

Full-Scale Application of EHC® Liquid Technology for the ISCR and ERD Treatment of an Aquifer Contaminated with Tetrachloromethane and Chloroform in Italy

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Introduction

EHC® Liquid Reagent is an *in situ* chemical reduction (ISCR) product for the treatment of impacted groundwater. It is a cold-water soluble formulation that is specially designed for injection via existing wells or hydraulic injection networks for the treatment of a wide range of groundwater contaminants. EHC® Liquid creates strong reducing conditions and promotes both biotic and abiotic dechlorination reactions. EHC® Liquid is composed of two parts: EHC® Liquid Reagent Mix, an organo-iron compound, and ELS® Microemulsion, which are easily combined and diluted for injection. As bacteria ferment the ELS® Microemulsion, they release a variety of volatile fatty acids (VFAs) such as lactic, propionic and butyric, which diffuse from the site of fermentation into the groundwater plume and serve as electron donors for other bacteria, including dehalogenators. The soluble organo-iron compound is comprised of a ferrous iron (Fe^{+2}) that can form a variety of iron minerals (e.g. magnetite, pyrite) that are capable of reducing contaminants as they oxidize further to the ferric (Fe^{+3}) state via one electron transfer.

SITE BACKGROUND

The site is situated in a highly industrialized area of northern Italy, where groundwater is historically contaminated with tetrachloromethane ($> 10 \text{ mg/L}$), chloroform ($> 10 \text{ mg/L}$), hexavalent chromium and, to a lesser extent, Tetrachloroethene (PCE) and Trichloroethene (TCE). The main impacted area was approximately 2000 m^2 with a 9 meters saturated thickness. As an initial intervention phase, hydraulic containment barrier (Pump & Treat) was selected as emergency action. In September 2017, values measured in groundwater for Carbon tetrachloride (CT) and Chloroform (CF) were still highly above the site-specific reclamation target values ($66 \text{ } \mu\text{g/L}$ for CT and for CF at $65 \text{ } \mu\text{g/L}$).

