ESTABLISHING CLEAN-UP CRITERIA AT THE SOURCE AREA BIOREMEDIATION (SABRE) SITE: THE DEVELOPMENT OF UNCERTAINTY-BASED METHODS TO QUANTIFY DNAPL MASS REMOVAL AND FLUX REDUCTION.

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SUMMARY

Considerable research effort has been directed to the development of effective source zone remediation technologies, yet little attention has been given to establishing robust clean up criteria to quantify the achievement of remediation targets. Here we describe the development of uncertainty-based methods for three types of performance metrics; DNAPL mass depletion, contaminant transformation and mass flux reduction. A highly instrumented research facility allowed comparison of performance metrics for enhanced in-situ bioremediation (EISB) of chlorinated solvents. The study concludes that EISB is effective at reducing DNAPL source mass and that reducing uncertainty in whether targets have been reached requires increasing investment in performance monitoring.

BACKGROUND

Chlorinated solvents have been used extensively in industry and are common groundwater contaminants. Their limited aqueous solubility often leads to the presence of dense non-aqueous phase liquid (DNAPL) source zones, which may persist due to mass transfer limitations from the DNAPL to groundwater.

Whilst recent research effort has been directed to the development of effective source zone remediation methods, considerably less attention has been given to establishing reliable methods to quantify the progress toward, and achievement of, remediation targets. At many sites, particularly early in the release history, a significant proportion (>90%) of the mass is present as a DNAPL (Pankow and Cherry, 1996). Evaluating remediation against cleanup objectives therefore requires quantification of DNAPL mass depletion. Deriving accurate mass estimates is not trivial. Currently available methods typically fail to provide a complete description of the total DNAPL mass. Furthermore, uncertainty in mass estimates that result from limited spatial resolution are rarely quantified, despite having significant bearing on whether the remediation has met the clean up criteria.

Here we describe the development of uncertainty-based performance metrics for quantifying the treatment of a trichloroethene DNAPL source zone. Conclusions and recommendations are presented relative to concentration, flux and mass-based performance metrics, based on the lessons learned at the Source Area BioREmediation (SABRE) site and by reference to current literature and best practice.

SITE SETTING

A former chemical manufacturing plant in UK was the focus for project SABRE. The site was occupied by a mono-chloro acetic acid (MCA) production plant that used TCE in the

production process. TCE releases from the drains and sumps are assumed to have occurred during the 25-27 year operational period.

The near-surface geology at the site comprises a variable thickness of fill over a sequence of alluvium (1 to 2.5 m thick) and gravels (3 to 5 m thick). The sediments rest on a significant thickness (>60 m) of mudstone bedrock, which is fractured and weathered near the surface (Lelliott et al., 2009). A reconnaissance survey at the site revealed a DNAPL source zone, comprising approximately 71% trichloroethene (TCE), that had penetrated the superficial deposits and approximately the uppermost metre of the mudstone. Groundwater sampling in existing monitoring wells identified a plume of TCE, cis 1-2-dichloroethene (cDCE), vinyl chloride (VC), and ethene (ETH) contamination in groundwater downgradient from the source zone, demonstrating degradation of dissolved phase TCE migrating from the source, but at rates that were too low to protect a nearby receptor.

The spatial distribution of the site-wide DNAPL source was used to guide the location of a 30 m long by 4 m wide cell that was the focus for the EISB research study. The cell was located to intersect the DNAPL source zone (Figure 1) and was aligned sub-parallel to the prevailing groundwater flow direction (south-south east).

