

GROUNDWATER REMEDIATION OF CHLORINATED ETHENES – IMPLEMENTATION OF A PILOT STUDY IN AN IRISH CONTEXT

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ABSTRACT

This paper presents the findings of a remediation pilot study completed at a former industrial facility in Co. Laois. Historic operations at the facility included jewellery making, soap manufacturing and aerosol production. The facility, an Integrated Pollution and Control (IPC) licensed facility, was closed in 2000. During site decommissioning, investigative works identified elevated levels of chlorinated solvents in the groundwater beneath the site, in particular Trichloroethene (TCE). Monitored Natural Attenuation (MNA) was the remedial approach agreed with the EPA as part of the site owners exit strategy. In early 2007, the EPA requested that our Client assess alternative remedial strategies for the site. A remedial options appraisal was completed and the most technically viable remedial strategy was selected. A pilot study to validate the effectiveness of the chosen strategy, enhanced anaerobic bioremediation (reductive dechlorination), commenced in 2007. The pilot study consisted of applying a hydrogen releasing compound to the subsurface within a portion of the inferred source area onsite. Groundwater monitoring wells upgradient, downgradient and cross gradient were monitored over an eighteen month period to observe the effects.

Enhancing reductive dechlorination using hydrogen donors effectively accelerates the breakdown of chlorinated solvent contaminants from the parent compound to its daughter products in this instance from TCE, to 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-DCE) or trans-1,2-dichloroethene (trans-DCE), vinyl chloride (VC) and eventually to ethene. During the pilot study and following application of the organic substrate i.e. a hydrogen releasing compound, a sharp decrease in concentration of the parent compound, TCE, was observed with concentrations decreasing from 20.374mg/l to <1mg/l measured at Day 19 post application. A corresponding increase in the daughter products was observed. The pilot study demonstrated that reductive dechlorination is a viable and effective remediation strategy for this site.

GENERAL INTRODUCTION

The site is located in Co. Laois and is bordered by a mix of residential, commercial and agricultural developments. The site was Greenfield prior to its development in the 1970s. Historic site operations included jewellery making, soap manufacturing and aerosol production. The site was licensed by the EPA in September 1998 under an Integrated Pollution and Control (IPC) Licence. In 1999 the site owners announced their decision to close the site and a gradual shutdown of operations took place between 1999 and the first half of 2000. Our Client purchased the site in 2000 and the site is currently unoccupied.

GEOLOGY

Quaternary Geology

The subsoil beneath the site comprises glacial tills (boulder clay) and sand and gravel deposits, which vary in thickness and occurrence across the site.

Bedrock Geology

The bedrock underlying the site is mapped as the Calp Formation which comprises of limestone with some shale. The bedrock is fractured in places, with the most highly fractured zone in the central portion of the site. Fractures have a moderate to steep dip (30° to 60°) which is similar to the orientation of the bedding planes. Some calcite and black mineralisation with similar orientation were

identified at the site. The limestone bedrock has been locally dolomitised and has exhibited varying amounts of weathering and fracturing which control hydraulic conductivity in the formation.

HYDROGEOLOGY

The aquifer beneath the site is located within the Cushina Groundwater Body (GWB) which has an areal extent of 170m². The aquifer of the Calp Formation in this area is classified as a locally important aquifer which is moderately productive only in local zones. In general, the Calp Formation is considered to have a low permeability in the order of 1m/d (Wright, 2000); however, high permeability is associated with fault zones.

The groundwater vulnerability beneath the site has been classed by the Geological Survey of Ireland (GSI) as 'high' with the exception of a small area in the northern portion of the site which is classed as 'Extreme' and 'Extreme with rock near surface or karst'.

