

Session 1C.9 - Bioremediation of chlorinated solvents in groundwater 1

## **MEETING THE CHALLENGES FOR BIOREMEDIATION OF CHLORINATED SOLVENTS POSED AT OPERATIONAL SITES: A COMPARISON OF CASE STUDIES**

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This paper examines two case studies where remedial strategies employed complementary approaches or treatment trains to address historic losses of tetrachloroethene (PCE) and trichloroethene (TCE) at operational sites in the UK.

At the first site, TCE concentrations averaging 2900µg/l showed little evidence of natural degradation, with degradation products being less than two orders of magnitude to that of the parent compound (*cis*-1,2-dichloroethene (DCE)) <10µg/l in the source zone and vinyl chloride (VC) <1µg/l. Groundwater was mostly aerobic, so conditions were unsuitable for reductive dechlorination, and elevated concentrations of competing electron acceptors such as sulphate were also present. The remedial strategy consisted of an injection of a lactate-based, hydrogen release compound (HRC®). This was accompanied by HRC primer to acclimatise the groundwater for reductive dechlorination, which was duly demonstrated by successive increases, followed by decreases in the degradation products, DCE, VC and ethene. An order of magnitude reduction in total chlorinated ethenes was achieved within the source area in two years and, despite the initial absence of any significant reductive dechlorination, no inoculation with *Dehalococcoides* was necessary. A soil vapour extraction scheme, undertaken in parallel with the groundwater injection regime, successfully reduced vadose zone concentrations of TCE in soil above the impacted area. The aeration had no effect on redox conditions and no inhibitory effects on reductive dechlorination proceeding within the underlying groundwater.

The second site by contrast had been subject to a much greater degree of impact (primarily by PCE), including the presence of localised Dense Non Aqueous Phase Liquid (DNAPL) in a more cohesive geological formation consisting of a gravelly clay. Intrinsic reductive dechlorination was already well advanced but access to significant areas of the source of the contamination was restricted. Therefore, the overall aim was to mitigate the potential for off-site migration as a first priority, whilst achieving a reasonable degree of mass removal within the source and plume subject to the constraints of on-site operations.

A three-stage strategy was implemented involving (i) periodic injection of HRC as a migratory 'barrier' hydraulically down gradient of the source at the site boundary to protect off-site receptors, (ii) application of a percarbonate-based chemical oxidation reagent, Regenox® followed by HRC in the source area and (iii) HRC alone in the downgradient plume, the HRC applications comprising both a primer and an extended release formulation HRC-X. Notwithstanding some continuing dissolution into the aqueous phase within the source area and immediately down hydraulic gradient from it, degradation had been proceeding at a steady rate in localities towards the boundary. At the periphery of the site, total chlorinated hydrocarbons rose from tens of thousands to over 100,000µg/l following initial mobilisation before being reduced by two-orders of magnitude to concentrations of less than 1,000µg/l, five years after treatment commenced.

The paper will discuss the variation in Chlorinated Hydrocarbon Compound (CHC) behaviour in response to the various active remedial intervention according to its nature, severity and distribution and how remedial progression can be assessed using the 'Chloride Index', in conjunction with mass removal.