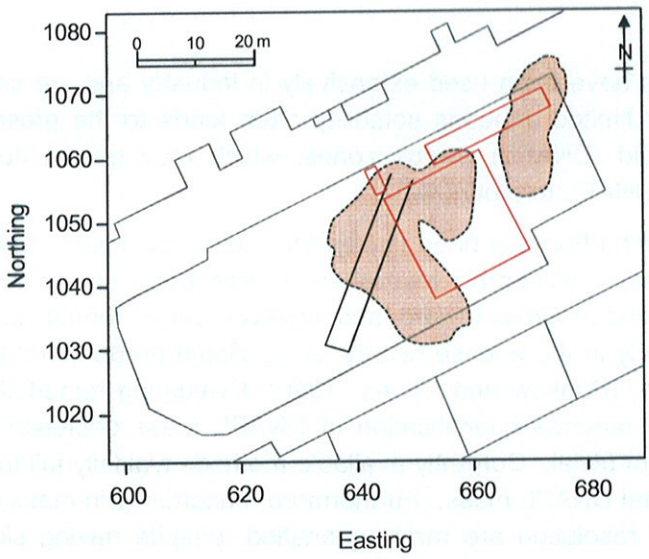


Figure 1. Extent of the DNAPL source zone is shown in dotted outline and shading. The three bold outlines in the vicinity of the DNAPL source zone indicates the location of the historical MCA production plant. The U-shaped bold outline identifies the location of the SABRE research cell.

The cell was constructed from plastic sheet piles that were keyed into the top of the mudstone. The cell was open to the aquifer at the upgradient end, and pumping wells were installed at the closed (downgradient) end to create forced gradient flow conditions. The design residence time was set at 40 days for one complete cell volume. The cell was instrumented with fully-screened monitoring wells, plus multilevel sampler transects that were aligned transverse and parallel to flow (Figure 2).

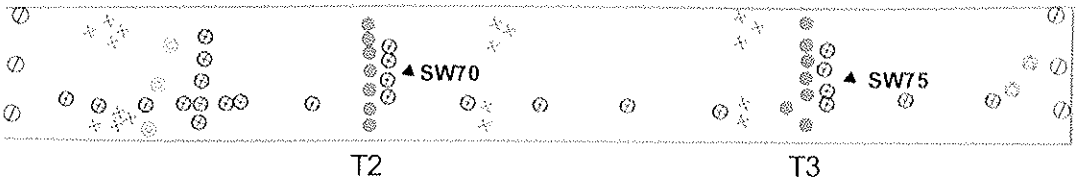
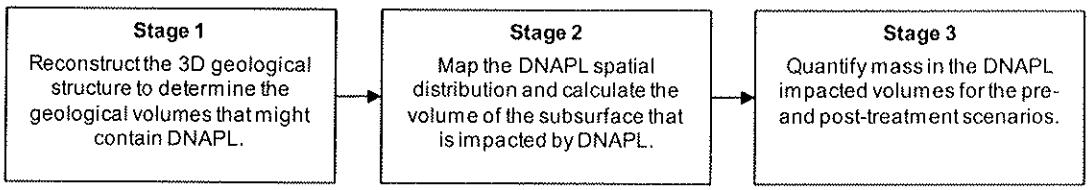


Figure 2. Schematic of the SABRE test cell, showing location of the fully-screened monitoring wells (SW70 and SW 75) and multilevel sampler transects in the source (T2) and plume (T3) zones.

PRE- AND POST-REMEDIATION DNAPL MASS ESTIMATES

The approach adopted in this study was to develop a methodology that simplified the description of contaminant distribution, yet allowed robust sensitivity analysis and quantification of uncertainty. The approach was considered to be of more practical utility than three dimensional multiphase flow and transport simulators, which are rarely validated at real field sites and are not as yet standard desktop tools. The methodology is based on standard site investigation methods, simplifying assumptions regarding DNAPL distribution and statistical descriptions of DNAPL mass.

Estimates of pre- and post-treatment mass were determined using a three stage process:



Stage 1 concerned the reconstruction and visualisation of the geological sequence at the site to provide geologic context for the DNAPL mass estimates within the SABRE cell during Stage 2. The 3D geology model was based on detailed lithostratigraphic logs and constructed using the software GSI3D (Kessler et al. 2009).

Analysis of the uncertainty in the geological volume estimates was undertaken, based on the confidence in predicting the depth to a given geological contact (Lelliott et al. 2009). The results informed the stochastic modelling methodology in Stage 3.

Stage 2 involved mapping the spatial distribution of the volatile organic compounds (VOCs) in the cell before and after treatment, using a 2-step process involving: i) detailed vertical profiling of the VOCs at each of the transect borehole locations, and ii) interpolation of these data across the entire cell volume. Vertical profiling in the cell involved using two main techniques:

- Combined membrane interface probe (MIP) and electrical conductivity (EC) profiling. The MIP tool supplied qualitative data on the vertical distribution of contamination and depths of geological interfaces.

