CL:AIRE

SAB 5

(September 2010)

sabre bulletin

CL:AIRE SABRE bulletins describe specific, practical aspects of research from the LINK Bioremediation Project SABRE, which aimed to develop and demonstrate the effectiveness of *in situ* enhanced anaerobic bioremediation for the treatment of chlorinated solvent DNAPL source areas. This bulletin focuses on the contained area field test.

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Overview of the SABRE Field Tests

1. INTRODUCTION

This bulletin describes the contained area field test carried out as part of the SABRE (Source Area BioREmediation) project. It also describes in less detail, field tests conducted in an uncontained area designed to test alternative electron donors and electron donor delivery methods.

SABRE is a field and laboratory demonstration of *in situ* bioremediation of a chlorinated solvent dense non-aqueous phase liquid (DNAPL) source zone. The field test site ("site") is located at a former manufacturing plant within an operational chemical manufacturing facility in the UK. Between the mid-1960s and 1990, trichloroethene (TCE) was stored in a bulk storage tank and used for purification of the product formerly manufactured at this site.

Investigations carried out in 2002 showed that made ground, alluvium, and River Terrace sandy Gravel (RTG) soils are contaminated with TCE DNAPL, as well as an underlying mudstone formation. A dissolved phase plume emanating from this source area has migrated a distance of 400 m to reach a river at the boundary of the facility property. The dissolved phase plume contains the TCE degradation products cis 1,2-dichloroethene (cDCE), vinyl chloride (VC), ethene, and chloride.

In 2003, the site was selected as the SABRE field demonstration site, based on:

- Source characteristics - DNAPL in a sandy gravel aquifer;
- Good access to the source and plume for extensive characterisation investigations;
- Central location of the site in the UK - convenient for researchers from the UK and US; and
- Cooperation of the site owner.

Objectives of the field pilot trials included:

- **Demonstrate and quantify the effectiveness** of the process-bioremediation of DNAPL source zones;
- Establish the most **applicable and cost-effective monitoring techniques** for application at other sites; and
- Develop **detailed process understanding.**

2. CONTAINED AREA TEST CELL CONCEPT

The test cell was constructed to create an "*in situ* laboratory" for quantifying DNAPL remediation. The test cell was designed to:

- Enforce a steady and simplified flow field to allow for detailed monitoring with a reasonable number of monitoring points arranged in flux fences[1];
- Increase mass balance accuracy and provide a check on flux fence calculations;
- Impose an advective timescale compatible with the bidegradation process and the experimental design, flushing approximately 10 pore volumes through the cell over the 600 day period of the experiment; and
- Monitor a DNAPL source area in its upgradient portion, and the dissolved plume migrating from the source area in its downgradient portion.

[1] a flux fence is a monitoring well transect used to estimate the total mass discharge of groundwater plume passing through the transect by measuring and integrating estimates of concentration and groundwater flow rate at measurement points within the transect.

Figure 1. Site layout: test cell, DNAPL source and dissolved plume.

3. CELL DESIGN, SETUP AND OPERATION

Additional design objectives for the test cell included:

- Hydraulic isolation of a narrow flow path within the RTG;
- Limited edge disturbance and non-interference with planned geophysical testing programme sensitive to metallic construction materials; and
- Simple gradient control and limited susceptibility to bio-fouling.

The as-built test cell is shown in Figure 2.

Design features include:

- A "U" shaped containment wall (4 m wide by 30 m in length) of fibre-reinforced polyester (FRP) sheet piles (non-metallic) seated in the mudstone (Figure 2); and

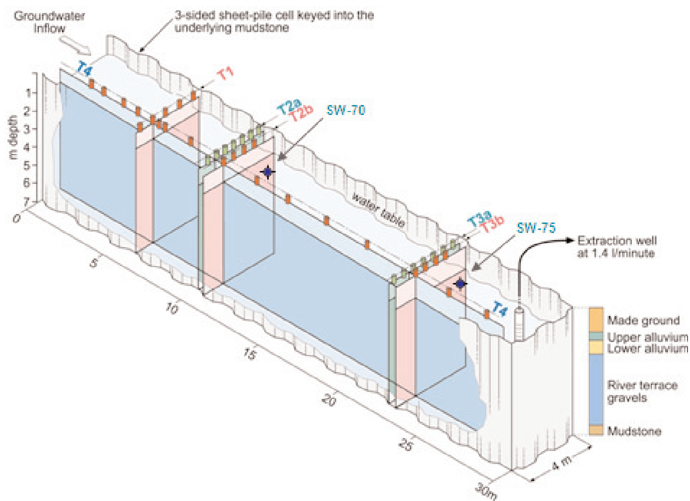

Figure 2. Schematic of test cell.

