Table 2). Overall observed retardation of the other partitioning tracers was low compared to other studies using the same tracers (Jawitz et al., 2000; Noordman et al., 2000), in keeping with the residual and heterogeneous nature of the DNAPL distribution at this site. Retardation was strongest for the tracers TMH and SDBS (Table 2). Due to their strong retardation, breakthrough was not complete (Fig. 3). To minimize truncation errors in the tracer-derived estimates (Annable et al., 1998b), the breakthrough curves were extrapolated to 100 days using an exponential decay function that was fit to the last 20 days (day 40–60) of the PITT to complete the breakthrough data for the zeroth and first moment calculations. Resulting fits were relatively poor, except for sweepzone 2 (SDBS and TMH) and 3 (SDBS) with $R^2 > 0.86$. The breakthrough of TMH in sweepzone 3 could not be extrapolated because of a lack of an exponential decay trend (Fig. 3c). Extrapolation of the tail of the breakthrough curves increased the calculated retardation factors by up to 6.2% for the TMH (sweepzone 1, Fig. 3a) and up to 8.2% for the SDBS tracer (sweepzone 2, Fig. 3b) representing up to 35% and 21% of initial S_n and a_{NW} estimates before correction for background sorption.

Natural background sorption of non-conservative tracers onto sedimentary components such as organic matter proved to be a significant factor. Therefore, NAPL saturation estimates were corrected using Eq. (4) and the retardation factors obtained from the laboratory background sorption tests using sediment not exposed to DNAPL (Table 2). The background corrected average NAPL saturations for the four sweep volumes were calculated for 2-octanol, TMH and DMP (Fig. 4). The trend in the estimated NAPL saturation across the four sweepzones was similar for the various tracers. The highest DNAPL saturation estimates were obtained for sweepzone 2 and the lowest for sweepzones 1 and 4. These differences in estimated NAPL saturation are consistent with the GPR-derived DNAPL

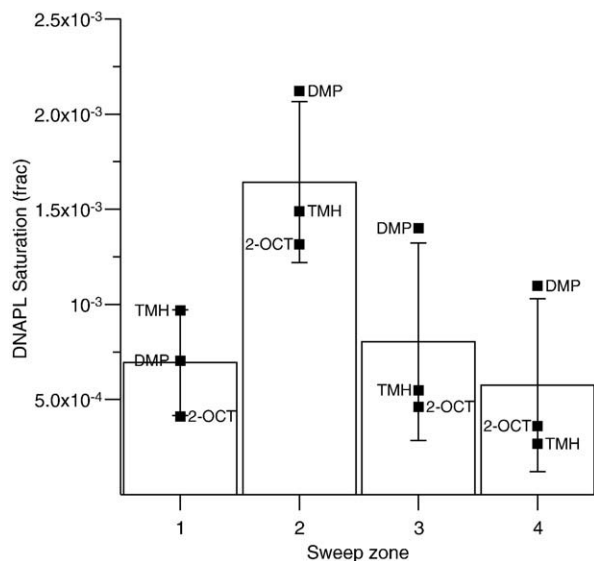


Fig. 4. Average DNAPL saturations in the swept aquifer volumes, corrected for natural background retardation (Table 2). Error bars indicate standard deviations for the plotted tracer values.

distribution 2 years after DNAPL infiltration as shown in Fig. 1 (Hwang et al., 2006).

For sweepzones 2 to 4, DMP resulted in the highest estimates of average NAPL saturations, while lower, similar estimates were derived from the BTC of 2-octanol and TMH (Fig. 4). The higher estimates for DMP are likely an overestimation given its small retardation factor (1.02–1.06, Table 2), causing higher uncertainties in the NAPL saturation estimates (Brooks and Wise, 2005). Therefore, DMP derived saturation data was not further processed. Sweepzone 1 differed from the other sweepzones in that TMH rather than DMP resulted in the highest NAPL saturation estimate, while 2-octanol resulted in the lowest NAPL saturation estimate. Overall, 2-octanol seemed to behave as the most consistent tracer across the four sweepzones, likely since it did not require extrapolation of its BTC, showed good retardation and excellent recovery. However, as the retardation factors for 2-octanol of less than 1.2 are less favourable (Jin et al., 1995; Jin et al., 1997) than for TMH (1.13–1.41, Table 2) the behaviour of both partitioning tracer is further evaluated in this study.

