CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791

DOI: 10.3303/CET1332006

A Comparison between Pump & Treat Technique and Permeable Reactive Barriers for the Remediation of Groundwater Contaminated by Chlorinated Organic Compounds

Immacolata Bortone*[a], Simeone Chianese[a], Armando Di Nardo[a], Michele Di Natale[a], Alessandro Erto[b], Dino Musmarra[a]

[a]Seconda Università degli Studi di Napoli, Dipartimento di Ingegneria Civile, Via Roma 29, 81031, Aversa (CE), Italia
[b]Università degli Studi di Napoli Federico II, Dipartimento di Ingegneria Chimica, P.le Tecchio 80, 80125, Napoli, Italia
immacolata.bortone@unina2.it

This paper deals with the design and the preliminary optimization of the remediation of a Tetrachloroethylene (PCE)-contaminated aquifer by Pump and Treat technique (P&T) or Permeable Reactive Barrier (PRB). The experimental site is located near a solid waste landfill in the metropolitan area North of Naples (Italy) where a considerable amount of solid waste has been deposited over the past decades. For both remediation technologies, adsorption onto granular activated carbon was adopted to remove PCE from water. In particular, a comparison of the results obtained, both in terms of efficacy of pollutant removal and the corresponding preliminary overall cost, was conducted. The design of both remediation techniques was conducted by using a commercial 3D hydrodynamic code to simulate groundwater flow and contamination transport and a second code, developed by the authors, to describe the adsorption phenomena involving the pollutant.

1. Introduction

Anthropogenic activities using chlorinated hydrocarbons (e.g. metal-degreasing facility, automotive industry, etc.) are the main reasons for the massive presence of these chemicals in the environment nowadays. In solid waste landfills, unintentional discharge of leachate and plastic material degradation due to leaching by rainwater are the main causes of chlorinated groundwater contamination (June et al., 2009; Kjeldsen et al., 2002). Tetrachloroethylene (PCE) is one of the most common chlorinated organic compounds in groundwater (Erto et al., 2009). The exposure to PCE represents a great danger for human health and environment, because of its high toxicity and slow degradation rate (U.S. EPA, 1988). Moreover, according to IARC (International Agency for Research on Cancer) classification, PCE is "probably carcinogenic to humans" (group 2A of carcinogens) (IARC, 1995). For all these reasons, the European Directives 2000/60/EC and 2006/118/EC indicate Tetrachloroethylene as one of the most dangerous contaminants and subject to a strict regulation.
Various options can be adopted for the remediation of aquifers contaminated by chlorinated hydrocarbons (Rivett et al., 2006), both in situ (such as PRB and anaerobic reductive dechlorination), and ex situ (such P&T). Pump and Treat technique (P&T) is a classic ex-situ technology. It consists in two different steps: a pumping step, in which the contaminated plume is extracted from groundwater by pumping wells, and a treatment step in which the pollutants are removed from the water by a specific operation, such as adsorption (U.S. EPA, 1996). Permeable Reactive Barriers (PRB) - an in-situ technology (Di Nardo et al., 2010) – are a possible alternative to P&T. PRB consists in the introduction of a "wall" of reactive media (e.g. an adsorbing material) in the subsurface, which groundwater naturally can pass through, as it is more permeable than the surrounding media while the adsorbing material captures the pollutants (Di Natale et al., 2008; Erto et al., 2011a).

In this work P&T and PRB for the remediation of an aquifer contaminated by chlorinated hydrocarbons, by using a modelling tool, are compared. A PCE-contaminated groundwater near a solid waste landfill in the metropolitan area North of Naples (Italy) is analysed as a case study.

2. Remediation method design and preliminary optimization

Remediation technology design can be effectively assisted by computational fluid dynamics (CFD), considering all the information about the site provided by a specific hydraulic, geotechnical and contaminant characterization of the polluted groundwater (U.S. EPA, 2008). To this purpose, a calculation domain large and long enough to contain the whole contaminant plume, considering the natural stream direction of the groundwater, might be considered.

In a P&T technology design, the first step includes the definition of the number and the location of pumping and/or recharge wells and the flow rate pumped and/or injected by each well. In the second step, the design consists in an appropriate "on site" treatment, i.e. an adsorption column specifically dimensioned for the whole amount of pumped water (U.S. EPA, 2008). Differently, the design of a PRB consists in the identification of the barrier location and orientation, in the definition of its dimensions (length, height, and thickness) and, consequently, in the determination of the amount of adsorbing material (Erto et al. 2011a). For both technologies, due to the high number of variables to be calculated, the design requires the use of an iterative procedure by the application of a *trial and error* approach, verifying that contaminant concentrations downstream the treatment achieve the water quality standards. In particular, for a PRB, a preliminary optimization process consists mostly in thickness minimization, once the other dimensions fixed; while for a P&T, it consists in the minimization of both the number of wells and the pumped rates. Of course, the overall objective is to minimise the total cost and the time required for an effective remediation of the site.