- A downgradient extraction trench and upgradient influent trench backfilled with pea-shingle (Figure 3).

FRP sheet piles were driven to the top of the mudstone using a specially-designed steel mandrel. This mandrel facilitates percussion advancement of plastic piles in a range of geologic conditions.

The test cell was located to enclose part of a DNAPL source area in its upgradient end, while its downgradient portion contained only a small quantity of residual DNAPL.

Biostimulation design was based on laboratory studies summarised in CL:AIRE SABRE Bulletin #3. These studies indicated that an emulsified vegetable oil (EVO) donor was effective at supporting dechlorination, and that bioaugmentation helped achieve rapid dechlorination with minimal lag time.

The test cell was instrumented (Figure 2) with:

- Three fully-screened wells (upgradient of the cell and at two locations along its centreline);
- Three multi-level flux fences with a monitoring density of approximately 1 per 0.5 m^2 of cross sectional area (transects T1, T2a/T2b, T3a/T3b); and
- An additional longitudinal transect of multi-level wells installed along the length of the cell (transect T4).

Project Streamtube (CL:AIRE Research Bulletin RB11) installed and provided data from transects T4 and T1 in the source area and enhanced detail at the SABRE flux fences permitting the quasi 3-D visualisation of data shown in later figures. In total, over 400 groundwater sampling points were established inside the 30 m by 4 m test cell, making it one of the most densely instrumented *in situ* groundwater testing facilities ever constructed. During installation of the monitor wells, 450 soil samples were collected and analysed.

The test cell was operated initially for a 90 day baseline period to establish steady-state pre-treatment conditions. Groundwater was extracted at an average of 1.4 litres per minute (lpm), corresponding to an average residence time within the cell of 45 days.

A total of 2,400 kg of SRS^{TM} EVO was injected at a 5% concentration through 16 small diameter wells for biostimulation. Approximately 80% of the EVO was targeted at the source zone area in the upper third of the cell, with the remainder distributed in the lower two-thirds of the test cell.

Bioaugmentation with KB-1® dechlorinating bacterial consortium was completed using the same injection wells two weeks after EVO injection.

Monitoring was conducted on the schedule shown in Figure 4 (with some variability as to the precise day of sampling). The starting point for treatment time measurement was defined as the day following completion of EVO injection, which took approximately one week to complete. Negative day numbering represents the baseline period.

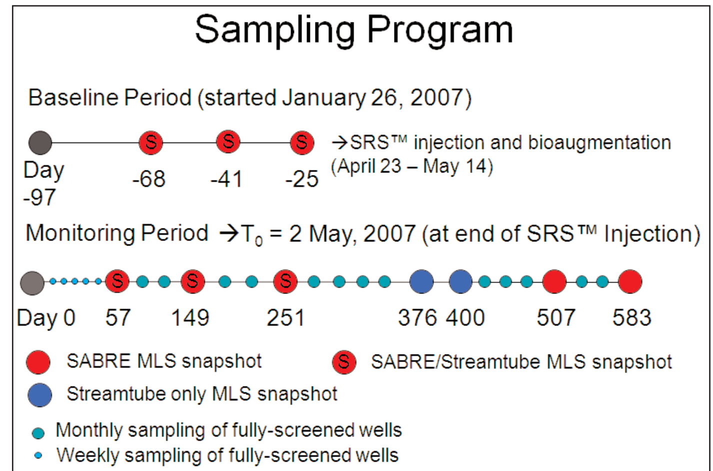

Figure 4. Sampling schedule.