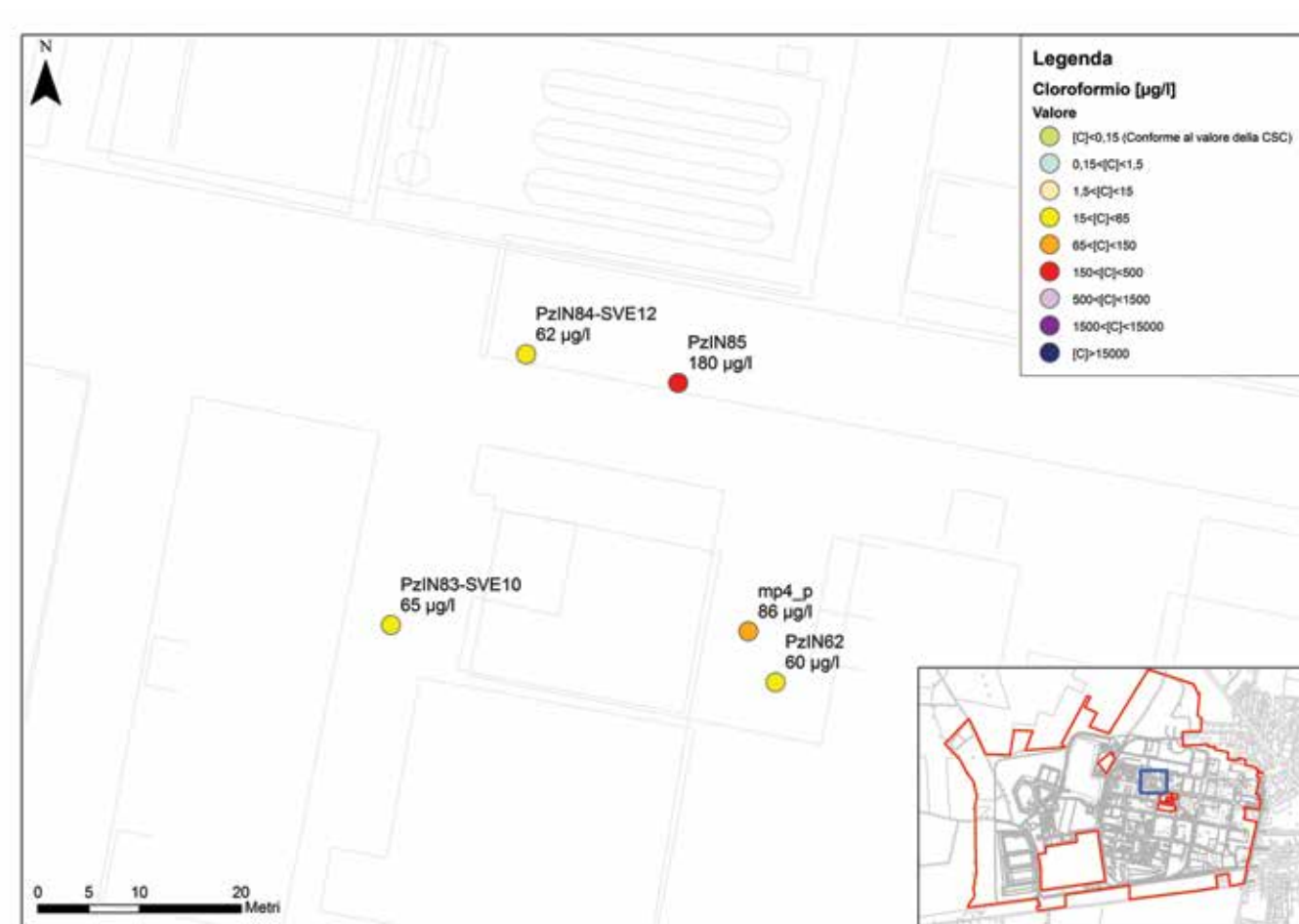
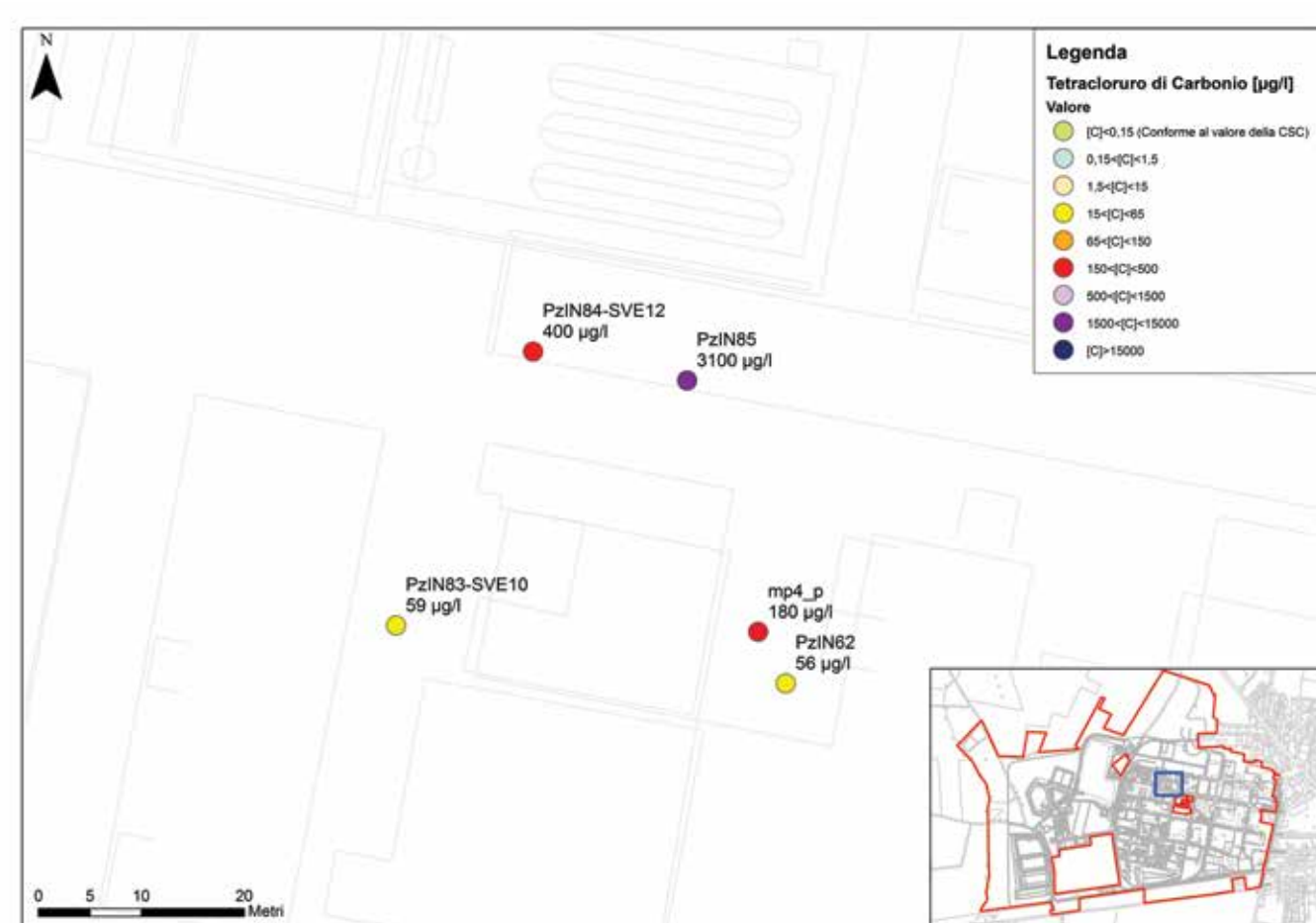
The contaminated superficial aquifer consists of a coarse sand with permeability between 3.6×10^{-4} and $1 \times 10^{-4} \text{ m/s}$. Consequently, linear velocity of the groundwater flow is equal to about 284 m/year , considering a hydraulic gradient equal to about 0.3% and an effective porosity of the saturated medium of 12%.



