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FIELD APPLICATION OF A REAGENT FOR IN SITU CHEMICAL REDUCTION AND ENHANCED REDUCTIVE DICHLORINATION TREATMENT OF AN AQUIFER CONTAMINATED WITH TETRACHLOROETHYLENE (PCE), TRICHLOROETHYLENE, 1,1-DICHLOROETHYLENE, DICHLOROPROPANE AND 1,1,2,2-TETRACHLOROETHANE (R-130)

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Abstract

Groundwater at an abandoned industrial area near Bergamo, Italy, was historically contaminated by tetrachloroethylene (PCE) (>100 µg/L) and, to a lesser extent, by trichlorethylene (TCE), dichloropropane (DP) and 1,1,2,2-tetrachloroethane (R-130). A liquid reagent (EHC® Liquid) was selected for remediation of groundwater at the site. The reagent is provided in two parts: EHC® Liquid Mix (a soluble organo-iron salt), and ELS® Microemulsion (a lecithin-based carbon substrate), and is designed to promote both *in situ* chemical reduction (ISCR) and enhanced reductive dechlorination (ERD) to destroy chlorinated organic compounds. The two components are mixed with water and injected into the subsurface. Once in groundwater, EHC® Liquid rapidly generates highly reduced conditions, favouring both biotic and abiotic dechlorination reactions. Less than 6 months after the injection of EHC® Liquid in the main source area, concentrations of the target contaminants had reached the site-specific remediation target values (CSC Legislative Decree 152/06) in the main monitoring piezometers present in the area, thus demonstrating the effective establishment of enhanced biotic and abiotic reducing conditions and degradation of the target compounds.

Keywords: aquifer, chlorinated solvents, enhanced reductive dichlorination, lecithin microemulsion, treatment

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1. Introduction

Enhanced *in situ* anaerobic bioremediation can be an efficient method of degrading various chlorinated solvents dissolved in groundwater, including 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 groundwater with limited impacts on infrastructures and relatively low cost compared to other common engineered remedial systems (Borden, 2006; Lewis et al., 2000). However, the addition of organic carbon into saturated zones is a well-known technology to promote conventional enzymatic reductive dechlorination reactions (Hartmans et al., 1985; Vogel, 1994). This happens because the organic carbon substrate in the subsurface will support the growth of indigenous microbes in the aquifer (Aulenta et al., 2006). As bacteria feed on the soluble carbon media, they consume dissolved oxygen and other electron acceptors, thereby reducing the redox potential in groundwater (Bradley et al., 1998). In particular, as bacteria ferment the ELS® (Emulsified

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Lecithin Substrate) component (Leombruni et al., 2020), they release a variety of volatile fatty acids.

(VFAs) such as lactic, propionic and butyric, which diffuse from the site of fermentation into the saturated contaminated plume, and serve as electron donors for other bacteria, including dehalogenators. Enhanced anaerobic bioremediation may fit sites where site-specific data indicate that the contaminants 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.

Treated area: background

Groundwater at an abandoned industrial area near Bergamo, Italy, was historically contaminated by tetrachloroethylene (PCE) (>100 µg/L) and, to a lesser extent, by trichlorethylene (TCE), dichloropropane (DP) and 1,1,2,2-tetrachloroethane (R-130), as shown in Fig. 1 and Fig. 2. Based on the results of a characterization analysis, the contaminated source area aquifer subject to intervention consisted of a saturated area approximately 400 m^2 wide and 18 meters of thick. The piezometric surface is located at approximately 20 meters below ground level, while the base of the investigated aquifer, represented by a stratification of thick silty sand, is approximately 38 m from the ground level (Fig. 3). The surficial contaminated aquifer is constituted by a fine sand with hydraulic conductivity in the order of 1.2 x 10^{-3} cm/s, considering a hydraulic gradient of about 7% and an effective porosity of the saturated medium of about 34%. Linear interstitial velocity of the groundwater flow is calculated to approximately 76 m/year. Before treatment, the aquifer showed natural aerobic conditions (Eh ≈ 150 mV, DO ≈ 4 mg/L), an average sulphate content of about 1 mg/L, and pH values in the neutral range (pH ≈ 6.7). In April 2019, limited evidence of anaerobic degradation catabolites (e.g. Trichloroethylene, 1,1-Dichloroethylene, Vinyl chloride) together with DP and R-130 concentrations were present in solution. Moreover, multi-levels monitoring data have shown a clear uniform distribution of the main contaminant levels along the saturated treatment zones.