- Sonic percussion drilling and coring. Sub-samples of the core provided quantitative data on the vertical distribution of contamination, organic carbon, porosity and the locations of geological interfaces. Sudan IV tests on sub-samples of the cores supplied qualitative data on the vertical distribution of DNAPL.

The combined lines of evidence from the MIP profiles and cored boreholes were used to construct composite data plots and to determine where DNAPL was present in the vertical profile (Figure 4). Estimates of DNAPL saturation were determined according to the partitioning calculation of Feenstra et al. (1991).

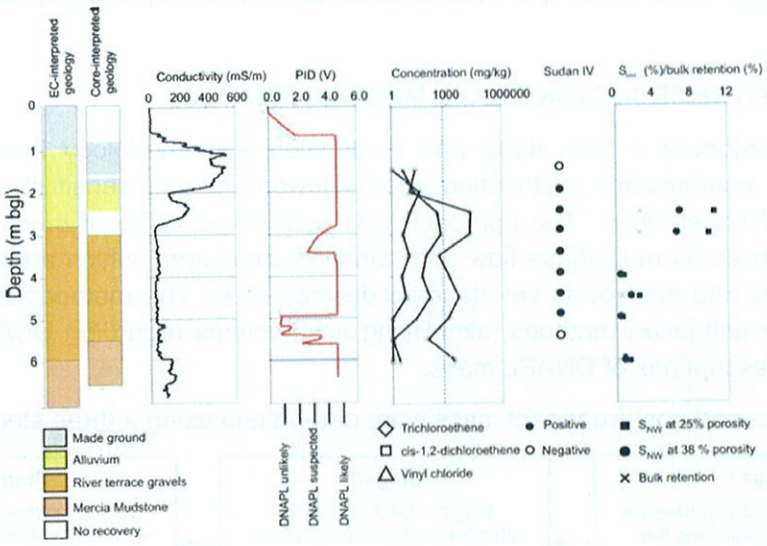


Figure 4. Vertical profile data used to determine DNAPL presence and estimate non-wetting phase saturation and bulk retention capacity.

The amount of the vertical profile that contained DNAPL was expressed as a proportion of the total profile depth, termed here the percentage occupancy. By calculating the percentage occupancy at each borehole location a point-source based distribution of DNAPL could be determined.

The SABRE cell modelled area (30 × 4 m) was gridded to allow interpolation between the grid cells that contained the point-source vertical profile data. Earlier investigations, undertaken at the site scale (100 × 80 m), examined the effect of grid sizes (5.0, 0.5, 0.1 m) on volume estimation and, ultimately, DNAPL mass. The smaller grid size of 0.1 m (equivalent to the soil core borehole diameter) was selected for the analysis of data from the SABRE cell.

The interpolated plots (Figure 5) indicate that the volume of aquifer impacted varies in the cell as a function of the DNAPL distribution. The change in the DNAPL impacted aquifer volume (Figures 5a and 5b) reflects mass depletion due to enhanced in-situ bioremediation. Uncertainty is influenced principally by sampling density and is lower in the vicinity of the multilevel sampler transects (Figure 2, T2 and T3).