The results of hydrogeological testing at the site indicate that the hydraulic conductivities ranged from 1.39x10⁻⁹m/s (0.00012m/d) to 2.08x10⁻⁴m/s (18m/d) with an average of 2.41x10⁻⁵m/s (2.08m/d). In general, the higher permeability values were associated with wells screened across highly fractured and weathered or dolomitised zones within the limestone. Groundwater beneath the site flows to the northeast towards the River Barrow which is located 500m from the site and is the primary environmental receptor of groundwater contamination in the area. It was established that all houses and industries within a 1 km radius of the site are served by public mains water supply. The measured hydraulic gradient across the site ranges from 0.003 to 0.005.

CONTAMINANTS

In accordance with the requirements of their IPC Licence, the former site owners undertook an investigation of the property to determine whether there were any residual impacts on the subsoil and groundwater as a result of 25 years of industrial activities on the site. This investigation revealed the presence of elevated levels of an industrial chlorinated solvent, namely Trichloroethene (TCE) in the groundwater downgradient of the factory building. TCE was commonly used in industrial and commercial activities in the 1970s and 1980s in particular as a degreasing agent for cleaning metal parts and also for dry cleaning. It is reported that TCE may have been used on the site from 1974 to the early 1980s. The contamination onsite resulted from site operations and waste management practices associated primarily with jewellery manufacturing although there were no reports of significant releases at the site. Maximum TCE concentrations reported in the inferred source area, located downgradient of the factory building, were in the region of 130mg/l in a sample collected from Borehole 401 in May 2000. Low level contamination was detected at depths of 75metres below ground level (mbGL) although the highest concentrations were generally observed at a depth of approximately 25-30mbGL. Low level concentrations of Tetrachloroethene (PCE) and chlorinated ethene daughter products were also observed.

ROLE OF THE REGULATOR

Monitored Natural Attenuation (MNA) was the remedial strategy approved by the EPA and implemented by the former site owner in 2000. It was considered at that time based on available data that the process of natural attenuation was already occurring. MOR has undertaken groundwater monitoring on site since 2001. Monitoring reports were submitted to the EPA after each monitoring event. These reports reveal the continued presence of TCE in the groundwater and although the plume size has remained stable over the monitoring period, the EPA were no longer willing to accept MNA as a viable remediation strategy due to the slow degradation of the contamination. In January 2007 the EPA requested that our client consider alternative remediation. Following this request from the EPA, MOR commenced a detailed evaluation of possible alternative remediation technologies.

REMEDIAL OPTIONS APPRAISAL

Various remedial options were examined by MOR to determine their technical feasibility for use on this site including those listed in the Contaminated Land Report No. 11, more commonly known as CLR 11 (Environment Agency, 2004). The remedial options evaluated included:

Civil Engineering Methods	<ul style="list-style-type: none"> • Hydraulic Barrier • In-ground Barrier
Biological Methods	<ul style="list-style-type: none"> • Biosparging • Enhanced Anaerobic Bioremediation
Chemical Methods	<ul style="list-style-type: none"> • Chemical Oxidation
Physical Methods	<ul style="list-style-type: none"> • Dual Phase Soil Vapour Extraction (DPSVE) • Air Sparging • Permeable Reactive Barriers (PRBs) • Ex-situ Pump and Treat • Thermally enhanced remediation techniques

The remedial options were evaluated in terms of the initial cost of implementation, ongoing operational and maintenance costs, duration of treatment, disturbance of land and specific technical constraints. Some of these remedial options were easily discounted given the specific site characteristics. For example, given the depth of contamination, it was clear that PRBs, in-ground barriers or thermal treatment would not be effective solutions for this site. It was also considered that hydraulic containment would not be effective for this site as it is likely that groundwater flow within the bedrock aquifer rather than flushing due to infiltration is responsible for much of the mass transfer of contaminants.

Techniques that involve the use of air injection (e.g. biosparging and airsparging) were also discounted due to difficult application in bedrock conditions, the depth of contamination and also given the heterogenous subsurface conditions present which could result in some areas remaining untreated.

