Full-scale application of ELS® microemulsion Technology for the Treatment of an Aquifer Contaminated with perchloroethylene and trichloroethylene via Ehnanced Reductive Dechlorination.

Applicazione ad ampia scala della tecnologia ELS® microemulsion per il trattamento di un acquifero contaminato da percloroetilene e tricloroetilene mediante declorurazione riduttiva potenziata

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Riassunto: Pennacchi di contaminazione mista composti da solventi organo-clorurati e metalli pesanti sono piuttosto comuni in molti siti. I metalli pesanti possono essere trattati attraverso l'instaurazione di condizioni moderatamente riducenti in falda. Differentemente, i composti organo-clorurati hanno dimostrato di essere degradati biologicamente da specifici microrganismi decloranti come Dehalococcoides sp. La declorurazione anerobica potenziata richiede, però, la presenza di un efficace elettro-donatore tale da fornire idrogeno molecolare (H$_2$) in acqua per la completa declorurazione degli eteni clorurati. La distribuzione in falda dell'elettro-donatore determina la creazione di condizioni altamente riducenti nella zona di trattamento. Questo trattamento biologico comporta anche la riduzione e la precipitazione dei metalli pesanti attraverso l'instaurazione di processi indotti solfati-riducenti. Peroxychem LLC ha sviluppato un elettro-donatore innovativo, dal nome ELS® Microemulsion Reagent (ELS) per il trattamento in situ di composti organo-clorurati e metalli pesanti. Questo substrato è stato applicato con successo in numerosi siti al fine di trattare le varie tipologie di contaminanti presenti negli acquiferi.

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ELS® è un elettro-donatore costituito da un substrato organico facilmente fermentabile a base di lecitina ed ingegnerizzato per potenziare i processi in situ di biorisanamento anaerobico di acque sotterranee contaminate da composti organo-clorurati e metalli pesanti come il Cromo esavalente Cr [VI]. Il prodotto è facile da miscelare con acqua e iniettare nel sottosuolo. Una volta in falda, i microrganismi indigeni utilizzano ELS® per generare rapidamente condizioni altamente riducenti, favorendo le reazioni di declorurazione biotica e la riduzione di metalli ossidati come Cr [VI].

Questa tecnologia innovativa è stata applicata con successo in un ex sito produttivo nel centro Italia, dove le acque sotterranee risultavano storicamente contaminate con Tetracloretilene (PCE> 5,5 milligrammi per litro; mg / L), Tricloroetilene (TCE> 2 mg/L), 1,2 -Dicloroetene (1,2-DCE> 1 mg / L) e, in misura minore, Cloruro di Vinile (VC) e 1,2-Dicloropropano (DP). Un sistema di pompaggio e trattamento (Pump-and-treat; P&T) installato nella zona sorgente era attivo da anni come misura di contenimento della sorgente e, contemporaneamente, per accelerare la rimozione complessiva dei contaminanti dalle acque sotterranee. Tuttavia si riteneva che il regime di pompaggio avesse potuto influire sull'efficacia del trattamento ELS® a causa della maggiore velocità del flusso di falda e, quindi della possibile rimozione del substrato organico iniettato. Per mitigare questa possibilità, si è proceduto a disattivare alcuni pozzi ed a modulare le velocità di pompaggio di altri in modo da garantire la compatibilità con l'iniezione del prodotto a base di lecitina. In particolare, durante il periodo di trattamento mediante ELS®, è stato mantenuto attivo, a monte della zona iniettiva, un sistema di trattamento a bassa portata di emungimento, principalmente per ritardare la diffusione verso valle di ELS® nell'acquifero e, quindi, per potenziare ulteriormente il trattamento della zona sorgente. Dopo la modifica del sistema P&T, circa 4.900 kg di ELS® in formula concentrata sono stati miscelati con acqua e, quindi, iniettati ad alta pressione in 51 piezometri fissi nell'area sorgente. In poco più di 12 mesi dall'iniezione della microemulsione ELS® nelle acque sotterranee nell'area sorgente principale, le concentrazioni in falda di PCE, TCE ed i rispettivi cataboliti, come DCE e VC, si sono rapidamente ridotte, rispetto alle concentrazioni pre-trattamento, fino al raggiungimento i valori obiettivo normativi di trattamento (CSC D.lgs 152/06) nei principali piezometri di monitoraggio dell'area, evidenziando anche la creazione di evidenti e potenziate condizioni di riduzione biotica. Non sono stati osservati fenomeni di nuovo incremento delle concentrazioni durante i tre successivi anni di monitoraggio.