2.1 Modelling equations

Generally, in the saturated zone of an aquifer, the advection and dispersion phenomena determine the solute contaminant transport. In a two-dimensional system, for a porous media with a uniform porosity distribution, the mass transport equation can be written as in the following (Bear, 1979):

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(v_i C)+\sum_{k=1}^{N}R_k \tag{1}$$

where C is the concentration of pollutant (e.g. PCE) dissolved in groundwater, t is the time, x_i is the distance along the respective coordinate axis, D_{ij} is the hydrodynamic dispersion coefficient, v_j is the seepage or linear pore water velocity, while $\sum_{k=1}^{N}R_k$ is a chemical reaction rate.

The hydrodynamic dispersion coefficient, D_{ij}, is a second-rank tensor consisting in the sum of mechanical dispersion tensor and the molecular diffusion coefficient (a scalar).

The linear pore water velocity, v_j, can be calculated by the Darcy equation, which can be written as:

$$v_j = K_{ij}\cdot\frac{\partial h}{\partial x_j} \qquad i,j=1,2,3 \tag{2}$$

where K_{ij} is the hydraulic conductivity of the porous medium (a second-order tensor), and h is the hydraulic head, that can be calculated starting from Laplace equation (1).

In a PRB, where adsorption phenomena take place, the chemical reaction term of equation (1) is represented by adsorption and can be expressed as follows:

$$\sum_{k=1}^{N}R_k = \frac{\rho_b}{n_b}\frac{\partial\omega}{\partial t}=K_c a\left[C-C^*(\omega)\right] \tag{3}$$

where ω represents the pollutant concentration on solid, ρ_b the dry bulk density of the adsorbing material, n_b its porosity, $C^*=C^*(\omega)$ is the pollutant liquid concentration at thermodynamic equilibrium with adsorbing solid; C^* derives from the adsorption isotherm and defines the mass transfer driving force in the transport model equation, a is the specific surface area of the adsorbent, K_c is the global mass transfer coefficient.

Throughout the entire flow domain, the initial PCE concentration in the groundwater is known and it is assumed to be zero on the surrounding soil.

In a P&T technology, the adsorption in a fixed-bed column can be used as the remediation step of the global treatment. In this case, assuming one-dimensional flux, negligible axial variation of speed and diffusivity and negligible variation of concentration of PCE dissolved in groundwater, the equation (1) can be written as follows:

$$v_1 \frac{\partial C}{\partial x_1} = \frac{\rho_b}{n_b} \frac{\partial \omega}{\partial t} \tag{4}$$

Where v_1 is the relative velocity into the column along the x_1 direction. (v_1 ranges between 0.0005-0.01 m s^{-1} for adsorbing phenomena to take place). The right term of equation (4) describes the accumulation on the adsorbing solid, as stated by equation (3).

In this work, an implicit finite difference method was used to carry out the numerical integration of the modelling equations with their appropriate boundary conditions, by adopting a commercial 3D software for groundwater flow and pollution dynamics simulation, e.g. PMWIN (Chang and Kinzelbach, 1998). In particular, the Darcy equation (2) and the Laplace equation was solved by PMWIN-MODFLOW toolbox, while the mass transport equation (1) was solved by PMWIN-MT3D toolbox (Erto et al., 2011a). A second code called ADSORB-CODE was developed to describe the adsorption phenomena involving the pollutant both for PRB and P&T (Di Natale et al., 2009), in which the equations (3) and (4) were solved with the appropriate boundary conditions, after the choice of a specific absorbing material for PCE removal from polluted groundwater.

2.2 Absorbing material characterization

A granular activated carbon (GAC), commercially available, Aquacarb 207EA^{TM} (provided by Sutcliffe Carbon,) was chosen as adsorbing material. This GAC has the following characteristics (Erto et al., 2010): a BET surface area of 950 m^2 g^{-1}, an average pore diameter of 26 Å, a dry bulk density (ρ_b) of 500 kg m^{-1}, a porosity (n_b) of 0.4 and a hydraulic conductivity of about 0.001 m s^{-1}. The experimental characterization of the GAC for PCE adsorption was reported in previous papers (Erto et al., 2011b; Erto et al., 2012), and the Langmuir adsorption equation showed to be the more suitable isotherm model:

$$\omega = \frac{\omega_{max} K \cdot C^*(\omega)}{1 + K \cdot C^*(\omega)} \tag{5}$$

At a temperature of 10 °C, the following parameters were estimated for equation (5):
ω_{max} = 913.9 mg g^{-1} K = 19.830 l mol^{-1}.