Even though the GPR-derived data (Hwang et al., 2006) allowed a tight design of the PITT zone (about 10 m³ soil volume) around the extent of the DNAPL source zone, the range in estimated NAPL saturations of 0.0007–0.002 are among the lowest field PITT-based estimates reported in the literature (Annable et al., 1998a,b; Brooks et al., 2002; Meinardus et al., 2002; Divine et al., 2004), in keeping with the aged nature of the studied source zone. Our estimates for average pore saturation (Fig. 4) are closest to those found by a PITT ($S_n = 0.001$ –0.0032) that followed the remediation of a PCE DNAPL source zone using alcohol flushing (Jawitz et al., 2000).

The PITT-derived average NAPL saturations (Fig. 4) allow the estimation of total DNAPL mass remaining (Table 3). The total estimated volume of DNAPL was 6.6 L and 8.3 L based on 2-octanol and TMH retardation data, respectively. These volumes represent 13.2% and 16.6% of the initially released multi-component DNAPL volume, or 29–37% of the original PCE volume fraction. These PITT-derived estimates are slightly higher than the independent estimate of 10% DNAPL remaining that was derived from cumulative mass discharge calculations for a high-resolution transect located immediately down-gradient of the DNAPL source zone. However, the PITT-derived estimates of DNAPL remaining, are higher than estimates (4.4% and 9%) from the GPR measurements taken shortly after the PITT (Hwang et al., 2006). These lower GPR estimates may be due to the inability of GPR to detect part of the DNAPL that is present at very low pore saturations. This is supported by the observation that, already 3 years before the PITT, the integrated GPR reflection signal could not be discerned from the background signal (100%), for all but the area of sweepzone 2. Consequently, the background corrected signal of sweepzone 2 (120%) accounted for 98% of the total background corrected signal.

Due to the residual nature of the distributed DNAPL, PCE dissolution might have had a significant effect on DNAPL volume estimates. Calculated PCE fluxes during the PITT recorded at the extraction wells were highest for OUT-2 (up to 13.9 g/day) followed by OUT-3 (up to 1.8 g/day), in agreement with the highest calculated NAPL saturations (S_n) for their respective sweepzones (Fig. 4). PCE concentrations were non-detect in extraction wells OUT-1 and OUT-4. Overall, the total PCE

Table 3

Estimated DNAPL saturations (S_n) and volumes, DNAPL–water interfacial areas (a_{NW}), morphology indices (H) and average spherical radius equivalent (ASRE) values for the four sweepzones are also shown. All data are corrected for natural background sorption of tracers. Values for TMH are based on extrapolated breakthrough curves (Fig. 3), except for sweepzone 3.

| Tracer | Sweepzone | | | |
|--------|------------------------|---------|---------|---------|
| | 1 | 2 | 3 | 4 |
| | S_n (-) | | | |
| 2-OCT | 4.1E-04 | 1.3E-03 | 4.6E-04 | 3.6E-04 |
| TMH | 9.7E-04 | 1.5E-03 | 5.5E-04 | 2.7E-04 |
| | PCE (L) | | | |
| 2-OCT | 0.99 | 3.09 | 1.21 | 1.33 |
| TMH | 2.33 | 3.50 | 1.44 | 0.99 |
| | Total PCE (L) | | | |
| 2-OCT | | | 6.63 | |
| TMH | | | 8.26 | |
| | a_{NW} (cm^{-1}) | | | |
| SDBS | 64 | 88 | 77 | 41 |
| | H (cm^{-1}) | | | |
| 2-OCT | 156,308 | 67,027 | 166,683 | 112,530 |
| TMH | 66,461 | 59,232 | 140,417 | 152,118 |
| | ASRE (μm) | | | |
| 2-OCT | 0.19 | 0.45 | 0.18 | 0.27 |
| TMH | 0.45 | 0.51 | 0.21 | 0.20 |

dissolution during the PITT amounted to less than 0.1% of the estimated NAPL volume present.

3.3. NAPL–water interfacial areas

Calculation of DNAPL–water interfacial areas was based on the breakthrough behaviour of the SDBS tracer. Values for DNAPL–water interfacial areas followed a pattern keeping with the NAPL saturation estimates, with the highest for sweepzone 2. However the contrast between the interfacial values determined for the individual sweepzones were smaller than for NAPL saturation. In particular, the estimated interfacial area was relatively high for sweepzone 1 (Table 3).