Abstract: *Mixed plumes of chlorinated organics and oxidized metals are a common contaminant at many sites. The oxidized metals can be mediated by the establishment of moderately reducing conditions. The chlorinated organics have been demonstrated to be degradable by specific dechlorinating microrganisms in anaerobic environment such as Dehalococcoides sp. Enhanced biological dechlorination requires the presence of an effective electron donor to provide molecular hydrogen (H2) to completely degrade chlorinated ethenes. Distribution of the electron donor results in the biologically mediated establishment of highly reducing conditions in the treatment zone. This process also results in the reduction and precipitation of the oxidized metals via sulphate-reducing conditions. Peroxychem LLC has developed an innovative electron donor, ELS® Microemulsion Reagent (ELS) for in situ treatment of chlorinated organics and metals. This substrate has been successfully applied at numerous sites to address a variety of contaminants.*

ELS® is an organic electron donor composed of an easily fermentable organic substrate based on lecithin, and designed to enhance in situ anaerobic bioremediation aquifers contaminated by organochlorine compounds and heavy metals such as hexavalent chromium Cr{VI}. The product is easy to mix, dilute and inject into the subsurface. Once in the groundwater, indigenous microorganisms utilize ELS to rapidly generate highly reducing conditions, favoring biotic dechlorination reactions and the reduction of oxidized metals such as Cr{VI}.

This innovative technology was successfully applied to a former manufacturing site in the center of Italy, where groundwater was historically contaminated with Tetrachloroethylene (PCE > 5.5 milligrams per Liter; mg/L), Trichloroethylene (TCE > 2 mg/L), 1,2-Dichloroethene (1,2-DCE > 1 mg/L) and, to a lesser extent, Vinyl Chloride (VC) and 1,2-Dichloropropane (DP). A pump-and-treat system (P&T) installed in the source was active as a source containment measure and to speed up the overall groundwater remediation. However, there was concern that the pumping could affect the ELS treatment effectiveness because of the increased groundwater flow velocity and the potential for removal of the injected bioremediation substrate. To mitigate this potential some wells were switched off the flow rates of others was adjusted to ensure compatibility with the planned product injection. In particular, an upstream low-flow-rate pump and treat system was maintained over the ELS® treatment period, primarily to delay the fast-downstream diffusion of the amendments in the aquifer, thus enhancing the source treatment. Following the calibration of the P&T system, approximately 4,900 kg of ELS® concentration was injected under high pressure at 51 locations into the source area. In about 12 months from injection of ELS® Microemulsion into the groundwater in the main source area, concentrations of PCE, TCE and the recognized catabolites, such as DCE and VC, rapidly reduced, compared to the pre-treatment concentrations, until they reached the statutory national limits (CSC D.lgs 152/06) in the main monitoring piezometers of the area, also highlighting the establishment of clear and enhanced biotic reducing conditions. No rebound effects have been observed in the next three years of monitoring.

Introduction

Enhanced in situ anaerobic bioremediation can be a cost-effective method of degrading various chlorinated solvents dissolved in groundwater, including chloroethenes, chloroethanes, chlorinated pesticides, chloromethanes, chlorinated cyclic hydrocarbons and some dissolved metals (e.g., hexavalent chromium) (Bradley 2000; Lee et al. 2000) Advantages of enhanced anaerobic bioremediation include complete mineralization of the contaminants in situ with limited impact on infrastructures and relatively low cost compared to other engineered remedial systems (Borden 2006; Lewis et al. 2000). However, the addition of organic carbon into saturated zones is well-known to promote conventional enzymatic reductive dechlorination reactions (Hartmans et al. 1985; Vogel 1994). This happens because the carbon in the subsurface will support the growth of indigenous microbes in the groundwater environment (Aulenta and Majone 2006). As bacteria feed on the soluble carbon, they consume dissolved oxygen and other electron acceptors, thereby reducing the redox potential in groundwater (Bradley et al. 1998). As bacteria ferment the ELS® reagent, 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 contaminated plume, and serve as electron donors for other bacteria, including dehalogenators. Enhanced anaerobic bioremediation may be appropriate at sites where site-specific data indicate that the contaminants present can be readily degraded by native microbial populations under anaerobic conditions (Lee et al. 1999; Newell et al. 2003). Moreover, the use of microemulsion such as ELS should be strongly recommended where subsurface conditions (e.g., aquifer permeability) are conducive to adequate emplacement and distribution, and creation of an in situ reactive zone conducive to anaerobic degradation of the targeted contaminants.