ELS® Microemulsion 25%



EHC® Liquid Dry Mix (Iron Salt)

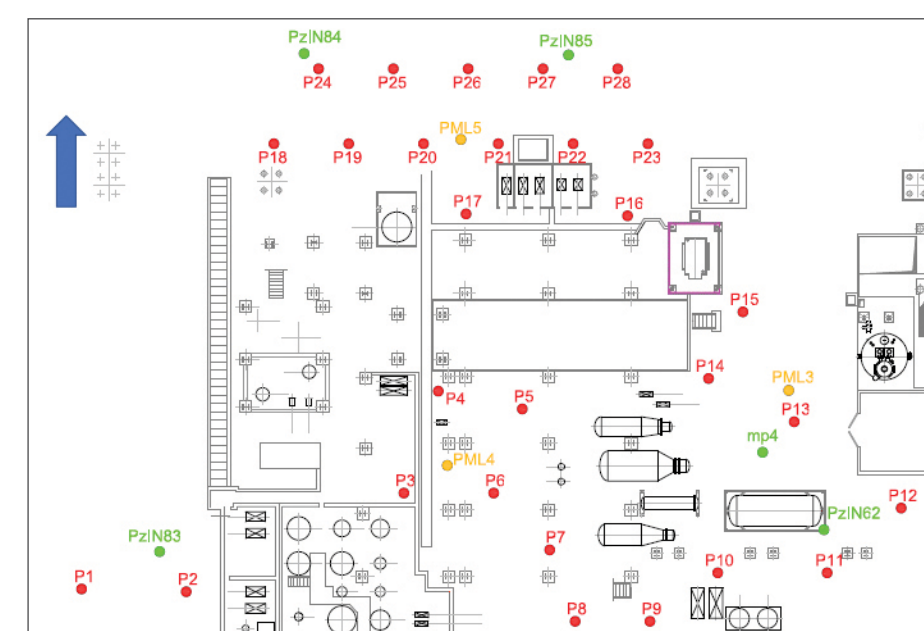


Pre-treatment CT (top) and CF (bottom) concentrations in the source zone in September 2017.

FULL SCALE IMPLEMENTATION

The piezometric surface is located 8 meters from the surface, while the base of the contaminated aquifer, represented by a layering of compact clay, is 17 m from ground level. Furthermore, before treatment, the aquifer showed naturally occurring aerobic conditions ($\text{Eh} \approx 50 \text{ mV}$, $\text{DO} \approx 7 \text{ mg/L}$) and an average sulphate content of about 70 mg/L and pH values in the neutrality range. ($\text{pH} \approx 7.3$).