All reported interfacial areas are within the range of those reported in other field studies (e.g. Annable et al., 1998a). A first impression on the morphology of DNAPL present in the sweepzones was obtained by calculating the morphology index ($H = a_{NW} / \theta S_n$). The relatively high ($>30,000$) indices obtained (Table 3) suggests that no DNAPL is present as pools (Annable et al., 1998a).

3.4. Evaluation of PITT-derived DNAPL characterization

3.4.1. Comparison with core-derived NAPL saturations

An earlier study by Thomson (2004) on sediment cores through the source zone allowed comparison of the PITT-derived average NAPL saturation estimates for the 4 sweepzones with core-data derived NAPL pore saturation data. Detailed, depth discrete sampling (1 cm spacing) of three continuous cores was performed two years prior to the PITT (Fig. 1). The S_n estimates based on total VOC mass concentrations in these samples show the heterogeneous vertical distribution of DNAPL

in this source zone (Fig. 5). The highest DNAPL saturations were estimated for core 2A, with local peaks of NAPL saturation of up to 4% (Fig. 5). DNAPL saturation estimates were lower for core 1A, with a peak of 1.3%. DNAPL presence was concentrated across 4 to 20 cm intervals for core 1A and core 2A, respectively. DNAPL presence was not detected in core 3A (Thomson, 2004). These observations are not in contrast with the highest estimated NAPL saturation (S_n) values for sweepzone 2 and 3 (Fig. 4).

The high level of characterization of the studied source zone allowed a relatively tight design of the PITT in both the horizontal (Fig. 1) and vertical directions (Fig. 2). This minimized the flushing of uncontaminated sediments by the injected tracer volume and maximized the detectability of DNAPL in the sweepzones. However, due to the heterogeneous vertical distribution of DNAPL, as observed in the sediment cores, a large fraction of the injected tracer solution did not interact with DNAPL. In comparison to the sweep height of the PITT (1.5 m, Fig. 2), DNAPL was only detected in a layer of 4 cm thick for core 1A. For core 2A, all DNAPL was present within a vertical range of 76 cm, with high variability within this interval. To enable comparison with the PITT-derived saturation values, the core-derived saturations were averaged over a 1.5 m interval. These “sweep-averaged” pore saturations for cores 1A and 2A were 0.014% and 0.39% respectively (Fig. 5). These core-based values represent estimates of PITT-derived average NAPL saturations (S_n), assuming identical vertical DNAPL distribution throughout the swept aquifer volumes. In comparison to the actual S_n estimates for the PITT (Fig. 4), the sweepzone averaged value for core 1A is five times lower than the lowest averaged S_n value (sweepzone 4), while the sweepzone averaged value for core 2A is two times higher than the highest averaged S_n (sweepzone 2). As core 2A is just down-gradient of the original DNAPL release point (Fig. 1), the DNAPL distribution observed in this core is probably

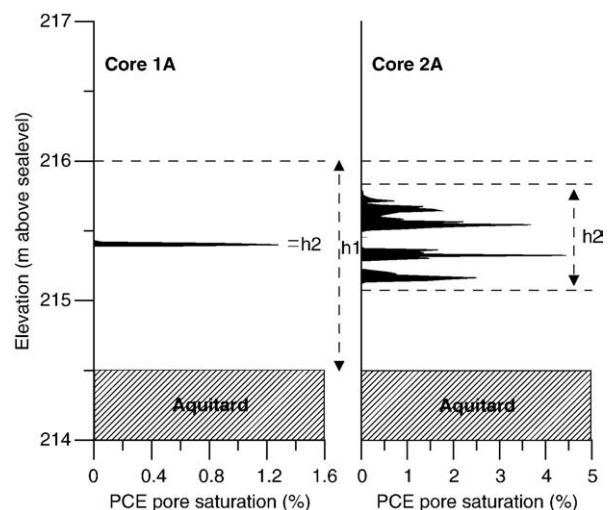


Fig. 5. NAPL saturation of source cores 1A and 2A (3A did not contain free phase DNAPL), (Thomson, 2004). The average saturation over the PITT vertical sweep height is 1.5 m (h_1 , Fig. 2) is 0.014% (core 1A) and 0.39% (core 2A). Calculated average NAPL saturation for an imaginary sweep height (h_2) across the height of the DNAPL containing interval for core 1A (4 cm) and 2A (76 cm) is 0.54% and 0.77% respectively.

representative for the most contaminated part of the remaining residual source zone. Thus, the PITT-derived estimates of NAPL saturation fall within the range of expected average NAPL saturations for the sweepzones based on the available core data.