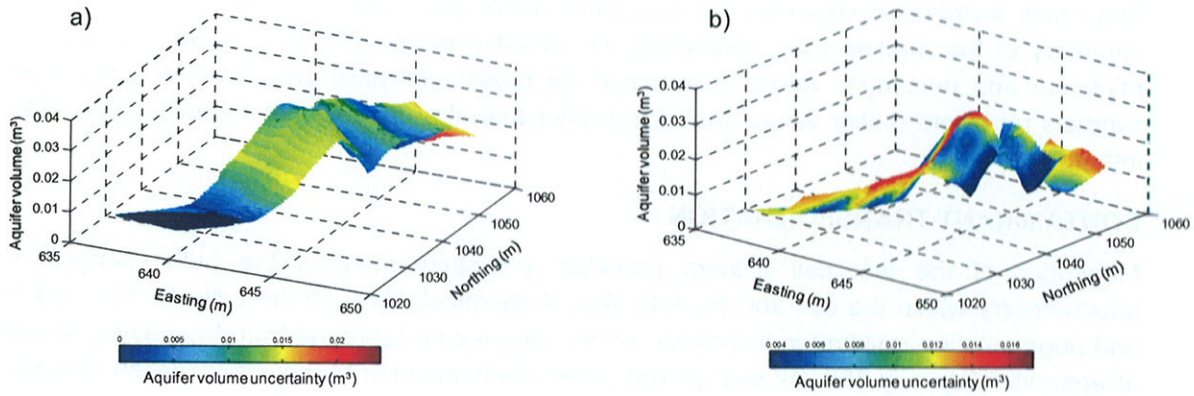
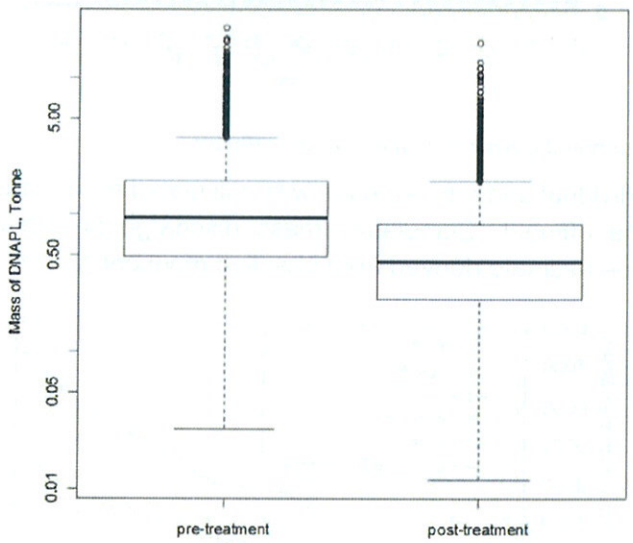


Figure 5. Estimates of the volume of aquifer impacted by DNAPL for the Pre-remediation (a) and post-remediation trial (b) scenarios for a 0.1 m grid. The colour drape indicates the uncertainty in volume estimates for each grid location.

Stage 3 involved uncertainty based estimates of DNAPL mass. The effect of variability in impacted aquifer volume and the distributions of DNAPL saturation and porosity were investigated using a modified bulk retention capacity expression. Monte Carlo simulations (10,000 realisations) were undertaken to determine the plausible range of DNAPL mass estimates, both before and after treatment of the DNAPL source zone by enhanced in situ bioremediation (Figure 6).



Percentile values	10th	25th	50th	75th	90th
Pre-treatment mass (tonne)	0.27	0.49	0.94	1.76	3.13
Post-treatment mass (tonne)	0.14	0.24	0.45	0.85	1.51

Figure 6. Pre- and post treatment DNAPL mass estimates.

The mass distribution shown in the box-and-whisker plot (Figure 6) provides a graphical summary of the median (50th percentile), interquartile range (25th to 75th percentiles) and minimum and maximum values determined by preset statistical criteria. The open circle symbols represent outlier values that are greater than the upper quartile plus 1.5 times the interquartile range.

CONTAMINANT TRANSFORMATION

Monitoring of the test cell effluent provided a measurement of the bulk changes in geochemistry within the cell and the total flux of chemicals through the cell. Biostimulation and augmentation resulted in increases in total ethenes in discharge from the cell beginning at approximately day 150, as well as enhanced dechlorination to vinyl chloride and ethene (Figure 7).

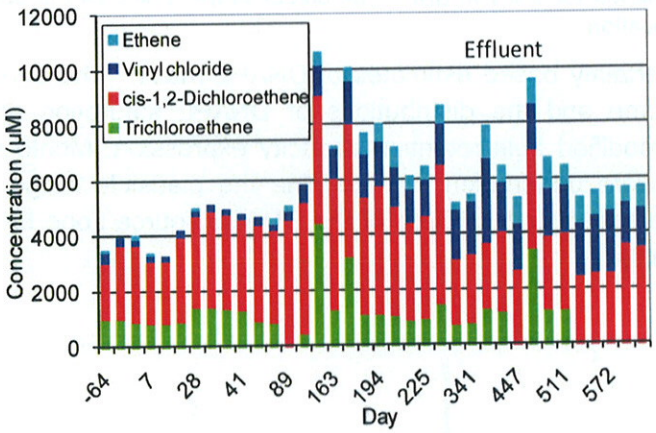


Figure 7. Change in chlorinated ethene speciation in the effluent

Mass discharge of individual and total ethenes was calculated from measured concentrations and flow rate for the effluent. Cumulative mass discharge is charted in Figure 8 and compared to a baseline estimate derived from baseline monitoring.