## INTRODUCTION

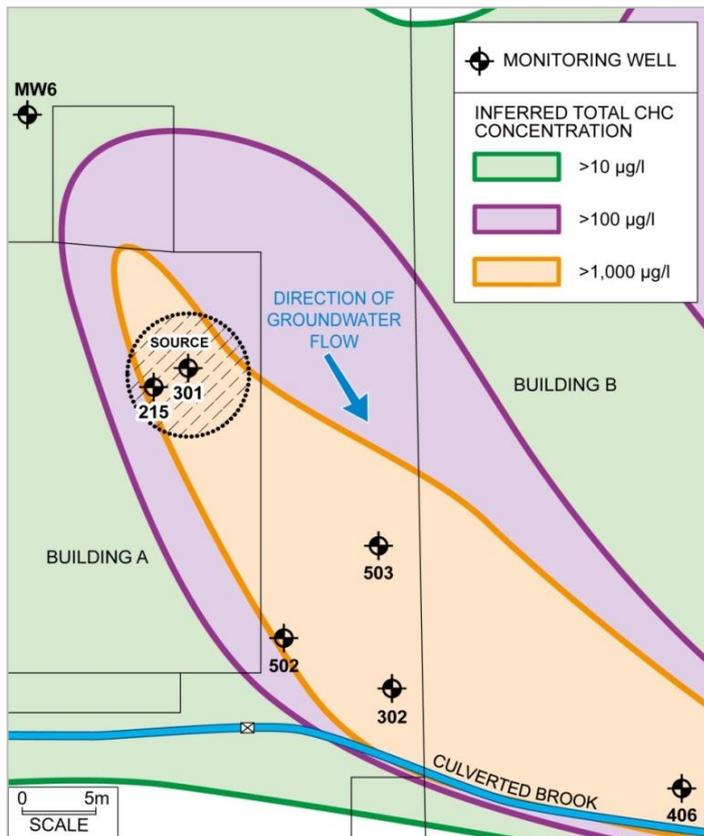
Remediation of chlorinated solvents faces particular challenges at operational facilities due to constraints imposed by operational, and health and safety issues. This paper compares the remediation of two contrasting, historically contaminated sites, one involving relatively moderate concentrations of TCE (Site 1), the other with DNAPL primarily originating from PCE (Site 2).



## SITE 1

At Site 1, investigations that had taken place during a change in site ownership identified the presence of trichloroethene (TCE) at several locations across the site, relating to a series of historical losses. Most of the plumes associated with these losses were attenuating, apart from one that originated from the site of a former storage tank, where up to 20mg/l of TCE had previously been detected (Figure1).

**Figure 1: Plan of Site 1 illustrating location of groundwater source area**



The presence of TCE (but none of its degradation products) was also identified in samples taken from a culverted brook within the site boundary and hydraulically downgradient from the source area, although concentrations had not exceeded the Environmental Quality Standard (EQS) of 10µg/l. The geological sequence beneath the site comprised between 1m and 6m of made ground, typically consisting of clayey sand with varying proportions of gravel, underlain by alluvial deposits. Shallow groundwater was encountered towards the base of the made ground or top of the alluvial deposits typically at a depth of between 1.8m and 2.4m in the proximity of the source area. The inferred groundwater flow regime was convergent upon the line of the culverted brook.

A remedial target for TCE of 1000µg/l was agreed with the regulator (the Environment Agency) as being suitably protective of the brook as the key receptor.

A review of the chemical and geochemical parameters demonstrated that conditions within the groundwater were sub-optimal for reductive dechlorination (Table 1), particularly the presence of elevated nitrate, sulphate and non-detectable iron (II). This was supported by the relatively low concentrations of *cis*-1,2-dichloroethene (DCE) in relation to TCE at the site and the absence of vinyl chloride (VC) above detection limits: Whilst a maximum concentration of 20,200µg/l TCE was identified, with DCE mostly non-detectable or below 50µg/l. No evidence of DNAPL had been provided or inferred from any of the previous site investigations.

Due to the operational nature of the site, an in situ remedial approach was essential and bioremediation through Enhanced Reductive Dehalogenation (ERD) was selected as the best practicable technique. The remedial design was facilitated using in-house software provided by Regensis, according to the groundwater characteristics set out in Table 1, and incorporated both a microbial demand factor and a safety factor of respectively three times and two times greater than the theoretical requirement.