Materials and Methods
The science behind ELS® Microemulsion

ELS® Microemulsion is a lecithin-based reagent of food-grade organic carbon used to enhance anaerobic bioremediation in contaminated aquifers. Lecithin is a complex mixture of phospholipids, polysaccharides, complex carbohydrates, fatty acids, triglycerides and antioxidants such as tocopherols (i.e., vitamin E). Phospholipids are the main components in lecithin. These compounds are present in all living cells and serve as nature's main surface-active agents. Lecithin is used in a wide variety of food products including infant formula, chocolate, baked goods, and cheese products. Phospholipids contain structural nitrogen and phosphorus which are slowly released into to the microbial population of the aquifer as they metabolize the phospholipids. This ensures a long-lasting and stable supply of essential nutrients, important for the growth of bacteria in ERD applications in groundwater. Lecithin offers a valuable advantage over other common carbon substrates, particularly in nutrient-stressed aquifers. Moreover, lecithin's organically-bound nutrients are

superior to some ERD products that simply combine lactate or vegetable oil with inorganic forms of nitrogen and phosphorus; in fact, the inorganic nutrients can be rapidly consumed, precipitated in forms that are not bioavailable, or washed out of the treatment zone with groundwater flow. A second valuable feature of phospholipids is their surface-activity. Phospholipids are amphiphilic, simultaneously hydrophilic (water-loving) and lipophilic (oil-loving). Consequently, they are easy to emulsify and form stable aqueous emulsions with very small droplets (ca. 60 percent less than 1 µm diameter) that are not prone to breaking. This enables easy application through existing wells and good distribution throughout the treatment saturated zone. The high molecular weight and branched structure of phospholipids enable them to serve as long-lasting source of molecular hydrogen and nutrients for ERD and ISCR applications. The molecular weight of the main components of lecithin is between 760 g/mole and 744 g/mole, nearly 300 percent greater than the main component of soybean oil (i.e. linoleic acid: molecular weight of 280 g/mole). The other major phospholipids in lecithin have similarly high molecular weights. Moreover, the antioxidant property of lecithin, which enables it to protect organic compounds (i.e., enzymes and DNA) and inorganic species (e.g., ferrous iron, $Fe+2$) from undesirable oxidation reactions, make it particularly well suited for use as the carbon substrate for ISCR applications because it enables the inclusion of ferrous iron and creation of an easily-applied, fully liquid ISCR reagent. It is recognized that ferrous iron on mineral surfaces such as iron oxyhydroxides (e.g., goethite), magnetite, pyrite, and even simple clays (e.g., smectite), can create reactive minerals that are capable of mediating dechlorination of chloroethenes and chloromethanes, including complete dehalogenation of PCE and TCE to chloroacetylenes (Penny et al. 2010; Cope et al. 2001; Hendrickson et al. 2001). It has been suggested that ferrous iron can be viewed as the abiotic equivalent of bacteria in reductive dehalogenation processes. Moreover, the formation of reactive iron and iron sulfide minerals can enhance dehalogenation rates even if only small amounts of the minerals are formed, because concentrations of mackinawite or green rust as low as 0.1 percent by weight are capable of transforming chlorinated hydrocarbons at environmentally significant rates (Robertson et al. 2000; Adamson et al. 1999). Therefore, such reactive minerals can be repeatedly regenerated by the activity of iron reducing bacteria, so long as a supply of organic electron donor remains available; thus, they can provide a long-term contribution to groundwater cleanup. In general, biotic anaerobic reductive dechlorination via ELS Microemulsion occurs by sequential removal of chloride ions. The most thoroughly studied anaerobic dechlorination pathway is degradation of PCE to TCE to cis-dichloroethene (DCE) to vinyl chloride (VC), and finally to ethene. Sequential reductive dechlorination from PCE to TCE to the DCE isomers (cis-DCE or trans-DCE) to VC to ethene is illustrated in Figure 1.

In this reaction, hydrogen is the electron donor, which is oxidized. The chlorinated ethene molecule is the electron acceptor, which is reduced. While other fermentation products (e.g., ELS microemulsion) may serve as an electron donor, hydrogen appears to be the most important electron donor for anaerobic dechlorination of CAHs (Aziz et al 2001; Maymo-Gatell et al. 1997; Fennell and Gossett 1998).
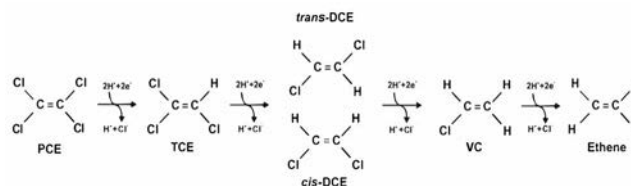

Fig. 1 - The biogenolysis/hydrogenolysis reaction for the reductive dechlorination of PCE in groundwater.
Fig. 1 - La reazione di biogenolisi/idrogenolisi per la declorazione riduttiva di PCE nelle acque sotterranee.

