# Long Term Treatment of 1,2-Dichloropropane Contaminated Groundwater in Low-Permeability Media using Micro-Scale ZVI and Organic Carbon Amendment

## Summary

Following a truck accident on one of the main motorways in northern Italy, about 3,000 L of 1,2-dichloropropane was released into the ground, causing an immediate contamination of the soil and groundwater. As an emergency remedial action, approximately 900 $m^3$ of shallow soil was excavated and landfilled. In addition, the contaminated aquifer was physically contained by emplacing metal sheet piles to a depth of 6 meters below ground surface (bgs) to limit further contaminant migration. To remediate the residual groundwater contamination 55,000 kg of EHC® Reagent was injected into a triangular grid of 42 injection points from one to six meters bgs. A recirculation system was maintained during the EHC treatment period to enhance diffusion of the amendments in the aquifer. The site's remedial goal was to achieve at least a 90 percent reduction in 1,2-dichloropropane compared to baseline concentrations. This paper describes the implementation and results of the treatment that lead to site closure in 2015.

## Introduction

The combination of *In Situ* Chemical Reduction (ISCR) with bioremediation via enhanced reductive dechlorination (ERD) is an effective and widely applied remediation method for groundwater contaminated with chlorinated solvents. In situ groundwater remediation is often accomplished by injecting liquid or solid reactive amendments to stimulate biological and/or abiotic degradation mechanisms. This approach can be challenging to apply in low permeability media due to the difficulty of distributing amendments in the targeted treatment zone. In situ remediation of low-permeability soils using common rapid releasing and short-lived reagents is often complicated by at least two factors: (1) clayey formations generally contain a higher proportion of the contaminants sorbed to the soil matrix, and (2) it is often difficult to achieve effective distribution of remedial reagents in tight soils. As a result, contaminant destruction is often limited and concentration rebounds are commonly observed. Once the reagents have been consumed, further desorption of chlorinated volatile organic compounds (CVOCs) present in the soil will predictably recontaminate the groundwater. Since degradation reactions are aqueous-based, removal kinetics are ultimately limited by desorption rates, and total removal rates are largely governed by the longevity of the remediation reagent.

Figure 1. EHC Slurry for DPT Injection

EHC ISCR reagent is a combination of controlled-release hydrophilic organic carbon and micro-scale zero valent iron (ZVI) used for the treatment of groundwater and saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides and organic explosives (Figure 1). Following emplacement of EHC into the subsurface, various physical, chemical, and microbiological processes combine to create strongly reducing conditions that stimulate rapid dechlorination of many oxidized compounds, such as chlorinated ethenes, ethanes, and other chlorinated solvents. This typically yields safe, rapid and effective destruction of targeted contaminants without the accumulation of conventional, dead-end intermediates. EHC degrades chlorinated ethenes through a combination of both biotic and abiotic pathways, including dehalogenation, beta-elimination, and hydrogenation. The 1,2-dichloropropene reductive reaction pathway to propene utilized with the use of EHC can be seen in Figure 2.

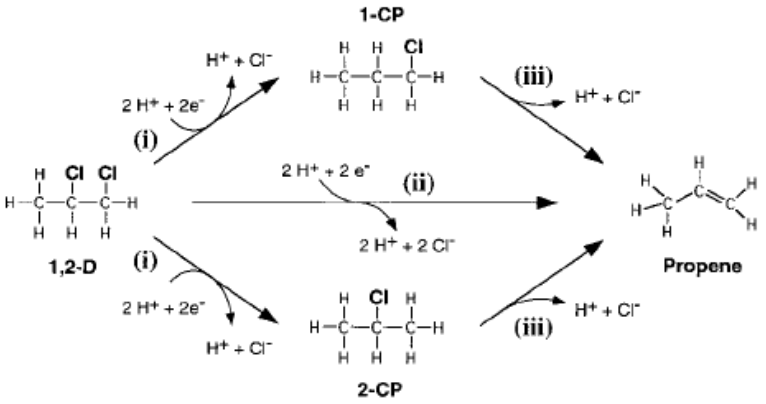



Figure 2. Anaerobic transformation of 1,2-dichloropropane by (i) hydrogenolysis of 1,2-dichloroproene resulting in the formation of monochlorinated propanes (1-CP and 2-CP), (ii) dichloroelimination (vicinal reduction) of 1,2-dichloropropane resulting in the formation of propanes[1]

