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**Organic solvent contaminated groundwater
bioremediation:
study and development of advanced in-situ
processes and definition of an evaluation
protocol for the better remediation strategy**

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Abstract

Groundwater and soil contamination by chlorinated hydrocarbons has recently become of increasing concern and extensive researches have been conducted to develop technologies for remediating both contaminated groundwaters and soils. In this framework *in-situ* technologies are promising for remediating contaminated groundwater in that they would keep the ecosystem largely undisturbed and would be cost effective.

The aim of the present study is the assessment of natural attenuation potential at a TCE-contaminated site in Northern Italy, near Milano, where contamination of aquifers by TeCA, PCE and TCE has been documented.

This site has a long history of contamination (approximately 50 years) mainly due to industrial activities.

The study illustrates the steps involved in implementing natural or enhanced attenuation screening protocols at this site and represent an outstanding example of effective coupling of process analysis and modeling. In fact microcosm studies properly integrated with modeling results might suggest the feasibility for enhancing *in-situ* reductive dechlorination at the investigated site in order to achieve the stringent legislation limits. Such promising results will be verified through a field test performance before implementing the process at full-scale.

In-situ enhanced anaerobic reductive dechlorination (RD) is a promising technology for remediation of chloroethane and chloroethene contaminated groundwater. Indeed it is ideally suited for integration into long-term site management programs to address chlorinated solvents dissolved in groundwater. That's because such contaminants often are encountered in the form of DNAPL, which is characterized by a slow release, thus requiring long-term decontamination activities. Consequently active processes (e.g., conventional groundwater pumping and treating) often result costly and quickly reach a point of diminishing returns.

In situ enhanced RD can be accomplished by either enhancing halo respiratory activity of native microbial dechlorinating population (e.g. through the addition of electron donors and/or nutrients to produce favorable reducing conditions), or by inoculating the aquifer with microorganisms that are capable of degrading the target pollutants.

The protocol to be developed will describe a phased-approach for the assessment of the feasibility of bioremediation, either enhanced or as a part of a natural attenuation objective, at a contaminated site. The "Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water" (EPA/600/R-98/128) and the "Treat ability test for evaluating the potential applicability of the reductive anaerobic biological in situ treatment technology

(RABITT) to remediate chloroethenes” (US Department of Defence) will be the reference reports for the implementation of this new protocol.

The phase-approach included chemical, hydrogeological, and microbiological characterization of the site, monitoring and modelling of the contamination plume, and field tests.

Site description and characterization



Fig. 1 – Aerial view of the tested site

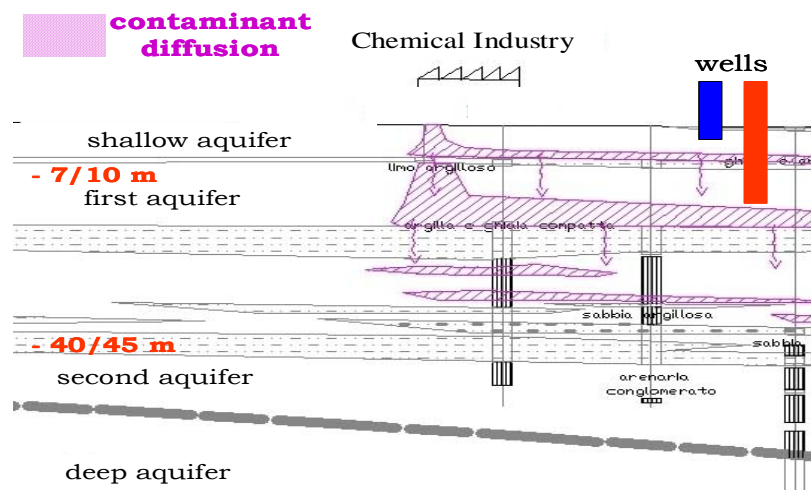


Fig. 2 – Section of the aquifer system

In the first phase an extensive review of existing site data (hydrogeological information and aquifer parameters), and sampling and analyses of groundwater at

existing wells (20 monitoring wells located in different parts of the plume) has been carried out.