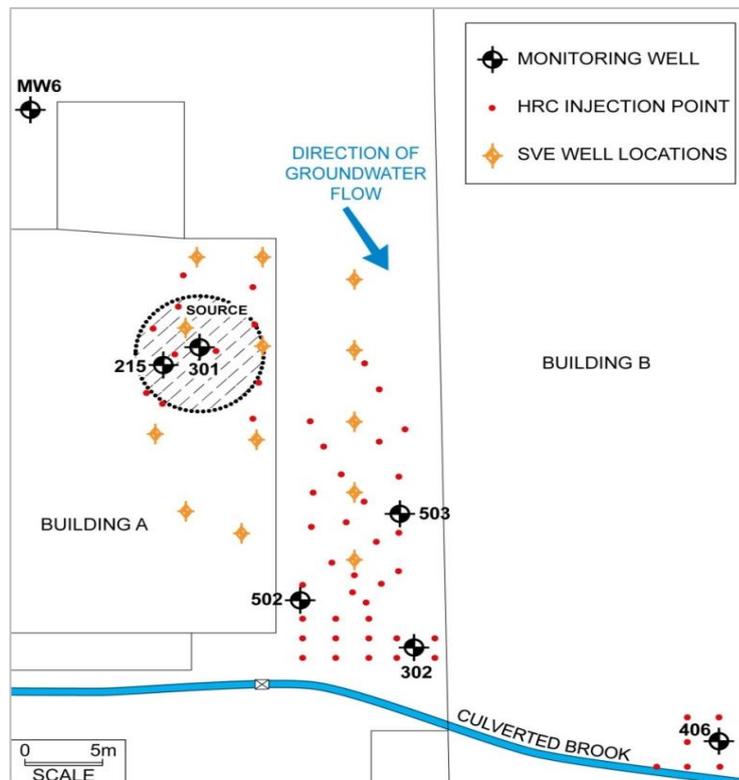
**Table 1: Key geochemical properties of groundwater: Site 1**

Parameter	Geometric mean and/or comments
Dissolved Oxygen	1.7mg/l (mostly >1mg/l)
Nitrate	4.0mg/l
Sulphate	230mg/l
Methane	7.4µg/l
TOC	4.8mg/l
Ethane & ethene	<1µg/l
Vinyl Chloride	<1µg/l
cis-DCE	<5% of [TCE]

The primary source of carbonaceous substrate required to promote reductive dehalogenation through prolonged release of lactate was HRC® supplied by Regenesis. This additionally incorporated HRC primer, a modified version of HRC, to achieve acclimation of the saturated zone through a more rapid reduction in redox potential and to overcome competing electron acceptor sinks, primarily sulphate.

The remedial design had identified a requirement for 52 injection points in total, 10 within the source area and the remainder within the plume at approximately 3m spacings. Due to access constraints, it was not possible to achieve a uniform grid spacing, however a total of 11 points were located within Building A, encompassing the source area with an additional 42 hydraulically downgradient (Figure 2).

**Figure 2: Location of injection points for HRC and soil vapour extraction wells at Site 1**

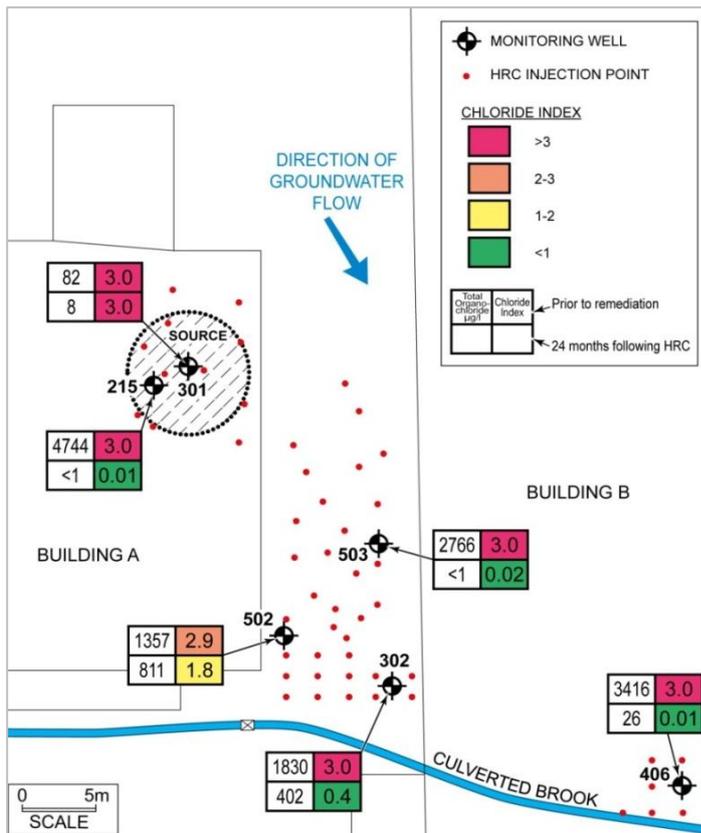


The majority of the latter (34 in total) were installed in a 10m width corridor running between Buildings A, and B, the distance between each point ranging from approximately 2.5m to 5m. A cluster of 8 injection points were also installed around monitoring well BH406, located towards the southern edge of the plume within Building B.