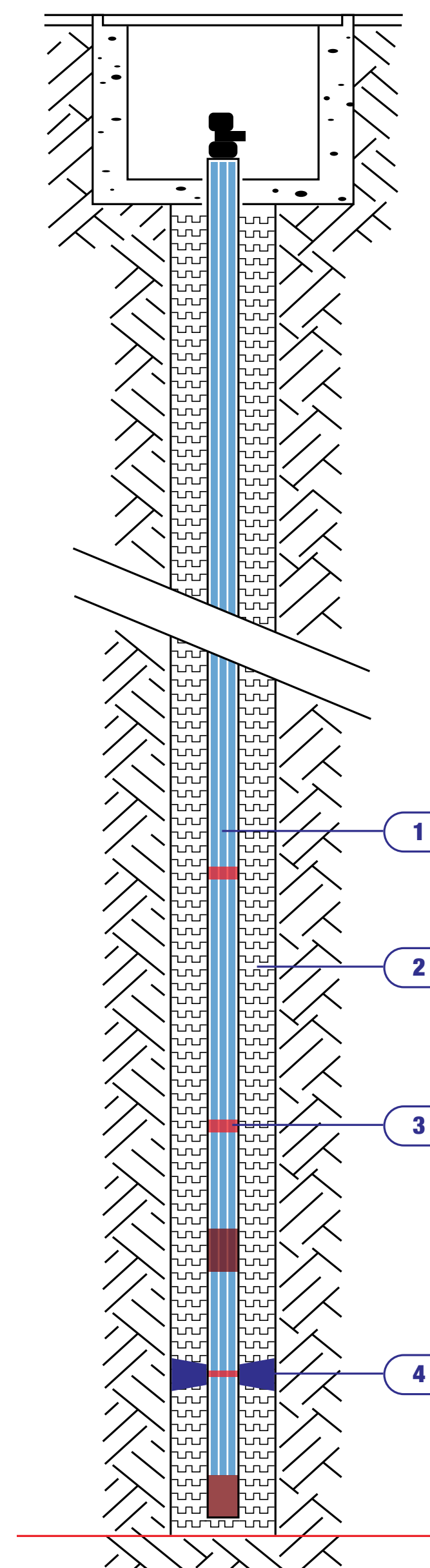
In December 2017, approximately 8568 kg of ELS® concentrate was emulsified with 10% dilution water along with 1960 kg of a EHC® Liquid Reagent Mix. It was then injected under pressure ($\approx 7 \text{ bar}$) in the contaminated subsurface through 28 fixed injection points and distributed in the source area. The main objective established in the reclamation plan was to obtain compliance with site-specific CSR limits ($\text{CT} = 66 \text{ } \mu\text{g/L}$, $\text{CF} = 65 \text{ } \mu\text{g/L}$) at the monitoring points present in the treatment area. A high viscosity volumetric transfer pump was used for the transfer of the ELS® concentrate from the drums to the pre-mixing tank, with 5000 to 10000 RPM capable of handling a maximum viscosity of 20000 cP .



Grid of the injection points (in red) and monitoring points (in green and orange) together with the subsurface direction.