The subsurface below the site shows two clayey layers at different depths which allow to define two aquifer up to about 50 m (Figure 2).

The contaminant concentration data collected at the site show that majority of contaminant mass is present in the deep permeable zone, named First Aquifer, probably due to the small thickness of the first clayey layer (0.5-3.5 m) and possible hydraulic connection between the two aquifers.

The second as well as the deep aquifers are still not involved in the contamination. Generally in each sampling point two wells were installed at different depth in order to investigate both the shallow and the first aquifer.

Groundwater collected from the well located about 20 m down-gradient the contamination source area was mainly contaminated by TeCA (13435 µg/l), PCE (1300 µg/l), TCE (1970 µg/l), along with cis-DCE (290 µg/l and VC at 13 µg/l. The presence of TCE reductive dechlorination daughter products along with an hydraulic conductivity $> 10^{-3}$ cm/sec indicated that the site has the potential for natural or enhanced bioremediation.

The second phase of the approach relied on the implementation of a network of monitoring wells (12 piezometers have been installed) close to the source of contamination along groundwater flow direction. This was aimed at increasing the number of groundwater sampling points in order to better monitoring contaminant transport and biodegradation.

During this phase aquifer material has been also collected for microcosm studies. The high concentrations detected in the wells all trough the long-term monitoring have suggested the possibility of a DNAPL. Numerical simulations based on different source hypotesis have confirmed that such high level of contamination can result only as a consequence of a DNAPL presence.

Future steps will be to realise a packer-test monitoring campaign.

Microcosms studies

Microcosms studies are carried out at the Department of Chemistry, University of Roma La Sapienza.

The microcosm study were designed to assess the potential for microbial in-situ anaerobic reductive dechlorination (RD) at the contaminated site. In particular, this study was aimed at evaluating whether RD by native population could be enhanced by addition of substrates (i.e. yeast extract, lactate, butyrate, hydrogen) or growth factors (i.e. yeast extract, vitamin B12) and whether it could proceed past cis-DCE; at evaluating the influence on RD of competitive metabolisms (i.e. nitrate reduction and sulfate reduction); and at evaluating the application of a *Dehalococcoides* spp. containing inoculum for the treatment of the TeCA, PCE and TCE contaminated groundwater.

In conclusion, results from the microcosm study indicate the potential for enhancing full dechlorination at the chlorinated solvent contaminated site, through a proper addition of a suitable electron donor (e.g. lactate or butyrate) and/or through bioaugmentation with a *Dehalococcoides*-containing culture.

Field test

Final steps of protocol application suitability are the design and execution of a field test for an in situ evaluation of the remediation strategy for the contaminated site.

This implies first selecting a testing location, which met all technical and administrative screening criteria. Based on the results of the characterization different viable locations have been hypothesized and VISUALMODFLOW simulations have been carried out in order to select the most suitable configuration of the well and monitoring system.

In order to obtain an easier regulatory approval it was decided that the test will have been located in the hot spot area, which had previously been confined by constructing a low permeability cement barrier.

The selected area results then completely isolated from the aquifer system; the barrier in fact provides lack of hydraulic connection with the shallow aquifer while the first clayey layer serves as the aquitard.

The proposed field testing system, illustrated in figure 3, distributes feed solution by forcibly injecting amended groundwater at the head of the testing zone while extracting groundwater near the end of the zone. This technique creates a hydraulic gradient designed to direct the flow of amended groundwater through the test plot.

VISUALMODFLOW simulation have been carried out in order to determine the size of the area interested by the forced water circulation system. This is necessary in order to calculate the amount of electron donor to be supplied for effectively enhancing the biological activity, thus ensuring a proper process performance.

The behavior of the system has also been investigated, in terms of electron donor dispersion in the system. No consumption from biomass was considered in order to have a conservative estimate of the dispersion area.