A single injection of HRC (pre-heated in a water bath to achieve an appropriate viscosity) took place using direct push hydraulic equipment. Drive rods were inserted to the base of the contaminated zone (typically 10m below ground level) and the HRC was injected across a 5.5m saturated thickness as the rods were withdrawn. Approximately 422kg of HRC and 218kg of HRC primer were injected within the source area, with the corresponding amounts for the remainder of the plume being 4,858kg and 1,386kg respectively.



**Figure 3: Changes in organochloride content and Chloride Index 24 months following HRC injection**



To address a localised source of TCE in the vadose zone that posed a potential human health risk, a soil vapour extraction (SVE) scheme was implemented in parallel with the groundwater remediation works to treat an area of approximately 375m<sup>2</sup>. This consisted of 13 vapour extraction wells installed on a nominal 5m grid across the core area to a maximum depth of 2m, linked together in three rows by interconnecting pipework, connected via a manifold to a soil vapour extraction plant. This was operated over an eight month period.

Groundwater monitoring was undertaken prior to treatment at intervals of one, three, six, 12, 18 and 24 months following application of reagents. The results of the treatment are illustrated in Figure 3 for individual wells in terms of the total organochloride content and the 'Chloride Index' prior to and 24 months following remediation.

The latter is defined as:

$$\frac{\sum(\text{concentration cVOC} \times N)}{\sum(\text{concentration cVOC})}$$

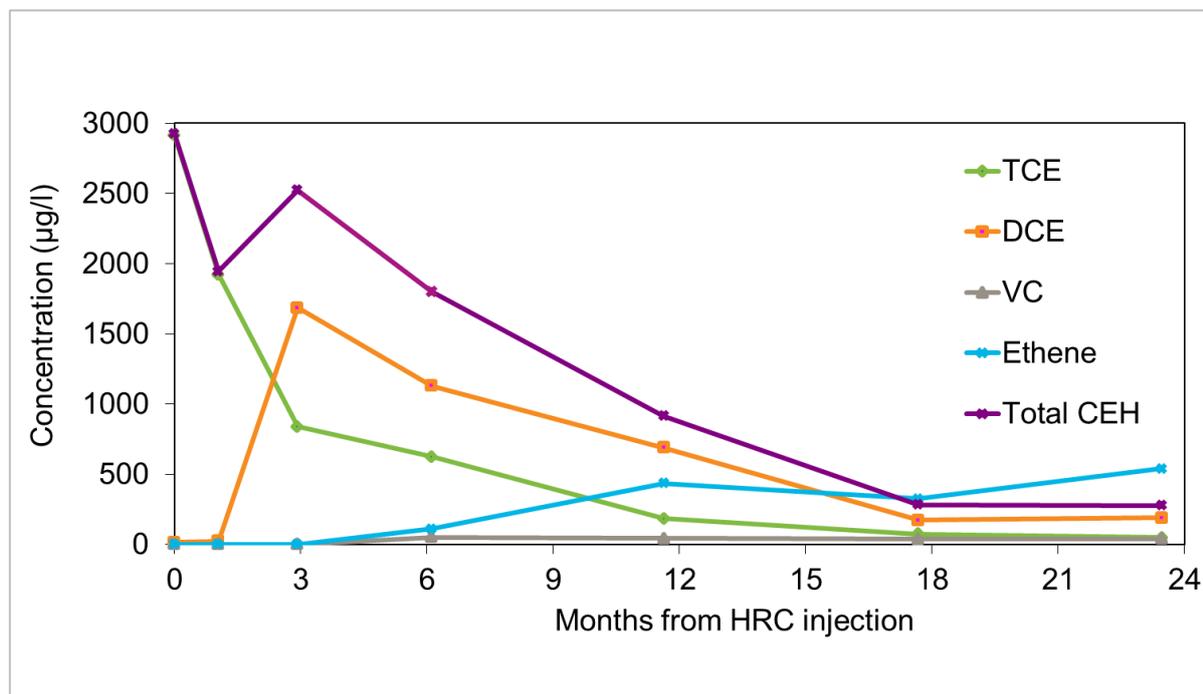
with N being the number of chlorine atoms of the individual cVOC compound and concentration being expressed in moles/l.