Any method involving the extraction of groundwater (e.g. DPSVE or ex-situ pump and treat) were not considered to offer viable technologies in the context of site specific conditions due to the high operation and maintenance costs associated with treating such large volumes of water and difficult application conditions given the depth of the contamination.

Chemical oxidation ranked strongly as a remedial option however it was also considered to be unviable due primarily to the requirement for oxidants to come into contact with all areas of contamination, the potential for frequent reapplication, in addition to health and safety concerns.

Following a detailed evaluation, enhanced anaerobic bioremediation (and the reductive dechlorination process) was ranked as the preferred option, on the basis that it would enhance mildly reducing conditions already present, that the contaminant levels are within the treatable range and that substrate addition would facilitate the reductive dechlorination of the competing electron acceptors present in the groundwater onsite followed by a reduction in chlorinated solvent contamination. Two organic substrates that are readily available on the market were evaluated as part of the appraisal, HRC-Advanced and ethanol.

HRC-Advanced is a glycerol poly lactate/polyoleate produced by Regenesis. It provides effective reductive dechlorination over large plume volumes as naturally occurring microorganisms create hydrogen and, in turn, reducing conditions in the aquifer when they metabolise the lactic and fatty acid supplied by HRC-Advanced. The hydrogen acts as an electron donor within the reducing environment and facilitates reductive dechlorination of the contaminants. This product is used to accelerate the in-situ biodegradation rates of chlorinated hydrocarbons via anaerobic reductive

dechlorination processes. The indigenous microorganisms capable of reductive dechlorination use the hydrogen to progressively remove chlorine atoms from chlorinated hydrocarbon contaminants.

Ethanol (CH₃CH₂OH) is a volatile flammable colourless liquid that is miscible with water. Similar to HRC-Advanced, when ethanol is applied to the subsurface naturally occurring microorganisms utilise the ethanol for energy creating hydrogen. Under anaerobic conditions, ethanol can be biodegraded to acetic acid and hydrogen or to carbon dioxide and hydrogen. The hydrogen acts as an electron donor within the reducing environment and facilitates reductive dechlorination of the contaminants.

Some of the main difficulties of in-situ treatments include achieving contact with all areas of contamination as without direct contact breakdown will not be observed. Ethanol has a short electron donor release profile as it rapidly ferments when compared to the longevity of the HRC-Advanced (4-5 years). Therefore, while ethanol is cheaper upon initial application than HRC-Advanced, its short lifespan within the aquifer would warrant a number of subsequent reapplications at a substantial additional cost. In addition, HRC-Advanced migrates from the application wells via advection, therefore allowing for significant distribution of HRC-Advanced and over its functional longevity. Similarly hydrogen will travel in the subsurface from the migrated HRC-Advanced via diffusion and advection allowing for a greater radius of influence of the treatment which should in turn minimise the number of application wells and reduce the potential for a requirement for repeat application events.

PILOT STUDY IMPLEMENTATION

PILOT STUDY OBJECTIVES

In undertaking the pilot study the primary objectives were to establish whether the technology would provide a viable remedial strategy for the site while at the same time remedially addressing a focused area of high contamination within the source area at the site. Additional objectives for the pilot study included gaining information on:

- The degradation kinetics as a result of the application of the slow release electron donor;
- The longevity of the product and the associated metabolic acids which are released within the pilot area;
- The requirement for electron donor in order to facilitate degradation, and
- Confirmation of the site conceptual model.