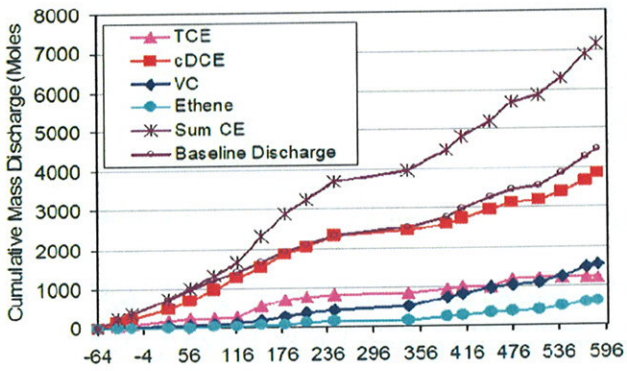


Figure 8. Cumulative total mass discharge of ethenes from the cell

Cumulative mass discharge from the cell over the test duration is equivalent to 943 kg of TCE, exceeding an estimated baseline value of 590 kg by 353 kg. This result represents a 1.6x flux enhancement factor due to: a) the higher effective solubility of the lesser chlorinated daughter products; b) enhanced mass transfer from DNAPL to the aqueous phase resulting from larger concentration gradients; and c) possible surfactant or co-solvency effects of metabolites resulting from biostimulation.

An ethene and chloride mass balance was conducted to determine the fate of TCE released from DNAPL during the test. The net discharge of each ethene and chloride was determined from the difference in cumulative mass discharge in the effluent and an estimate of the mass entering the cell based on influent groundwater monitoring data (Table 1).

Table 1. Relative proportions of the total TCE mass removed from the cell.

Constituent	Net Discharge (moles)	Free Cl- Created (moles)	TCE-Eq (kg)
PCE	0		0
TCE	1,108		146
cDCE	3,575	3,575	470
VC	1,455	2,910	191
Ethene	544	1,632	71
Total Ethenes in Effluent	6,682	8,117	878
Free Cl-	12,585	4,467	196
		Total TCE removed or degraded (kg)	1,074

Of the net discharge of 12,585 moles of chloride from the cell, 8,117 moles are accounted for based on dechlorination of TCE to cDCE, VC, and or ethene. The remaining 4,467 moles of chloride in the discharge is therefore likely the result of complete degradation of TCE. It is also possible that some of the excess chloride is associated with ethene that was lost to volatilization; regardless, the chloride balance suggests that 1,074 kg of TCE was lost from the cell through degradation and discharge.

VOC MASS FLUX

Conventional long screen wells can provide some qualitative information, but because they do not accurately capture the spatial complexity often present in a contaminant plume, data can be misleading and estimates of degradation rates carry considerable unquantifiable uncertainty. Instead mass discharge performance metrics are increasingly being applied to DNAPL site risk assessments and source zone remediation techniques (Basu et al., 2009). A key attribute of mass discharge measured using multilevel sampler transects is the preservation of spatial complexity, which permits monitoring of key processes that may be spatially discrete in complex heterogeneous aquifers.

A comparison of process level understanding obtained via multilevel sampling versus that from monitoring well data is shown in Figure 9, which compares the distribution of the chlorinated species monitored across the SABRE plume zone MLS transect at two different times during the experiment, to the concentrations found in the monitoring wells on those two occasions.

