

# Treatment of a large industrial site impacted with chlorinated solvents, using a combination of electron-donor substrates and a liquid activated carbon barrier

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## **1** About the Site

This poster describes the full-scale in situ remediation of a 60,000m<sup>2</sup> disused industrial site located in the Northeast of Italy, following previous attempts to remediate the site via ex situ methods.

The site was contaminated with chlorinated solvents in a heterogeneous geology (see fig. 1), resulting in a complex distribution of contamination, ranging from DNAPL to very low groundwater concentrations. In addition, the site is bounded by a tidal river and groundwater depth and flow direction are periodically affected.

## **Characteristics:**

High heterogeneitySilty sands and sandy silts

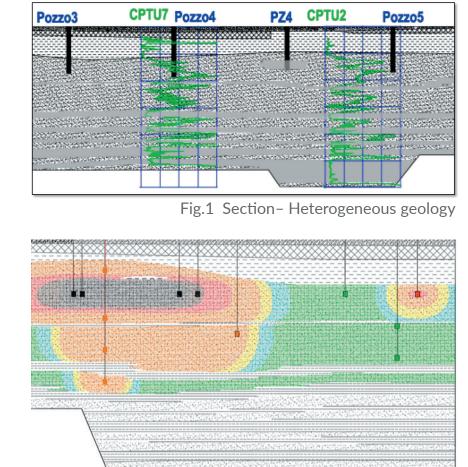
#### Total Site Area: 60.000 m<sup>2</sup> Extent of Contamination: 20.000 m<sup>2</sup>

#### Soils

TCE: max 65 mg/kg VC: max 110 mg/kg 1,2-DCA: max 5.5 mg/kg

#### Groundwater

TCE: max 155,000 μg/L 1,2-DCE: max 108,000 μg/L VC: max 8,900 μg/L



## 2 Remedial Approach

Previous remediation had comprised of excavations in the source areas, with pump and treat used at the site boundaries to hydraulically contain the impacted groundwater onsite. However the remediation targets within, and at the boundary of the site, were not met. Natural attenuation was not practical, as it would result in long-term ongoing risk and high costs. Furthermore, it was determined that groundwater concentrations of up to  $155,000 \mu g/L$  TCE presented an unacceptable risk to both on- and off-site receptors. It was therefore determined that an active in situ remedial approach should be used to address the residual contamination onsite.

The new remediation approach was based on targeted excavation of highly impacted soils, plume treatment through Enhanced Reductive Dechlorination (ERD) and the installation of a downgradient treatment zone through the injection of a liquid activated carbon barrier to prevent further contamination of the river beyond the site boundary.

#### **Remediation Activity**

2008-2012: Site characterisation

2008-2009: Primary source removal

2009: Hydraulic containment (Pump & Treat) installed along downgradient site boundary to





- Surface aquifer: from 1-4 m to 25 m from ground level
- Aquifer slightly under pressure
- Less permeable levels at 11, 17 and 19 m from ground level
- River valley deposits
- Site bounded by tidal river
- Seasonal variations in groundwater depth and flow direction

Fig.2 Section – Extent of contamination

# **3 Pilot Test Phase 1**

A dual pilot test was carried out on site, to test two different remedial approaches: ISCO using permanganate was tested in one area, and ERD using 3D-Microemulsion<sup>®</sup> (3DMe) was tested in another area on the site.

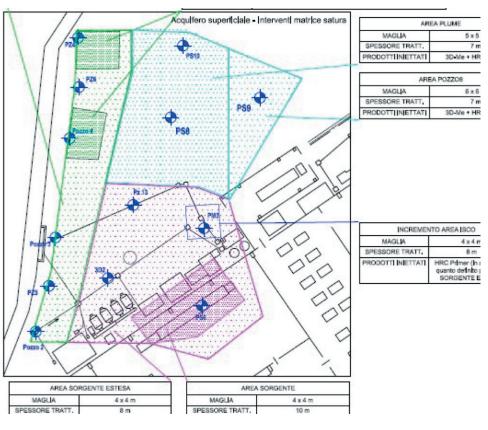
#### **Comparative pilot test results:**

In Situ Chemical Oxidation (ISCO)	Enhanced Reductive Dechlorination (ERD)
Requires high volumes to be applied	Lower mix volumes needed
Application difficulties	Manageable application difficulties
Pilot results showed contaminant rebound effect	Pilot results showed a significant and continuing degradation trend of the contaminants
Multiple injection campaigns required	Only one injection campaign needed
Closely-spaced injection grid, requiring more points	Wider injection grid possible, reducing the number of points
Poor efficacy	Good efficacy
Longer implementation time	Faster implementation time