Therefore, in consideration of the asymptotic trend of the contaminant concentrations in the solution, with values above the GD 152 (2006), it was considered appropriate to apply the EHC® Liquid technology; an innovative *in situ* treatment able to favour the establishment of both biotic and abiotic reductive dechlorination processes. The distribution of PCE and 1,1-DCE concentrations in the source area groundwater pre- treatment are shown, respectively, in the following maps.
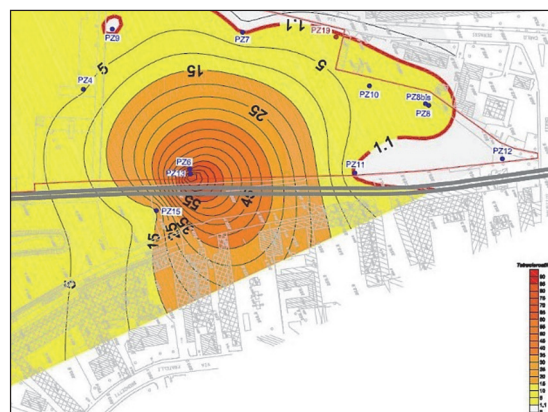

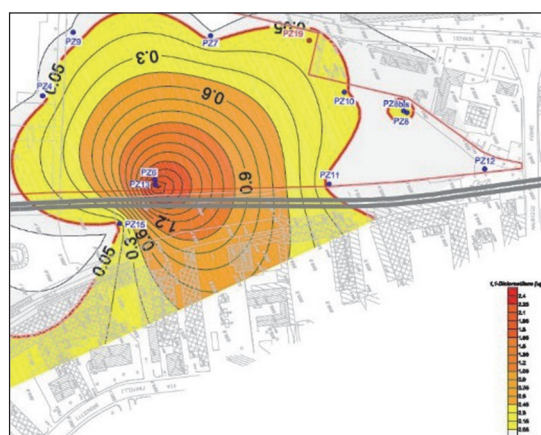**Fig. 1**. PCE concentrations (µg/L) in the source area before treatment (April 2019)

Fig. 2. 1,1-DCE concentrations (µg/L) in the source area before treatment (April 2019)

2. Material and methods

2.1. The science behind EHC® Liquid ISCR Reagent

EHC® Liquid is composed primarily of ELS® Microemulsion; a slow-release organic carbon substrate, and EHC® Liquid Mix; an organo-ferrous compound (both food-grade). Key characteristics include,

• The ELS® component is based on soy lecithin, which is comprised of a high weight molecular phospholipid organic substrate ideal for the slow and sustained release of electron donors. ELS® also contains polysaccharides that are easily fermented to rapidly establish reducing conditions *in situ*. ELS® concentrate is shipped in 200 litre/204 kg steel drums and has a honey-like appearance with viscosity of about 3,700 N-s/m^2, at 20°C (Fig. 4).

• The iron in EHC® Liquid Mix is an organo-ferrous iron compound, provided as a soluble dry powder packaged in 11.7 kg bags (Fig. 4).