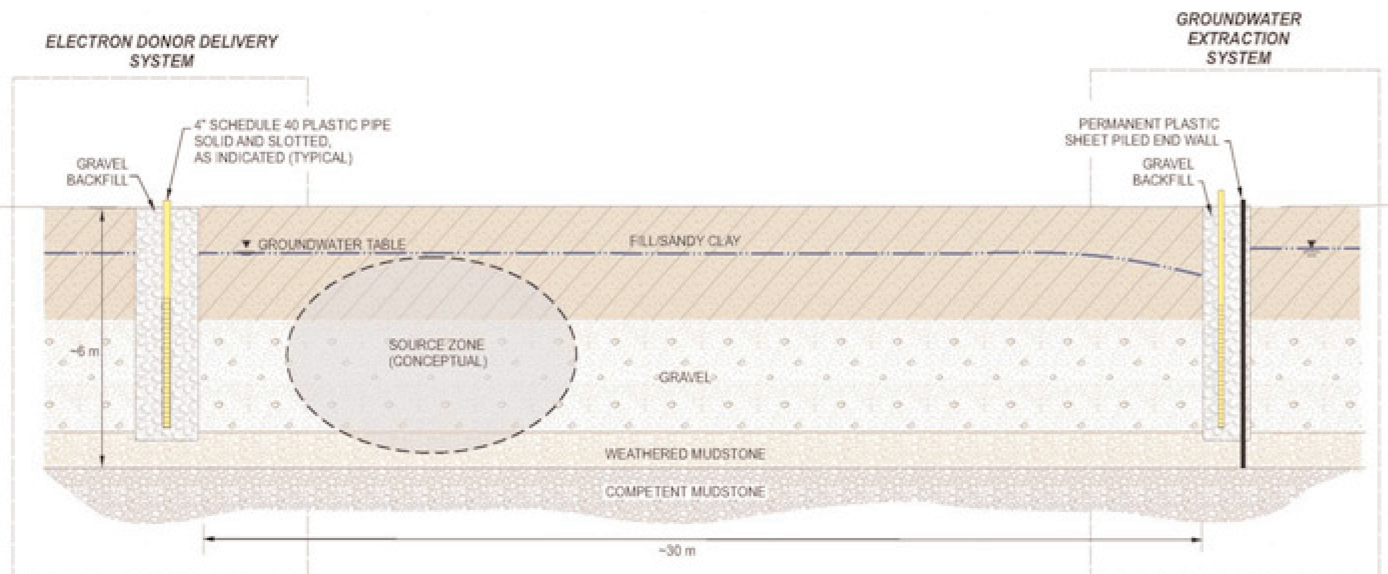

Figure 3. Cross-section through test cell.

4. OUTCOMES OF SRS™ INJECTION AND BIOAUGMENTATION

Widespread distribution of the SRS™ was achieved within the test cell, resulting in an increase in Total Organic Carbon (TOC) in groundwater which remained at 200-500 mg/L through early 2008. Iron reduction directly followed biostimulation, as evidenced by an increase in iron at the fully screened wells and in cell effluent from a pre-treatment baseline of 16-50 mg/l to approximately 100-250 mg/L. An initial decrease in sulphate concentration from 500 mg/L to less than 50 mg/L suggests stimulation of sulphate reduction; subsequently variable inputs of sulphate from the underlying mudstone caused corresponding variability within the test cell. Moderate methanogenesis was observed starting from about day 160; methane of less than 1 mg/L increased to between 3 and 10 mg/L. These trends are illustrated in Figure 5, which charts monitoring data for monitoring well SW-70. Similar trends were seen in SW-75. These monitoring wells are located in the downgradient area of the source (SW-70) and in the plume zone (SW-75), as depicted in Figure 2.

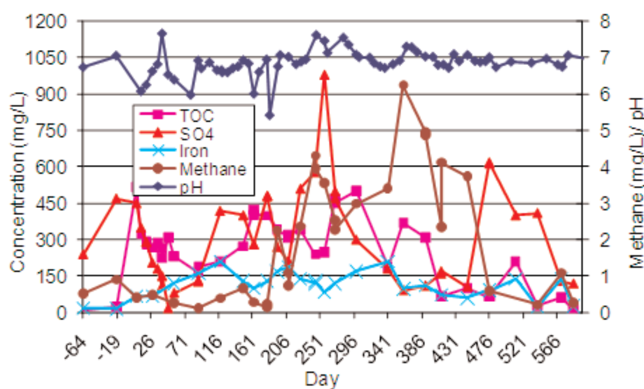

Figure 5. Geochemical measurements at SW-70.