Results of the simulation, referred to 150 days continuous injection of lactate in the system, are reported in figure 4.

It's noteworthy that lactate dispersion is confined to a quite limited volume.

The field testing system, illustrated in figure 3, has been realized on July 2004 and a general view is reported in figure 5.

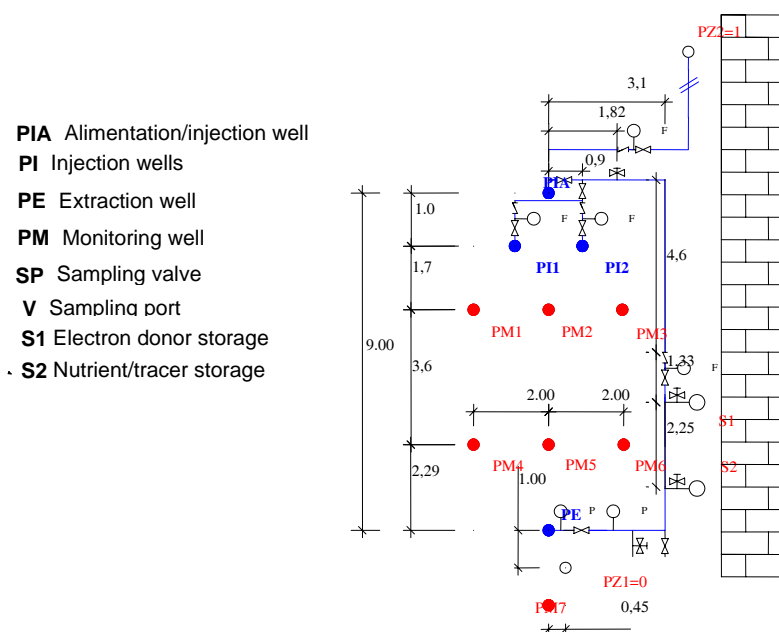


Figure 3 – Field test layout

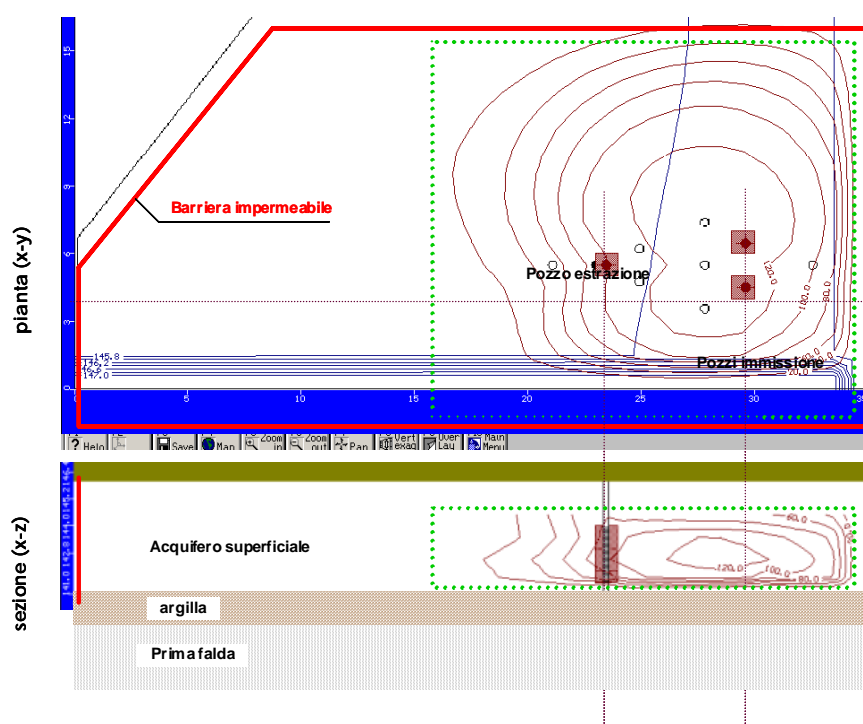


Figure 4 – Typical example of simulation with VISUALMODFLOW. Substrate concentration distribution on the plane x-y after 150 days



Figure 5 – Realization of field test (July 2004)

During the last year of the present study, the field test project has been completed and implemented. Tracers studies have been performed in order to verify the results of the computer-aided simulations. A 150 days monitored ENA is hypothesized.