- contain risk of offsite migration
- 2013-2014: Double Pilot Test (In situ) for groundwater remediation Phase 1
- 2014: New Remediation plan for soil and groundwater
- 2015-2016: Full scale groundwater remediation works Phase 1 with ERD (by REGENESIS) and hotspot soil excavation (by others)
- 2017: Pilot Test (In situ) for groundwater remediation Phase 2
- 2018: Full scale groundwater remediation works Phase 2 with Liquid Activated Carbon (LAC) by REGENESIS

## The conceptual site model:

- Differing hydrogeological conditions and contaminant distribution were considered to determine the type and dosage of substrate injection across the site.
- The results of the pilot tests demonstrate how these provided further information to create the most accurate full-scale design.



## 4 Full-Scale Treatment Phase 1 (ERD)

#### Main critical factors:

- Area to be treated was large:  $6,500 \text{ m}^2$  (with an average thickness of 8 m).
- Highly variable contaminant concentrations across the site.
- Complex geology, including lenses of lower permeability.
- The area adjacent to the downgradient site boundary is affected both by the river (riparian zone) and the hydraulic containment (pump and treat) system.

## Implementation strategy:

ERD of the chlorinated solvents was achieved through a grid of direct push injections, introducing a suite of REGENESIS products into the subsurface. The site was first divided into different areas based on the distribution of contamination and differing permeabilities.

A tailored product mix and dosage was then created for each area. Our widedistribution substrate (3DMe) was used in the up-gradient zones on a widely spaced injection grid, to minimise injection points and therefore cost, while providing optimum treatment of the contamination. Treatment layer: 3 m – 11 m BGL Grid: 3 m x 3 m Technologies injected: HRC, HRC X, HRC Primer

Treatment layer: 4 m – 11 m BGL Grid: 5 m x 5 m Technologies injected: 3-D Microemulsion, HRC Primer

Treatment layer: 3 m – 11 m BGL Grid: 6 m x 6 m Technologies injected: 3-D Microemulsion, HRC Primer

Treatment layer: 3 m – 11 m BGL Grid: 4 m x 4 m Technologies injected: 3-D Microemulsion, HRC Primer

Partial treatment of the deep aquifer: Treatment layer: 11 m – 17 m BGL

# 5 Full-Scale Treatment Phase 2 (LAC)

The second phase focuses on the downgradient site boundary, adjacent to the river. The proximity of the river and Italian legislative rules, have determined that the site boundary targets are very stringent (<1  $\mu$ g/L). Although the previous ERD treatment has reduced the contaminant influx dramatically; for such low targets, biodegradation alone may not reach these low targets.

Therefore, a second phase treatment has been implemented to combine contaminant sorption and biodegradation using an injectable colloidal activated carbon. A double pilot test of this approach was performed in two areas on site, in order to demonstrate the technology's efficacy and to design an accurate dose for the full-scale works. The full-scale barrier was implemented in autumn 2018 in the portions where in situ interventions Phase 1 have not met the stringent targets.

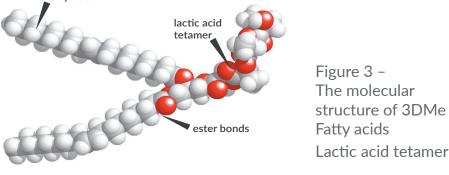
This in situ barrier is meant to replace the costly P&T system and allow the owner to cease all remediation activities with full regulatory site closure.

## 6 About the Technologies Used

## 3-D Microemulsion<sup>®</sup> (3DMe<sup>®</sup>)

3DMe is designed to distribute over very wide areas from each injection point. This is achieved through the molecule having hydrophilic and oleophilic properties (see figure 3), hence upon mixing with water, 3DMe forms a microemulsion made of tiny micelles, which propagate through and coat the aquifer, creating a wide and effective treatment zone. 3DMe provides an immediate, mid-range and long-term, controlled release supply of hydrogen (electron donor) to rapidly create and then sustain anaerobic conditions:

- Stage 1 the immediately available free lactic acid (lactate) is
- fermented rapidly
- Stage 2 the controlled-release lactic acid (polylactate ester based portion) is metabolized at a more controlled rate
- Stage 3 the free fatty acids and fatty acid esters are converted to hydrogen over a mid to long-range timeline giving 3-D Microemulsion an exceptionally long electron donor



Hydrogen Release Compound Primer<sup>®</sup> (HRC Primer<sup>®</sup>)