As degradation proceeds the Chloride Index falls: theoretical plumes consisting solely of PCE, TCE, DCE, VC or ethene would have respective chloride indices of four, three, two, one, or zero. As seen in Figure 3, the reduction in total mass of organochloride was accompanied by a substantial shift in Chloride Index in most wells, the exception being well MW301, where less than 10µg/l TCE was detected.



The overall shift in the predominance of degradation products is illustrated in Figure 4.

**Figure 4: Mean concentrations of chlorinated ethenes (CEH) following HRC injection**



The remedial target was reached or surpassed in all wells after 12 months and concentrations of total CHCs continued to fall over the following year. After 24 months, concentrations of TCE fell from  $2,913 \pm 830 \mu\text{g/l}$  prior to treatment to  $49 \pm 46 \mu\text{g/l}$ . Whilst VC (non-detectable prior to treatment) was now present, its concentration ( $38 \pm 26 \mu\text{g/l}$ ) was less than an order of magnitude to that of ethene ( $540 \pm 344 \mu\text{g/l}$ ) after 24 months (mean  $\pm$  standard error).

Soil concentrations of TCE in the vadose zone were also reduced to below the remedial target of 144 mg/kg after eight months of operation of the SVE system and, on this basis, it was agreed with the regulators that no further remedial action was required.

## SITE 2

At the second site, which had experienced a number of historical losses of primarily PCE, the geology consisted of made ground to a maximum depth of approximately 2.3m underlain by natural soft to stiff brown sandy gravely clay encountered at depths of between 1.75m and 5.0m. Shallow groundwater was encountered (typically at less than 1m depth) in the made ground and the drift deposits although it was discontinuous across the site with low recharge rates. Several separate sources of contamination were present (illustrated by the pink areas in Figure 5) and there was already evidence of significant reductive dechlorination taking place with elevated DCE, VC and ethene detectable, in contrast to Site 1 (Table 2). Also the concentrations of PCE present, typically in the tens and hundreds of mg/l in source areas were indicative of DNAPL.



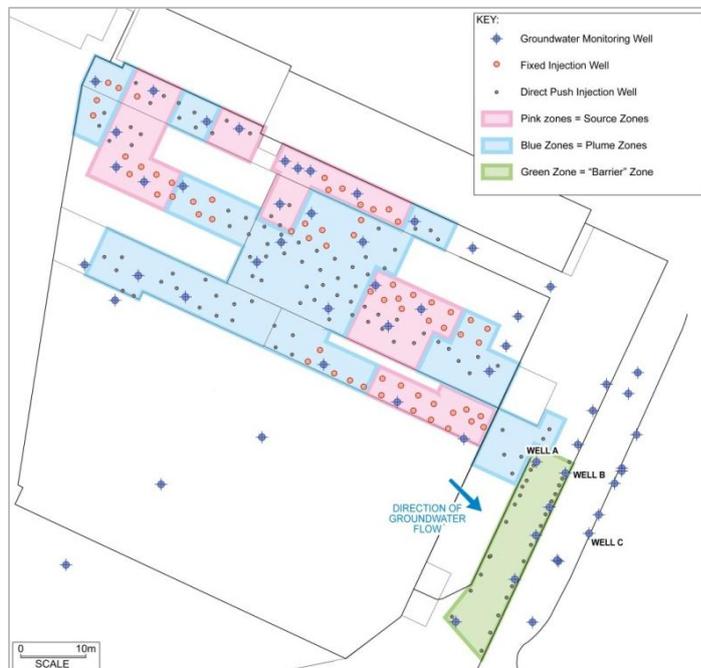
Table 2: Key geochemical properties of groundwater: Site 2

Parameter	Geometric mean and/or comments
Dissolved Oxygen	1.0mg/l
Nitrate	11mg/l
Sulphate	220mg/l
Methane	340µg/l
TOC	74mg/l
Ethane	13µg/l
Ethene	560µg/l
Vinyl Chloride	1900µg/l
cis-DCE	Typically > 2x [PCE]