EHC® Liquid Mixing and Dilution



Injection point details

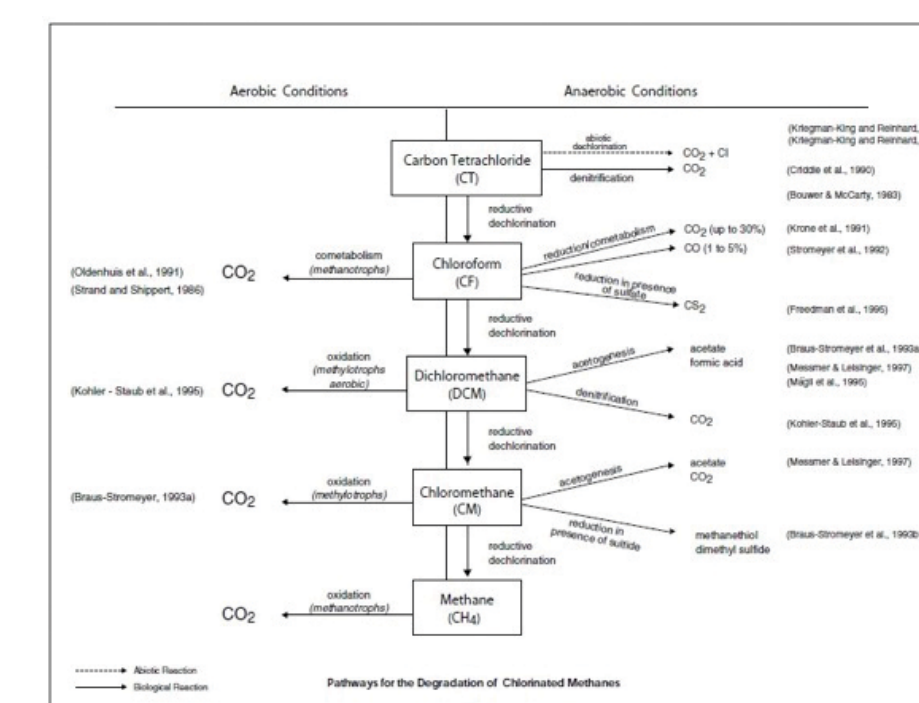
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