The change in chloroethene speciation at monitoring well SW-70 is charted in Figure 6. TCE was rapidly and completely converted to cDCE throughout much of the test cell by day 7; VC production was readily apparent by day 100 (from 300 μM to over 3000 μM). Ethene production was also detected starting at day 100, but peaked above its baseline value of ~50 μM, at 1000 μM, later in the pilot test.

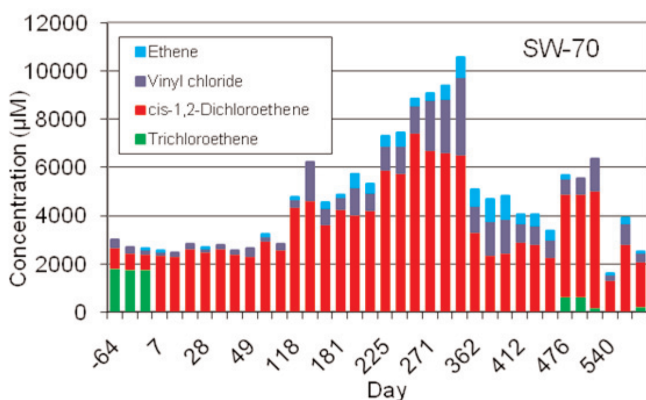

Figure 6. Change in chlorinated ethene speciation in SW-70.

Peak values of total ethenes between day 240 and 340 may have been enhanced by inconsistent operation of the test cell pump during this period. At SW-70 a decrease in total chlorinated ethenes and degradation extent is observed after day 340, corresponding with decreasing TOC and potentially greater rainfall and leakage into the test cell.

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. As illustrated in Figure 7, biostimulation and augmentation

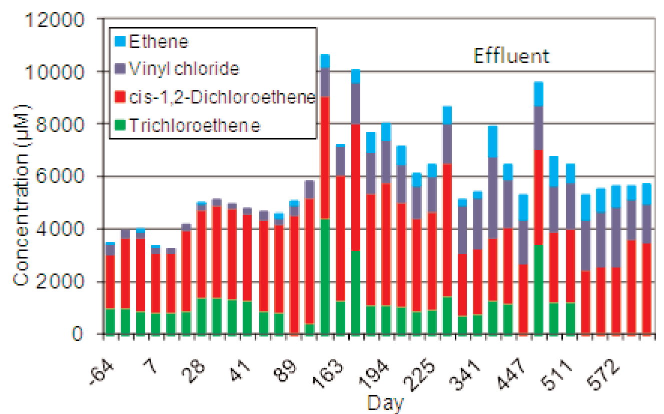

Figure 7. Change in chlorinated ethene speciation in effluent.

resulted in increases in total ethene discharge from the cell beginning at approximately day 150, as well as enhanced dechlorination to VC and ethene. Although some TCE discharge was evident through most of the test period, TCE is essentially absent from the discharge at the endpoint of the test. Based on the absence of TCE in upgradient monitoring points from day 7 - day 476 (i.e. SW-70) a previously unidentified source of TCE may have been present in the downgradient portion of the cell. During this same period, measured vinyl chloride reductase (VCRa) gene copies, indicative of the abundance of bacteria capable of VC reduction, increased by three orders of magnitude (Figure 8).

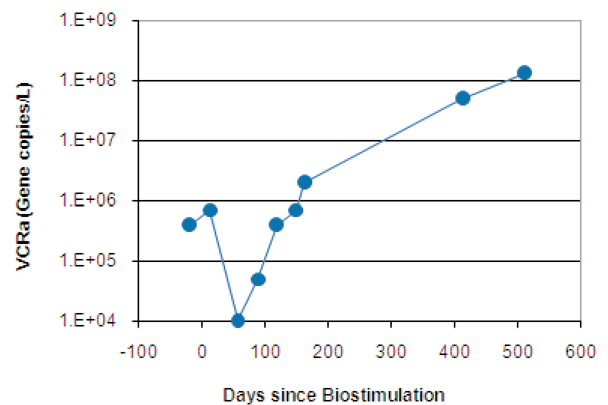

Figure 8. Vinyl chloride reductase in test cell effluent.