The primary objective of the remedial strategy at this site was to protect neighbouring properties hydraulically downgradient, with the secondary objective being to effect reductions in contaminant mass within the source and plume areas such that natural attenuation could address residual concentrations. As with Site 1, operational constraints required an in situ remedial strategy, with the additional challenge of DNAPL in areas of limited access. A three-stage approach was implemented:

- Installation of a ‘bio barrier’ on the hydraulically downgradient site boundary as a protective measure, with periodic replenishment
- Treatment of the source areas (chemical oxidation followed by ERD)
- Treatment of the plume areas by ERD

Figure 5: Plan of Site 2 illustrating areas for treatment: source, (pink), plume (blue) and barrier (green)



The barrier, located in the green area in Figure 5, comprised two parallel rows of 10 off-set injection points at approximately 2m to 3m spacings (i.e. 20 injection points in total). During January 2009, approximately 54.45kg of HRC was injected at each location via the direct push methodology, between 2m and 6m below ground level. This was repeated some 14, 31, and 50 months later (March 2010, August/September 2011 and March 2013), the latter including a further five points extending back into the site along the assumed flow path.



For the source areas, the remedial strategy consisted of two elements:

- Beginning March 2009, treatment with RegenOx®, a proprietary formulation of sodium percarbonate and activator, via 61 fixed wells installed across five areas in off-set herringbone rows, at approximately 2.5m – 3.5m spacing. Injection was undertaken across a 2m - 4m thickness (depending on location) with 27.2kg RegenOx® per linear metre per application. The purpose of this being to promote dissolution of PCE from the adsorbed phase mass (i.e. the soil) and initiate mass destruction through chemical oxidation. Three rounds of in situ chemical oxidation (ISCO) were undertaken over a period of three months.
- Following a three month stabilisation period, additional treatment using HRC was initiated via the same 61 wells in September 2009 to accelerate anaerobic degradation of desorbed and partially degraded PCE and its intermediates. A total of 2,965kg HRC was injected across the source areas, equivalent to 13.6kg per linear metre (within a 2m – 4m aquifer thickness).

Owing to the significant dissolved contaminant mass within the source areas and the resultant accelerated depletion of HRC in these areas, further injections of both HRC and also 'Extended Release Formula' HRC (known as HRC-X) took place within the source zones in August and September 2011. In total, 8,038kg of HRC and 3,516kg of HRC-X were injected via a combination of existing fixed injection wells and new direct push locations across four source areas.

At the same time HRC was injected within the plume area (blue zones in Figure 5) at 95 locations in a herringbone pattern at approximately 2m – 3m spacings, predominantly in new direct push locations, as well as a number of existing fixed wells. A total of 4,658kg of HRC were injected in these areas.

Localised pumping and manual removal of DNAPL from a couple of locations (i.e. where access permitted) was also undertaken. Since 2011 approximately 88 litres of DNAPL have been removed.

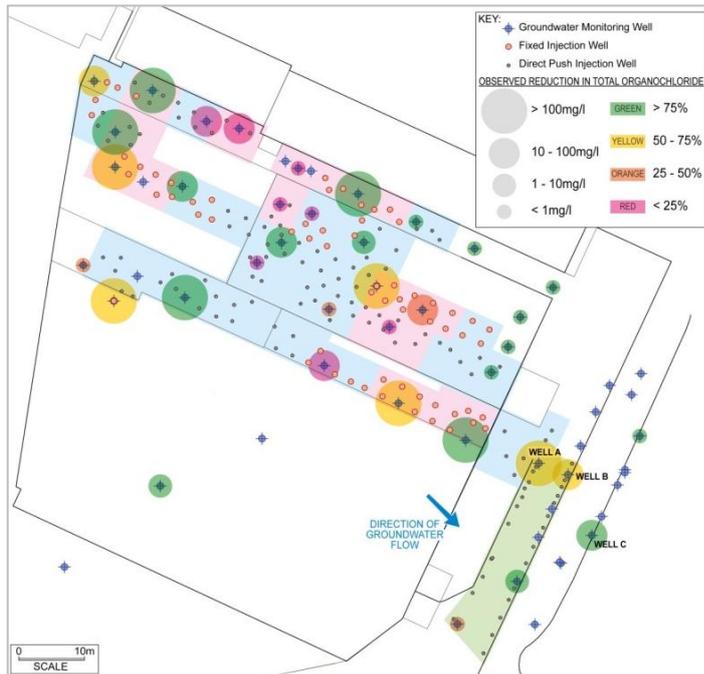
Groundwater and vapour monitoring have been undertaken regularly since the commencement of the remedial treatment. Monitoring of selected dedicated indicator wells across the source, plume and peripheral areas has allowed the observation of trends and assessment of the remedial treatment program.