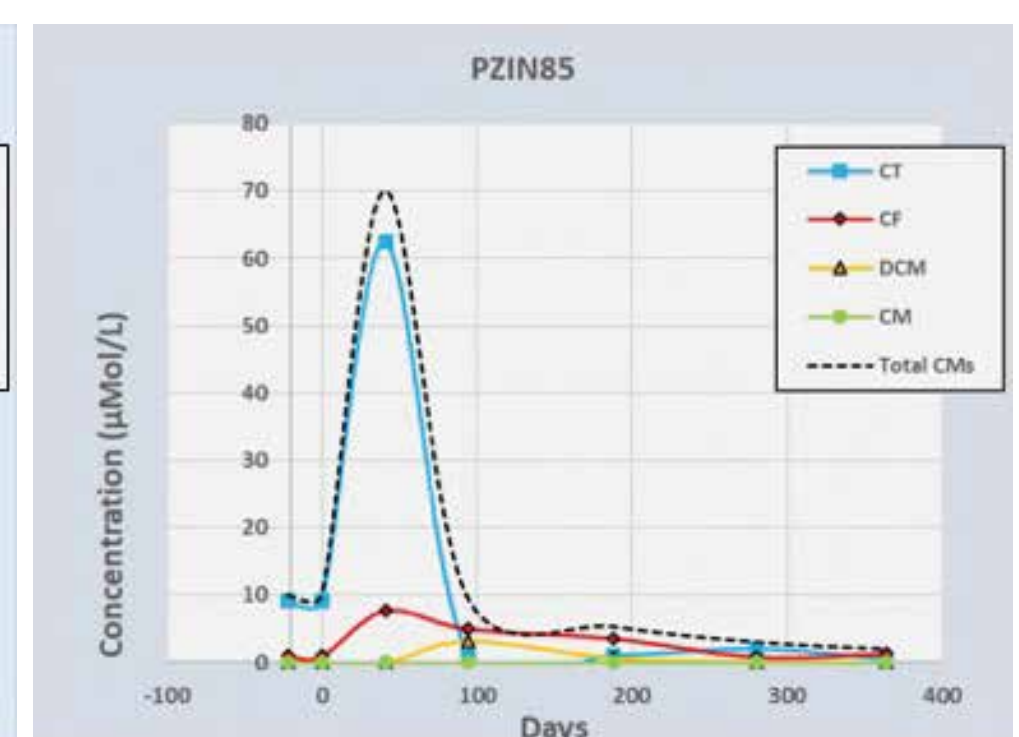
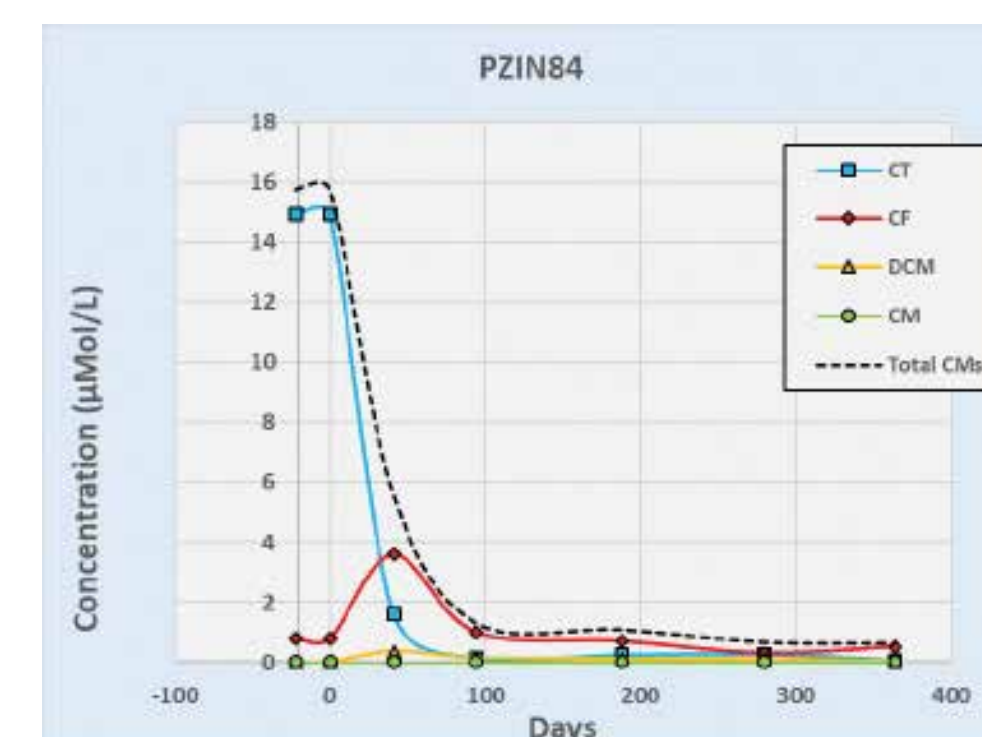
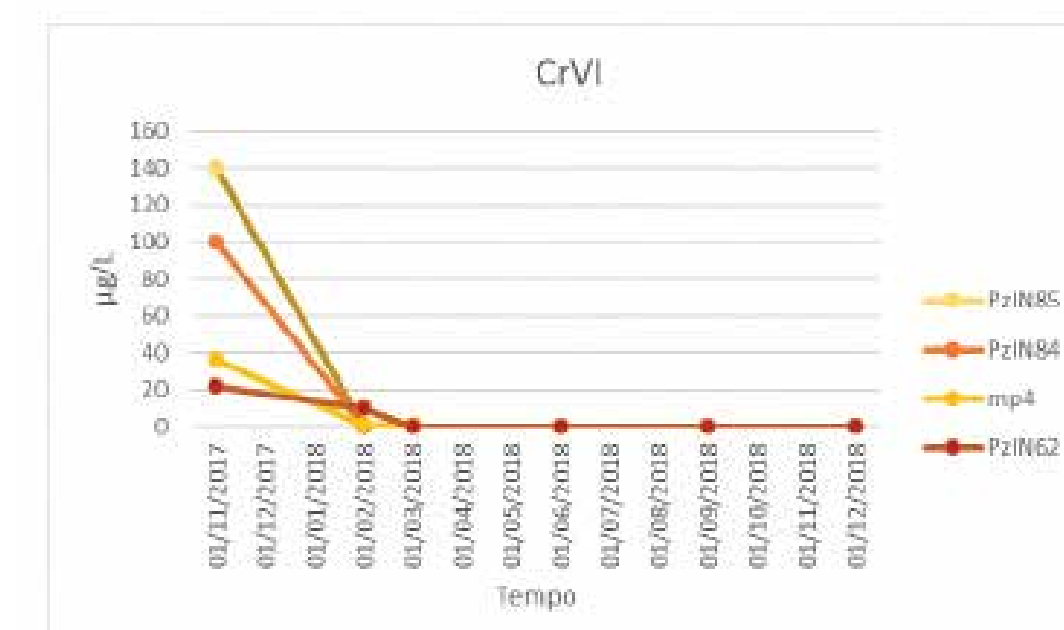
FULL SCALE RESULTS