5. IMPLEMENTATION CHALLENGES

The SABRE contained area pilot test highlighted several implementation challenges for this technology, including acidification, aquifer clogging, electron donor depletion, and heterogeneity in both source distribution and migration pathways.

Fermentation and dechlorination generate acid. Because dechlorinating bacteria are most efficient in the range of 6.5 - 8.5 standard pH units, acid production can inhibit dechlorination and limit remedial performance. Decreases in pH from approximately 7 to approximately 6 (Figure 5) were noted following oil injection. A pH control system employing injection of a potassium and sodium bicarbonate solution was implemented approximately 4 months after biostimulation, resulting in increases in pH throughout the test cell.

Increases in the hydraulic gradient within the upper portion of the test cell were observed beginning approximately 6 months following oil injection, and 2 months after the start of bicarbonate injection. Partial clogging of the aquifer in this area was suspected, and several potential causes were hypothesised, including: bio-fouling, carbonate precipitation, iron sulphide precipitation, ion exchange and coagulation of emulsified oil. While this clogging condition was investigated, pH control was suspended. Analysis of

soil borings did not provide any evidence of biofouling or mineral precipitation. Semi-solid organic material consistent with oil residue was discovered in a limited area of the cell. A pumping and injection by-pass system was installed to eliminate the flow restriction and allow the pilot test to continue as designed.

EVO injection does not typically cause permeability reduction, provided a dilute EVO mixture is used, generally <5%, and excessive quantities of oil are not injected. The large quantity of EVO injected into the enclosed test cell in this case may have exceeded the aquifer's capacity, and resulted in local clogging. For treatment of DNAPL areas, multiple, smaller EVO injections are less likely to result in formation clogging.

As discussed in Section 4, decreases in TOC within the cell after approximately one year of operation were correlated with decreases in dechlorination extent. While enhanced dechlorination was observed for an additional year, replacement of electron donor would be required to achieve optimised performance at full-scale.

Described in more detail in CL:AIRE SABRE Bulletin #2, a tracer test was conducted during the pilot test. Consistent with the geological variability recorded in boring logs, this test illustrated that flow paths with residence times as short as 10 days exist within the test cell (average residence time 45 days). Thus, even when geochemistry, electron donor availability, and bacterial ecology are optimal, the extent of degradation within the test cell may be limited along short flow paths. Further, the existence of lower permeability zones, including the underlying mudstone, represent a potential longer term source of TCE, with diffusion-limited transport into higher velocity flow zones.

6. CONTAINED AREA PILOT TEST PERFORMANCE

CL:AIRE SABRE Bulletin #6 considers performance metrics for DNAPL bioremediation in detail. A summary of the main outcomes is provided here.

Increase in total ethene discharge from the test cell results from the enhanced transfer of mass from the DNAPL and sorbed phase to the aqueous phase due to: 1) an increased concentration gradient due to the biological treatment of groundwater, and 2) the enhanced effective solubility that results from the degradation of TCE (solubility of 1,100 mg/L) to cDCE and VC, with solubility of 3,500 mg/L and 8,800 mg/L, respectively. In this case, up to a two-fold increase in discharge was observed. Over the pilot test period, a total of 1000 kg of ethenes were removed in the test cell effluent, calculated as TCE equivalent.

Pre-treatment soil sampling verified the distribution of DNAPL within the cell as shown in Figure 9, which depicts the volume within which TCE exceeds 622 mg/kg, a concentration threshold that corresponds to inferred DNAPL presence. Warmer colours (yellow - 1000 mg/kg and red - 10,000 mg/kg) exceed this threshold, while cooler colours (green - 100 mg/kg, light blue - 1 mg/kg, and dark blue - 0.1 mg/kg) are below this threshold.

Treatment during the pilot test phase resulted in a reduction in the DNAPL zone as delineated by the 622 mg/kg TCE boundary, comparing Figure 10 to Figure 9 (See CL:AIRE SABRE Bulletin #2).