Most source areas of Site 2 tended to demonstrate an initial increase in TCE and/or DCE following application of RegenOx®, representing desorption of the parent compound from the solid phase into aqueous solution with rapid conversion to DCE. This was also observed in plume area wells subjected to only HRC, which is considered to represent the release of sorbed contamination or dissolution of NAPL through biosurfactants production resulting from stimulation in microbial activity.

The changes in concentration of the key determinands arising as a result of degradation at most locations have been compounded by the migration of degradation products from treatment areas hydraulically up gradient and also the application of repeat injections of HRC. Whilst this makes the tracking of progress difficult, three illustrations are provided of the substantial progress made in the overall treatment.



**Figure 6: Reduction in groundwater contamination achieved through ERD, based on comparison of November 2014 data with maximum concentrations**

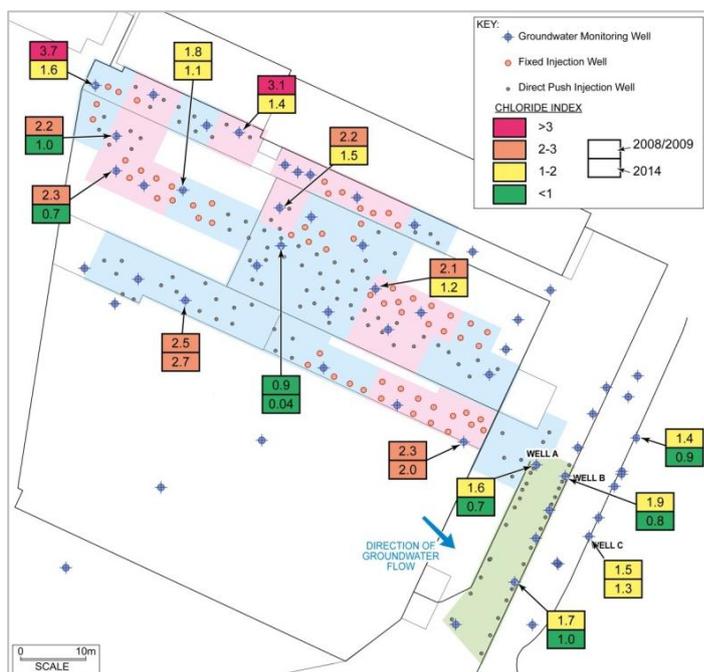


The first lies in an examination of the treatment results in terms of the degree of reduction achieved compared to the maximum recorded concentration in the groundwater, as illustrated in Figure 6.

Notwithstanding the access constraints and the presence of DNAPL (particularly in the 'pink' zones), it is evident from Figure 6 that there has been a substantial mass loss taking place, with greater than 75% reduction being achieved at around half the well locations across the site, and more than 90% reduction at over a third.

The second indicator is the use of the 'Chloride Index' to represent the status of the reductive dechlorination process, as was used for Site 1. The Chloride Index for all wells, where a full suite of data were available prior to treatment commencing and at the most recent monitoring round in November 2014, is illustrated in Figure 7.

**Figure 7: Changes in Chloride Index after approximately 5 years of treatment**



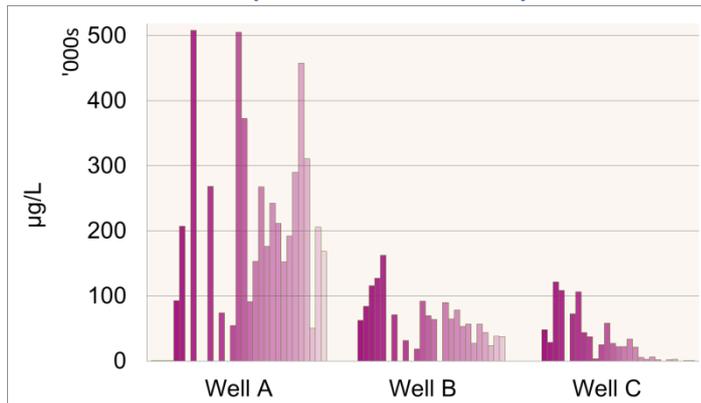
As seen from Figure 7, there has been a substantial shift in the Chloride Index over the course of the treatment across most locations, including some of the key source areas illustrated in Figure 5. Degradation was already well-advanced in the more peripheral wells such as Well C, where there have been fewer changes in relative composition.