3.4.2. DNAPL morphology

Recent studies have demonstrated the importance of particle and pore size characteristics with respect to PITT-derived interfacial areas (Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2008). Therefore, the data for the average NAPL saturations (S_n) and interfacial areas (a_{NW}) in the four sweepzones studied were used to calculate the effective radius that DNAPL blobs would have, assuming that all blobs are spherical and of equal size. We define this as the “average spherical radius equivalent (ASRE)” and is calculated using:

$$ASRE = \frac{3S_n\theta}{a_{NW}} \quad (8)$$

Note that morphology index values ($H = a_{NW}/\theta S_n$, e.g. Annable et al., 1998a) can be converted into ASRE values using:

$$ASRE(\mu\text{m}) = \frac{30,000}{H(\text{cm}^{-1})} \quad (9)$$

When DNAPL is present in interconnected multi-pore ganglia or pools (Dobson et al., 2006) the assumption of spherical geometry is not justified and the ASRE value would only provide an indication of relative dimensions. However, if DNAPL is largely present as residual, as in this study, blobs are more likely contained within single pore spaces (Powers et al., 1994; Conrad et al., 2002), rendering the assumption of spherical geometry reasonable.

The calculated ASRE values for the four sweepzones studied range from 0.18 to 0.51 μm (Table 3). These values are similar to the ASRE values calculated for a field PITT that evaluated the performance of interfacial tracers (Fig. 6, Annable et al., 1998a). In contrast, recent detailed lab studies on the determination of DNAPL morphology were performed under high average NAPL saturation and resulted in much lower interfacial area estimates than would be expected at field sites where DNAPL source zones have undergone considerable aging (Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2008). Consequently, the calculated ASRE values for these laboratory studies, as presented in Fig. 6, are much higher than those found under field conditions.

To further evaluate their potential use, ASRE values were calculated using tracer test data from Dobson et al. (2006). In that laboratory study, NAPL phases were entrapped within various grain size fractions with a range of median grain diameters between 300 and 1100 μm . They concluded that the entrapped NAPL was likely present as non-spherical multi-pore ganglia. Analysis of the ASRE values (91–1845 μm , Fig. 6) calculated for that study, supports their conclusion, as these values are in excess of the expected pore sizes within these grain size fractions.

In the presence of pore size indications, evaluation of ASRE values may be able to provide more detailed evaluation of

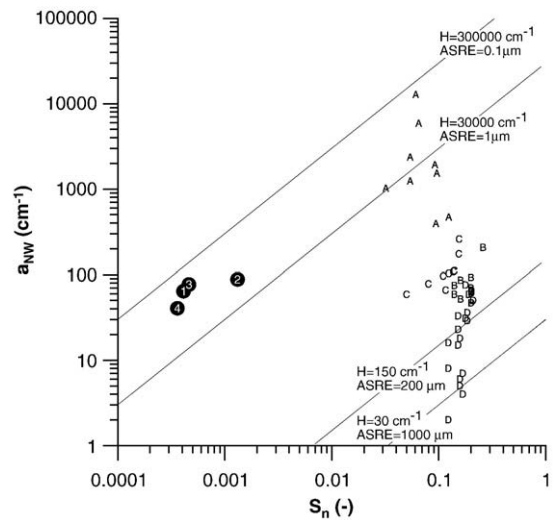


Fig. 6. Sweep-averaged NAPL saturations (S_n) versus estimated NAPL–water interfacial (a_{NW}) areas. Values for sweepzones 1–4 in this study (black circles) are derived from the 2-octanol retardation data, corrected for the natural background sorption (Table 2). The average spherical radius equivalent ($ASRE = 3 * S_n \theta / a_{NW}$) represents the average radius that the DNAPL blobs would have if they were all spherical. H represents the morphology index. A–D represent data from (Annable et al., 1998a; Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2008). Except for A, these were all derived from lab experiments.

NAPL morphologies. The few studies that have investigated pore sizes in the Borden aquifer point to effective pore sizes of a few (<3) microns (Ball et al., 1990; Hinedi et al., 1993). In this range, the calculated DNAPL saturation values for the obtained submicrometer ASRE values for the four sweepzones would indicate pore saturations up to 1% based on spherical volume calculations. Although these pore saturation estimates are highly sensitive due the third-power dependency on pore size, the order of magnitude is similar to that of the core-derived DNAPL pore saturations (Fig. 5).