3. Case study

A PCE-contaminated aquifer near a solid waste landfill in Giugliano in Campania, in the metropolitan area North of Naples (Italy), was examined as a case study. In this area (2.25 km^2), several solid landfills are located and an enormous amount of solid wastes was deposited in the last decades. A complete characterization of the groundwater was previously made (Di Nardo et al., 2010). The aquifer is located at a depth of about 35-40 m from the soil surface, it is confined by an impermeable layer (at about 50 m from soil surface) and it is contaminated by various types of pollutants, both inorganic and organic. The soil can be considered as made of a single mineral type (Neapolitan yellow tuff), with a hydraulic conductivity of $5*10^{-5}$ m s^{-1}. Throughout the entire flow domain, the pollutant concentration onto soil can be considered to be zero due to its very low adsorption capacity towards organic compounds (Erto et al., 2011a). In Figure 1, the map of the area is reported, with the PCE iso-concentrations and the piezometric lines of the groundwater, as in the present state. As shown in the figure, the flux lines are directed from East to West, with piezometric heights between 5 and 12.5 m a.s.l., under a piezometric gradient of 0.01 m m^1. The PCE concentrations are variable into the area and a maximum value of more than 20 times higher than the Italian regulatory limit for groundwater quality, established at 1.1 μg L^{-1}, can be individuated. Once the aquifer contaminated volume identified, it is possible to carry out both the remediation method designs.

4. Results

The best design for both remediation technologies was identified through various numerical simulations considering different working conditions.

For the PRB, the best results were obtained with the following dimensions: thickness equal to 3 m, length of 900 m and height of 12 m, and consequently a volume of adsorbing material equal to 27,000 m^3. To achieve the best capture efficiency of the contaminated plume, the wall is placed perpendicularly to the groundwater flow. In Figure 2, the numerical results of the remediation simulation by PRB are reported. As can be observed, during a working period of about 60 y the out-flowing PCE concentration is always lower than the Italian regulatory limit, also taking into account the possible occurrence of desorbing phenomena from GAC to groundwater.

For P&T, the best results were obtained with a configuration of 27 pumping wells and 12 recharge wells (Figure 3). As shown, after a run period of about 35 y, the PCE concentration is everywhere lower than the Italian regulatory limit so that the whole groundwater volume results to be decontaminated. In the adopted well configuration, when the PCE concentration reaches a value lower than the regulatory limit, a progressive turning off of pumping wells can be adopted in the pertinent zone. Similarly, when the increment of water level is no longer necessary for the remediation process, some recharge wells can be turned off too. For the P&T working time considered, the total amount of pumped water resulted about 1,500,000 m^3. Two adsorption columns were chosen by CFD simulations to treat this water volume, each with a height of 2.5 m, diameter of about 0.2 m, and a working time of 15 days (after which the absorbing material into the column is regenerated/substituted).

In addition, a preliminary cost analysis for the PRB and the P&T systems dimensioned, was carried out. The costs of the main variables considered for both PRB and P&T, and the corresponding amounts, are reported in Table 1 and Table 2, respectively. According to this cost analysis, it is not possible to establish clearly which is the most cost-effective remediation method for the case study presented. This is mainly due to the wide margin of uncertainty in the unit cost of the main variables examined; consequently a more accurate site-specific cost analysis is required. In any case for the PRB the cost of adsorbing material exceed the 70% of the total cost, therefore the use of low cost adsorbing material should make this technique cheaper than the P&T.

