



Application of a discontinuous permeable adsorptive barrier for aquifer remediation. A comparison with a continuous adsorptive barrier

G.F. Santonastaso^a, I. Bortone^{a,b}, S. Chianese^{a,*}, A. Erto^c, A. Di Nardo^a, M. Di Natale^a, D. Musmarra^a

^aDipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Via Roma 29, 81031 Aversa (CE), Italy, Tel. +39 081 5010387; Fax: +39 081 5037370; email: simeone.chianese@unina2.it (S. Chianese)

^bThe School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, UK

^cDipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

Received 23 May 2015; Accepted 3 December 2015

ABSTRACT

This work presents an innovative configuration of a permeable adsorptive barrier (PAB) for the *in situ* remediation of benzene-contaminated groundwater in the area of Naples (Italy). A PAB is a type of permeable reactive barrier (PRB) made with adsorbing materials (e.g. activated carbon). This particular PAB is a discontinuous permeable adsorptive barrier (PAB-D), consisting in an array of deep passive adsorptive wells whose hydraulic conductivity is higher than the surrounding soil. The design was based on COMSOL Multiphysics[®] simulations, which allow for the description of pollutant transport in groundwater and adsorption onto the barrier by means of a 2D model solved using a finite element approach. Based on a hydrological and geotechnical characterization of the entire polluted aquifer, the design and optimization of PAB-D parameters (location, orientation, number of wells and dimensions) were defined. The influence of hydraulic conductivity and dispersivity on the total number of wells for a complete aquifer remediation was investigated. Finally, a comparison with a continuous barrier (PAB-C), i.e. a wall of adsorptive material, in terms of total adsorbing material needed, is presented.

Keywords: Permeable adsorptive barriers (PAB); Passive wells; Adsorption; Groundwater remediation

1. Introduction

The contamination of groundwater in areas occupied by urban waste landfills is a very common problem. In these cases, many dangerous compounds can

be found in groundwater, both organic and inorganic, such as chlorinated (trichloroethylene, tetrachloroethylene, trichloromethane, etc.), aromatics (benzene, toluene, xylene, etc.), and metals (arsenic, thallium, lead, etc.), representing a serious risk for both human health and environment [1].

*Corresponding author.

Presented at EuroMed 2015: Desalination for Clean Water and Energy Palermo, Italy, 10–14 May 2015. Organized by the European Desalination Society.

The most traditional groundwater remediation technique is Pump and Treat, which consists in pumping the contaminated water out of the aquifer, then performing an *ex situ* treatment and finally reinjecting the treated water downstream into the aquifer [2]. This technology is listed among the most effective groundwater treatments as it can be successfully used for many different pollutants [3], even if it is also very expensive for the large consumption of energy in the pumping step [4]. More recently, some *in situ* technologies based on Permeable Reactive Barriers (PRB) [5,6] have been developed and efficiently proposed as a versatile technology for the removal of both heavy metals [7–10] and organic compounds [11–13].

These technologies consist in the insertion of a vertical permeable trench built with a material that is more permeable than the surrounding groundwater medium. In this way, the polluted water flows through the barrier under the natural groundwater gradient, so as to achieve a passive and cost-effective restoration of the aquifer. The barrier filling material must have specific physical and chemical properties. In particular, the design of PRBs relies on three main technical aspects: (a) the reactive media has to be matched to the target pollutant, (b) the PRB must be wide enough to ensure a sufficient residence time of the pollutant plume [14,15], and (c) the barrier must be large and deep enough and the reactive material must have a sufficient hydraulic conductivity so as to allow for the interception of the whole plume [6,16]. Moreover, clogging phenomena due to mineral precipitates in the barrier, if zero-valent iron is used as reactive media, have to be avoided [17].

In the last few years, different kinds of PRB configurations have been proposed [18]. For its simple conception, the continuous PRB is the most frequently used [19]. The Funnel-and-Gate (F&G) configuration has been used as an alternative when the geological aquifer properties are not homogeneous. It consists of two lateral impermeable walls embedded in the impermeable subsoil, directing the contaminant plume to a central permeable gate, where the reactive material is placed and where the groundwater treatment occurs [20].

