

First Pilot Test on the Integration of GCW (Groundwater Circulation Well) with ENA (Enhanced Natural Attenuation) for Chlorinated Solvents Source Remediation.

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The remediation of aged source zone affected by residual chlorinated aliphatic hydrocarbons (CAHs) represents one of the main challenges in contaminated aquifers. Groundwater Circulation Wells (GCWs) could be considered a strategy for the progressive source zone remediation; this *in situ* remediation technology is designed to create an *in situ* vertical groundwater circulation cells by drawing groundwater from an aquifer through one screened section of a multi-screened well and discharging it through another screened section. The pressure gradient between the two hydraulically separated screen sections in the well induces a circulation flow in the aquifer forcing water through less permeable layer where usually CAHs residual source are located. The groundwater moves through the treatment zone both horizontally and vertically and as a consequence the low permeable layer is constantly penetrated by the vertical flow of the GCWs. We tested the possibility to use GCW to enhance in-situ bioremediation (ISB) in an operative industrial site heavily contaminated by different chlorinated solvents (at concentration up to 100 mg/L) in a complex hydrogeological saturated zone. A 30 mts deep GCW, with three screen sections, was designed and installed at the site for a pilot testing. Groundwater is pumped towards two screen sections of the GCW and is reinjected into the aquifer by another screen section after passing through an external unit treatment. External treatment unit is composed of a sand filter tank and two reactors: one reactor was filled with a biodegradable polymer (poly-hydroxy-butyrate, PHB) and the other one with a mixture of zero-valent iron (ZVI) and PHB. Results from the first eight months of operation clearly demonstrated how groundwater recirculation through the PHB reactor allowed delivering continuously electron donors in the contaminated aquifer enhancing the mobilization of CAHs and stimulating Natural Attenuation biological processes.

1. Background/Objectives

Chlorinated aliphatic hydrocarbons (CAHs) are the most common source of DNAPLs (Dense Non-Aqueous Phase Liquids) contamination [McCarty, 2010; Pankow and Cherry, 1994]. Due to their higher density respect to water DNAPLs tend to migrate downward through the unsaturated zone and often accumulate in low permeable layers creating DNAPLs source zones/pools [Schwille, 1988; Anderson et al., 1992]. Traditional technologies, such as Pump and Treat (P&T), are usually adopted to control/manage the contaminated persistent plumes that develop from DNAPL pools, which act as a long-term source of groundwater contamination. On the other hand, source zone treatment is advantageous over plume management or containment strategies in that it effectively reduces the mass of contaminant. In Situ Bioremediation (ISB) is one of the effective removal approaches on active secondary sources [ITRC 2005]. However, ISB for a source zone removal should face several limitations [ITRC, 2008]. Effective delivery and distribution of electron donors other than bioavailability of contaminants in heterogeneous aquifers are some of the primary limitations in most hydrogeological settings. By this regards, Groundwater Circulation Well (GCW) was chosen as a more

appropriate remediation strategy to enhance ISB in an operative industrial site heavily contaminated by a wide spectrum of CAHs located in the northern part of Italy.

A large source zone, probably characterized by a significant amount of residual DNAPL, has been identified below operative industrial warehouses in a quite complex hydrogeological setting, from high permeable transmissive zone to low permeable zone. As a consequence, even though an intensive pumping is active since 9 years to avoid contaminant spreading outside the site, dissolved CAHs concentration still remain significantly high. A typical specific site hydrogeological setting is reported in Figure 1; it shows a multiple-layered heterogeneous aquifer which consists of materials that vary in their water-transmitting properties laterally and vertically (fine to middle sands with intercalation of less permeable sandy silts to clayey silts layers with permeability in range of 10^{-7} - 10^{-4} m/s). In this situation, trapped DNAPL in low k zones act as continuous persistent source releasing contaminants in the more permeable layers by slow back diffusion; contamination present at the site consists of quantities of pooled or trapped DNAPL-phase (hotspots) and various dissolved plumes are generated from the residual phase.