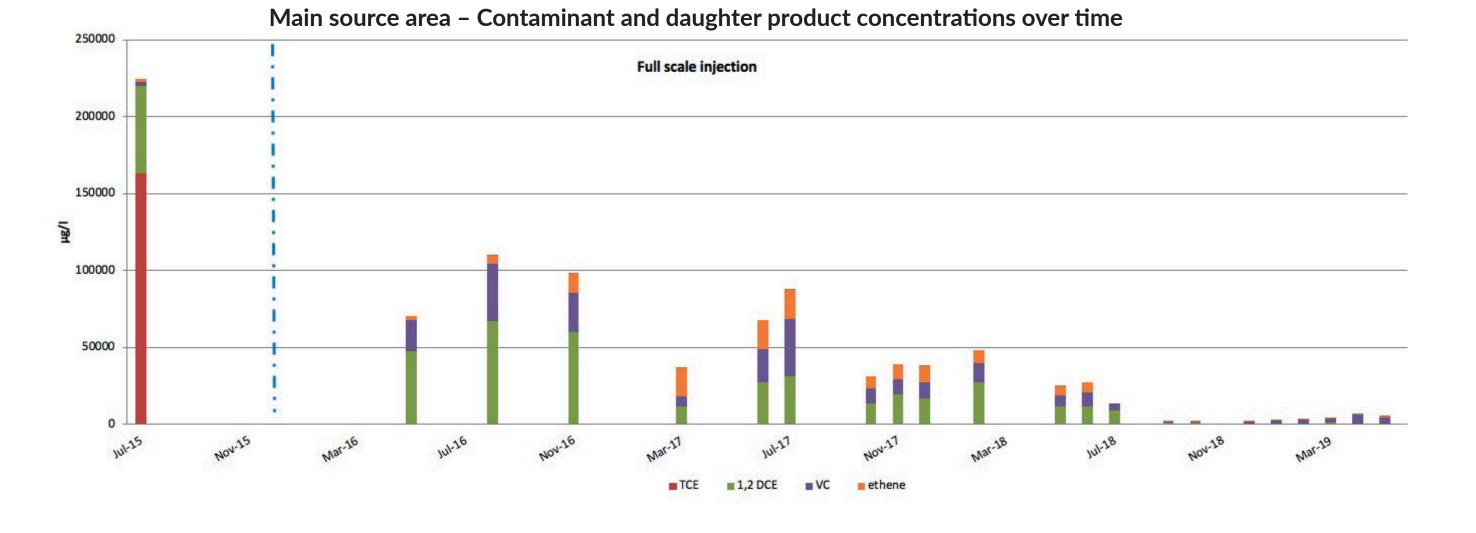
A faster-releasing version of HRC, designed for use in rapidly priming an aquifer for longer-term 3-D Microemulsion, HRC or HRC-X treatment. 3DMe<sup>®</sup> was used in all of the internal areas of the site (source zone):
This technology offers wide distribution (very wide meshes)
Longevity up to 3-5 years

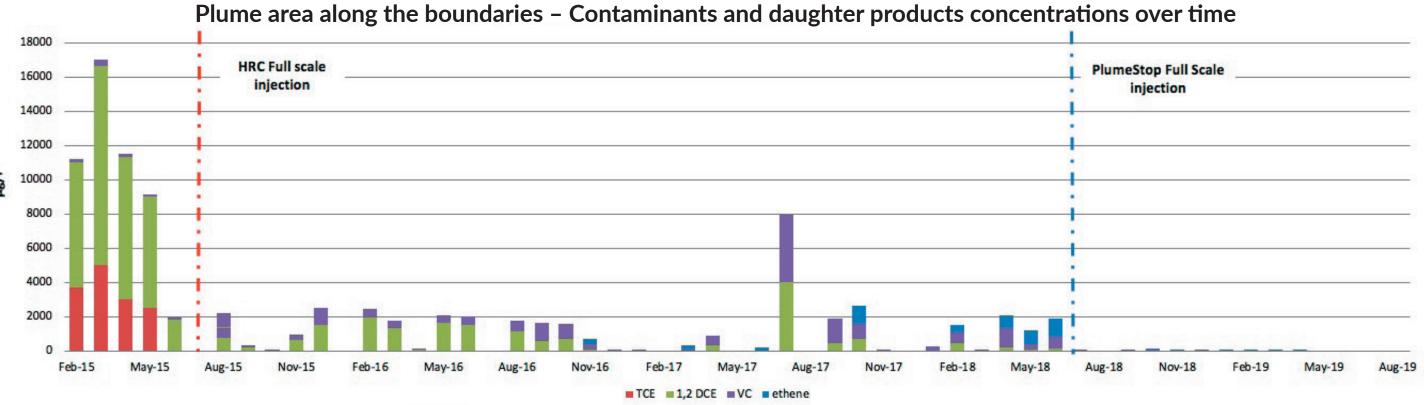
The downgradient treatment zone required application very close to the river at the site boundary. A mixture of low volume, high viscosity (HRC) products were used here to prevent contaminant egress from the site for up to five years from a single injection while remediation of the source area is completed upgradient.

