Control of the Effectiveness of Source Removal and ZVI Barrier Treatment in a DNAPLs Contaminated Site Using CSIA

/ CARME AUDÍ-MIRÓ (1*), ROBERTO ESPINOLA (2), CLARA TORRENTÓ (1), NEUS OTERO (1), MONICA ROSELL (1), ADRIANA ROSSI (1), JORDI PALAU (1, 3), ALBERT SOLER (1)

(1) Grup de Mineralogia Aplicada i Medi Ambient. Facultat de Geologia, Universitat de Barcelona, C/ Martí i Franques s/n, 08028 Barcelona, Spain.
(2) Agència Catalana de l'Aigua, C/ Provença, 204-208, 08036 Barcelona, Spain
(3) Université de Neuchâtel. CHYN, Centre d'hydrogeologie. Rue Emile-Argand 11, CH-2000, Neuchâtel, Switzerland.

INTRODUCTION

The study site is polluted with dense non aqueous phase liquids (DNAPLs): tetrachloroethylene (PCE), trichloroethylene (TCE) and dichloroethene (cis-DCE). Contamination was caused by a poor management of waste generated by an automotive industry, which was discharged into a seepage pit. As a result, soil contamination was produced in the seepage pit area and a plume of contaminated groundwater by DNAPLs was generated along the Can Ninou torrent (Granollers, Barcelona) (Fig. 1).

As a remediation strategy, a dual action was necessary: the removal of the source of contamination and the treatment of the groundwater plume of DNAPLs. The source removal consisted of a selective excavation of the seepage pit and an offsite management of the contaminated soil. To restore the groundwater quality, a passive treatment system using a Permeable Reactive Barrier (PRB) of Zero-Valent Iron (ZVI) was implemented, in order to remove DNAPLs from groundwater via abiotic reductive dechlorination.

As a valuable tool for monitoring a ZVI-PRB in the field, compound specific isotopic analysis (CSIA) has been proposed. When the chlorinated compound is degraded, a carbon isotope fractionation occurs producing an enrichment in ^{13}C in the residual compound (Slater et al., 2002; Prommer et al., 2008). The carbon isotopic composition of the residual compound can be related to the amount of compound degraded using the Rayleigh model (Prommer et al., 2008). Therefore, stable carbon isotope analysis permits the evaluation of the extent of degradation, excluding all the processes that produce a decrease in concentration but not a degradation (dilution, diffusion, dispersion, sorption), which don't generate a significant isotope change. In consequence, carbon isotopic composition permits to determine the specific efficiency of the degradation produced by the PRB in the field.

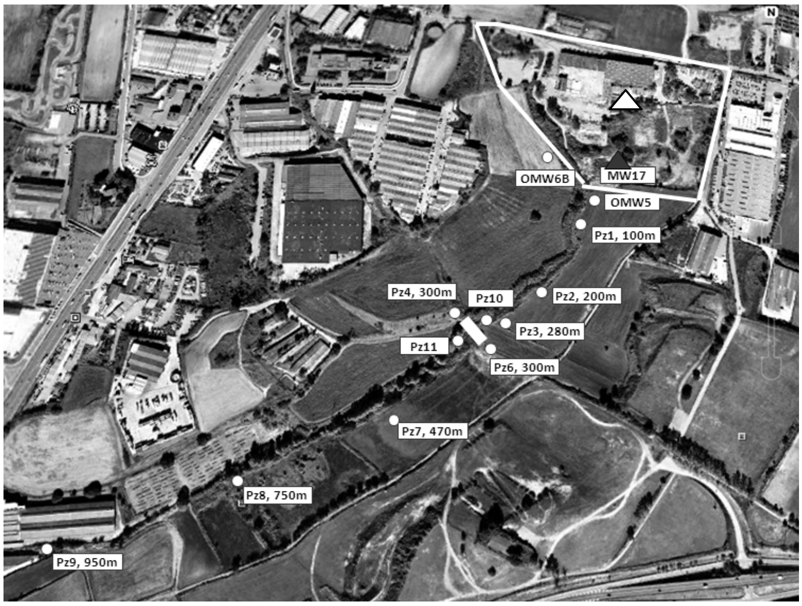

fig. 1. Aerial view of the contaminated site. The area surrounded by the white line corresponds to the industrial area and the white triangle to the contamination focus. The white circles correspond to wells installed along the torrent Can Ninou with their distance from the focus indicated. The wide white line represents the ZVI-PRB.

OBJECTIVES

The aim of this study is a) to monitor the pollution attenuation of a site contaminated by DNAPLs after the source removal; b) to determine the efficiency of the ZVI reactive barrier treatment already installed.

METHODOLOGY

A total of eleven piezometers of 10-12 m deep were installed along the *Torrent de Can Ninou* between May 2009 and March 2010 (Fig. 1) -Pz1 to Pz11-; other piezometers had been previously installed in 2005 (MW17, OMW5 and OMW6B). An initial sampling campaign of the wells was done before the removal of the source, in May 2009; and a total of four sampling campaigns were done approximately every six months since the removal of the source, from June 2009 until April 2011. Within this period of time, in March 2010, the ZVI barrier of 5 m high, 20 m long and 0.6 m thick was placed at a 7 m depth. Concentration of PCE, TCE and cis-DCE was determined from all the campaigns.

palabras clave: Barrera reactiva permeable, Fe(0) metálico, Fraccionamiento Isotópico, Etilenos Clorados	***key words:*** Zero Valent Iron, Permeable Reactive Barrier, Isotopic Fractionation, Chlorynated Ethylenes

* corresponding author: **carmeaudi@ub.edu**

The last campaign, in April 2011, also included the carbon isotopic analyses of PCE, TCE and cis-DCE. In March 2012, 5 additional piezometers were installed, two upstream of the barrier and three downstream of it. The new piezometers were multilevel piezometers with sampling tubes every half meter, until a total depth of 14 m.

