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CL:AIRE research bulletins describe specific, practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin overviews the Streamtube Project that uses longitudinal transect monitoring to assess dissolution and remediation of the SABRE research site DNAPL source zone.



# Streamtube Project Overview: Longitudinal Transect Assessment of the SABRE Site DNAPL Source Zone

## 1. INTRODUCTION

Industrial use of DNAPL (dense non-aqueous phase liquid) chlorinated solvents began in the 1930s and hence groundwater contamination arising from DNAPL releases at some sites may date back decades. Widespread occurrence of plumes of solvents such as trichloroethene (TCE) is often attributed to their generation from DNAPL residing below the water table. Sources typically comprise a complex architecture of DNAPL pooled on low permeability strata with residual ganglia spread throughout the post-spill DNAPL migration pathway. Combined complexities of DNAPL architecture and groundwater flow may lead to heterogeneous dissolution with DNAPL contained in low permeability strata or pools taking decades to dissolve. DNAPL sources pose a significant remediation challenge internationally.

The SABRE (Source Area BioRemediation) site located at a UK industrial site has afforded an opportunity to undertake high resolution assessment of a DNAPL source zone arising from industrial TCE releases some 19 - 45 years ago. In January 2007, the SABRE Project installed a 3-sided sheet-pile cell that enclosed 720 $m^3$ of soil and subsoil. The cell was estimated to contain 0.3 - 2.9 (median 0.9) tonnes of DNAPL. The cell was 4 m wide and had the long 30-m axis oriented parallel to groundwater flow that was drawn towards an extraction well at the closed cell end (Fig. 1). The 6 m deep cell was keyed into a mudstone aquitard and enclosed made ground, alluvium and a 3 - 4 m thick river terrace gravel (RTG) aquifer of primary interest.

This bulletin presents an overview of research conducted by the Streamtube Project (also CL:AIRE Research Project RP14) under the umbrella of the SABRE project that had a primary goal of bioremediation performance assessment (CL:AIRE SABRE Bulletin #1). Streamtube contributed to this goal through its specific aim to evaluate the use of detailed longitudinal monitoring transects in assessing DNAPL source zone architecture, dissolution and remediation at the field-scale. An array of multilevel samplers (MLSs) was installed within the SABRE cell to generate detailed 2-D longitudinal transect snapshots of dissolved concentrations along a flowline, or 'streamtube', through the DNAPL source zone (Fig. 1). Data obtained represent the most detailed field-scale longitudinal transect through a real site DNAPL source observed to date.

## 2. FIELD PROGRAMME

The constrained flow regime afforded by the cell meant that the vagaries of flow direction variability were removed that can be a significant cause of concentration variability at sites (Davis et al., 1999). The cell was positioned to locate delineated DNAPL in the up-gradient portion of the cell allowing its dissolved plume to be observed down-gradient. Streamtube installed a longitudinal transect (T4) of MLSs offset, but parallel to the cell centreline (Fig. 1). Groundwater samples were obtained from MLSs that comprised a central piezometer surrounded by >14 narrow Teflon® tubes spaced at 0.3 m increments (per Rivett and Feenstra (2005)). Cross-cell variability was also assessed by Streamtube transverse fences (Fig. 1: T1, T2b, T3b) and DNAPL occurrence quantified by coring. Primary field data collected by SABRE included