Data from this site in Italy confirmed an effective EHC lifespan of at least three years allowing the successful long-term treatment of the site's clayey formation. The EHC slurry was observed to displace into discrete fractures in the soil matrix. Long-term monitoring suggested that diffusion, advection, and dispersion serves to enhance the distribution of the reagent in the subsurface and provide treatment beyond the observed fractures. As a result, homogenous distribution of EHC into the soil matrix was not necessarily required for effective treatment, as may be required for other reagents.

## Site Background

In 2005, following a truck accident along one of the main motorways in the north of Italy, about 3,000 L of 1,2-dichloropropane were released into the ground, causing an immediate contamination of the shallow soils and groundwater for more than 18,500 $m^2$ (Figure 3) at the site near Portogruaro, in the province of Venice, Italy. The primary CVOCs found at the site prior to treatment included 1,2-dichloropropane at concentrations up to 10,196 µg/L in the groundwater and 61 mg/kg in the shallow soils.

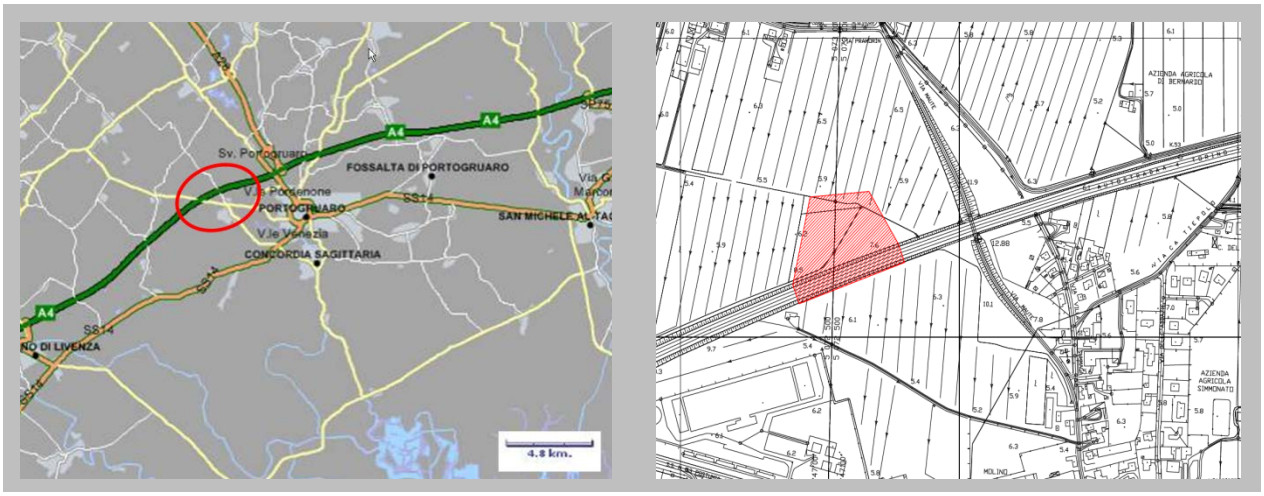



Figure 3. Accident location (left) and detailed focus on the remediation site (right)

Additional site investigation showed that the groundwater table was approximately one meter bgs and the groundwater flow velocity was assumed to be very low due to the type of soils at the site and the shallow hydraulic gradients measured. Lithology at the targeted depth interval (from one meter to 6 m bgs) was composed of interbedded saturated layers of silt and silty clay ($K \approx 5.6 \times 10^{-7}$ m/s).

The local authorities required an urgent remediation action due to the high contamination levels detected at the site.