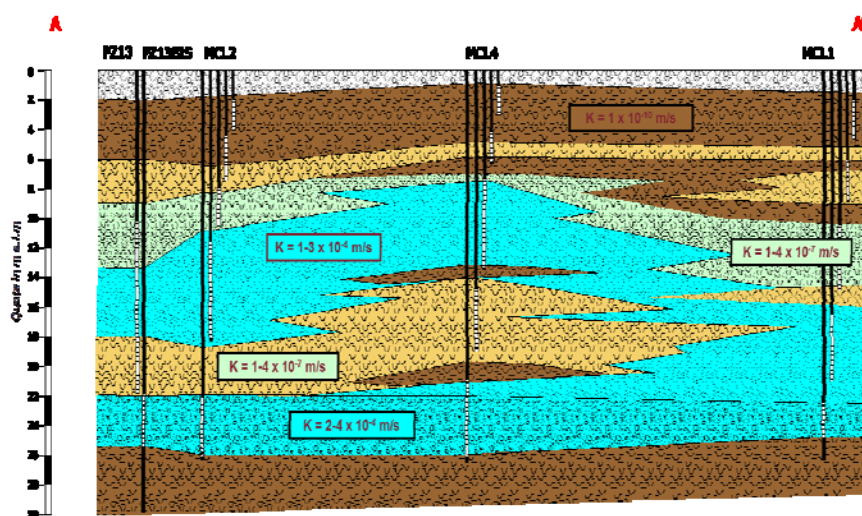


Figure 1: A representative geological cross section across the main contamination area

Site characterization surveys also indicated that natural attenuation is already ongoing in the investigated site: the presence of *cis*-DCE (*cis*-dichloroethene) and VC (vinyl chloride) indicates an intense but incomplete microbial dechlorination activity, who had led the formation of more toxic compounds such as VC. Due to the decreasing of the reductive dechlorination rate, under anaerobic conditions, an accumulation of *cis*-DCE or VC is often observed at CAHs contaminated sites [Tiehm et al 2011]. Therefore, laboratory microcosm experiments were set up to assess the possibility to significantly enhance the biodegradative potential of natural microbiota with the addition of electron donors as well as the interactions of dechlorinating populations with other microbial populations which can compete for the supplied electron donor [Fennel et al. 1997; Aulenta et al. 2002, Heimann et al 2007] and their effect on the dechlorination process in the subsurface. Microcosms were also used to evaluate the applicability of PHB as carbon releasing source at the studied site. PHB is a biopolymer produced (synthesized) by numerous microorganisms as an intracellular energy-storage material under unbalanced growth conditions [Brennan et al 2006], such as limited essential nutrients or excess carbon sources. This polymer was chosen as electron donors based on previous studies [Aulenta et al, 2008; Baric et al 2012, 2014] conducted at the lab scale which clearly demonstrated the ability of PHB fermentation products (volatile fatty acids, VFA and molecular hydrogen) to stimulate/sustain CAHs biological reduction dechlorination. Based on the geophysical characterization of the site and the distribution of the contamination, two locations were selected for saturated soil sampling for the microcosm investigation: one close to piezometer (Pz 6) downgradient the hydraulic barrier at the outer boundary of the site and the other one close to piezometer (Pz 14) inside an industrial warehouse close to the source area (metal industrial washing machines). Results of microcosm study indicated how an approach based on the delivery of electron donor in the area characterized by the presence of very high concentration of chlorinated solvents (source zone) could be successful in quantitatively degrade the contaminants in harmless compounds such as ethene and ethane (Figure2).