Thirdly, it is these wells located on the periphery of the site that provide the best representation of the effects of the treatment across the site as a whole. This is because the results reflect both the loss of parent compound, the release and subsequent degradation of intermediates originating from within the source and plume zones, as well as in the area adjacent to the barrier itself.

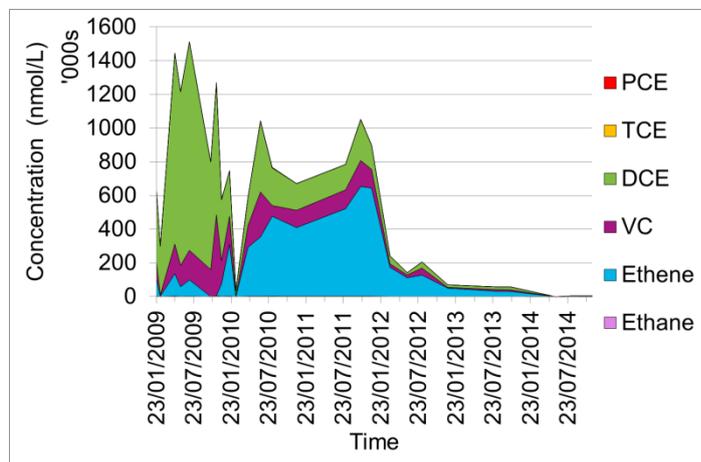
These findings are presented in Figure 8 as the total CHCs in wells from within the barrier zone. Refer to Figure 7 for well locations.



**Figure 8: Changes in total CEHs in wells hydraulically downgradient from source areas from baseline conditions in 2009 (darkest shaded bars) to 2014**



**Figure 9: Molar concentrations of CHCs and ethene/ethane in peripheral Well C**



The findings from Well A closest to the source reflect the various applications of reductant (and RegenOx® within the source itself), being characterised by increases and subsequent decreases as the product is mobilised and subsequently degraded. Further downgradient within Well B however there is more evidence of a general decrease, whilst continuing along the flow path in peripheral Well C there is greater evidence of an overall mass reduction.

The results of the peripheral Well C are of most importance not only for reflecting the activities within the contaminant plume but also the effectiveness of the bio-barrier in mitigating risks to off-site receptors. The progress achieved over the lifetime of the project is illustrated in Figure 9, which represents data on a molar basis to allow like for like comparisons.

## CONCLUSIONS

Conditions at Site 1 were unfavourable for natural attenuation of TCE, with no evidence of *Dehalococcoides* activity through minimal DCE and the absence of VC and ethene. Despite these circumstances, a steady mass reduction accompanied by a sequential increase and subsequent decrease of daughter compounds were clearly evident following a single injection round of HRC, without any additional requirement for bioaugmentation by *Dehalococcoides*.

Reductive dehalogenation was already well established at Site 2, but it was apparent that a significant mass of contamination (assumed to be present as DNAPL) was present within areas of limited accessibility. Its ongoing diffusion into the aqueous phase presented significant challenges not only in terms of providing the requisite amount of hydrogen to achieve degradation but also understanding the overall extent of degradation achieved. Nonetheless, a comparison of current concentrations with peak concentrations encountered has demonstrated a substantial reduction in overall mass across the site as a whole, following a sequential application of chemical oxidation and ERD. The effects of the latter were also observed in changes to the Chloride Index, and the success of the bio barrier in attenuating the residual contamination migrating to the site boundary is also clearly evident.

In situ ERD can therefore be an effective approach at active sites for protecting off-site receptors, despite heterogeneous conditions, DNAPL and restricted access.