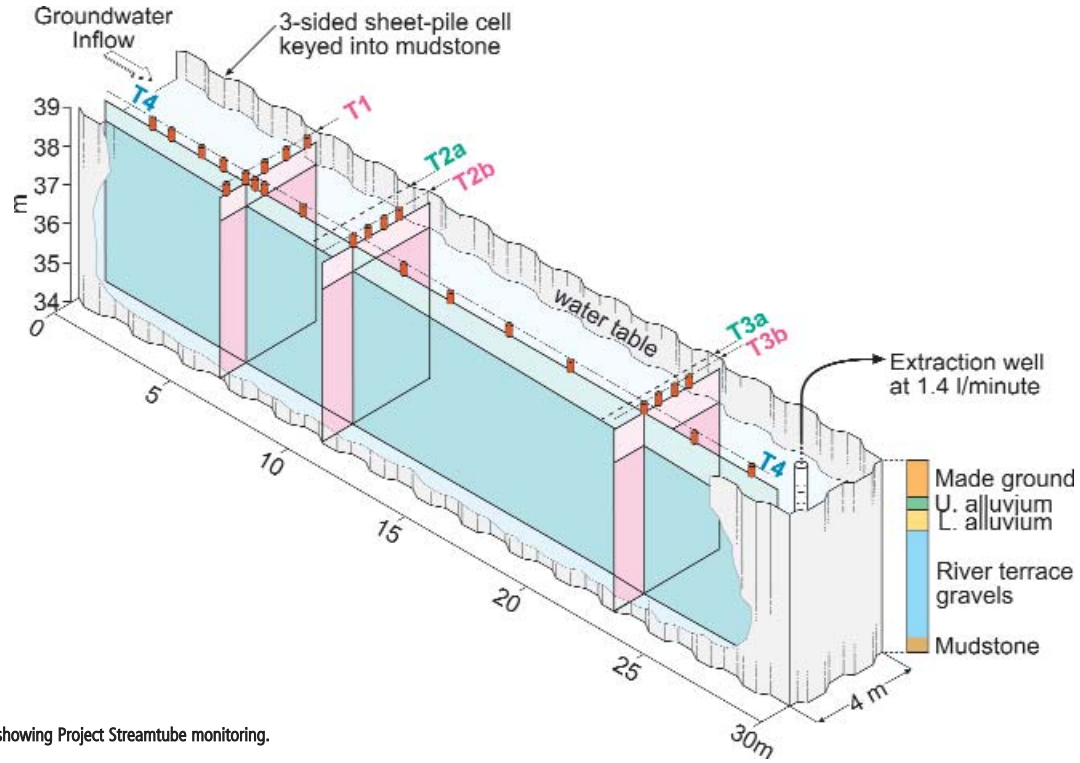


Figure 1. SABRE test cell showing Project Streamtube monitoring.

transverse MLS flux fence (T2a, T3a) data, conventional monitoring and extraction well discharge data, and soil and microbiological data (CL:AIRE SABRE Bulletin #5).

The abstraction rate from the cell was 1.4 l/min giving a mean groundwater velocity within the streamtube of 0.65 m/d and a residence time of 45 day (d). Baseline monitoring was conducted under pumped, but otherwise un-amended, conditions for 80 d prior to bioremediation. Treatment involved injection of 2.9 $m^3$ of SRS™, an emulsified soybean oil that provided a slow release of partitioning electron donor to promote sequential dechlorination of dissolved TCE to cDCE (cis-dichloroethene) to VC (vinyl chloride) to Ee (ethene). Other products are chloride, acidity (unless buffered) and reduced species (e.g. iron (II), sulphide, methane). Suitable dechlorinating bacteria such as *dehalococcoides* were naturally present, but enhanced by bioaugmentation with commercially available KB-1® culture, a consortium of dechlorinating bacteria.

T4 longitudinal transect snapshots were obtained over the 80 d baseline period corresponding to flushing of 2 cell volumes prior to the bioremediation phase (implemented at 0 d, 2 May 2007). T4 was monitored to 385 d by Streamtube over which a further 6.5 cell pore volumes were flushed. After completion of the bioremediation phase (monitored to 600 d by SABRE), a tracer test was conducted involving injection of a pulse of conservative bromide tracer in wells located 6 m along T4 with a single T4 transect snapshot collected after 6 d transport.

## 3. DNAPL SOURCE ZONE

### 3.1 Architecture

Pre-baseline soils data plotted relative to DNAPL threshold and percent saturation reference lines (where saturation is the proportion of void space filled with NAPL) revealed complex source zone architecture (Fig. 2). Data from T4 indicated DNAPL was present over the 5 - 15 m interval with local-scale similarity evident against a general, but irregular, trend of increasing then decreasing saturations with depth. Peak DNAPL saturations varied in elevation along T4. Cross cell T1 data also revealed significant lateral heterogeneity with concentrations varying by orders of magnitude at specific elevations. Sub-zones of DNAPL presence and absence existed in close proximity with concentrations peaking at some 55 g/kg in the RTG unit. Lateral data (Fig. 2 and other data not shown) indicated DNAPL occurrence was greatest on the opposing side of the cell to T4 at both 5 m and 13 m distance, but coincident with T4 at 10 m.