## Full Scale Implementation

As an emergency response, approximately 900 $m^3$ of shallow soils were immediately excavated and disposed into landfill. In addition, the contaminated aquifer had been physically contained, emplacing metal sheet piles to a depth of 6 m bgs to limit further contaminant migration (Figure 4).

To address the residual groundwater concentrations of 1,2-dichloropropane, 55,000 kg of EHC Reagent was injected into a triangular grid of 42 injection points between 1 m and 6 m bgs, resulting in an average application rate of 0.6 percent to soil mass. EHC was supplied as a dry powder and mixed with water onsite into slurry containing about 29 percent solids. The annular space of the well outside the PVC pipe was filled with a sand mixture and granular EHC (see Figure 5). A subsurface recirculation system was maintained over the EHC treatment period, designed to enhance diffusion of the amendments in the aquifer.

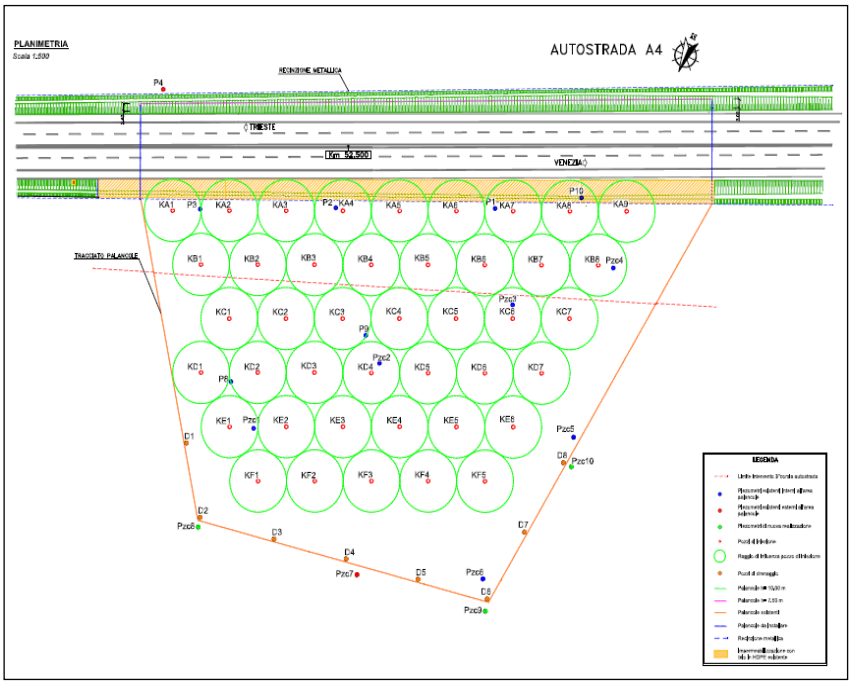



Figure 4. Grid of injection points and site border. View from above.

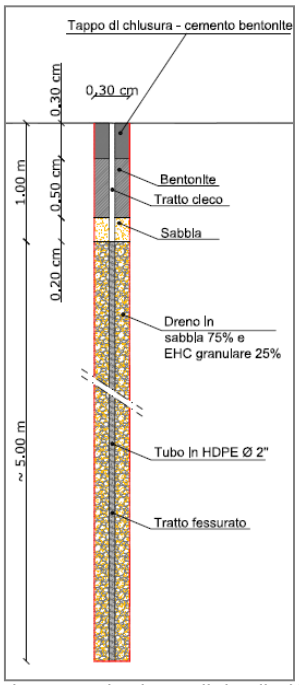



Figure 5. Injection well details (Scale 1:20)

The target goal for the grid set forth in the Clean-up Plan developed for the site was to obtain at least a 90 percent reduction in 1,2-dichloropropane compared to baseline concentrations located in the treatment area, corresponding to 0.16 µg/L in the points of compliance (Pzc6) as depicted in Figure 6.