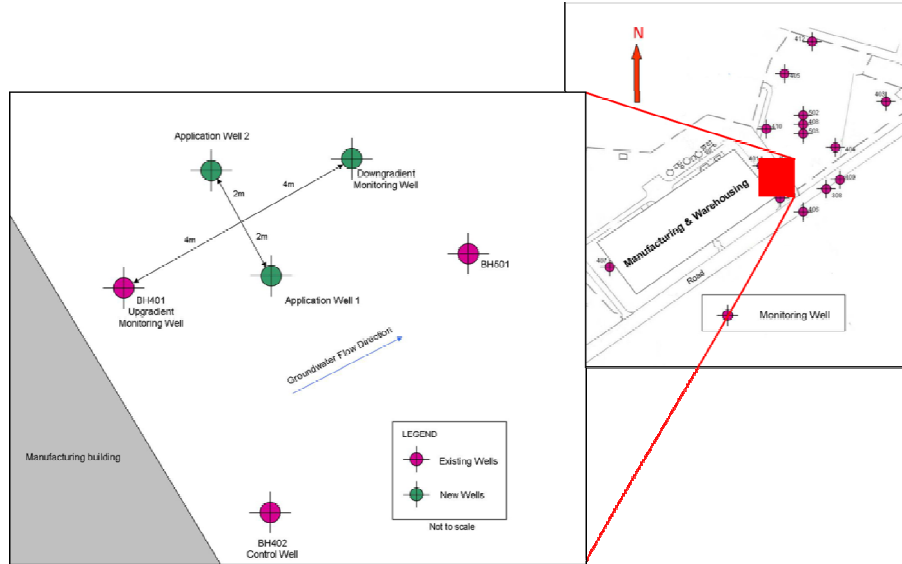
PILOT STUDY DESIGN AND IMPLEMENTATION

The location of the pilot study was based on a review of all analytical data available for the site and targeted elevated concentrations of TCE within the source area. Wells 401 and 402 consistently contain the highest concentrations of TCE and are considered representative of the source area. It was considered important from the perspective of carrying out the pilot study, to have a large volume of baseline information on both the control well (Well 402) and the upgradient well (Well 401).

Design Rationale:

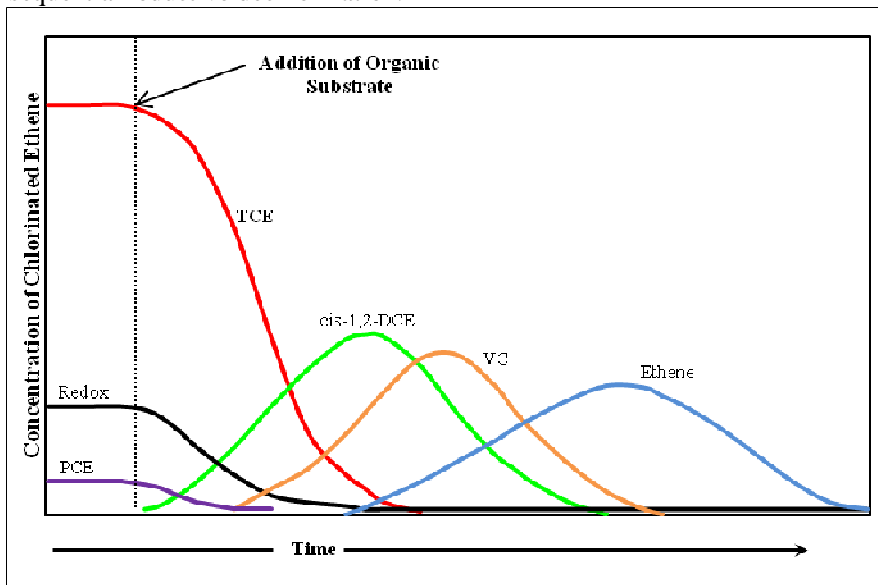
- Background/Control well (402): Allowed for the changes in natural attenuation conditions to be compared to background levels.
- Well upgradient of treatment zone (401): Provided a measure of contaminant and competing electron acceptor flux entering the treatment zone.
- Well inside treatment zone (APP1 and APP2): application wells.
- Well downgradient of the treatment zone (DGW): Provided information on the effect HRC-Advanced had on the biodegradation rates of contaminants and on aquifer conditions.