Very elevated saturations were notably rare. The source-area data (5 - 15 m interval; n=352) had 45% of samples below the DNAPL detection threshold with 50%, 2%, 2% and 1% of samples respectively in the 0.1 - 5%, 5 - 10%, 10 - 20% and >20% DNAPL saturation ranges. Thus 95% of the source contained a near equal split of non-detectable and low (< 5%) saturation DNAPL. The widespread occurrence of low saturations may in part reflect the source had been exposed to some 19 - 45 years of natural groundwater flushing with preferential DNAPL depletion from more permeable horizons and up-gradient portions of the source. The orthogonal pair of core transects provided good understanding of the source architecture, nevertheless the resolved complexity suggests full 3-D investigation was still warranted. The number of samples analysed (>350 samples, 20 cores) within a 10 x 4 x 5 $m^3$ aquifer volume is substantial and suggests typical site investigations will inevitably face major uncertainties in source-zone architecture.

### 3.2 Dissolution

Dissolved-phase TCE concentrations observed close to the source prior to remediation are illustrated by the -20 d plume snapshot data over the 5 - 15 m source zone interval (Fig. 3). Detailed comparison of these data with T4 soils data (Fig. 2) indicated dissolved concentrations >1-10% solubility surrounded the area of DNAPL contamination and were fairly continuous within mid to lower RTG elevations to 18 m distance. Concentrations approaching TCE solubility were, however, rare and located close to elevated DNAPL saturations.

Literature indicates solubility may occur from groundwater contact with quite low DNAPL saturations (>~2%) occurring over at most tens of centimetres for typical to high groundwater velocities (Rivett and Feenstra, 2005). Rate-limited,

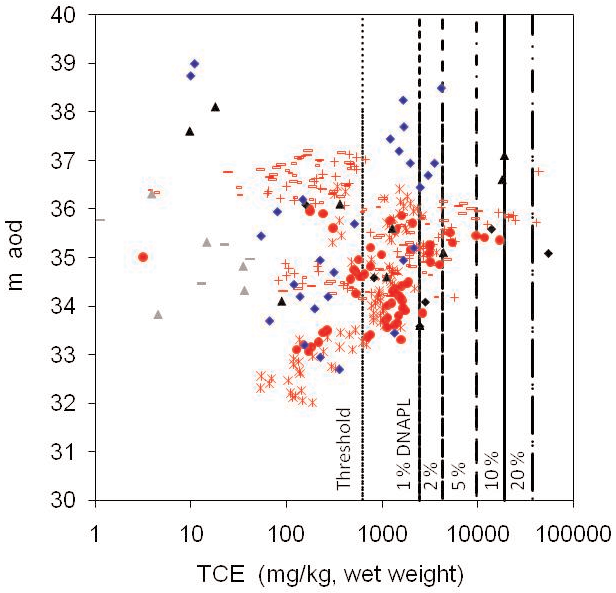


**Figure 2. Pre-baseline TCE soil-concentration depth profiles for the T1 transect (red symbols) and T4 transect (other colour symbols, and red-filled circles for the T1 - T4 intersection profile).**

less-than-solubility, dissolution may however develop at low contact length to velocity ratios when NAPL-water interfacial areas and/or saturations and contact lengths reduce with dissolution (Grant and Gerhard, 2007). Rate-limited dissolution of the source was promoted by frequent low saturations, but offset by long, albeit discontinuous, DNAPL contact lengths of potentially metres.

It additionally proved necessary to consider local TCE biodegradation and dechlorination product concentrations to account for the less-than-solubility TCE data. Baseline total ethenes (TCE + cDCE + VC + Ee) data in fact demonstrated concentrations at, or exceeding, equivalent TCE solubility over much of the 10 - 14 m T4 interval with cDCE dominant. Local over saturation of the aqueous-phase with elevated degradation products was indicative of biologically-enhanced dissolution processes occurring prior to bioremediation (Glover et al., 2007). Bio-activity was hence shown to influence DNAPL dissolution.