3.5. Sources of background sorption of tracers

3.5.1. Background sorption by sedimentary components

The NAPL saturation (S_n) and NAPL–water interfacial values discussed so far were corrected for the natural background tracer sorption on sediment using data from the background lab tests. As a check on the representativeness of the lab-derived background retardation factors a comparison was made with data from a background field PITT previously performed at Borden (1996, unpublished data), 50 m down-gradient from the studied DNAPL source zone. As this field PITT had used different partitioning tracers, the excellent linear correlation between the calculated K_d values and the K_{NW} values (Brooks et al., 2002) for partitioning tracers in both lab and field (not shown, $R^2 > 0.97$, through origin) was used to assume that PCE–water partitioning is proportional to sediment–water partitioning for the Borden aquifer. The calculated field background retardation factors are in good agreement with those measured in the laboratory column experiments of this study (Table 2), supporting the representativeness of the background sorption data derived from the lab tracer tests,

although the slight differences could be due to natural sediment variability within the relatively homogeneous Borden aquifer.

The determined background sorption to sedimentary components proved to be significant in this study. Not correcting for this would result in an overestimation of total PCE volumes by up to 159% (2-OCT) for the partitioning tracers and up to 235% (sweepzone 4) for the interfacial areas (SDBS) compared to the background corrected estimates (Table 3). Previously, background sorption of tracers by sedimentary organic matter and mineral components present in aquifer sediment has also been shown to be significant in post-remediation tracer tests (Jin et al., 1997; Jawitz et al., 2000). The current study shows that, even under pre-remediation conditions, sediment background sorption can be significant, given sufficient time for natural dissolution of DNAPL to form a highly residual source zone.

3.5.2. Background sorption by residual high-molecular components

NAPL phases commonly contain high-molecular weight components, such as the non-solvent concentrations found in the well-characterized DNAPL at the Savannah River Site (Dou et al., 2008) which contains long chain alkyl esters at about 0.5 g/L. Residualization of these high-molecular weight components is likely to impact tracer retardation of particularly interfacial tracers as this process adds hydrophobicity to the surfaces of sedimentary components which may cause false-positive signal for presence of NAPL during PITTs (Jawitz et al., 1998; Lee et al., 1998; Rao et al., 2000), such as the “pitch-like” fraction as found after surfactant/alcohol flush remediation of a complex multi-component LNAPL (Jawitz et al., 1998). As about 15% of the originally infiltrated 50 L of DNAPL remained at the time of the PITT (Table 3), it is likely that residualization of Sudan IV has occurred to some extent in the source zone studied. Therefore, we tested the significance of elevated background sorption by residual Sudan IV, the hydrophobic high-molecular weight dye (MW = 380.44) that had been added to the DNAPL mixture originally infiltrated at the study site. The presence of Sudan IV was previously observed in core samples at the study site by a distinct light pink color upon sample preparation in methanol, including samples that did not show detectable presence of DNAPL components (Thomson, 2004). Therefore, a lab tracer test was conducted on a sediment sample selected from a post-PITT core in the source zone of the study site as the pink coloration in methanol and the absence of chlorinated solvent components in this sample indicated the presence of residual Sudan IV. The tracer retardation factors determined for this sample were elevated for both partitioning and interfacial tracers, as compared to the natural background sorption determined for sediment unaffected by residual Sudan IV. For the interfacial tracer SDBS, this effect is particularly strong (Table 2). Unfortunately attempts to develop a reliable method to spectrophotometrically quantify Sudan IV concentrations in methanol extracts were unsuccessful. For some perspective, however, the upper limit of residualized Sudan IV content in this sediment sample would be 0.016% (dry weight), based on the initial Sudan IV concentration (0.94 g/L) in the DNAPL and assuming 100% initial pore saturation. Even at more realistic initial pore saturations, this amount, equivalent to 0.01% organic carbon, would be a significant addition to the

natural OC content (f_{oc}) of 0.02%, reported for the Borden aquifer (Ball et al., 1990).