The EHC® Liquid formulation has been specially engineered for easy on-site handling, and can be applied through fixed well injection systems, hydraulic injection systems or via "direct push technologies".
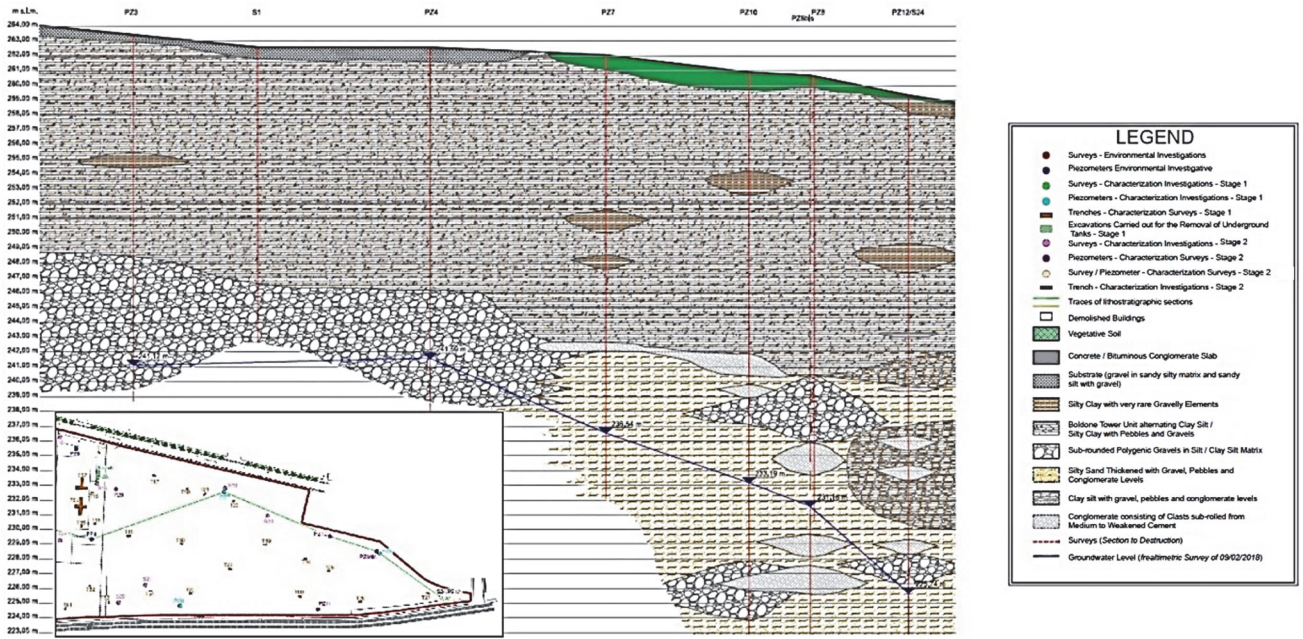
Fig. 3. Geological section aquifer being treated

Fig. 4. ELS® Microemulsion barrel (a) and pails with the EHC® Liquid Mix compound (b)

The components are readily mixed in water on site prior to injection. Once in the aquifer, the EHC® Liquid components rapidly generate reducing conditions and act as an electro-donor, favouring enhanced reductive dechlorination processes (ERD). Furthermore, through fermentation of the ELS® Microemulsion, bacteria release a variety of volatile fatty acids (VFAs) such as lactic, propionic and butyric acid. These then spread from the injection zone throughout the contaminated plume, acting as electron donors for other bacteria, including dehalogenators (Fennell and Gossett, 1998; Maymo-Gatell et al., 1997). The lecithin molecule itself is composed mainly of phospholipids. It is also a zwitterion, which has a positively charged head and a negatively charged tail. Consequently, the ELS® Microemulsion has both hydrophilic and hydrophobic properties, which tend to be more stable and long-lasting in the subsurface compared to compounds consisting of only a hydrophobic part (e.g. emulsified vegetable oils). Furthermore, in addition to serving as a long-lasting carbon source, phospholipids promote bioremediation in groundwater by providing highly bioavailable organic nutrients, including nitrogen and phosphorous: essential elements for bacterial growth (Leombruni et al., 2020).