The figure 6 illustrates the results of simulation with VISUALMODFLOW injecting 10.000 mg/l of NaCl.

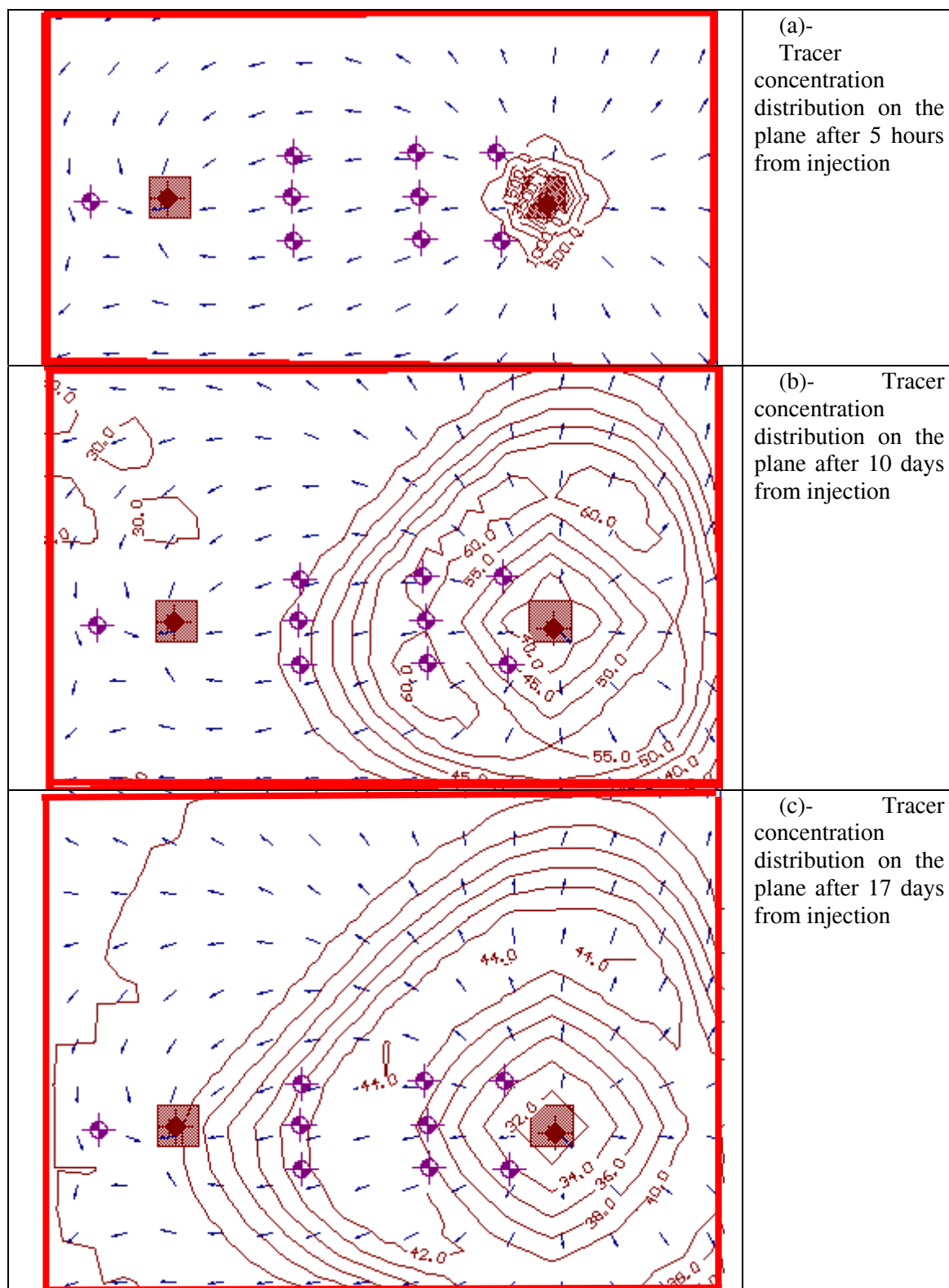


Figure 6 – Conservative tracer distribution injected in PI1, PI2 wells at a concentration of 10.000 mg/l.

The difficulties encountered in the field test realization, due to well problem construction have brought to a change in the injection and extraction wells. So the new test configuration sees the PM2 as the injection well and the PM7 as the extraction well.