As the presence of locally residualized Sudan IV likely resulted in elevated tracer sorption within areas of the flow domain of the sweepzones, the question arises to what extent this has affected the overall PITT-derived parameters and how correction could be achieved. At least the total amount of Sudan IV introduced into the source zone is known, although its distribution is presumably as heterogeneous as that of the initial DNAPL. Further complicating a correction for this phenomenon at any site would be the unknown extent to which the Sudan IV, or other hydrophobic high-molecular weight (HMW) equivalent, is either residualized or concentrated in the remaining DNAPL in the source zone, as this would depend on the degree of homogeneous dissolution or DNAPL interconnectedness within the source zone architecture. Finally, a meaningful correction would also require the reliable quantification of residualized HMW in relation to observed tracer retardation.

In assessing whether the effects of residual Sudan IV in the current study would require a correction of PITT-derived parameters, the total amount of Sudan IV introduced to the source zone was compared with the total amount of sedimentary organic matter that was present in the sweepzones. This analysis brought forward that sedimentary organic matter represented an amount of organic carbon that was more than 300 times larger than the 49 g of Sudan IV introduced. So even though tracer sorption was affected locally, it is not likely that residualized Sudan IV significantly affected overall tracer sorption in the sweepzones even if this amount completely residualized. This is especially the case for the sweepzones through the hot spot of the DNAPL source zone, which shows lower degrees of DNAPL depletion. For sweepzone 1, where DNAPL depletion was strongest based on the disappearance of DNAPL reflection observed by GPR after 2 years (Fig. 1), the relatively high estimates for S_n by the TMH tracer (Fig. 4; Table 3) and the interfacial area by SDBS (Table 3) may have partly resulted from increased sorption by residualized Sudan IV in addition to the advanced dissolution that has likely further reduced DNAPL blob sizes.

Although the effect of residualized Sudan IV was not likely significant for overall tracer sorption in our study, the observed increased tracer sorption in individual samples represents the potentially significant effect of residualized HMW compounds on PITT-derived parameters. Compared to the NAPL source zone studied, most significant effects would be expected at sites that have 1) higher fractions of HMW compounds in NAPL (Lee et al., 1998; Dou et al., 2008), 2) have a smaller fraction of the initially spilled DNAPL remaining and 3) a higher ratio between initial spill volume and sweepzone volume. The assessment under which conditions residualized HMW components cause significant tracer sorption should be subject for further study.

3.6. Evaluation of PITT-derived source zone characterisation

Although the inherent uncertainty associated with PITT estimates of NAPL volume is relatively small (Dwarakanath et al., 1999), multiple potential sources for error and uncertainty exist when performing PITTs (Brooks et al., 2002). While some of the well-known limitations in the presence of DNAPL pools, such as poor hydrodynamic accessibility of tracers and

non-equilibrium mass transfer, were not likely to have occurred in the highly residual source zone in this study, some other limitations should be considered.

When extrapolation of the tails of the tracer BTCs becomes a significant part of estimating NAPL saturation or interfacial area, as was the case for TMH and SDBS in this study, additional estimation errors are introduced (Jin et al., 1997). Based on the quality of the extrapolated fit, the associated uncertainty would be smallest for sweepzone 2, which is the most relevant sweepzone based on the highest NAPL presence. Therefore the most reliable estimate of S_n and overall DNAPL volume was probably provided by the behaviour of 2-octanol as it showed distinct retardation without the requirement of extrapolation. In addition its recovery was better than that of TMH and DMP (Table 2). Except for sweepzone 1, TMH-based estimates of S_n matched the 2-octanol based estimate quite well (Fig. 4, TMH value for sweepzone 3 not based on extrapolated data). Larger deviations were observed for the estimate based on the behaviour of DMP, the partitioning tracer that showed minor retardation.

In this study, the estimated S_n values and DNAPL volumes for the four sweepzones compared favourably with measurements from various independent methods, particularly core sampling and ground-penetrating radar. However, without a method that can measure field representative NAPL–water interfacial areas (Rao et al., 2000), the field PITT-derived a_{NW} values could not be evaluated, and separate tests at the studied source zone at other concentrations and/or other interfacial tracer types would be required to verify whether field PITT-derived estimates are at least consistent, as was shown for the lab tracer tests (Kim et al., 1999).