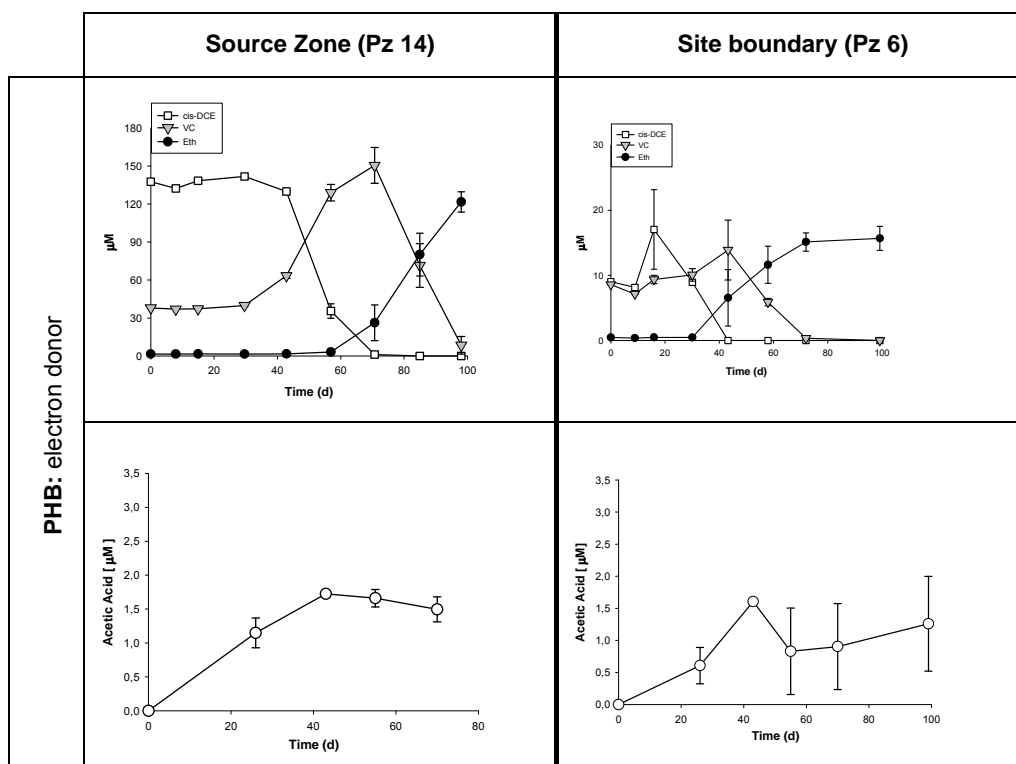


Figure2: Reductive dehalogenation of chlorinated solvents and acetic acid in anaerobic reactors amended with PHB. Error bars indicate the difference between two duplicate microcosms.

Based on the satisfactory results of the laboratory investigations, indicating that reductive dechlorination might be enhanced successfully at the considered site, the design of a pilot test was performed in order to select the best remediation strategy. As well known, one of requirements for successful *in situ* bioremediation implementation for chlorinated DNAPLs is the homogenous electron donor distribution. In this case, because of geochemistry and hydrogeology of site, the conventional addition methods are not suitable; traditional injection approaches are often limited by preferential migration of injected fluids through better permeable zones, while delivery through less permeable and contaminated layers is usually limited. On the other hand, Groundwater Circulation Well remediation technology allows creating in-situ vertical groundwater circulation cells by drawing groundwater from an aquifer through one screened section of a multi-screened well and discharging. The typical GCW configuration consists of installation of a single operating well with at least two isolated screen section. Groundwater is extracted from one screen and after treatment (or amendment) it is injected back into the aquifer through the second screen, creating a three-dimensional flow pattern (circulation cell) in the aquifer. The pressure gradient between two hydraulically separated screen sections in the well induces a circulation flow in the aquifer [Xiang and Kabala 1997, US EPA1998]. The groundwater moves through the treatment zone both horizontally and vertically and as a consequence the low permeable layer is constantly penetrated by the vertical flow of the GCW (Figure 3).

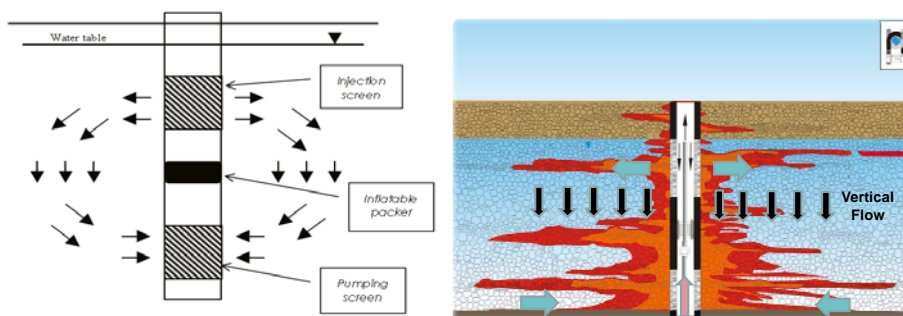


Figure3: Schematic overview of an operating Groundwater Circulation Well

2. Pilot (Field) Test

On the basis of the geological and hydrogeological characteristics of the site, a 30 mts deep GCW was designed in order to obtain an *in-situ* vertical groundwater circulation by drawing groundwater from two lower screened sections (-24mts and -14mts) of a multi-screened well separated by packers and discharging it through an upper screened section (-7mts). Thus, GCW worked under standard flow conditions: water flow comes in through the lower and intermediate screen and out to the upper screen. As consequence, two pumps were installed on the surface to extract groundwater from deep permeable layer and low permeability intermediate layer, hereafter called pump 1 and pump 2, respectively. Following that, groundwater is pumped upward inside an above-ground installed external treatment unit. Figure 4 illustrates the P&ID of the above-ground set-up plant connected to the GCW. According to P&ID, nine different possibilities are made available to change process and work under favorable condition.