Figure 1: Pilot Study Layout



The volume of HRC-Advanced applied during this pilot test was calculated based on a number of factors including the area to be targeted, representative contaminant concentration, contaminated saturated zone thickness requiring treatment, estimated groundwater velocity, groundwater geochemistry and competing electron acceptor demand for HRC-Advanced supplied electron donor. The remediation pilot study commenced on the 27th July 2007. HRC-Advanced was mixed with water on site to form a micro-emulsion (5:1 dilution). In total 278.8 kg of HRC-Advanced was applied to each of the injection wells (2No.).

Figure 2: Conceptual model of the predicted change in chlorinated ethene concentration on site over time due to sequential reductive dechlorination.



Following the addition of an organic substrate and in the presence of appropriate microbial communications, reductive dechlorination of the parent compound occurs. For this particular site it was anticipated that TCE would be reduced to the following daughter products, 1,1 dichloroethene (DCE), cis-1,2-dichloroethene (cis-DCE) or trans-1,2-dichloroethene (trans-DCE). These daughter products are reduced to Vinyl Chloride (VC) which is ultimately reduced to ethene.

DISCUSSION OF RESULTS

Following application of the hydrogen releasing compound groundwater monitoring of the pilot study wells was completed on 7No. occasions over a 14 month period.

Chemical Parameters – Parent and Daughter Compounds

A baseline monitoring event was completed prior to the application of the hydrogen releasing compound. This identified elevated concentrations of TCE in groundwater in DGW (20mg/l). The baseline monitoring event illustrated that minimal degradation of the chlorinated ethene parent compound was taking place with low levels of one daughter product, trans-DCE, evident (0.034mg/l). Low levels of tetrachlorethene (PCE) were also observed (0.004mg/l).

Table 1: Chlorinated Ethene Concentrations - DGW

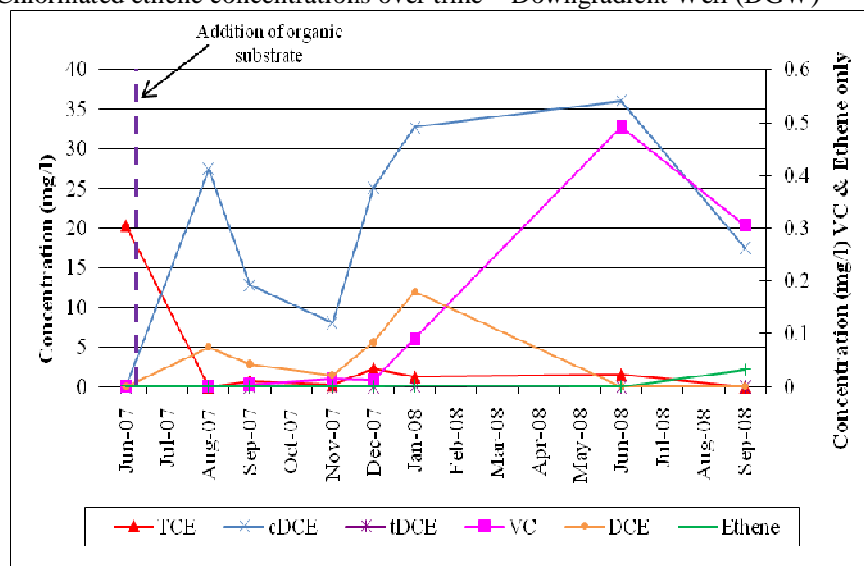
Compound	Unit	Baseline	Event #1	Event #2	Event #3	Event #4	Event #5	Event #6	Event #7
			June 2007	August 2007	September 2007	November 2007	December 2007	January 2008	June 2008
Tetrachloroethene	mg/l	<0.001	0.004	-	-	-	-	-	-
Trichloroethene	mg/l	<0.001	20.374	0.008	0.720	0.260	2.353	1.276	1.539
trans-1,2-Dichloroethene	mg/l	<0.001	0.034	-	-	0.019	0.048	0.104	-
cis-1,2-Dichloroethene	mg/l	<0.001	-	27.487	12.834	8.069	25.112	32.748	36.070
1,1-Dichloroethene	mg/l	<0.001	-	0.075	0.043	0.022	0.085	0.180	-
Vinyl Chloride	mg/l	<0.001	-	-	0.005	0.015	0.014	0.091	0.492
Ethene	mg/l	<0.001	-	-	-	-	-	0.003	-