While the estimated a_{NW} values in this study seemed reasonable based on morphology and ASRE evaluation, the potential error in these estimates is especially dependent on the use of a constant concentration for the interfacial tracer, which represents an important simplification for field PITTs. Unlike lab PITTs, continuous input of tracer solution is most often impractical and therefore a pulse input is used. Transport and sorption processes cause interfacial tracer concentration to vary within the flow domain. This requires the selection of a “representative” tracer concentration for the K_i calculation which is strongly dependent on the non-linear relationship with interfacial tension. The calculated interfacial data presented in this study (Table 3), have been based on the maximum SDBS concentration observed in each extraction well for a particular sweepzone. If instead, as an approximation for the case of a single extraction well, the averaged concentration value for the sweepzone maxima would have been used, then estimates of the DNAPL–water interfacial area for individual sweepzones (Table 3) would have deviated by up to 60%.

Variable or changing composition of NAPL can have a significant effect on partitioning coefficients (Lee et al., 1998; Wang et al., 1998). The multi-component DNAPL infiltrated at the study site initially consisted of PCE, TCE, and chloroform (CF), with molar fractions (x) of 0.41, 0.47 and 0.12, respectively. By the time of the PITT, five years later, the more water soluble CF and TCE components were no longer detected in groundwater, illustrating their depletion from the DNAPL phase. With PCE remaining as the only component by the time of the PITT, the partitioning coefficients are

expected to have decreased significantly, for example over 25% for n-hexanol as compared to the original multi-component composition (Wang et al., 1998). Although the addition of Sudan IV (0.98 g/L) probably has had some effect on the partitioning coefficient of tracers, these are expected to be negligible (Dwarakanath and Pope, 1998) for the very low molar fraction that Sudan IV represents in PCE ($x = 0.000263$), even if it is assumed that Sudan IV did not residualize and was fully concentrated in the remaining DNAPL ($x = 0.00176$). Similarly, the minor potential of Sudan IV for surface activity will likely be negligible in the competition with surfactants (Tuck et al., 2003), as was shown to be the case by Jeong et al. (2002), who found that the addition of a similar hydrophobic dye in PCE did not affect interfacial tension in the presence of surfactants.

Overall, the ability to use PITTs as a metric in the evaluation of in-situ remediation aimed at NAPL source removal (Rao et al., 2000; Divine et al., 2004), will depend on the balance between the actual reduction achievement and the uncertainties associated with the field PITT-derived estimates. For this study, the evaluation with independent methods suggests a range of 25–50% for the PITT-derived DNAPL volume estimates. The PITT-derived DNAPL–water interfacial area estimates could not be independently assessed, but are likely more sensitive to error. However, even in a relative sense, they provide useful insight in NAPL morphology and in the assessment of remediation approaches.

4. Conclusions

The field PITT was able to detect a small volume (6.6–8.3 L) of chlorinated solvent DNAPL in a heterogeneous residual ($S_n \sim 0.1\%$) DNAPL source zone that had formed after substantially dissolution ($\sim 85\%$) under the influence of natural groundwater flow. PITT estimates provided realistic indications of DNAPL pore saturations, lateral distribution and volumes remaining, as supported by independent estimates based on time-integrated mass discharge, soil core analysis and ground-penetrating radar.

The estimated lateral distribution of DNAPL was in keeping with previous GPR measurements, although the PITT was more sensitive to detecting the presence of the most residual DNAPL. PITT-derived pore saturation values S_n were within the range of values expected based on the detailed analyses of vertical distribution of DNAPL saturation in sediment cores. In addition, the use of both partitioning and interfacial tracers allowed the inferring of DNAPL morphology and the new metric “average spherical radius equivalent (ASRE)” was introduced. ASRE represents the radius that NAPL blobs have if they are assumed to be spherical and provides a potentially helpful tool to assess the expected size of residual DNAPL blobs, based on the relationship between average NAPL saturation and interfacial area estimates for residual source zones. Taking into account pore size restrictions, ASRE allows evaluation of the occurrence of NAPL in pools, ganglia or single pore blobs.

Due to the residual nature of the source zone PITT estimates had to be corrected for significant background sorption of tracers on the Borden aquifer sediment. The background tracer retardation factors determined in the lab were similar to those determined in a background field PITT. In addition to

background sorption of a sedimentary origin, a hydrophobic, high-molecular weight component (Sudan IV) that residualized on sediment surfaces likely presented a significant source of background sorption in areas where DNAPL was present initially but had dissolved away. As the distribution of these residualized components is as heterogeneous as the distribution of the initial DNAPL, such source of background sorption would become increasingly important in highly residual source zones of NAPL that contain significant amounts of hydrophobic, high-molecular weight components.

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