A further experimental campaign has been carried out, in the month of February 2005: the conservative tracer (NaCl) was injected for three times (on 16th, 20th, 22nd February) to verify the suitability of the new site configuration.

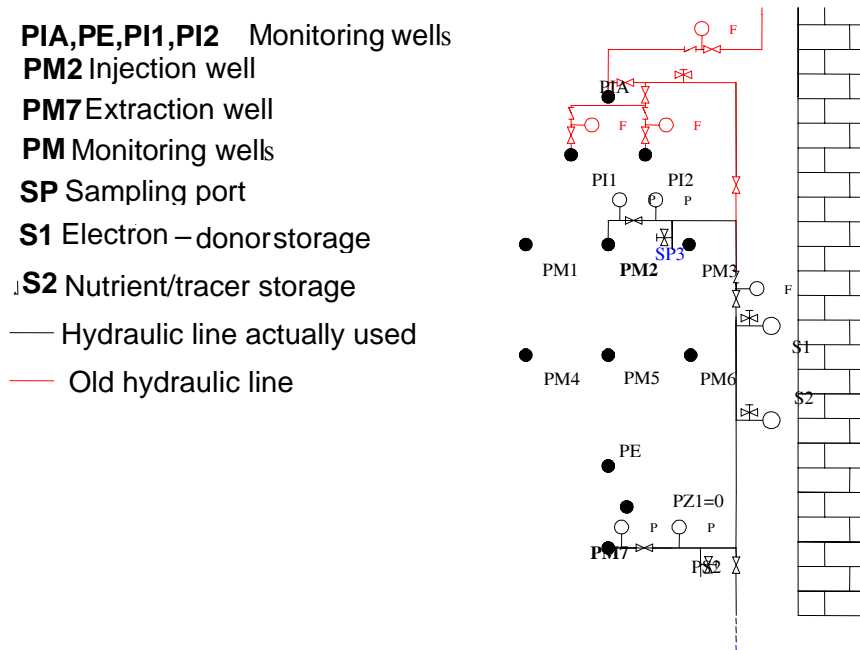


Figure 7 – New field test layout

One of the experimental breakthrough curves is reported in the following figure.