Pre- and post-treatment soil data have been evaluated in detail to produce estimates of non-aqueous phase mass and quantify the uncertainty in those estimates (See CL:AIRE SABRE Bulletin #2). Upper confidence limit non-aqueous phase mass estimates are consistent with the removal of 1000 kg ethenes in the test cell effluent, and suggest that, pre-treatment, the test cell contained in excess of 1 tonne of TCE, of which 60-75% was removed and/or completely treated during the field test.

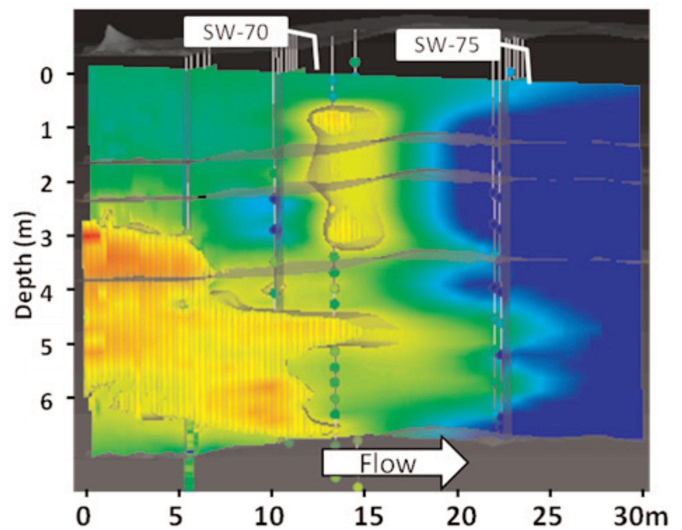

Figure 9. Pre-treatment TCE DNAPL distribution.

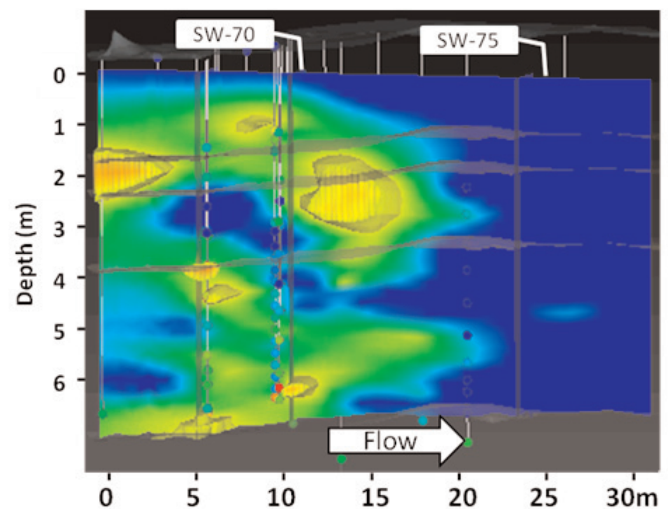

Figure 10. Post-treatment TCE DNAPL distribution.

The flux enhancement factor (ratio of post-biostimulation to pre-biostimulation flux) was approximately 1.6, averaged over the life of the field test, representing a potential decrease in DNAPL source lifetime of 40%. Continued *in situ* biological treatment of residual sources (sorbed and diffused) can effectively truncate long plume "tails", achieving a substantially greater reduction in remediation timeframe, depending on cleanup standards.

Aside from the effects of electron donor depletion, TCE remained only partially-degraded in the test cell effluent due to the high concentration source and the short residence times in the cell. However, even in the presence of persistently high cDCE concentrations (4,000 μM or 400 mg/L), up to 25% of TCE was degraded to ethene and other non-chlorinated degradation products, demonstrating complete dechlorination along slower flow paths.

The SABRE contained area field pilot test has confirmed the findings of a number of laboratory studies. In particular, biostimulation of DNAPL source zones can:

- Substantially reduce source lifetimes by enhancing mass transfer from the non-aqueous phase;
- Lead to rapid degradation of TCE to cDCE and VC even in the presence of DNAPL; and
- Support complete dechlorination of TCE provided sufficient residence time and electron donor.

Full-scale design of this technology is not without implementation challenges, but the SABRE contained area field test has made a substantial contribution to demonstrating the benefits of this technology *in situ*.