ELS® Microemulsion

ELS® microemulsion reagent is specially designed for easy on-site handling and addition to the subsurface via existing wells, hydraulic injection networks, or direct push technology once mixed with water at about 10% dilution. ELS® comes as a 25% microemulsion or a 100% concentrate. ELS® concentrate is shipped in 200 L (204 kg) steel drums. It has a honey-like appearance and viscosity (about 3,700 centipoise (cP), at 20 ° C) (Figure 2).

Fig. 2 - Barrel of ELS® concentrate before mixing with water.
Fig. 2 - Fusto di ELS® concentrato prima della miscelazione con acqua.

Site Background

Based on the results of an extensive Risk Analysis, the shallow aquifer in the intervention area (Fig.3) was contaminated due to the old manufacturing activities of the site. The impacted source area was approximately 2000 m^2 with a 3 meters thickness in the saturated zones.

Fig. 3 - Satellite photo of the area. The intervention area is highlighted in yellow (source ESRI).

Fig. 3 - Foto satellitare dell'area. L'area di intervento è evidenziata con un rettangolo giallo (fonte: ESRI).

Groundwater was affected by concentrations of PCE and TCE up to 10 mg/L, while unsaturated soils have shown evidence of contamination about the national statutory limits (CSC D.lgs 152/06) just around the PCE underground storage tanks. The following action was selected as an initial intervention phase:

- Removal of the PCE underground storage tanks and excavation of the contaminated soils;
- Hydraulic containment barrier (Pump & Treat – P&T)

Monitoring data trends showed a significant reduction of PCE and TCE concentrations in groundwater during the first years of operation (P&T). However, in March 2016, values measured in groundwater for PCE and TCE were still highly above the site-specific national statutory limits values (PCE = 1.1 µg/L, TCE = 1.5 µg/L, DCE = 0.05 µg/L, VC = 0.5 µg/L). The pre-treatment (March 2016) distribution of PCE is shown in Figure 4. In addition, there was some evidence of natural degradation anaerobic catabolites, i.e. Dichloroethylene (DCE) and Vinyl Chloride (VC).

Therefore, given an asymptotic trend of the contaminant concentrations remaining above the national statutory limits values, ELS® Microemulsion reagent has been chosen to apply; an in-situ treatment technology developed to establish bioremediation processes.

The shallow contaminated aquifer consists of fine sand, in which hydraulic conductivity was measured to range from 0.00085 to 0.001 cm/s, and linear groundwater velocity estimated to be approximately 20 m/yr, considering a hydraulic gradient of about 2.3% and an effective porosity of the saturated medium of 35%. The water table surface is located 10 meters below ground surface (bgs), while the base of the shallow aquifer, represented by a layering of compact
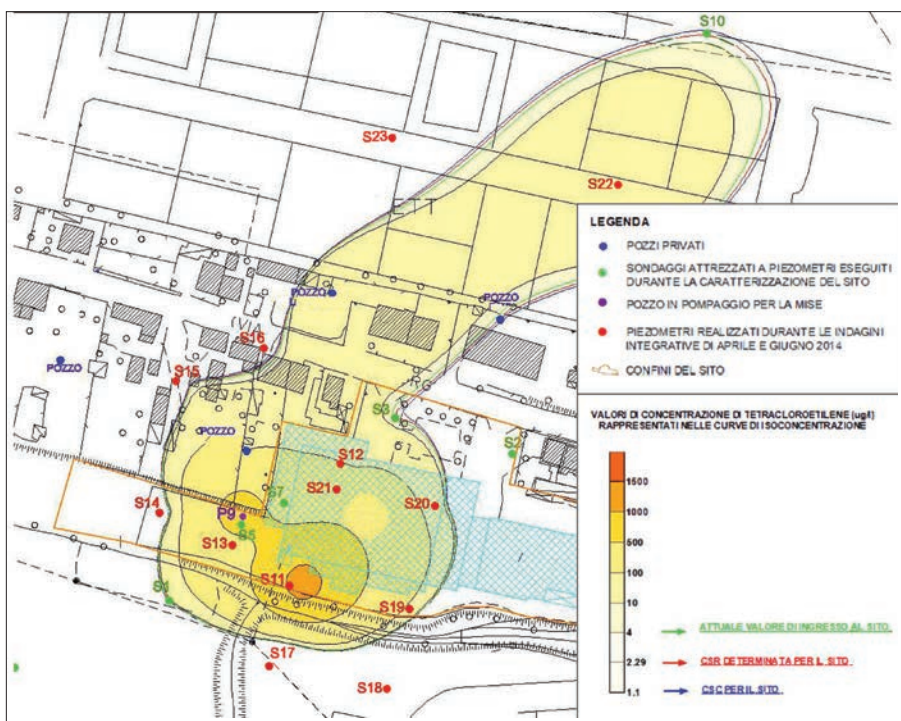

Fig. 4 - Pre-treatment PCE concentrations (µg/L) in the source zone.