Approximately one year after the EHC® Liquid reagent was injected into the subsurface, the remediation targets were achieved in almost all the treatment area's monitoring piezometers, with the exception of some downstream points where certain degradation catabolites were still slightly above the limits ($< 10 \text{ } \mu\text{g/L}$). The following graphs show how the concentrations of CT and its degradation catabolites in the subsurface have decreased below the treatment targets in two of the main control piezometers, thus showing a reduction of more than 95% in only twelve months of treatment.

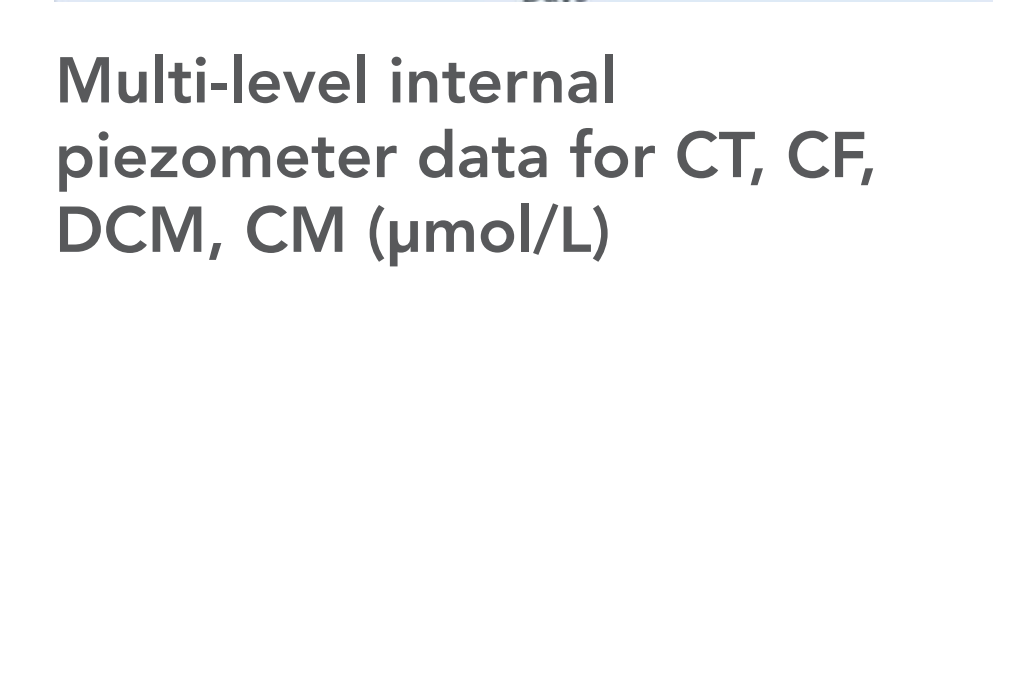
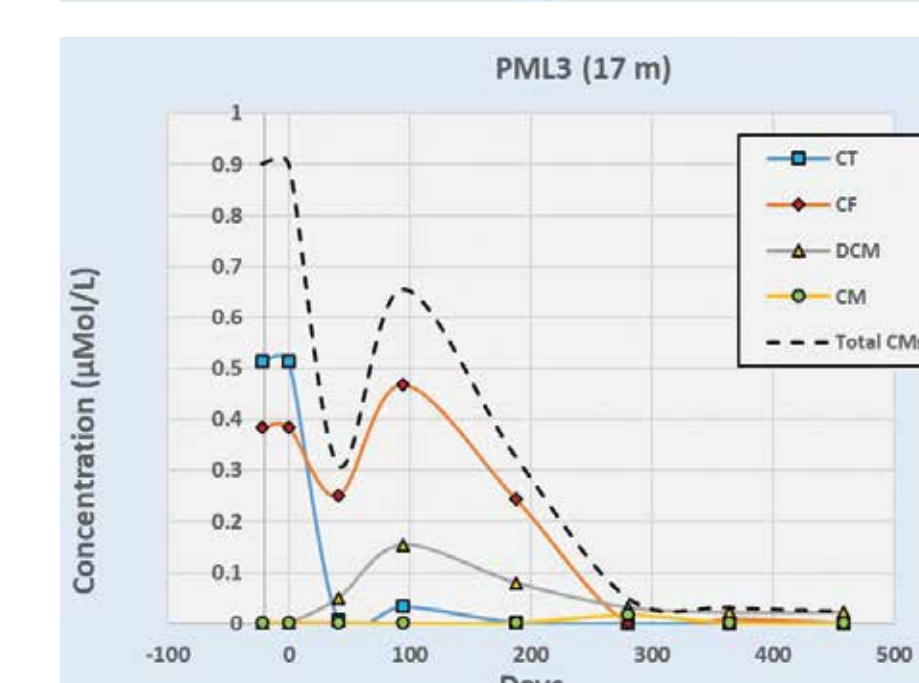
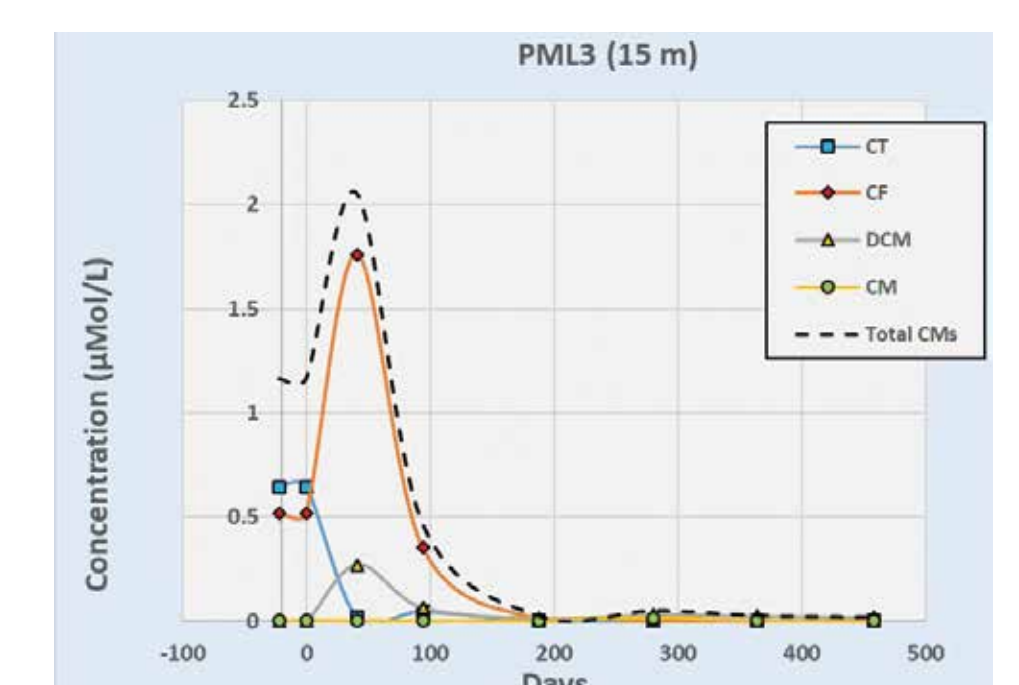
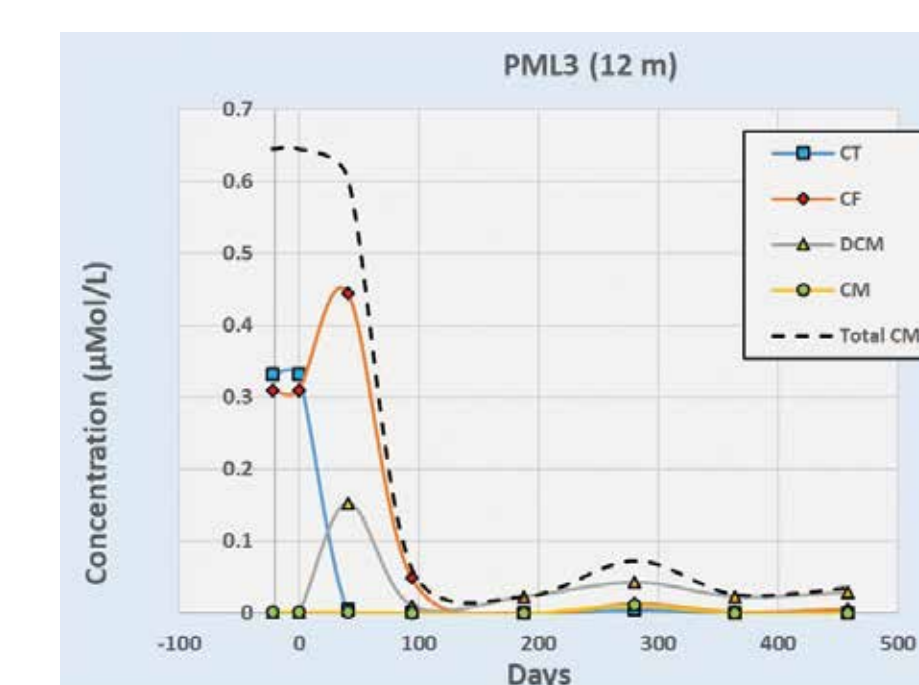
Additionally, all monitoring sites located in the enhanced anaerobic treatment zone indicated the complete elimination of hexavalent chromium concentrations in solution. Lastly, a significant decrease in the oxidation-reductive potential (ORP) was observed with negative values at all the monitoring points of the treatment area, as well as a decrease in the concentrations of the sulfates in solution, on average equal to one order of magnitude compared to the pre-treatment values between 50 and 100 mg/L , demonstrating the establishment of sulfate-reducing conditions.



ERD degradation pathways for chlorinated methane (Force, U. A. 2007).



Internal piezometer data for CT, CF, DCM, CM ($\mu\text{mol/L}$)



Multi-level internal piezometer data for CT, CF, DCM, CM ($\mu\text{mol/L}$)

CONCLUSIONS

In 2017, anaerobic remediation of an aquifer historically contaminated with tetrachloromethane and chloroform was successfully performed in Italy using EHC® Liquid reagent, an engineered slow-release compound of electrolyte donors in the subsurface. Once the injection phase was completed in the saturated zone, in less than 12 months, a rapid decrease in the concentrations of CT and CF in solution equal to about 95% was observed in all monitoring piezometers in the treatment area. Simultaneously, a temporary increase of daughter products, dichloromethane and chloromethane, were detected and monitored. This was followed by a subsequent rapid degradation of these values below detection limits in all piezometers, with the exception of some downstream points. No new increases in CT and CF concentrations were observed, demonstrating a successful dechlorination process. Also observed was the complete reduction for hexavalent chromium at all monitoring sites located in the treatment area.