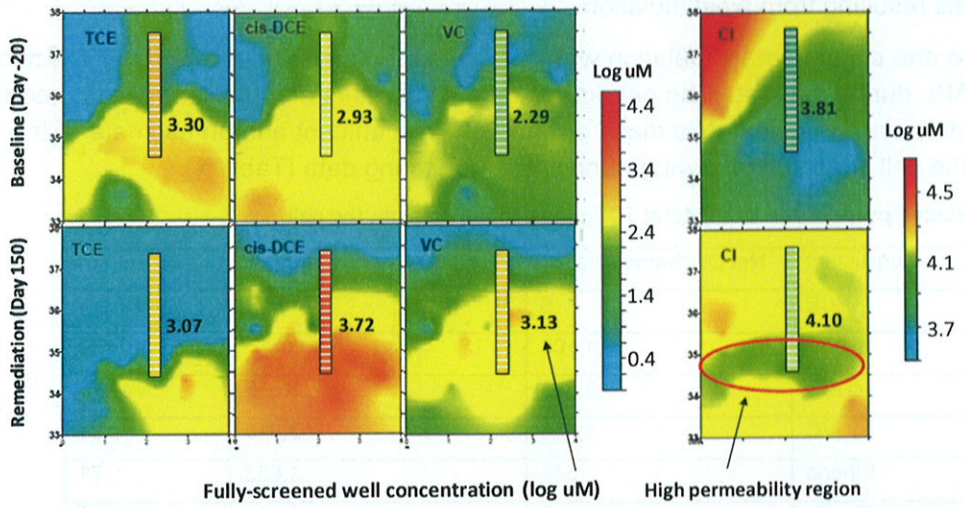


Figure 9. Comparison of plume area concentrations observed in monitoring wells and the spatial distribution of concentrations indicated by the MLS transects. Monitoring screen position is shown relative to the vertical and lateral MLS coverage. Top row is pre-remediation data; bottom row is 150 days after the start of remediation.

The well data suggest that monitoring wells must have preferentially sampled higher permeability horizons adjacent to the screen, yielding data that do not in all cases faithfully represent the areal average concentration in that transect plane, nor give any indication that chlorinated ethene concentrations vary over 4 orders of magnitude. In contrast, the spatially interpolated concentrations derived using the MLS data provide some useful insight into the state and evolution of parent and daughter contaminant distributions, which may contribute to remedial system optimisation. The nature of the mass discharge estimation method is such that uncertainty is an inherent product of the process. We used conditional simulation and Best Linear Unbiased Estimation (BLUE) techniques (Kitanidis, 1997) to spatially interpolate concentrations and Darcy velocity to estimate local mass flux values, which were then integrated to obtain mass discharge (Figure 10).

Based on integration of the MLS "snapshots", TCE discharge decreased after the start of remediation, but notably was not reduced to zero. There must therefore be mass flux paths in the test cell not sampled by that well. Assuming each discrete path has a different velocity, the state of dechlorination along the plume will undoubtedly be different asresidence times vary. Sporadic increases in TCE concentrations were observed in the plume monitoring well beyond Day 100, in some cases reaching concentrations similar to that during the pre-remediation period.