Fig. 4 - Concentrazioni (µg/L) di PCE nell'area sorgente prima dell'intervento.

clay, is 13 m bgs. Furthermore, before treatment, the aquifer conditions were slightly oxidizing and aerobic conditions (Eh ≈ 10 mV, Dissolved Oxygen ≈ 2 mg/L), had an average sulfate content of about 100 mg /L and near neutral pH (pH ≈ 6.8 SU).

Full-Scale Implementation

Prior to ELS substrate injection, a preliminary hydrogeological modeling of the site has been conducted (Edward R. Banta 2011; Harburgh et al. 2000). A P&T wells in the intervention area were active in order to speed up the removal and the treatment of contaminated groundwater and to ensure at least a partial containment of the source area (S11). However, the active pumping inside, or in the immediate vicinity of the area addressed by ELS® Microemulsion injections, could reduce its effectiveness, due to the increase in groundwater flow velocity and possible removal of the injected emulsion. For this reason, selected wells were de-activated and an upstream low-rate P&T system (≈10 L/h) was maintained over the ELS treatment period, designed primarily to delay the fast-downstream diffusion of the amendments in the aquifer, thus flatting the natural hydraulic gradient and enhancing the source treatment.

In September 2016, evaluating a concentration of lecithin in groundwater equal to about 2500 mg/L to meet H_2 demand based on site-specific input data provided (i.e., Transport Characteristics, Soil Data, Treatment Zone Dimensions, Geochemical Data and Aquifer Contaminant Information), approximately 4900 kg of ELS® concentrated was emulsified with 10% dilution water and then injected under pressure (≈ 7 bar) through 51 fixed injection points (Figure 5) in the contaminated source aquifer. The main objective established in the reclamation plan was to obtain compliance with national statutory limits values at the monitoring points present in the treatment area.

A high viscosity volumetric transfer pump (Figure 6) is generally used for the transfer of the ELS® concentrate from the drums to the mixing tank (Figure 7), with 5000 - 10000 revolutions per minute (RPM) capable of handling a maximum viscosity of 20000 centipoise (cP).

Fig. 6 - Detail of the hydraulic system used to transfer the ELS® concentrate from the drum to the mixing tanks and from the mixing tanks to the injection point.

Fig. 6 - Dettaglio del sistema idraulico usato per il trasferimento di ELS® concentrato dal fusto alla vasca di miscelazione e dalla vasca di miscelazione al punto iniettivo.

Fig. 7 - Pre-mixing tank (on the right) and final mixing tank with in-line recycling system (in the middle).

Fig. 7 - Vasca di pre-miscelazione (a destra) e la vasca finale di miscelazione con il sistema di ricircolo in linea (al centro).

Full-scale Results

Statutory groundwater protection levels were met in all the monitoring wells in about 12 months, except for some downgradient wells (S21, S12) where some VOCs catabolites were marginally above the standard of 1 ppb. Figure 8 shows the concentrations of TCE and PCE in groundwater below detection levels in all wells, indicating that a 99.8% reduction had been achieved in 12 months of treatment. DCE and VC levels were also below detection limits in all wells, except for a few downgradient wells (S21, S12), indicating a complete reductive dechlorination process in most of the treated aquifer (Fig.9).
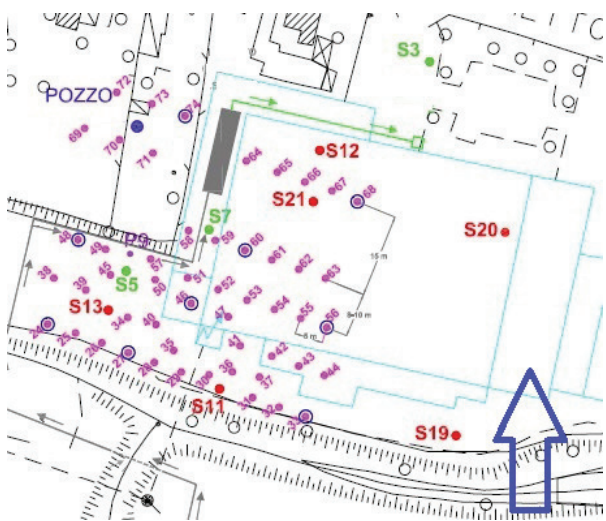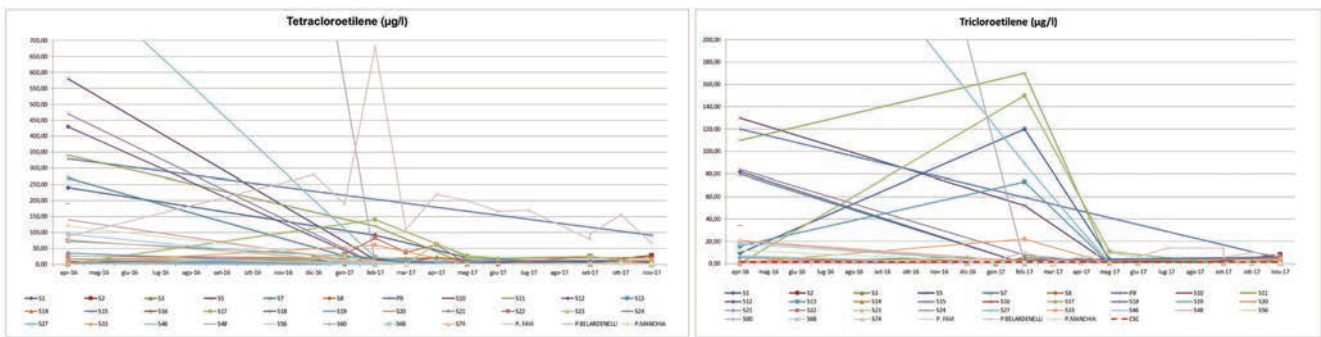