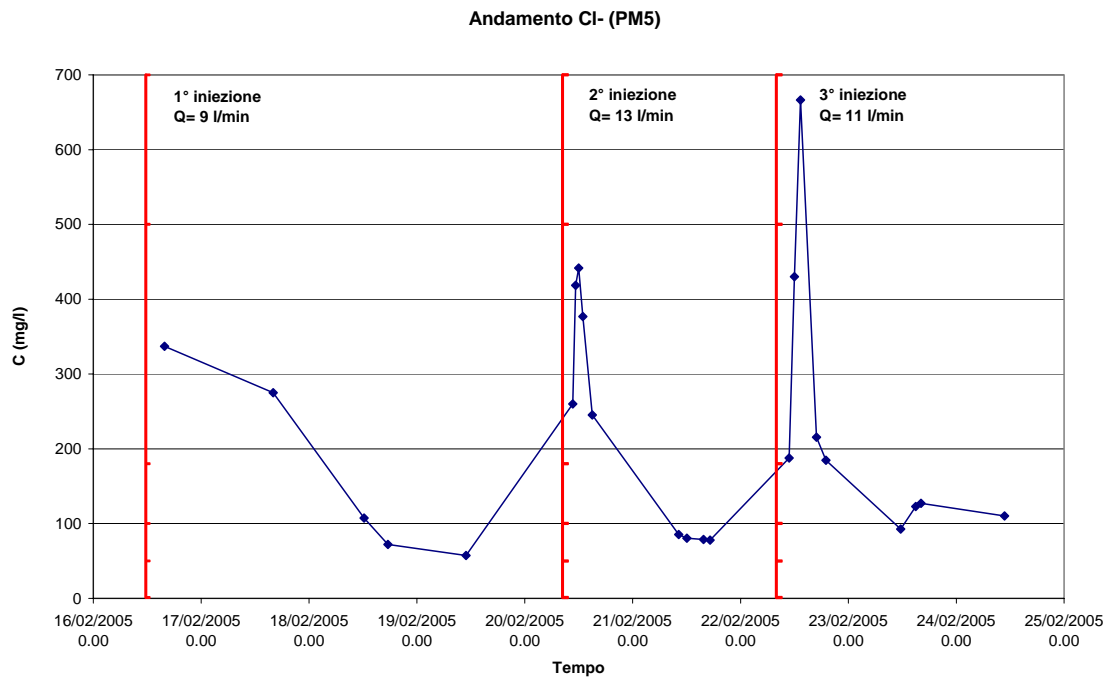


Figure 8 . – Tracer concentration curve after 3 injections in PM5 well

During tracer test levels of the wells are monitored for studying the hydraulics behaviour of the system. The observed results are reported in the figure 9.