2.2. Full scale implementation

In May 2019, approximately 8,160 kg of ELS® Microemulsion were first emulsified with water at 10% dilution (approximately 1 kg of ELS® Microemulsion mixed into 10 L of water), together with 1,872 kg of the EHC® Liquid Mix organo-ferrous compound. The solution was then injected under pressure (≈7 bar) into the impacted groundwater zone between 20 m and 38 m bgl through 8 fixed injection points distributed in the source area (Fig. 5). The main objective established in the reclamation plan was to obtain compliance with GD 152 (2006) limits (PCE = 1.1 μg/L, TCE = 1.5 μ/L, 1,1-DCE = 0.05 μ/L, 1,2-DP = 0.15 μ/L, R-130 = 0.05 μ/L) at monitoring points present in the treatment area (Pz6, Pz1, MLS1). The injection phase lasted approximately 7 working days

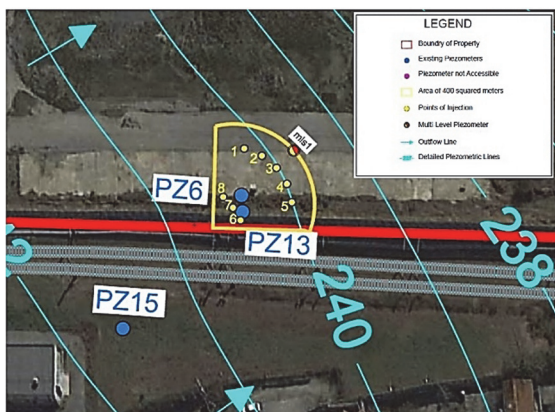and included the use of specific injection tools.

Fig. 5. Injection points grid (yellow) and monitoring points (blue and red) together with the GW flow direction

The ELS® Microemulsion component is easily emulsified directly on site, using a common high-speed centrifugal pump. Before mixing, a receptacle tank is filled with the appropriate amount of water needed to dilute the concentrate; this water is often pre-conditioned in order to remove the dissolved oxygen present. Afterwards, the ELS® Microemulsion and EHC® Liquid mix are added in sequence to the pre-mixing tank, and then transferred to a main mixing tank. A recirculation system with a centrifugal pump is then placed in-line, to provide continuous agitation of the reagents inside the main mixing tank (Fig. 6).

3. Results and discussion

Less than 6 months following EHC® Liquid injections, the remedial objectives were achieved in all monitoring piezometers present in the treatment area, except for a few downstream points where some degradation catabolites were still slightly above target limits (<0.3 μg/L). The concentrations in downgradient wells decreased but may still be above target limits. This may be due to matrix diffusion downgradient of the treatment area. It is anticipated that further treatment, or time, will result in achieving the goals in the highlighted wells. Fig. 7, for example, shows how the PCE concentrations and the respective biological daughter-products are reduced below clean-up goals (GD 152, 2006) in all the main piezometers, thus showing a reduction greater than the 95% in just 5 months of treatment.

Concentrations of individual degradation catabolites, such as DCE and VC, have remained substantially below detection limits in almost all monitoring points located within the treatment area. This data confirms the establishment of complete reductive dichlorination processes in the entire aquifer being treated (Fig. 8). Furthermore, the degradation processes in different portions of the treated aquifer were verified by sampling at different depths and observing the same degradation trends (Fig. 9). Finally, complete abatement of 1,2-DP and R-130 concentrations in

solution was also observed at all monitoring points located in the enhanced anaerobic treatment zone (Figs. 10-11). No rebound in PCE, DP or R-130 concentrations was observed subsequent to treatment, demonstrating the effectiveness of the reductive dichlorination process and indicating treatment of both dissolved and adsorbed phase contaminants.