RESULTS

The source removal have produced a general decrease of all the compounds, that is more pronounced in the case of cis-DCE, which is the compound that, before the source removal, was found in a considerable higher concentration than the others. Before the removal of the source the concentration of cis-DCE was of 43000 µg/L in OMW5 (just before the source removal on May 2009) and was reduced to 100 µg/L in April 2011.

Moreover, the isotopic results obtained from the April 2011 campaign from the wells located before the barrier show that biodegradation is occurring after the source removal. $\delta^{13}C$ values obtained show an isotopic enrichment of TCE and cis-DCE, with values from -19.9‰ for both TCE and cis-DCE in the source area to -16‰ and -15.5‰ (Figs. 2 and 3) for TCE and cis-DCE respectively just before the PRB.

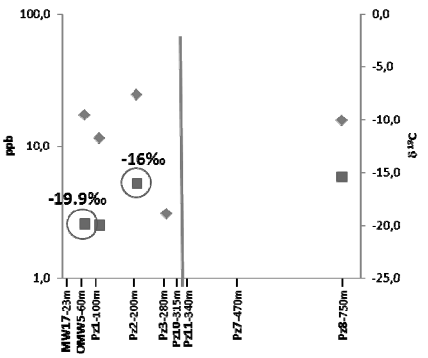

fig. 2. TCE isotopic signature ($\delta^{13}C$) (squares) obtained from the different wells installed along the plume and in distance from the focus. The vertical line corresponds to the place where the ZVI-PRB is installed. The diamonds indicate the concentration of TCE in each point.

With regards to the ZVI-PRB performance, $\delta^{13}C_{PCE}$ values analyzed upstream and downstream of the barrier in old piezometres don’t show isotopic changes (values are around -20‰ in all the sampling points) suggesting that PCE is not abiotically removed. In the case of TCE slight isotopic changes have been observed in the water flow in a far distance after the barrier (-15.4‰) (Fig. 2). Positively, cis-DCE showed increasing $\delta^{13}C$ values upstream to downstream of the barrier (from -15.5‰ to -11.5‰) (Fig. 3) indicating that a possible abiotic degradation due to the ZVI-PRB is being produced.

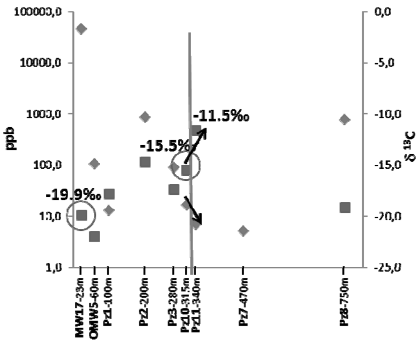

fig. 3. Cis-DCE isotopic signature ($\delta^{13}C$) (squares) obtained from the different wells installed along the plume and in distance from the focus. The vertical line corresponds to the place where the ZVI-PRB is installed. The diamonds indicate the concentration of cis-DCE in each point.

The fractionation ε_C of cis-DCE due to this specific type of iron has been previously obtained through laboratory batch experiments: -20.5‰ (Cretnik et al., 2011).

DISCUSSION

The results obtained confirm a successful removal of the source, which contributed to a significant decrease of cis-DCE, currently the most predominant contaminant.

The existence of biotic degradation in the field was demonstrated using the isotopic enrichment observed in TCE and cis-DCE upstream of the barrier.

These first results do not indicate an effective performance of the ZVI-PRB for the degradation of PCE, which doesn’t show any isotopic fractionation. Contrarily, isotopic fractionation has been observed in the case of TCE and cis-DCE from upstream to downstream of the barrier, which seems to indicate that the barrier is working for these compounds.

However, more information should be obtained in order to understand and characterize the barrier performance. Some hypothesis to explain these non totally successful results could be i) possible bypass processes occurring around the barrier, ii) an incorrect design of the barrier including length, highness and thickness, etc. The recently installed multilevel piezometers will let us determine the isotopic composition and the concentration of contaminants at different depths, allowing a better characterization of the contaminant plume, and, applying the isotopic analyses, potential bypasses occurring around the barrier may be detected.

CONCLUSIONS

Source removal has produced a significant reduction of the contaminant compounds, indicating successful pollution attenuation.

Isotope values have proved that natural TCE and cis-DCE degradation is occurring in the field.

Preliminary concentration and isotopic results seem to indicate that the PRB does not intercept the whole contaminated plume. The multilevel piezometers constructed around the PRB will let us know in detail the underground sections most affected by pollution and help to define patterns of DNAPLs migration in the subsurface, giving the possibility to improve the design of the ZVI-PRB.

AKNOWLEDGMENTS

This work has been financed by the projects CGL2011-29975-C04-01 from the Spanish Government and 2009SGR-00103 from the Catalan Government.

REFERENCES

Prommer, H., Aziz, L.H., Bolaño, N., Taubald, H., Schüth, C., (2008): Modelling of geochemical and isotopic changes in a column experiment for degradation of TCE by zero-valent iron. J. Contam. Hydrol. 97, 13-26.

Slater, G.F., Lollar, B.S., King, A., O’Hannesin, S., (2002): Isotopic fractionation during reductive dechlorination of trichloroethene by zero-valent iron: influence of surface treatment. Chemosphere. 49, 587–596.

Cretnik, S., Audí-Miró, C., Bernstein A., Palau, J., Soler, A., Elsner, M., (2011): Isotope measurements (C, Cl) can help assessing the efficiency of zero valent iron barriers. AIG-9 congress, book of abstracts.