## 4. DISSOLVED PLUMES

A selection of T4 dissolved-plume snapshots for baseline and bioremediation phases is shown in Fig. 3 and longitudinal profiles based on averaged T4 MLS concentrations in Fig. 4.

### 4.1 Baseline Phase

The -20 d T4 snapshot shown (Fig. 3) was similar to the other baseline snapshots with fairly repeatable longitudinal profiles also observed (Fig. 4). Snapshot repeatability, whilst endorsing sampling and analysis protocols, also confirmed DNAPL dissolution and plume transport and attenuation were temporally quite stable. Lateral flow transients that would typically occur without a constrained cell environment dictate such steady-state observations are typically difficult to make in the field. Lateral flow transients, due to spatially variable recharge or seasonal flow changes, may be a primary cause of temporal concentration variability at many sites rather than perhaps DNAPL source zone dissolution, or plume attenuation variability (Davis et al., 1999).

T4 baseline data contained elevated TCE concentrations in the DNAPL source zone, but also a 'bull's eye' of dissolved TCE at ~25 m (Figs. 3, 4). The presence of predominant cDCE and further dechlorination products VC and Ee local to the source area illustrates the potential for biodegradation and natural attenuation processes in the vicinity of DNAPL. Individual compound maxima within subsets of the baseline data shift progressively down gradient in accordance with their dechlorination sequence, however, complete dechlorination to elevated Ee concentrations was limited. The partial attenuation was consistent with wider site plumes of several hundred metres long with cDCE and VC predominant (CL:AIRE SABRE Bulletin #5).

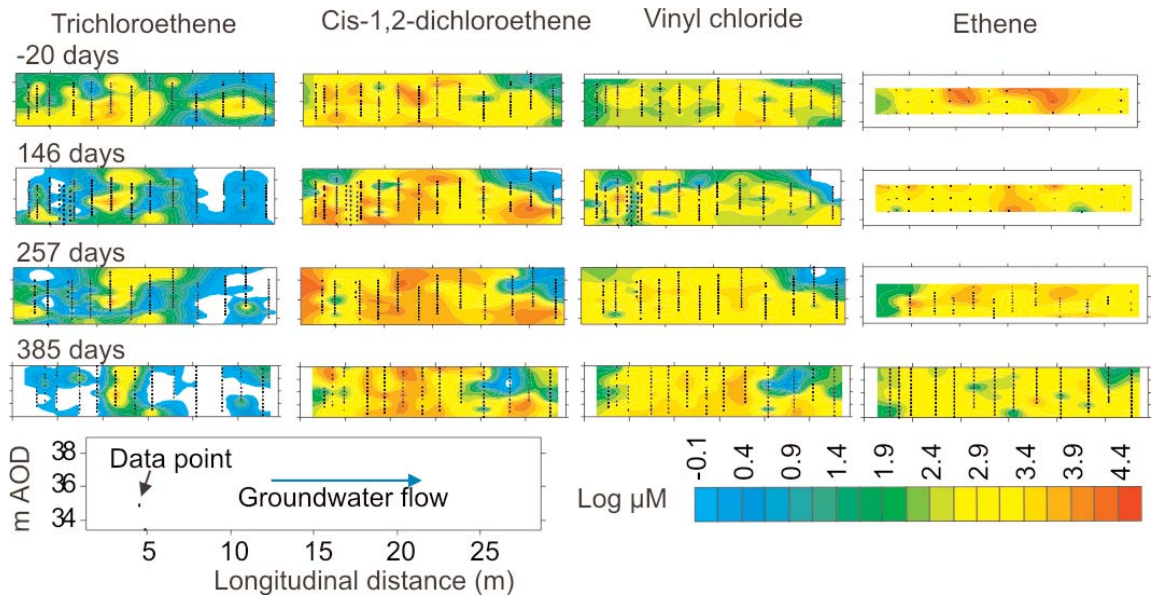


Figure 3. Example dissolved plume MLS snapshot data collected from T4 during the baseline and bioremediation phase.