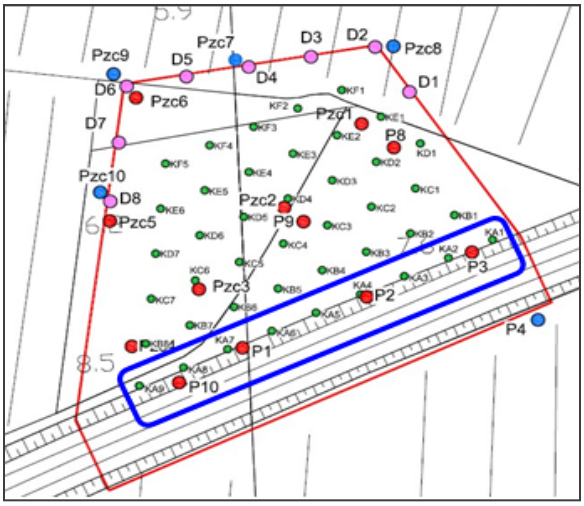
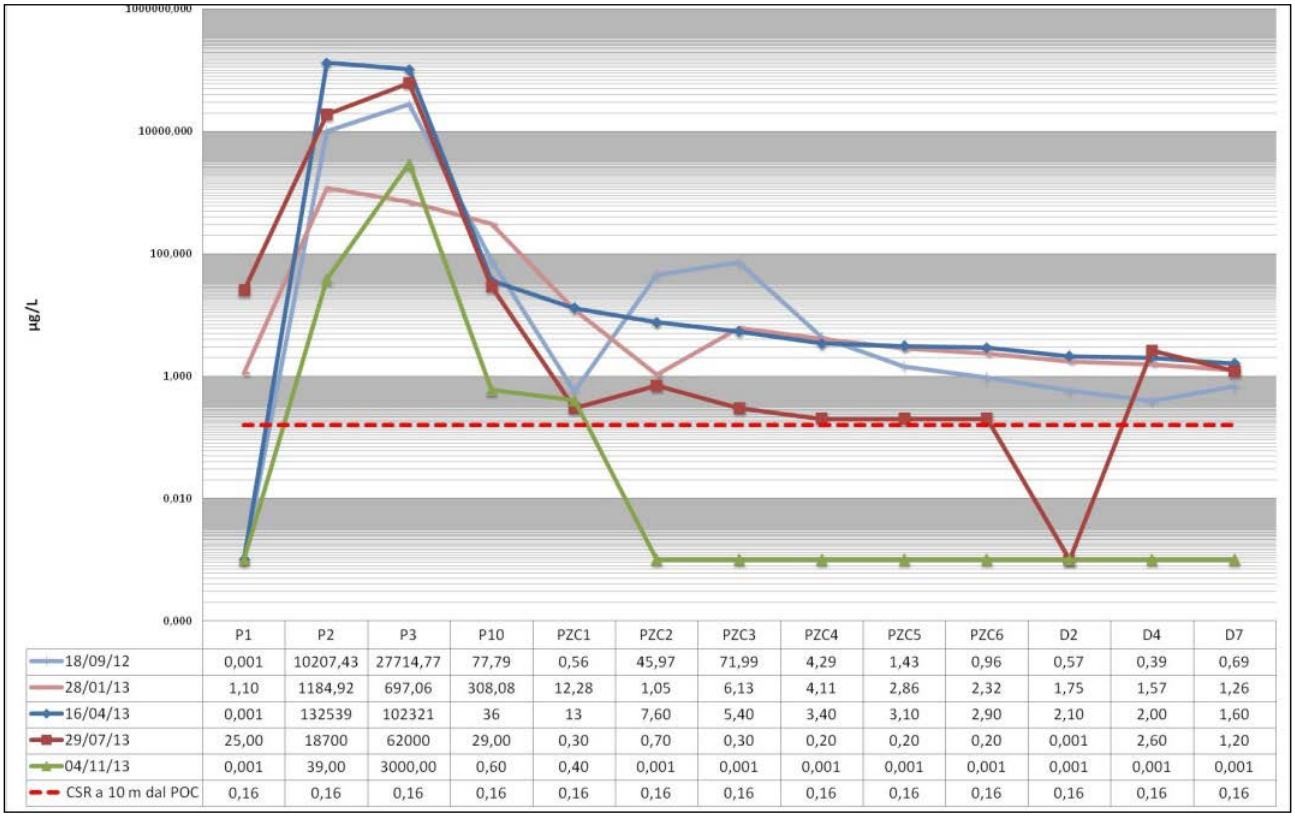