Fig. 5 - Grid of the injection points (in lilac) and monitoring points (in red, blue and green); the blue arrow represents the medium groundwater flow direction.

Fig. 5 - Griglia dei punti di iniezione (in lilla) e di quelli di monitoraggio (in rosso, blu e verde); la freccia blu indica la direzione media di flusso idrico sotterraneo.

Fig. 8 - First year post-injection monitoring data for PCE and TCE in the treatment area (µg/L).

Fig. 8 - Dati di monitoraggio delle acque sotterranee durante il primo anno post-iniezione per PCE e TCE nella zona di trattamento (µg/L).
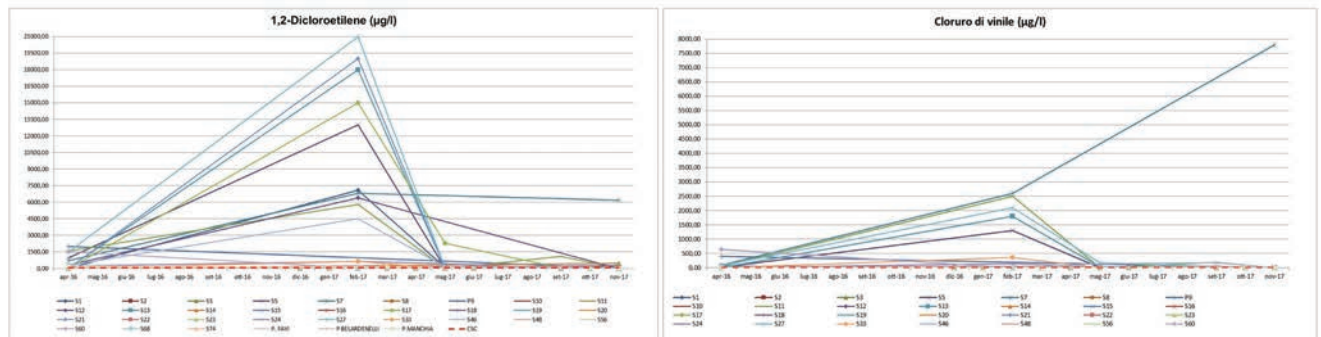

Fig. 9 - First year post-injection monitoring data for DCE and VC in the treatment area (µg/L).

Fig. 9 - Dati di monitoraggio delle acque sotterranee durante il primo anno post-iniezione per DCE e CV nella zona di trattamento (µg/L).

Moreover, during the second and third year of post-injection monitoring, the concentration levels of contaminants, such as PCE and TCE, along with the degradation catabolites, such as DCE and VC, reached the clean-up goals remaining below the detection limits in almost all the treatment area's monitoring points (Fig.10 and FIG.11). This confirmed the establishment of complete enhanced reductive dechlorination processes throughout the treated aquifer. No rebound effects have been observed (Fig.12 and FIG 13).
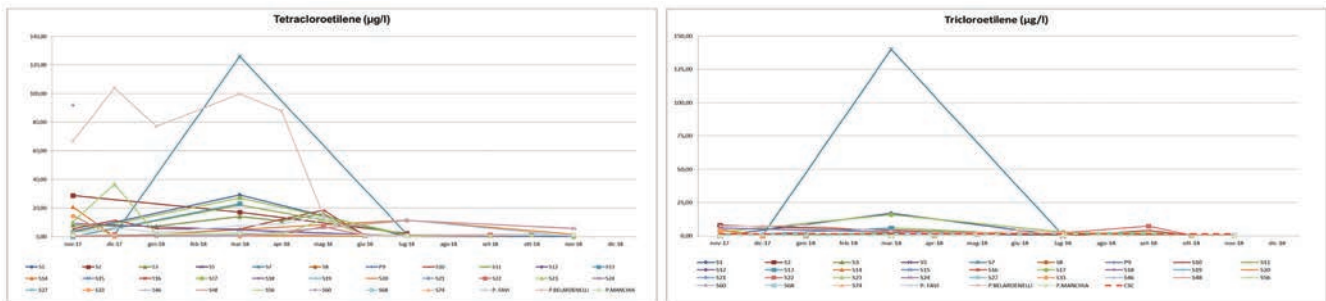