Fig. 6. ELS® Microemulsion component in 200 L steel drums, and EHC® Liquid mix component in 11.7 kg bags delivered in plastic pails
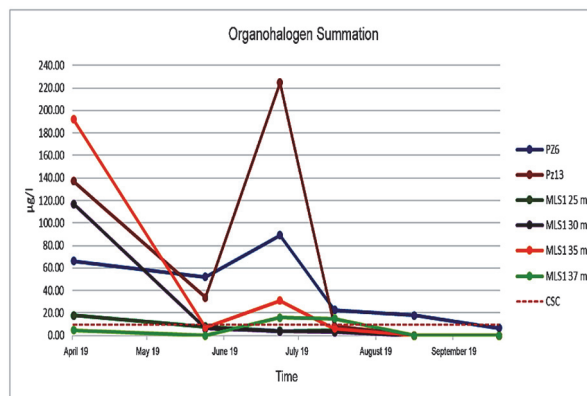

Fig. 7. Concentration trends for chlorinated ethylenes in groundwater at monitoring points in the treatment area, before and after EHC® L injections performed in May 2019
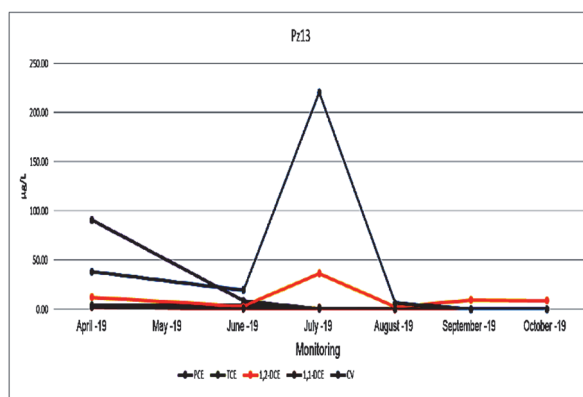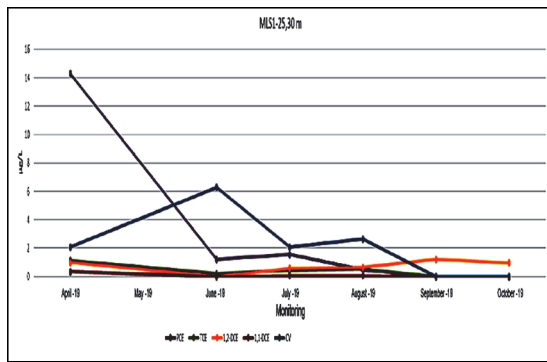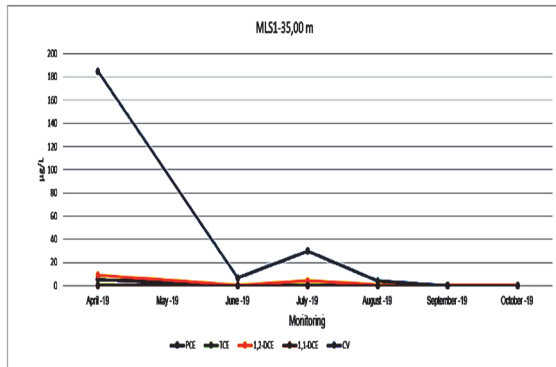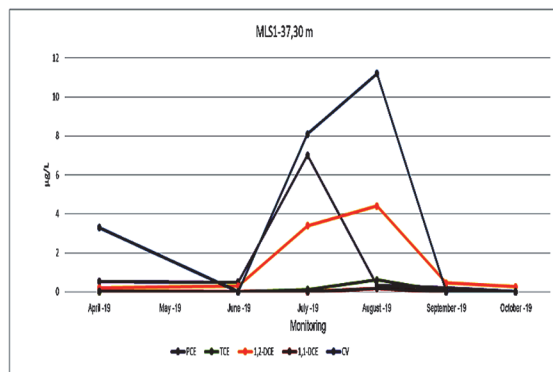