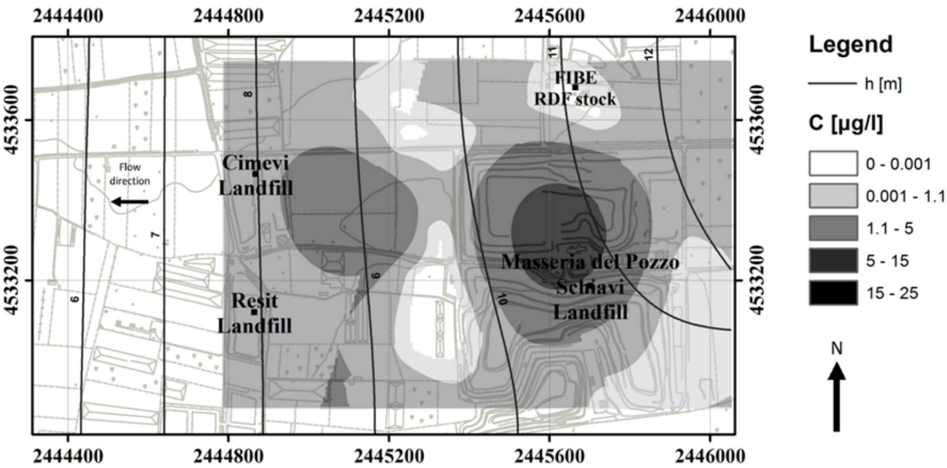

Figure 1: PCE iso-concentration and iso-piezometric contours at the initial condition

Table 1: Preliminary cost analysis for PRB (service life about 60 years)

Cost variables	**Unit cost**	**Amount**	**Cost [€]**
Construction	50-100 [€/m$^3_{soil}$]	27,000 [m$^3_{soil}$]	1,350,000-2,700,000
Adsorbing material	100-500 [€/m$^3_{GAC}$]	27,000 [m$^3_{GAC}$]	2,700,000-13,500,000
Monitoring	-	-	100,000-250,000
		Total:	4,150,000-16,450,000

Table 2: Preliminary cost analysis for P&T (service life about 35 years)

Cost variables	**Unit cost**	**Amount**	**Cost [€]**
Construction	0.2-0.4 [€/m$^3_{flow}$]	1,500,000 [m$^3_{flow}$]	300,000-600,000
Energy	0.1-0.2 [€/kWh]	280,000 [kWh]	28,000-56,000
Workers	20,000-30,000 [€/y]	6	4,200,000-6,300,000
Treatment	1-5 [€/m$^3_{flow}$]	1,500,000 [m$^3_{flow}$]	1,500,000-7,500,000
Monitoring	-	-	100,000-250,000
		Total:	6,128,000-14,706,000