Figure 6. Monitoring and Injection well details (Scale 1:20)

## Full Scale Results

Following injection of EHC into the aquifer, 1,2-dichloropropane removal rates peaked approximately 15 months after commencement of the remediation activities, at >89 percent removal. Two years post-application, these rates increased to approximately 96 percent removal, and have remained at that level for nine months, continuously supporting treatment of groundwater (Figure 7). Site closure was accomplished in 2015.



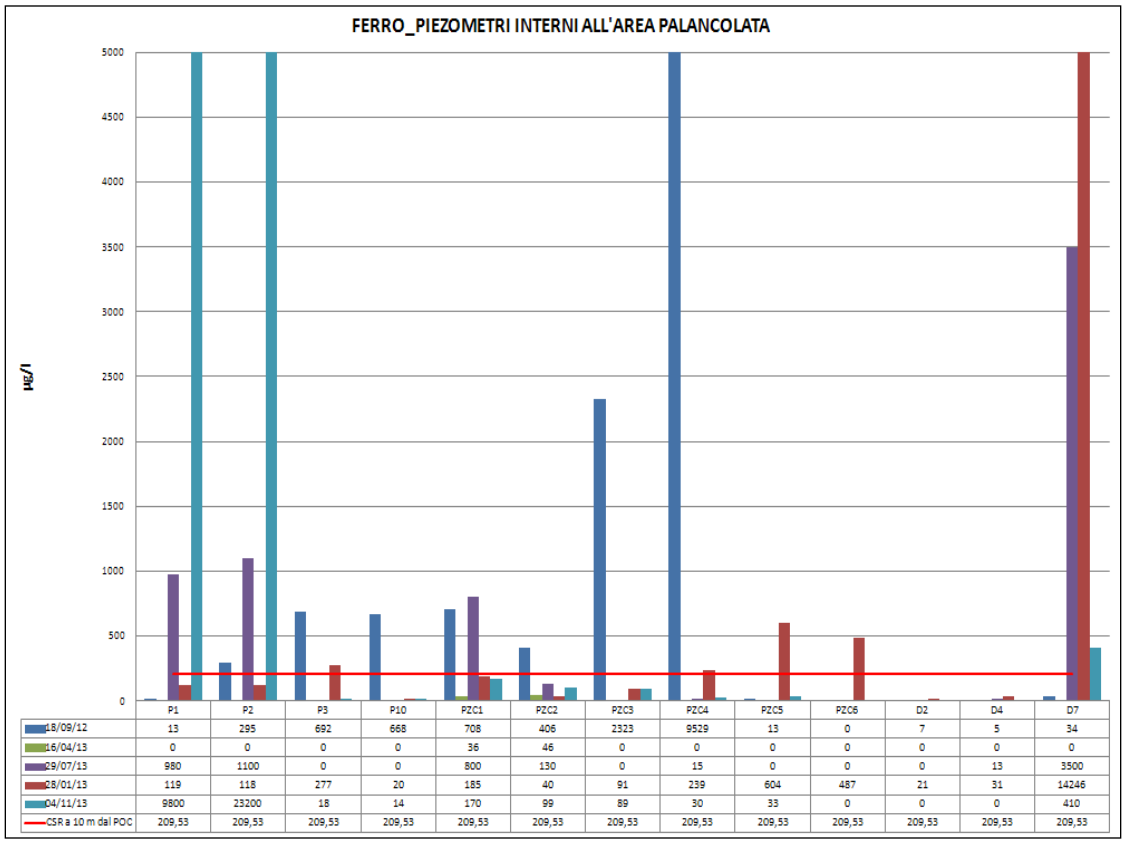

| | P1 | P2 | P3 | P10 | PZC1 | PZC2 | PZC3 | PZC4 | PZC5 | PZC6 | D2 | D4 | D7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18/09/12 | 0,001 | 10207,43 | 27714,77 | 77,79 | 0,56 | 45,97 | 71,99 | 4,29 | 1,43 | 0,96 | 0,57 | 0,39 | 0,69 |
| 28/01/13 | 1,10 | 1184,92 | 697,06 | 308,08 | 12,28 | 1,05 | 6,13 | 4,11 | 2,86 | 2,32 | 1,75 | 1,57 | 1,26 |
| 16/04/13 | 0,001 | 132539 | 102321 | 36 | 13 | 7,60 | 5,40 | 3,40 | 3,10 | 2,90 | 2,10 | 2,00 | 1,60 |
| 29/07/13 | 25,00 | 18700 | 62000 | 29,00 | 0,30 | 0,70 | 0,30 | 0,20 | 0,20 | 0,20 | 0,001 | 2,60 | 1,20 |
| 04/11/13 | 0,001 | 39,00 | 3000,00 | 0,60 | 0,40 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 |
| CSR a 10 m dal POC | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 | 0,16 |

Figure 7. Internal piezometer data for 1,2-dichloropropane

## EHC Performance Indicators

A significant increase in dissolved organic carbon (TOC) and ferrous iron (Fe(II)) was observed at all sampling locations, confirming that successful product placement and sufficient distribution had been achieved. TOC and Fe(II) were detected at maximum concentrations of 2,800 mg/L and 5 mg/L, respectively (Figure 8). Dissolved concentrations gradually decreased over time and stabilized slightly above the baseline range of less than 0.8 mg/L to 1.8 mg/L. At the latest sampling event conducted 24 months after installation, TOC was measured at concentrations ranging from 3.3 mg/L to 18.6 mg/L.