Fig. 8. Concentration trends for chlorinated ethylene in groundwater at monitoring point Pz13 in the treatment area before and after injection of EHC® L performed in May 2019
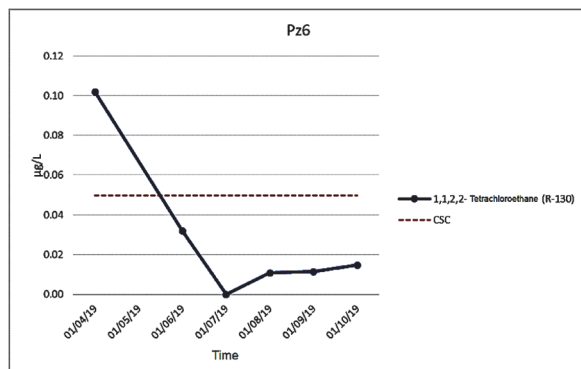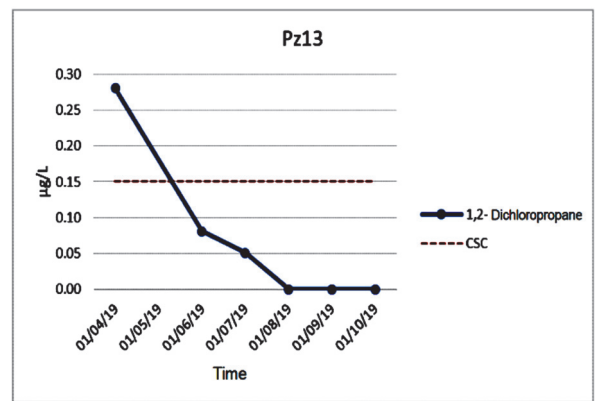
(a)

(b)

(c)

Fig. 9. Concentration trends for chlorinated ethylenes in groundwater at the MLS1 multi-level monitoring point: (a) 25 m bgl; (b) 35 m bgl; (c) 37 m bgl

Fig. 10. Trend in R-130 concentrations in groundwater at the Pz6 monitoring point in the treatment area before and after EHC® L injection performed in May 2019

Fig. 11. Trend in 1,2-DP concentration in groundwater at the monitoring point Pz13 in the treatment area before and after EHC® L injection performed in May 2019

3.1. Evaluation parameters of EHC® Liquid effectiveness

In order to determine if the piezometers were effectively under the influence of the EHC® Liquid reagent and, therefore, to demonstrate the effective distribution of the reagent in all the treated areas, aquifer field parameters including total organic carbon (TOC), dissolved oxygen (DO), hydrogen ion activity (pH), and oxidation-reduction potential (ORP) were measured. The extent of reducing conditions was also assayed by analysis of dissolved iron Fe (II), manganese Mn (II) and sulphate (SO_4). Along with DO, ORP, and pH as field parameters, Fe (II) and Mn (II) are viewed as good indicators of substrate effectiveness in establishment of reducing conditions.

A decreasing trend in DO was observed following substrate injection, indicating rapid establishment of anaerobic conditions necessary for biological reductive dechlorination. A significant increase in the concentrations of Fe (II) and Mn (II) in solution was observed in all the monitoring piezometers present in the treatment area, confirming the correct distribution of the reagent in the groundwater and the establishment of enhanced anaerobic conditions. Maximum concentrations of Mn (II) and Fe (II) of 4 and 13 mg/L were observed.
A decrease in the concentrations of sulphate in solution was observed, on average, equal to an order of magnitude compared to the pre-treatment values ranging from 0.5 to 1 mg/L, thus demonstrating the establishment of sulphate-reducing conditions, necessary for the achievement of complete biological reductive dichlorination.

4. Conclusions

In 2019, the ISCR and ERD treatment of an aquifer historically contaminated with tetrachlorethylene, 1,2-dichloropropane and 1,1,2,2-tetrachloroethane was successfully performed in Italy using EHC® Liquid. Following injection of EHC® Liquid into the treatment zone, highly reduced

conditions were established in the aquifer as indicated by the reduction in ORP, and geochemical changes including an increase in soluble manganese and ferrous iron and a decrease in sulphate concentrations. As reducing conditions were being established, a rapid decrease of the PCE, DP and R-130 was observed in all treatment area monitoring wells. Less than six months after application, PCE, DP and R-130 concentrations were reduced up to 95% compared to pre-treatment concentrations.