7. UNCONTAINED AREA PILOT TESTS

The uncontained area trials were conducted in parallel with the contained area pilot test, and focused on investigating two full-scale design issues:

- Alternative electron donors and their cost-effectiveness: relative performance of EVO and cheese whey electron donors; and
- Electron donor delivery method: effectiveness of (i) single-event delivery by injection through direct push drill rods and (ii) single-event delivery by simultaneous injection and recirculation using fully-screened wells.

Source mass estimates developed during the SABRE site investigation suggested that as much as 100 tonnes of TCE could be present in the source area. The test cell encloses only a small part (approximately 1%) of the total source; full-scale remediation could require a large quantity of electron donor. Therefore, the unit cost of the electron donor is a material design consideration. Cheese whey was identified as a low cost alternative to EVO. Low cost cheese whey is available fresh from the producer in liquid form. Dried cheese whey is a higher cost alternative, although a source of low cost reject dried whey was also found. Comparative laboratory testing of cheese whey, SRS™ and a cheese whey/SRS™ mixture was carried out before starting field trials.

In addition to the large areal extent of the source requiring amendment, delivery of electron donor is complicated by active and disused utilities and foundations, ongoing operations at the facility, the low yield of some geologic units (mudstone, alluvium and portions of the river terrace deposits), and the high degree of geologic heterogeneity. Therefore, efficient and effective electron donor delivery methods are needed for upscaling this technology. Direct injection and injection recirculation were identified as two methods for accessing residualised DNAPL in a variety of locations.

Three field trial areas were set up in the source area close to the test cell, with multi-level monitoring wells downgradient of the electron donor delivery zone:

- Direct injection of EVO (Terra SRS™);
- Direct injection of liquid cheese whey; and
- Injection recirculation of a EVO/cheese whey mixture.

The injection-recirculation (I-R) trial was started 4 months after the direct injection trials, using a pair of 150 mm wells fully-screened through the RTG.

Trial details are summarised in Table 1.

Electron Donor Delivery in Uncontained Area

Delivery during the direct injection/passive bioremediation trials was adversely affected by two factors:

- Preferential flowpaths: variable TOC concentrations were observed shortly after injection, with corresponding variation in degradation performance later in the monitoring period; and
- Surface emergence of electron donor: limited the quantity of donor that could be delivered.

Surface emergence occurred with cheese whey and not with SRS™. Whilst this could be due to geological differences between the trial locations, this is unlikely because they were immediately adjacent. It was concluded that the solids content of the cheese whey caused local pore clogging that then encouraged vertical flow to surface.

Table 1. Uncontained area pilot trial summary.

Parameter	Direct injection trials		Injection-Recirculation
	EVO	Cheese whey	EVO/Cheese whey
Formation treated	RTG	RTG	RTG
Total fluids injection (litres)	6,500	8,000	40,000 over 2 days
Electron donor delivered	900 kg	880 kg	1000 kg SRS™ and 500 kg cheese whey
Electron donor concentration	14%	11%	4%
Approximate material cost of electron donor	£2,500	£300	£2,750
Approximate installation and operating costs of donor delivery	£750	£2,500	£4,000
Total cost, per kg donor delivered	£3.60	£3.20	£4.50
Injection points/spacing	3 at 2 m spacing	9 at 1 m spacing	8 m between well pair
Surface emergence of donor	No	Yes, at 8 locations	No
Bioaugmentation	No		
Monitor well network	2 multi-level well installations, 4 m and 8 m downgradient	Separate, but identical to the EVO system	2 multi-level well installations, one between injection wells and one 6 m downgradient
Monitoring frequency and period	Monthly sampling for 16 months		Monthly sampling for 12 months
Analytical suite	Groundwater analysed for VOCs, ethene, ethane, methane, inorganics suite		

No difficulty was experienced in delivering the scheduled mass of electron donor by injection-recirculation, with a total of 40,000 litres delivered over 2 days. However, it was apparent that the electron donor followed preferential pathways as evidenced by (i) early breakthrough of electron donor at the extraction well in advance of theoretical, (ii) variable TOC concentrations achieved and (iii) variable degradation performance.

During subsequent monitoring of the I-R system, several litres of separate phase vegetable oil were found in the injection wells. This is indicative of breakdown of the oil emulsion in close proximity to the injection wells during and/or after injection. It is possible that the salt content of the cheese whey destabilised the EVO emulsion, causing accumulation of free phase oil close to the injection wells.