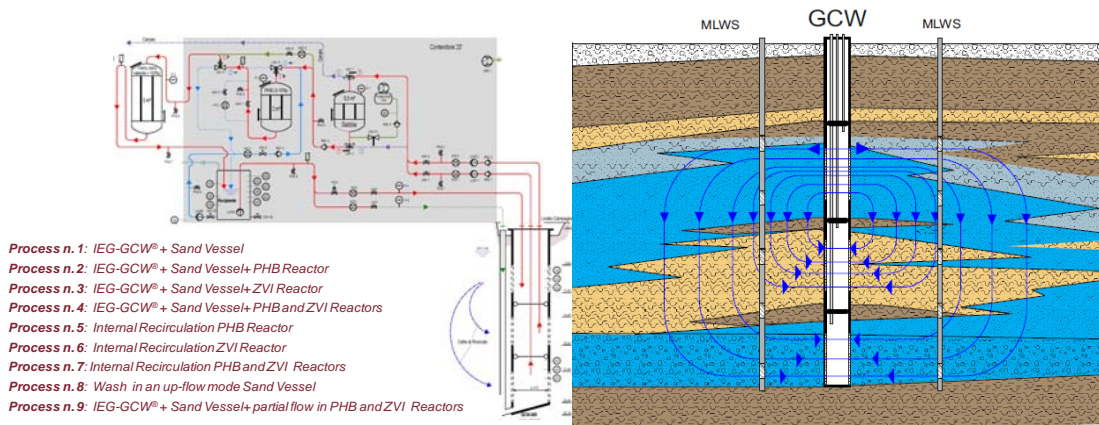


Figure 4: Piping and Instrumentation Diagram - P&ID, of the remediation plant with applicable processes and schematic diagram of groundwater flow pattern due to use of GCW.

As shown in Figure 5, the external treatment unit is composed of a sand filter tank, a PHB reactor (where fermentation takes place and dissolved VFA and H₂ are produced) and a ZVI reactor (where CAHs are partially removed before reinjection).

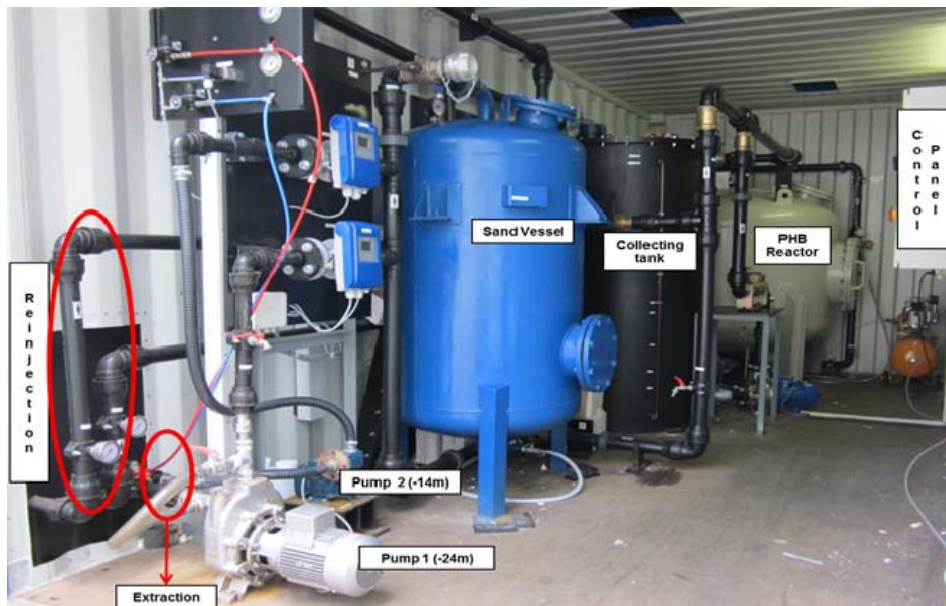


Figure 5: The external treatment unit.