MDL – Method Detection Limit

- below MDL

Approximately two weeks (19 days) following the application of the hydrogen releasing compound groundwater samples showed clear evidence of reductive dechlorination of the parent compound with a decrease in TCE concentrations to 0.008mg/l and a corresponding increase in daughter products such as cis-DCE (27.487mg/l) and 1,1-DCE (0.075mg/l) (refer Figure 3).

Figure 3: Chlorinated ethene concentrations over time – Downgradient Well (DGW)



Clear evidence of reductive dechlorination was observed in the downgradient well with significant increases in the concentrations of daughter products observed. Similarities were also observed between the conceptual model of the anticipated concentrations over time and the observed concentration distribution. Significantly since the pilot study was completed low levels of vinyl chloride and ethene initially observed following the application of the hydrogen releasing compounds have increased. The presence of ethene in the samples collected from the downgradient well, DGW, is evidence that reductive dechlorination is occurring as a result of the anaerobic conditions and substrate addition from HRC-Advanced. In contrast, the upgradient and control wells displayed minimal and certainly no long term reduction in chlorinated solvent concentration. The upgradient

well continued to contain elevated concentrations of TCE in the region of 40mg/l representing the influx of contaminants into the pilot study area on an ongoing basis.

Geochemical Parameters

Geochemical parameters provide supporting evidence that conditions are suitable for reductive dechlorination.

Table 2: Laboratory Analysis - DGW

		Baseline	Event #1	Event #2	Event #3	Event #4	Event #5	Event #6	Event #7	
		June	August	September	November	December	January	June	September	
		2007	2007	2007	2007	2007	2008	2008	2008	
Field Parameters										
pH		7.43	6.57	6.76	7.16	5.39	7.80	7.11	7.08	
Temperature	°C	11.9	11.9	11.8	11.9	11.0	10.0	12.3	11.6	
Conductivity	µS/cm	770	1320	1340	1013	479	1264	1114	1026	
	%	1.4	2.4	2.5	1.8	1.8	2.4	2	1.8	
	ppm	385	659	670	507	956	640	556	513	
Dissolved Oxygen	mg/l	3.67	0.26	0.21	NA	0.60	0.26	1.08	0.09	
ORP	mV	139	-21	-299	-236	-189	-157	-132	-193	
Laboratory Results										
Total Iron Low Level	mg/l	<0.05	-	0.56	31.24	3.679	5.57	1.52	12.97	1.958
Dissolved Iron Low Level	mg/l	<0.002	0.005	0.34	0.051	3.822	0.021	0.396	0.096	0.266
Total Manganese	mg/l	<0.05	-	2.56	11.74	8.845	5.740	8.140	7.57	2.746
Dissolved Manganese Low Level	mg/l	<0.001	-	2.803	8.415	10.930	5.384	7.798	10.810	0.129
Nitrite	mg/l	<0.05	-	-	-	-	-	-	-	
Nitrate	mg/l	<0.3	7.20	-	-	-	-	-	-	
Sulphate	mg/l	<3	30	24	16	-	-	-	-	
Chloride	mg/l	<1	84	71	109	107	92	113	90	97
Methane	mg/l	<0.001	-	-	0.003	0.006	0.004	0.051	0.190	1.300
Ethane	mg/l	<0.001	-	-	-	-	-	-	-	0.001
Ethene	mg/l	<0.001	-	-	-	-	-	0.003	-	0.033
BOD	mg/l	<2	-	467	108	101	52	-	8	35
Ferric Iron	mg/l	<0.05	-	-	-	2.1	-	2.3	-	0.180
Ferrous Iron	mg/l	<0.1	-	-	-	2.1	-	4.7	0.06 ^f	-
Lactate*	mg/l	<0.20	4.07	764	2.80	3.03	2.42	2.72	NA	NA
acetate*	mg/l	<0.20	-	<50	103	89.90	49.30	66.40	NA	NA
i-butyrate*	mg/l	<0.20	-	<2.0	<1.0	<10.0	<1.0	<1.0	NA	NA
n-butyrate*	mg/l	<0.20	-	6.82	<1.0	1.84	0.93	4.34	NA	NA
Propionate*	mg/l	<0.20	-	17.8	152	76.70	21.80	46.10	NA	NA
Pyruvate*	mg/l	<0.20	-	<2.0	<1.0	-	-	-	NA	NA
TOC (Chemex)	mg/l	<0.20	3.39	349	121	59.20	39.10	62.90	NA	NA