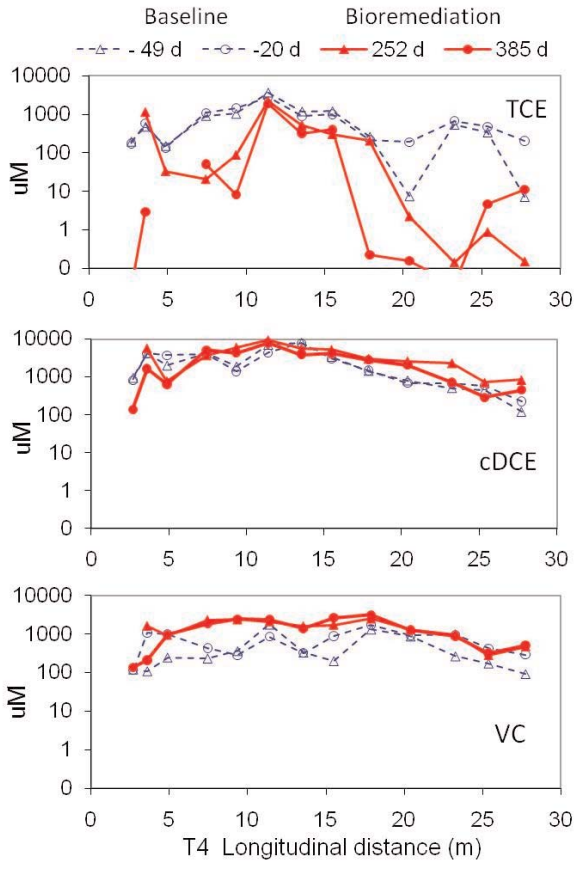


Figure 4. Example longitudinal concentration profiles based on averaged T4 MLS concentration data.

## 4.2 Bioremediation Phase

Semi-quantitative data based on T4 water-sample colouration confirmed SRS™ electron donor (of white milky appearance) was reasonably dispersed throughout the cell. A significant decline of dissolved TCE occurred over the monitored bioremediation phase and by 385 d much of the T4 snapshot was <100 µg/l (-0.12 log µM; Fig. 3) approaching drinking water standards for TCE (10 µg/l). Longitudinal profiles exhibited TCE declines and cDCE and VC increases down gradient relative to baseline data (Fig. 4). The main hotspot persisting at 11 m corresponded with maxima found in the baseline dissolved plume and soils data and was ascribed to local DNAPL persistence. Secondary lower concentration hotspots of TCE persisted, including the 25-m 'bull's eye'.

Predominance of cDCE continued during bioremediation with elevated concentrations most evident at 252 d, but with some decline by 385 d. cDCE decline was supported by SABRE data to later time and accompanying steady temporal VC increase. Trends in the Ee data were less clear. Widespread presence of Ee through the source area with localised elevated hotspots over 5 - 20 m indicated complete dechlorination was most significant in niche, sub-areas of the source zone. Local inspection of T4 data up-gradient of some Ee hotspots provided evidence of expected increases and declines in VC, cDCE and TCE over several metre length scales.

The temporal dissolved-phase cell mass was estimated from the T4 snapshot data assuming simple uniform extrapolation of T4 concentrations across the cell (Fig. 5). Although not a quantitative metric of remediation performance, such as temporal extracted mass (CL:AIRE SABRE Bulletin #5), this mass does provide semi-quantitative indication of remediation progress. Insufficient T4 Ee data exist for earlier time estimates, however, other Ee data (CL:AIRE SABRE Bulletin #5) suggest low to moderate Ee rises from concentrations somewhat below initial VC values.

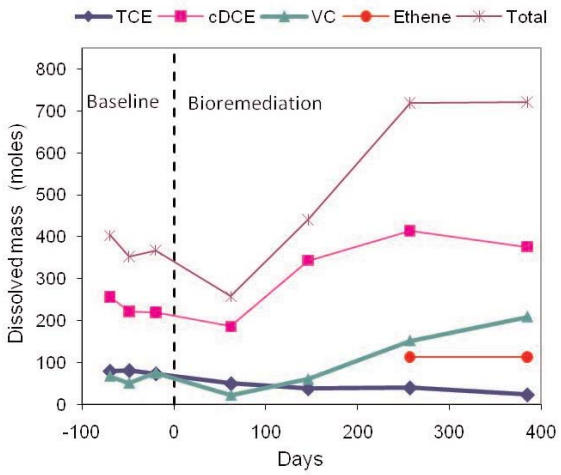


Figure 5. Estimated cell dissolved-phase mass with time estimated from the T4 transect data.