3. Results

3.1 Enrichment of groundwater with PHB fermentation products

Figure 6 depicts volatile fatty acids (VFAs) effluent concentrations as function of operating time as measured in the outlet of the PHB reactor and even in the outlet of the vessel where the groundwater that will be reinjected into the aquifer is collected.

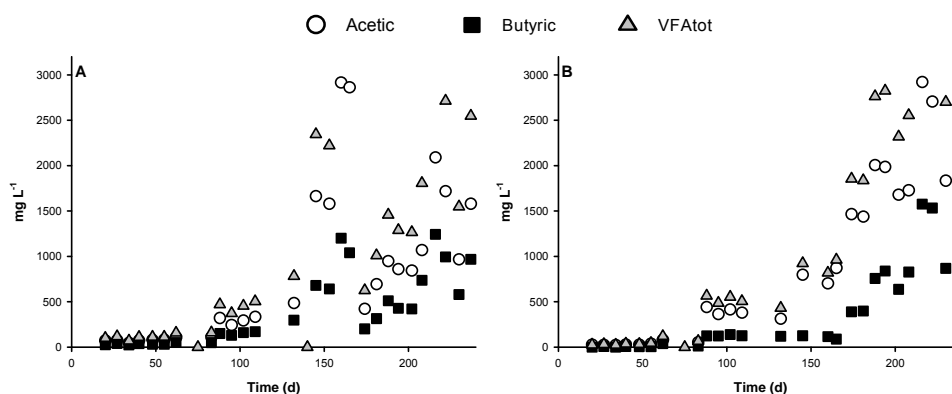


Figure6: VFA effluent concentrations of PHB reactor (A) and vessel (B)

Groundwater pumped from deep (-25m) and intermediate screen (-14m) was enriched with products from the continuous fermentation of PHB. Tuning the flow rate groundwater through PHB reactor allowed optimizing the concentration of the produced dissolved electron donors and the spreading of biostimulants in the subsurface can be varied accordingly.

3.2 Enhancing CAHs mobilization

Groundwater recirculation through PHB reactor allowed a continuous delivering of the PHB fermentation products in the contaminated aquifer also in the low permeable layer due to the vertical flow induced by the GCW installation. The field results clearly demonstrated that mobilization of chlorinated aliphatic hydrocarbons was strongly enhanced (Figure 7).

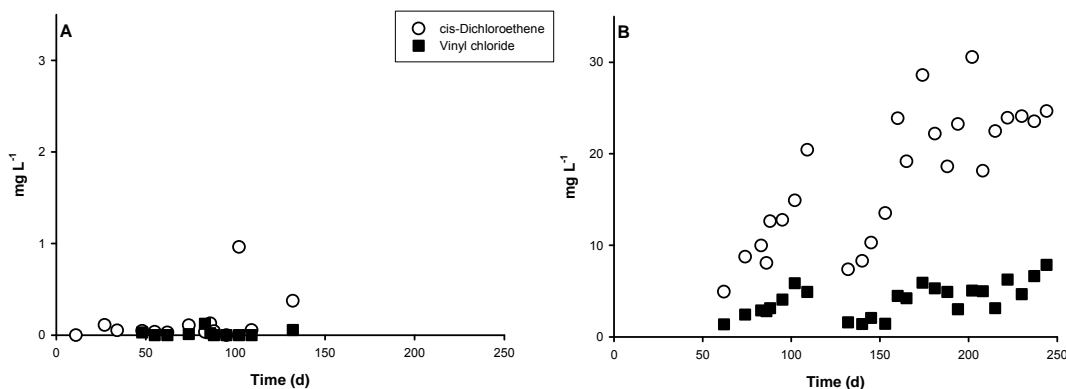


Figure7: CAHs concentration in the groundwater extracted from the lower (A) and intermediate (B) screen

The CAHs mobilization has been proven by analysing the mass of 1,2-DCE and VC extracted during the operation time (Table1).

Table 1: CAH mass extracted during the field test

	deep permeable layer	low permeability intermediate layer
Extracted volume [m ³]	4200	25
cis-DCE (g)	210	200
VC (g)	84	87.5

It is worth of noting that the calculated extracted amounts for both contaminants are very similar, but the relative volume at the two examined depths is strongly greater for the deep screen (-24 mts) than the intermediate screen (-14 mts).