Moreover, the oxidation-reduction potential (ORP) decreased within the injection zone. Sulfate concentrations decreased from a baseline concentration range of 11 mg/L to 632 mg/L to below the detection limit of 0.1 mg/L, suggesting that sulfate-reducing conditions were established within the injection zone.




| | P1 | P2 | P3 | P10 | PZC1 | PZC2 | PZC3 | PZC4 | PZC5 | PZC6 | D2 | D4 | D7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18/09/12 | 13 | 295 | 692 | 668 | 708 | 406 | 2323 | 9529 | 13 | 0 | 7 | 5 | 34 |
| 16/04/13 | 0 | 0 | 0 | 0 | 36 | 46 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 29/07/13 | 980 | 1100 | 0 | 0 | 800 | 130 | 0 | 15 | 0 | 0 | 0 | 13 | 3500 |
| 28/01/13 | 119 | 118 | 277 | 20 | 185 | 40 | 91 | 239 | 604 | 487 | 21 | 31 | 14246 |
| 04/11/13 | 9800 | 23200 | 18 | 14 | 170 | 99 | 89 | 30 | 33 | 0 | 0 | 0 | 410 |
| CSR a 10 m dal POC | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 | 209,53 |

Figure 8. Internal piezometers data for Fe(II)

## Discussion and Conclusion

EHC was successfully injected into the low-permeability formation to achieve greater than 96 percent removal of 1,2-dichloropropane. As expected, diffusion was the primary hydrogeological factor supporting reagent distribution, considering the low-permeability formation and the slow groundwater velocity. Over three years following the injections, redox indicators suggested that reducing conditions were maintained within the injection zone; ORP, DO and sulfate

were still significantly below baseline levels, and propene concentrations remained elevated. In conclusion, the EHC injections have promoted long-term treatment at the site in saturated intervals. This treatment is the result of several 1,2-dichloropropane destruction pathways that continue to remain active three years after the initial injections. Site closure was accomplished in 2015.

## BIBLIOGRAPHY

1. LOFFLER “Complete Reductive Dechlorination of 1,2-Dichloropropane by Anaerobic Bacteria” APPLIED AND ENVIRONMENTAL MICROBIOLOGY, July 1997, p. 2870–2875