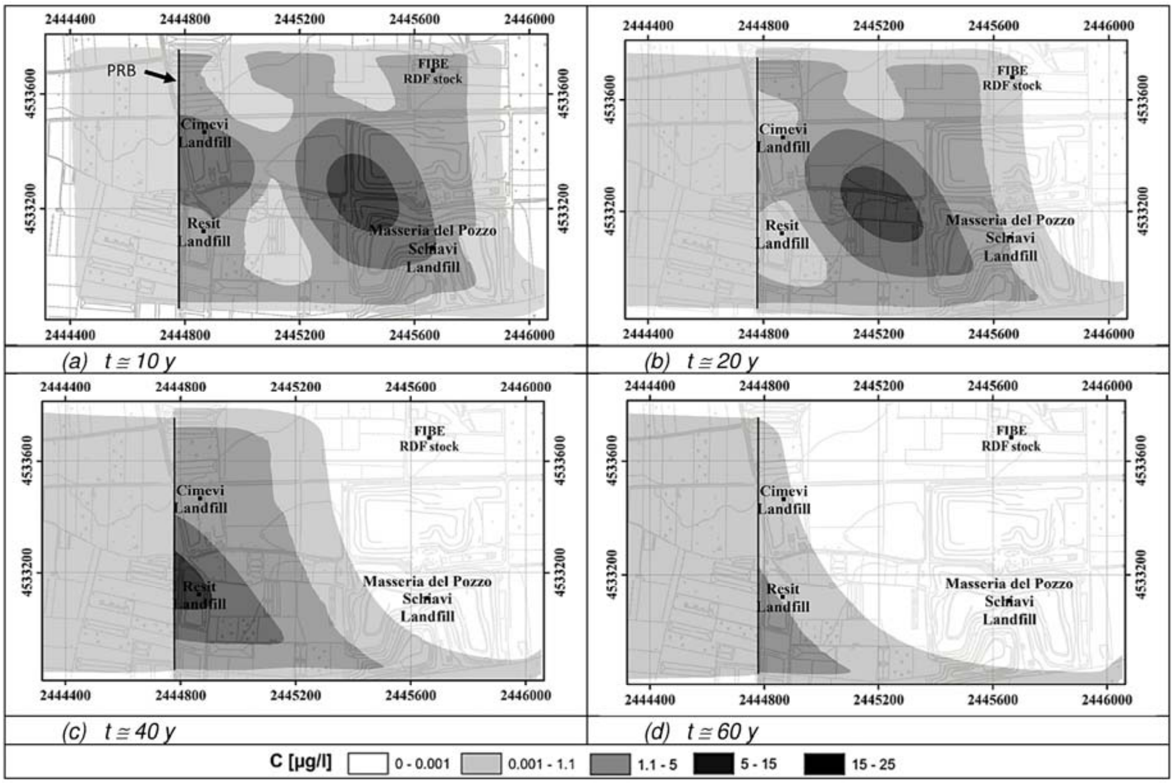

Figure 2: PCE isoconcentrations with PRB installation up to a run period of about 60 years

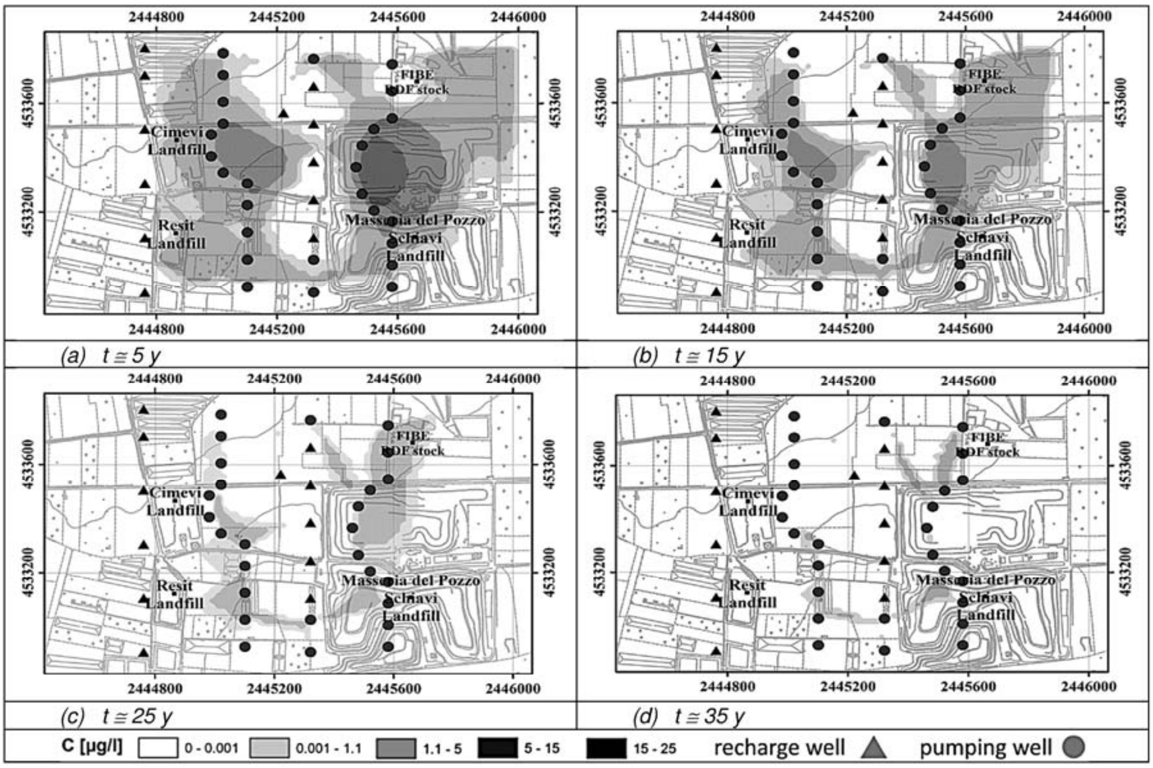

Figure 3: PCE isoconcentrations with P&T installation up to a simulation time of about 35 years

5. Conclusion

In this work, a comparison between Pump & Treat technique and Permeable Reactive Barriers for the remediation of a PCE-contaminated aquifer was carried out, and a preliminary cost analysis is been reported. Both decontamination technologies were applied to a polluted site in the metropolitan area North of Naples (Italy) and adsorption was chosen as remediation technology. The design was carried out using Computational Fluid Dynamics (CFD) by adopting specific software for groundwater flux simulation and adsorption phenomena on activated carbon. Numerical results showed that both PRB and P&T can be suitable to remediate the groundwater, reducing PCE concentration under the regulatory limit, and therefore respecting water quality standards. However, the preliminary cost analysis performed is not sufficient to establish which remediation methods is the most cost-effective, and a more accurate analysis site-specific is required.

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