The above findings highlight the need to:

- Minimise injection of solid matter; and
- Control both the concentration and total mass of EVO injected at each well (or direct push location) during each injection event.

Field Performance of Alternative Electron Donors

Laboratory trials carried out on cheese whey, SRS™ and a SRS™/cheese whey mix indicated that all three donors supported complete dechlorination to ethene, with SRS™ having marginally better performance.

Trends in TCE and its daughter products were similar in all three uncontained area field trials, and similar to trends observed in the test cell. TCE concentrations generally decreased following biostimulation, as observed in the test cell. The cheese whey direct injection trial performed best in this respect. cDCE was the dominant chlorinated ethene throughout all three trials in all monitor wells.

As in the test cell, production of VC and ethene was observed, generally after 100 days or longer. For VC, baseline concentrations were typically of the order of 1 mg/l, whereas maximum treatment phase concentrations were typically >30 mg/l. For ethene, baseline concentrations were typically <1 mg/l, whereas maximum treatment phase concentrations were generally in the range 30 to 70 mg/l. The maximum measured concentrations of VC and ethene were respectively 150 mg/l and 100 mg/l, which are two orders of magnitude higher than the corresponding baseline.

Electron Donor Selection Economics

Cheese whey can be obtained as both fresh liquid and as a dried powdered product. The fresh whey contains approximately 6% dry matter by weight. However, the fresh whey arrived with a floating crust of solid material. Dried whey mixes to a liquid relatively easily, but the final liquid product contains a significant mass of suspended solid matter. No attempt was made to measure the pore clogging effect of cheese whey in this study, but the experience cited above suggests that significant clogging occurred during the trial. It would be possible to improve the on-site mixing process or manufacture a cheese whey product with reduced solids content, but both these would add to the cost of cheese whey.

EVO showed no evidence of pore clogging during injection.

Separate costs of electron donor supply and injection are shown in Table 1. These costs are specific to this pilot trial, and may not be directly applicable to a full-scale commercial project or the entire range of project conditions. However, the trials indicated that the total cost of delivering EVO is competitive with cheese whey due to significantly lower operational costs for EVO injection. The trials reported above indicated that EVO was less likely to clog the formation and probably has superior delivery distribution characteristics.

It was concluded that EVO is likely to be the most cost-effective electron donor for this project at full-scale due to:

- Competitive overall delivery cost, taking into account cost of supply and cost of field injection; and
- Reduced potential for poor clogging, providing for better donor distribution throughout the treatment zone and better performance where multiple injections over a period of months or years are anticipated.

8. CONCLUSIONS

The SABRE test cell is one of the most highly instrumented field-scale groundwater test facilities constructed anywhere in the world. The test cell provides effective containment to groundwater in the sandy gravel aquifer enclosed within the cell, which enabled the SABRE field trials to be conducted with a constrained flow field, controlled residence times and relatively accurate quantification of mass fluxes.

The test cell contained approximately 2.4 tonnes of TCE DNAPL prior to treatment, of which approximately 60% was removed during the 20 month post-biostimulation monitoring period. Treatment comprised a single dose of electron donor only and was not designed to maximise DNAPL mass removal. Better treatment performance would undoubtedly have been achieved if a repeat application of electron donor had been delivered after approximately 12 months; this was not carried out for experimental reasons. The effective residence time in the test cell was limited by the physical length of the cell combined with preferential high velocity groundwater flowpaths. Although complete dechlorination to ethene was achieved, the majority of the chlorinated ethene mass discharged from the test cell was only partially dechlorinated, due at least in part to relatively short residence times. Performance data indicate that further mass removal and additional dechlorination could have been achieved given additional electron donor dose(s) and a longer treatment period.

Through a combination of laboratory microcosm and column tests, field trials and modelling studies, the SABRE project demonstrated that engineered *in situ* bioremediation can be an effective technology for the treatment of DNAPL source zones. The field trials described in this bulletin made an important contribution, showing that concepts demonstrated in the laboratory could be successfully transferred to and implemented at field scale.

Acknowledgments

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This Bulletin was prepared by members of the SABRE cell engineering work package team, Lawrence Houlden (Archon Environmental) and Peter Zeeb (Geosyntec Consultants).

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