MDL – Method Detection Limit

- below MDL

NA not available

- Dissolved Oxygen (DO): DO is the highest energy-yielding electron acceptor for the biodegradation of organic constituents. The results are a clear indication that anaerobic conditions were developed onsite which are required for anaerobic reductive dechlorination to take place.
- ORP is a measure of the oxidation/reduction potential. Measurements continued to remain negative and reflect strongly reducing conditions in the downgradient well.
- Thermodynamically nitrate is the next favourable electron acceptor after oxygen. The decrease in concentrations to below MDL following the application of HRC-Advanced reflect the fact that it is a favourable electron acceptor.
- Sulphate is also used as an electron acceptor in the biodegradation of organic constituents and is reduced to form sulphide (EA, 2000). Sulphate concentrations showed a steady decrease in concentration following the application of HRC-Advanced.
- Methane is an indicator of anaerobic conditions and of the degradation of organics by methanogenic bacteria. It is produced by the microbial reduction of carbon dioxide (EA, 2000). Methane concentrations in the downgradient well have shown a steady increase since the pilot study commenced.
- TOC provides a measure of the total concentration of organic material (natural and anthropogenic) (EA, 2000). TOC was analysed during the first six months of the pilot study and it was clear from the results that HRC-Advanced had a clear impact on the downgradient well immediately after application and for the duration of the sampling and analysis for TOC that took place.
- Metabolic acids provide an indication of the presence of HRC-Advanced in the subsurface. The metabolic acids analysed are short chain molecules which provide carbon and energy for

anaerobic bioremediation. In general, the highest concentrations were observed in the downgradient well following the application of HRC-Advanced.

- BOD is a measure of the amount of oxygen used by bacteria in the degradation of organic matter. As expected, BOD concentrations in the downgradient well have significantly increased following the application of HRC-Advanced and thereafter, generally decreased.

CONCLUSIONS

It can be concluded that:

- A significant reduction in the parent contaminant, TCE, was observed with a 99.95% reduction observed when the final samples were collected in September 2008 when compared to the baseline monitoring event.
- An increase in the daughter products of TCE such as cis-DCE, VC and ethene were observed. The presence of these compounds is a clear indication that sequential dechlorination is occurring (i.e. that the TCE is being broken down to its end products). The presence of these compounds, which will undergo degradation in time, either anaerobically or aerobically, is further evidence of reductive dechlorination occurring at the site due to the application of HRC-Advanced.
- Strongly reducing conditions were created and sustained within the bedrock aquifer during the pilot study. These conditions are required to facilitate the degradation of TCE.
- Competing electron acceptors such as dissolved oxygen, nitrate and sulphate all displayed a marked decrease in concentration following the application of HRC-Advanced illustrating that they have been consumed in the process. Conversely, total organic carbon measurements displayed an increase in concentration, illustrating that HRC-Advanced provides an on-going substrate for the reductive dechlorination process.
- The conceptual site model for the site was validated.
- This represents a viable and effective remediation technology for this and other sites.
- Technology improvements are facilitating the remediation of sites where previously remedial options were limited.

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