The rise in total ethenes mass was around a factor of 1.8 and indicative of the biologically enhanced dissolution achieved during bioremediation. This factor is intermediate between the flux enhancement factor of ~1.6 observed from SABRE cell extraction data and lab column studies that report enhanced dissolution factors ~2.1 (CL:AIRE SABRE Bulletins #3, #5). Processes that bio-enhance DNAPL dissolution include biodegradation inducing greater parent-solvent concentration gradients, greater concentrations of less hydrophobic metabolites more easily transported away from the source, enhanced dissolution by bio-surfactants and electron-donor co-solvency (Glover et al., 2007).

## 5. SUPPORTING FIELD TESTS

The bromide tracer test and hydraulic conductivity data proved fundamental to T4 interpretation. T4 data indicated the tracer plume comprised faster and slower sub-plumes with mean velocities of 3.0 and 1.4 m/d, both exceeding the mean cell extraction rate velocity estimate inferring tracer movement along preferential flow pathways. Fastest velocities were ascribed to transport in a conductive (>10 m/d) gravel at 34.5 - 36 m elevation observed on the opposing side of the cell to T4 at 10 m, but apparently trending laterally across cell allowing high velocity tracer to appear in T4 at 20 m by 6 days. This locality was close to the bull's eye anomaly of TCE which was hence ascribed to preferential oblique flow into the T4 transect within the cross-cutting gravel where residence times and/or conditions were likely less conducive to biodegradation. Some flow bypassing of the more contaminated parts of the DNAPL source area in T4 was probable due to preferential flow in the conductive, less contaminated, gravels located lateral to T4.

## 6. DEGRADATION RATE ESTIMATION ISSUES

Preliminary data analysis indicated degradation rate estimation from the longitudinal T4 data was problematic, when simple regression models based on analytical model centreline methods (Beyer et al., 2006), or related analytical models that allow for successive dechlorination steps such as the US EPA models BIOCHLOR or REMChlor (Falta, 2008) were implemented,. Although the cell provided a streamtube of flow to the extraction well, the data presented above do not support a streamline of flow occurred along T4 itself. Rather, some groundwater flow was oblique. The transect's proximity to a laterally heterogeneous DNAPL source zone architecture resulted in observed T4 transect concentrations being sensitive to such lateral flows. Work is on-going to evaluate if field-based degradation rates can be determined from analytical or numerical modelling approaches on sub-sets and the T4 dataset as a whole with support from SABRE datasets to better constrain estimates.

## 7. SOURCE-ZONE DEPLETION

Table 1 presents pre- and post-remediation DNAPL saturation data for soil cores from T4. Not all of the pre- and post-cores were from similar localities and hence data provide a semi-quantitative indication of remediation performance. Post remediation saturations were generally lower with 79% of samples below the DNAPL detection threshold. Elevated saturations were still detected, but were marginally less frequent and below 10% saturation. Detection of low saturations also decreased. Persistent elevated DNAPL saturations were sporadically distributed within the 7 - 15 m interval of T4 and in proximity to some dissolved concentration hotspots. DNAPL was not found in the vicinity of the persistent TCE bull's eye endorsing the lateral flow explanation given earlier.

**Table 1. Comparison of estimated DNAPL saturations from soil-core data pre-and post-remediation from transect T4.**

| DNAPL % saturation | Pre-remediation (n = 352) % | Post-remediation (n = 106) % |
|---|---|---|
| No DNAPL | 45 | 79 |
| >0.1 - 5 | 50 | 18 |
| 5 - 10 | 2 | 3 |
| 10 - 20 | 2 | 0 |
| >20 | 1 | 0 |

The observed lateral heterogeneity in DNAPL precludes the T4 data alone from giving a reliable estimate of DNAPL mass in the whole cell. Both the T4 dissolved-phase and solid-phase data do nevertheless confirm bioremediation had achieved a significant, although not complete, diminishment of the source term. SABRE cell effluent data indicated that over 0.8 tonnes of TCE (equivalent) was in fact removed from the cell during the bioremediation phase that was comparable with the median estimate of DNAPL initially present. Post-remediation soil core data throughout the test cell suggest pre-treatment, the cell contained in excess of 1 tonne of TCE, of which 60 - 75% was removed and/or completely treated during the field test (CL:AIRE SABRE Bulletins #2, #5). Hence, even with the high density of data compared to real sites, moderate uncertainty still remains in both the initial and final DNAPL mass estimates.