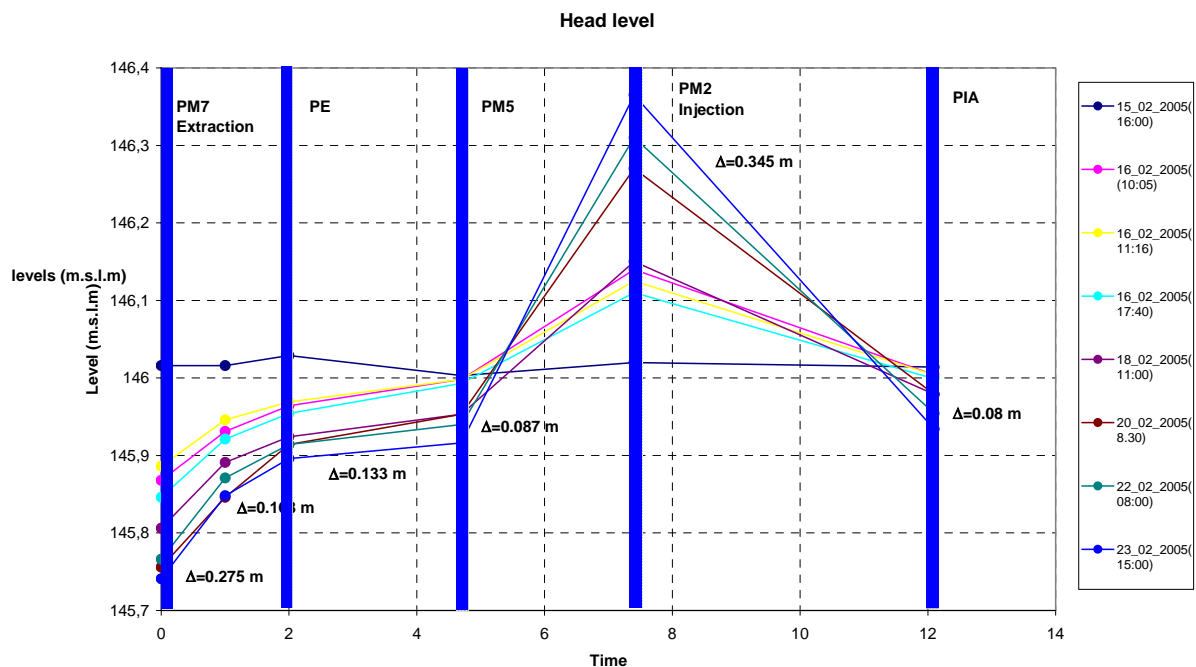


Figure 9 – Different levels of wells monitored during tracer test (February 2005)

In figure 10 an example of the calibration phase of MODFLOW is reported. The three peaks represent the three injections carried out in February; from fitting the simulation results with the experimental ones it has been possible to define the values of the conductivity parameter and of the dispersion one.

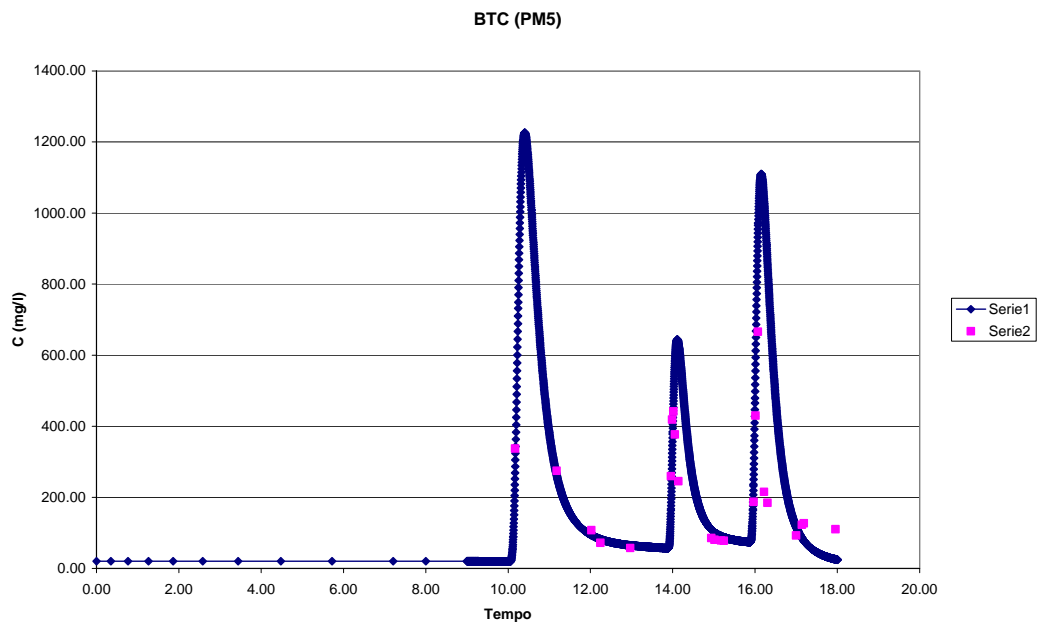


Figure 10 – Comparison between simulation results and observed results in PM5 well.

Conclusions

Assessing the potential for in-situ ENA of chlorinated contaminants requires real knowledge of both the processes involved and of the hydrogeological behavior of the aquifer. This can only be accomplished by means of a proper coupling of process analysis and modeling with respect to standardized procedures.

First results prove that, at the investigated site, ENA has the potential for effectively reducing the level of contamination by chlorinated solvents. However the effectiveness of such a strategy relies on a correct design and management of the treatment system at the field scale. Such aspects are being investigated by performing a field test.

The field test is the result of a large previous work based both on the lab tests and numerical simulation which have been carried out consciously with a friendly and used model like MODFLOW for allowing large use of the procedure.

The development of a protocol can be discussed basing the starting point from the results of this study where an application has been presented.

Acknowledgments

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