4. Conclusions

The installed GCW combined with the external treatment unit allowed the effective amendment of groundwater with the PHB fermentation products. The combined effect of groundwater recirculation with VFA production (probably by a co-solvent effect) clearly enhanced the mobilization of pollutants from less accessible low permeable zone where a significant mass of contaminants is strongly retained. By this regard the traditional Pump & Treat approach could allow the removal of contaminants mostly from the more transmissive zones of an aquifer but it has a negligible effect on the contaminant mass stored in low permeability media which are released out slowly by back-diffusion. Moreover, coupling GCW with the continuous production of electron donors should allow the enhancement of the biological reductive dechlorination inside the less permeable layer thus potentially reducing the remediation time.

Reference

- Anderson, M. R., R. L. Johnson, and J. F. Pankow, Dissolution of dense chlorinated solvents into ground water, 1, Dissolution from a well-defined residual source, *Ground Water*, 30(2), 250-256, 1992
- Aulenta F., Majone M., Verbo P., Tandoi V. Complete dechlorination of tetrachloroethene to ethene in presence of methanogenesis and acetogenesis by an anaerobic sediment microcosm. *Biodegradation* 13, 411-424, 2002
- Aulenta F., Fuoco M., Canosa A., Papini P.M., Majone M, Use of poly- β -hydroxy-butyrate as a slow-release electron donor for the microbial reductive dechlorination of TCE. *Water Science & Technology* 57,921-925, 2008
- Baric M.,MajoneM, Beccari,Papini P.M., Coupling of polyhydroxybutyrate (PHB) and zero valent iron (ZVI) for enhanced treatment of chlorinated solvents ethanes in permeable reactive barrier (PBRs); *Chemical Engineering Journal*, 195-196, 22-30, 2012.
- Baric M., L.Pierro L., Pietrangeli B, Papini M.P., Polyhydroxyalkanoate (PHB) as a slow-release electron donor for advanced in situ bioremediation of chlorinated solvent-contaminated aquifers, *New Biotechnology*, 31, 377-382, 2014.
- Brennan R., Sanford R., Werth C, Biodegradation of Tetrachloroethene by chitin fermentation products in a continuous flow column system. *J.Environment. Eng* 132(6), 664-673, 2206
- Fennell D.E, Gossett J.M, Zinder S.H Comparison of butyric acid, ethanol, lactic acid and propionic acid as hydrogen donors for the reductive dechlorination of tetrachloroethene. *Environ Science Technologies*. 31, 918-926, 1997.
- Heimann A.C, Friis A.K., Scheutz C.; Jakobsen R. Dynamics of reductive TCE dechlorination in two distinct H(2) supply scenarios and at various temperatures. *Biodegradation* 18, 167-179, 2007.
- ITRC. 2005. Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones. BioDNAPL-1. Washington, DC, USA. <http://www.itrcweb.org>. Accessed September 20, 2013.
- ITRC. 2008. Technical and Regulatory Guidance: In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones. BioDNAPL-2. Washington, DC, USA. <http://www.itrcweb.org>. Accessed September 20, 2013.
- McCarty, P. L. Groundwater contamination by chlorinated solvents: History, remediation technologies and strategies. *In Situ Remediation of Chlorinated Solvent Plumes*; Stroo, H. F., Ward, C. H., Eds.; Springer: New York, 2010; pp 805.
- Pankow, J. F.; Cherry, J. A. Dense Chlorinated Solvents and Other DNAPLs in Groundwater. Waterloo Press: Portland, OR, 1994; pp 522
- Schwillie, F., Dense Chlorinated Solvents in Porous and Fractured Media, Lewis, Chelsea, Mich., 1988
- Tiehm A and Schmidt K R Sequential anaerobic/aerobic biodegradation of chloroethenes—aspects of field application. *Current Opinion in Biotechnology* 22(3), 415-421, 2011.
- US Environmental Protection Agency (US EPA). Field applications of in situ remediation technologies: Ground-water circulation wells. Office of Solid Waste and Emergency Response, Technology Innovation Office: Washington, 1998
- Xiang J., Kabala Z.J., Performance of the steady-state dipole flow test in layered aquifer. *Hydrol. Process*. 11 (12):1595–1605, 1997.