As anticipated by sequential reductive dichlorination processes, a temporary increase of daughter products including DCE and VC was observed. These daughter products were rapidly reduced to below the method detection limit in all the monitoring wells, except for some downstream wells where EHC® Liquid had not been distributed. No rebound in PCE, DP or R-130 concentrations was observed subsequent to treatment, demonstrating the effectiveness of the reductive dichlorination process and indicating treatment of both dissolved and adsorbed phase contaminants.

References

Aulenta F., Majone M., Tandoi V., (2006), Enhanced anaerobic bioremediation of chlorinated solvents: environmental factors influencing microbial activity and their relevance under field conditions, *Journal of Chemical Technology and Biotechnology*, **81**, 1463-1474.

Borden R., (2006), Protocol for Enhanced in situ Bioremediation Using Emulsified Edible Oil, Air Force Center for Environmental Excellence (AFCEE), On line at: https://frtr.gov/costperformance/pdf/remediation/Final -Edible-Oil-Protocol-October-2007.pdf.

Bradley M., Chapelle F., Lovley D., (1998), Humic acids as electron acceptors for anaerobic microbial oxidation of vinyl chloride and dichloroethene, *Applied and Environmental Microbiology*, **64**, 3102-3105.

Bradley M., (2000), Microbial degradation of chloroethenes in groundwater systems, *Hydrogeology Journal*, **8**, 104-111.

Fennell E., Gossett J., (1998), Modeling the Production of and Competition for Hydrogen in a Dechlorinating Culture, *Environmental Science and Technology*, **32**, 2450–2460

GD 152, (2006), Governmental Decision No. 152/2006 Annex 5 Part IV, regarding the groundwater quality limits, On line at: https://www.camera.it/parlam/leggi/deleghe/06152dl2.htm.

Hartmans S., De Bont J., Tramper J., Luben K., (1985), Bacterial degradation of vinyl chloride, *Biotechnology Letteres*, **7**, 383-388.

Lee C.H., Lewis T.A., Paszczynski A., Crawford R.L., (1999), Identification of an extracellular agent [correction of catalyst] of carbon tetrachloride dehalogenation from Pseudomonas stutzeri strain KC as pyridine-2, 6-bis(thiocarboxylate), *Biochemical and Biophysical Research Communication*, **261**, 562-6.

Lee M.D., Buchanan R., Ellis D., (2000), *Laboratory Studies Using Edible Oils to Support Reductive Dechlorination*, Proc. 2nd Int. Symp. on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, vol.1, 77-84.

Leombruni A., Morlacchi F., Collina L., Leigh D., Mueller M., (2020), Full-scale application of ELS® microemulsion technology for the treatment of an aquifer contaminated with perchloroethylene and trichloroethylene via enhanced reductive dechlorination, *Acque Sotterranee - Italian Journal of Groundwater*, **9**, 19-26.

Lewis T.A., Cortese M.S., Sebat J.L., Green T.L., Lee C.H., Crawford R.L., (2000), A Pseudomonas stutzeri gene cluster encoding the biosynthesis of the CCl4-dechlorination agent pyridine-2,6-bis (thiocarboxylic acid), *Environement Microbiology*, **2**, 407-16.

Maymo-Gatell X., Zinder S.H., Anguish T., (1997), Reductive dechlorination of chlorinated ethenes and 1,2-dichloroethane by "Dehalococcoides ethenogenes" 195, *Applied and Environmental Microbiology*, **65**, 3108-3113.

Newell C.J., Rifai H.S., Wilson J.T., Connor J.A., Aziz J.A., Suarez M., (2003), *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies*, In: *Ground Water Issue*, U.S. Environmental Protection Agency.

Vogel T., (1994), *Natural Bioremediation of Chlorinated Solvents*, In: *Handbook of Bioremediation*, Lewis Publishers, Boca Raton, 201-225.