HRC<sup>®</sup> + HRC-X<sup>®</sup> were used in the downgradient treatment zone:

- These are extremely viscous technologies (no wash-out risk)
- Longevity up to 18-24 months (HRC) and up to 5-7 years (HRC-X)

## **Results & Conclusion**





Grid: 3x3 m Technologies injected: 3-D Microemulsion, HRC Primer

#### Application methods:

- Injection spacing in grid and barrier configurations:
  - Use of variable injection mesh (from 3 m x 3m, to 6 m x 6 m)
  - Variable dosing depending on area and depth
- Total of approximately 500 injection points across a 10,000m<sup>2</sup> area
- Injections took 6 months to complete

release profile

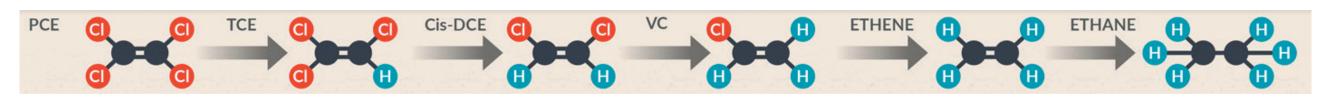
#### Hydrogen Release Compound<sup>®</sup> (HRC<sup>®</sup>)

HRC is an engineered, hydrogen release compound designed specifically for enhanced, in situ anaerobic bioremediation of chlorinated compounds in groundwater or highly saturated soils.

- Upon injection, HRC provides a controlled release lactic acid into the subsurface
- Anaerobic bacteria ferment lactic acid to obtain carbon and energy, generating other fermentable organic acids
- Microbial breakdown of the HRC produces a controlled-release of hydrogen for periods of up to 18-24 months on a single application
- Anaerobic dehalogenating bacteria use this hydrogen to degrade the chlorinated solvent contamination through enhanced reductive dechlorination

## Extended Hydrogen Release Compound® (HRC-X®)

An extended-release version of HRC for driving desorption, dissolution and degradation of higher dissolved phase chlorinated concentrations, including residual DNAPL.



## PlumeStop Liquid Activated Carbon®

PlumeStop Liquid Activated Carbon is an innovative groundwater remediation technology designed to rapidly remove and permanently degrade most groundwater organic contaminants. PlumeStop is composed of very fine particles of activated carbon (1-2µm) suspended in water through the use of unique organic polymer dispersion chemistry. Once in the subsurface, the material behaves as a colloidal biomatrix, binding to the aquifer matrix, rapidly removing contaminants from groundwater, and promoting permanent contaminant biodegradation.

This unique remediation technology accomplishes treatment with the use of highly dispersible, fast-acting, sorption-based technology, capturing and concentrating dissolved-phase contaminants within its matrix-like structure. Once contaminants are sorbed onto the regenerative matrix, biodegradation processes achieve complete remediation. The double stage treatment successfully reduced concentrations to the stringent onsite targets:

- Through ERD, primary compounds (PCE, TCE) decreased very rapidly.
- Full reductive dechlorination has occurred in most of the treatment areas, with vinyl chloride showing now low or negligible values.
- The liquid activated carbon barrier is further decreasing the concentrations at the site boundaries; up to now, approximately 70% of the boundary area has already achieved stringent targets, and costly P&T system has been partially dismissed.

The remediation results demonstrate how an accurate design of an integrative in situ approach can be tailored to different contaminant concentrations and aquifer permeabilities in order to provide cost effective treatment of large-scale chlorinated solvent sites.

- A very large site was treated cost effectively with in situ remediation.
- ERD was used to address DNAPL levels of contamination down to very low target concentrations.
- A suite of substrates was tailored to the requirements of different parts of the site. Successful ERD treatment was completed while hydraulic containment was maintained by a P&T system on the site boundary.
- The value of engineering controlled release electron donor substrates is shown here, with full reductive dechlorination of a high contaminated plume being achieved from a single injection.
- LAC was used to further decrease residual contaminant concentrations to very stringent targets where needed, allowing to finally switch off the P&T system.
- Full compliancy of the site and final closure is expected in 2020.