Fig. 10 - Second year post-injection monitoring data for PCE and TCE in the treatment area (µg/L).

Fig. 10 - Dati di monitoraggio delle acque sotterranee durante il secondo anno post-iniezione per PCE e TCE nella zona di trattamento (µg/L).
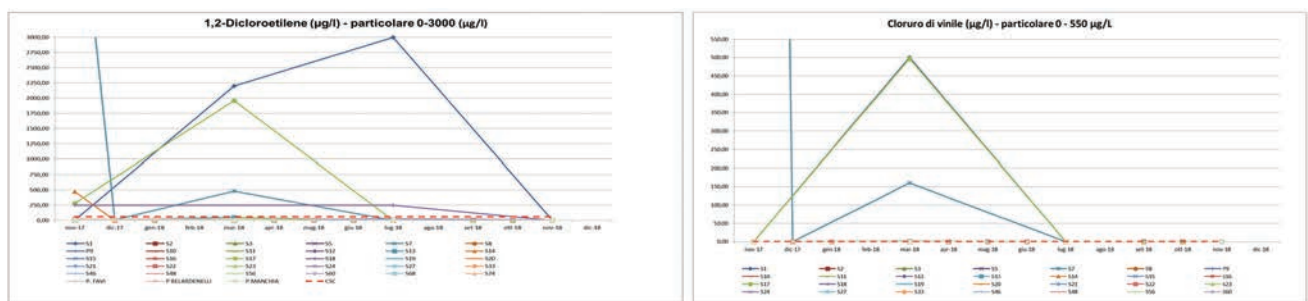

Fig. 11 - Second year post-injection monitoring data for DCE and VC in the treatment area (µg/L).

Fig. 11 - Dati di monitoraggio delle acque sotterranee durante il secondo anno post-iniezione per DCE e CV nella zona di trattamento (µg/L).

Fig. 12 - Third year post-injection monitoring data for PCE and TCE in the treatment area (µg/L).

Fig. 12 - Dati di monitoraggio delle acque sotterranee durante il secondo anno post-iniezione per PCE e TCE nella zona di trattamento (µg/L).
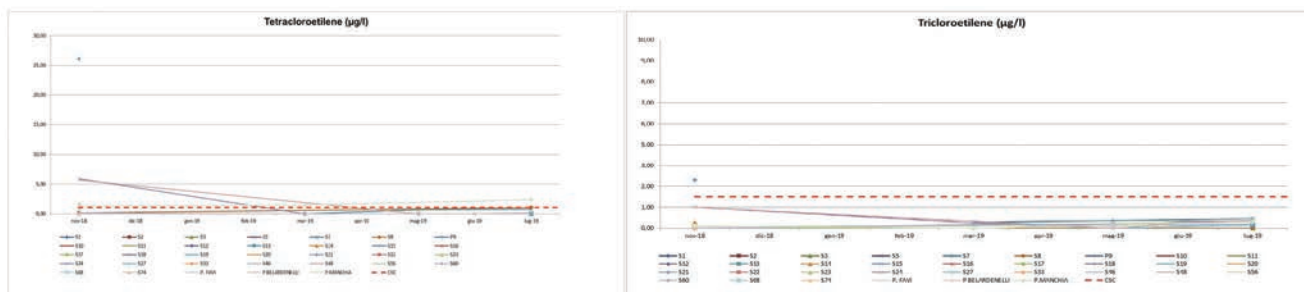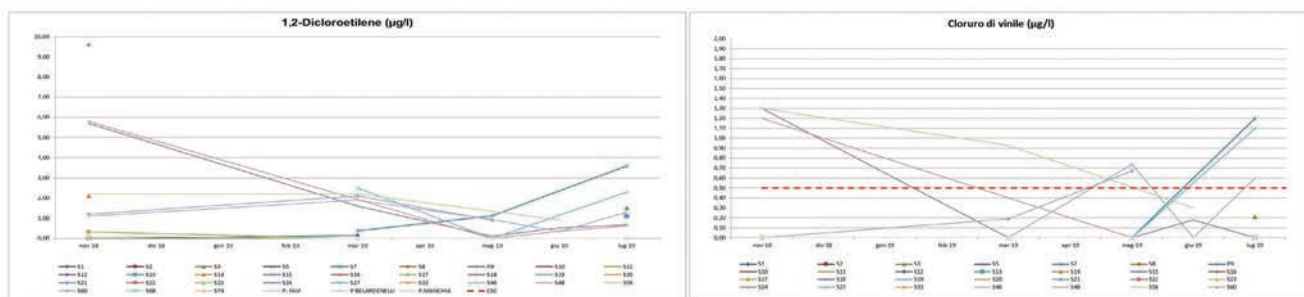