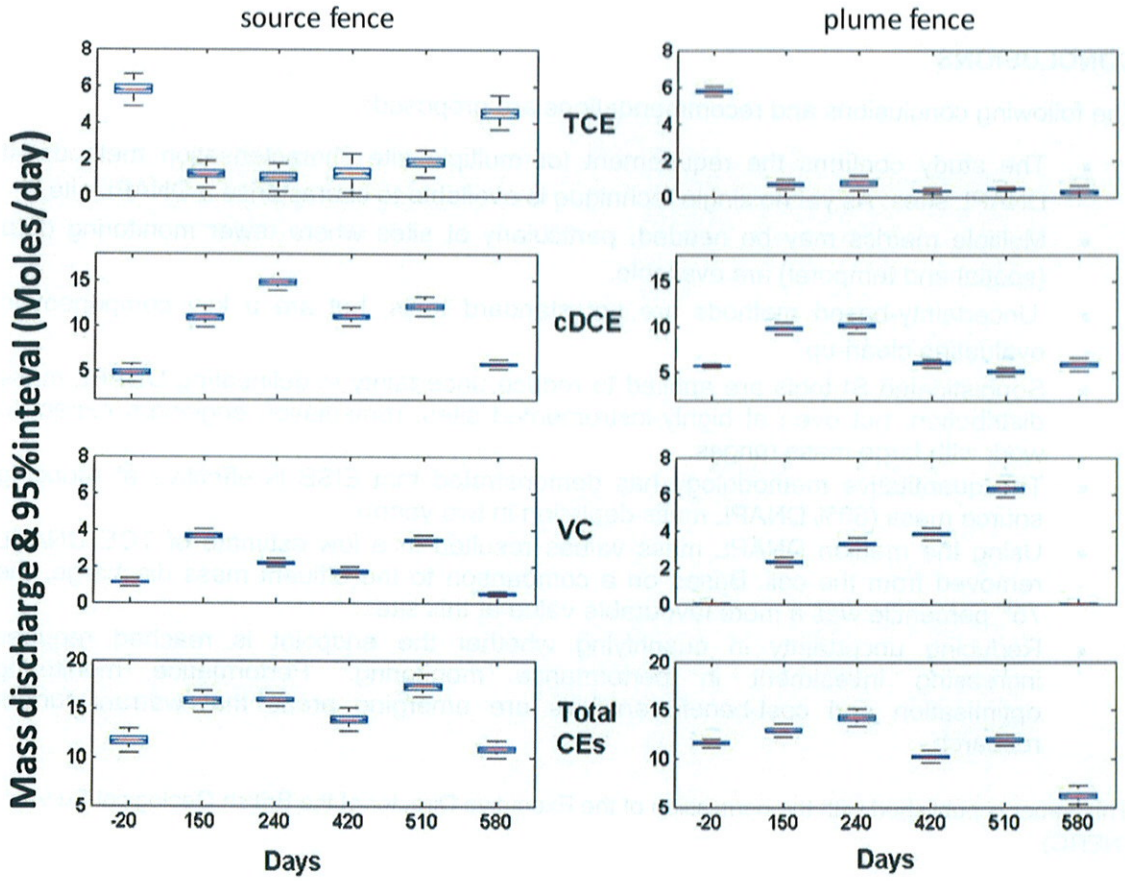


Figure 10. Mass discharges estimates of individual and total chlorinated ethenes calculated for the one pre-remediation sampling event and the 5 post-remediation sampling events. The source zone transect is on the left and plume zone transect on the right.

TCE mass discharge across the plume zone MLS transect decreased to a very low level and remained low throughout the entire remediation period. This implies that those TCE spikes either migrated in flux paths not sampled by the plume zone transect or that the mass discharge is sufficiently low that they contribute little to the integrated MLS transect estimate. This ambiguity suggests that the most robust monitoring strategy may be a combination of MLS transects and longer screened monitoring wells. The final snapshot reveals that total chlorinated ethene mass discharge across the source transect is approximately the same as that during the pre-remediation period, but is markedly reduced across the plume transect.

By assuming a constant volumetric discharge across the MLS transects, point mass discharge estimates can be temporally integrated to get an impression of the total amount of mass discharged over the experimental period. Using the total chlorinated ethene mass discharge values, approximately 714 kg TCE equivalent (c. 500 L of DNAPL) crossed the source zone transect and approximately 570 kg of TCE equivalent crossed the plume zone transect.

CONCLUSIONS

The following conclusions and recommendations are proposed:

- The study confirms the requirement for multiple site characterisation methods at DNAPL sites. As yet no single technique is available to characterise a DNAPL site.
- Multiple metrics may be needed, particularly at sites where fewer monitoring data (spatial and temporal) are available.
- Uncertainty-based methods are not standard tools, but are a key component in evaluating clean-up.
- Sophisticated SI tools are applied to reduce uncertainty in delineating DNAPL mass distribution, but even at highly-instrumented sites, remediation engineers expect to work with large mass ranges.
- The quantitative methodology has demonstrated that EISB is effective at reducing source mass (50% DNAPL mass depletion in two years).
- Using the median DNAPL mass values resulted in a low estimate of TCE DNAPL removed from the cell. Based on a comparison to the effluent mass discharge, the 75^{th} percentile was a more favourable value at this site.
- Reducing uncertainty in quantifying whether the endpoint is reached requires increasing investment in performance monitoring. Performance monitoring optimisation and cost-benefit analysis are emerging areas that warrant further research.

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