## 8. CONCLUSIONS AND RELEVANCE

Overall, the detailed longitudinal transect approach allowed insight into dissolution, attenuation and remediation processes and performance. The significant lateral heterogeneity in DNAPL saturation, dissolved phase and geological permeability does, however, suggest that a single detailed transect slicing through a source zone may differ quite significantly from a neighbouring parallel transect, even one just 1 m away. The value of 3-D, high resolution source-area data for fuller understanding is clearly recognised. Although such detailed 2-D or 3-D characterisation is the domain of research studies, nevertheless obtaining some high resolution data at real sites may be warranted to improve the conceptual site model and cost-effective remedial design.

Conclusions arising from the longitudinal transect study and remarks of relevance to practitioners managing DNAPL sites are summarised below:

- DNAPL source zone architectures are heterogeneous and may contain saturations that vary from <0.1% to >20% over centimetre length scales - most site investigations can therefore only obtain a crude assessment of a source zone without intensive investigation.
- Many sites contain sources decades old where it should be recognised DNAPL will have undergone preferential long-term dissolution from the more permeable strata and up-gradient portions of the source.
- Dissolved TCE was typically 1-10% of solubility within the source, however, total chlorinated ethenes were equivalent to TCE solubility, or greater suggesting bio-enhanced dissolution was naturally occurring prior to bioremediation; this possibility should be evaluated at sites.
- Anaerobic biodegradation may occur very close to DNAPL TCE; although cDCE was found to predominate, complete conversion to ethene was locally possible in the source.
- Bioremediation achieved significantly reduced dissolved and DNAPL concentrations of TCE with flux enhancement factors likely to be in the range 1.5 - 2 for TCE. Longer treatment zones, contact times or treatment periods than used here appear necessary for complete dechlorination.
- Simple conservative tracer testing and permeability data confirmed existence of high velocity pathways allowing significant flow by-passing of DNAPL and lateral flows; such supporting data may often provide critical insights.
- The use of longitudinal transects/profiles within a source zone to determine plume transport and attenuation parameters will be limited by the occurrence of oblique flows to the monitored plane. Transects within heterogeneous source zones will be particularly sensitive to the existence of lateral flows which are even more probable at sites without the benefit of a flow-constraining cell.
- The above does not invalidate more generally the use of plume centreline analysis methods in transport assessment as lateral concentration variability and flows may have a lesser influence in more homogeneous sources and larger scale plumes.

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**REFERENCES**

- Beyer C, Bauer S, Kolditz O , 2006. Uncertainty assessment of contaminant plume length estimates in heterogeneous aquifers. J. Contam. Hydrol. 87, 73-95.
- Davis GB, Barber C, Power TR, Thierrin J, Patterson JL, Rayner JL, Wu Q, 1999. The variability and intrinsic remediation of a BTEX plume in anaerobic sulphate rich groundwater. J. Contam. Hydrol. 36, 265-290.
- Falta RW, 2008. Mass conserving decision model for coupled source and plume remediation. IAHS, 324, 507-514.
- Glover KJ, Munakata-Marr J, Illangasekare TH, 2007. Biologically-enhanced mass transfer of tetrachloroethene from DNAPL in source zones: experimental evaluation and influence of pool morphology. Environ. Sci. Technol. 41(4), 1384-1389.
- Grant GP, Gerhard JI, 2007. Simulating the dissolution of a complex dense nonaqueous phase liquid source zone: 1. Model to predict interfacial area, Water Resour. Res. 43, W12410.
- Rivett MO, Feenstra S, 2005. Dissolution of an emplaced source of DNAPL in a natural aquifer setting. Environ. Sci. Technol. 39:447-455.

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