Fig. 13 - Third year post-injection monitoring data for DCE and VC in the treatment area (µg/L).

Fig. 13 - Dati di monitoraggio nelle acque sotterranee durante il secondo anno post-iniezione per DCE e CV nella zona di trattamento (µg/L).

Lastly, complete reductive dechlorination of 1,2-dichloropropane has also been observed in all the monitoring wells (Fig.14)

Discussion

To assess whether the wells were under the ELS® zone of influence, the groundwater was sampled for Manganese (Mn II) and ferrous iron (Fe II) during the first year following injections. A significant increase in manganese and ferrous iron was observed at all sampling locations, confirming successful product placement and that enhanced anaerobic conditions had been achieved (Fig.15). Moreover, the oxidation-reduction potential (ORP) decreased within the injection zone and sulfate concentrations decreased on average by an order of magnitude from baseline concentrations, suggesting that sulfate-reducing conditions were established within the injection zone.
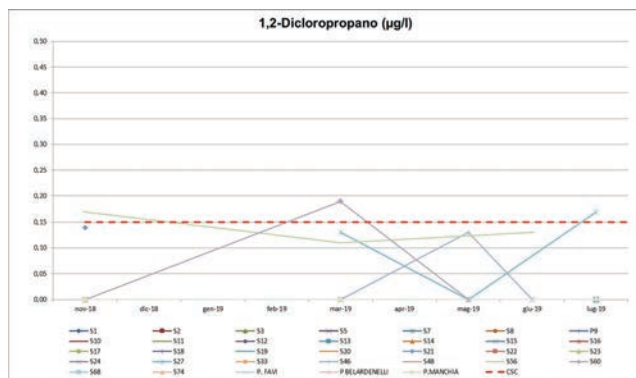

Fig. 14 - Post-injection monitoring data for 1,2-DP in the treatment area (µg/L).

Fig. 14 - Dati di monitoraggio delle acque sotterranee post-iniezione per 1,2-DP nella zona di trattamento (µg/L).

	Month				
	0	3	6	9	12
Nitrate (mg/L)	39	49	38	18	9
Sulfate (mg/L)	151	161	117	80	46
Ferrous Iron (µg/L)	<77	108	3,562	6,175	5,364
Manganese (µg/L)	<55	<55	1,821	3,158	2,398
Ph	6.50	6.66	6.56	6.24	6.39
ORP (mV)	203	49.24	12.8	-14.3	-56.7
OD (mg/L)	3.5	2.8	0.51	0.63	0.33

Fig. 15 - Average values over time of ELS® performance indicators for the monitoring wells in the treatment zone.

Fig. 15 - Valori medi nel tempo dei parametri indicativi del rendimento di ELS® nei punti di monitoraggio dell'area trattata.

research

Conclusion

A former manufacturing site had more than 2,000 m2 of groundwater impacted with PCE from an historical solvent release. The source was previously excavated; however, the main contaminated area and the down gradient plume showed maximum PCE concentrations up to 5,500 µg/L in the shallow aquifer. In Fall 2016, the environmental consulting firm successfully conducted a full-scale enhanced bioremediation approach using ELS® Microemulsion, a slow-release electron-donor reagent. Following injection into the saturated zone, PCE and TCE concentrations were significantly reduced in groundwater by 99.98% at all wells in less than 12 months; simultaneously cis-DCE and VC were produced and then degraded to below detection limits in majority of the wells. No rebound of PCE or TCE has been observed in the next years of monitoring, indicating that complete reductive dechlorination of these parent compounds have occurred. Moreover, degradation of 1,2-dichloropropane has also been observed in all the monitoring wells in the ELS® treated aquifer. The ELS® is expected to continue to treat potential residual contamination over the next 3 to 5 years. Based on the results of this application, Enhanced Reductive Dechlorination using EL®S has been demonstrated to be a highly cost-effective technology for in situ treatment of chlorinated organics.

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