Even if PRBs and F&Gs easily intercept the polluted water, they have two crucial disadvantages: (1) they are very expensive in case of wide and long barriers and (2) they are very difficult to build in deep aquifers [19]. For these reasons, more recently, some studies have put forward a discontinuous PRB composed of a certain number of passive wells arranged in one or several lines at a certain distance from one another [6,21]. Like in the continuous trench, the wells are more permeable than the surrounding soil, which

determines a natural deviation of the contaminated water flow toward the wells themselves, thus allowing for a thorough treatment. The main advantage of such a configuration is the reduced amount of the reactive material used to build the barrier itself, which also determines lower costs and simpler construction [21].

Whatever be the configuration used, adsorbing materials, like activated carbon, have gained growing interest because they can be effective for many different pollutants, such as chlorinated organic compounds, aromatic compounds, and metal ions, and they have a wide spectrum of applicability in terms of operational parameters and water properties [22–26]. The PRBs based on adsorption are commonly referred to as Permeable Adsorptive Barriers (PABs). When adsorption occurs, the pollutant is immobilized into the barrier; if the pollutant concentration entering the barrier varies in time during the whole barrier working period, the occurrence of desorption phenomena are also accounted for. Hence, a PAB assures both the immediate aquifer restoration and an effective long-term protection.

This study examines a real contaminated aquifer in the area of Naples (Italy), already investigated by the authors in previous papers [21,27–29], where the presence of several contaminants, both inorganic (e.g. Mg, Fe, Pb, Cr, etc.) and organic (e.g. benzene, toluene, dichloroethylene, tetrachloroethylene, etc.) was detected.

Groundwater pollution by aromatic compounds is a global environmental problem, typically caused by accidental releases from pipelines and storage tanks of petroleum products. Benzene is a major threat for water resources and is included in the EPA National Priorities List (NPL) [30,31] since it is carcinogenic [32]. The effectiveness of aromatic compound removal by adsorption is reported in several studies [22,33–37]. For instance, Lillo-Ródenas and coworkers [38] studied the influence of pore size distribution and surface oxygen groups of activated carbons on benzene removal. Liang and Chen [39] investigated the efficiency of activated carbon as a reactive medium in a permeable barrier for the removal of benzene-contaminated groundwater. Finally, experimental investigations in a fixed-bed column filled with granular activated carbon were performed by Plagentz and coworkers [40], aiming at the remediation of a contaminated groundwater. Although the effectiveness of activated carbon for benzene removal has been adequately addressed, its application as reactive media of PRBs needs to be tested further.

In this study, a discontinuous PAB (PAB-D) for the remediation of an aquifer contaminated by benzene is

presented. Moreover, a comparison between a continuous (PAB-C) [27] and a discontinuous (PAB-D) barrier applied to the same aquifer was also carried out to determine the type and amount of the building material, and the extent of the intervention needed in both cases.

The barrier was designed via iterative simulations made with COMSOL Multi-physics® [18,27], which allowed to simultaneously model the advection–dispersion processes into the aquifer and the adsorption occurring within the barrier.

2. PRB modeling equation

As reported in our previous works [21,28,29], the contaminant transport through a PAB in a 2D system (assuming constant pollutant concentration profiles throughout the height of aquifer) can be described via the advection–dispersion (AD) processes coupled with the adsorption phenomena (R) taking place into the barrier [41], written as follows:

$$\frac{\partial C}{\partial t} = AD + R \quad (1)$$

where the advection–dispersion mechanisms (AD) are modeled as proposed by Bear [41], via the following equation:

$$AD = \nabla(D_h \nabla C) - \frac{\vec{u} \nabla C}{n_s} \quad (2)$$

In Eq. (2), C is the dissolved concentration of pollutant in the groundwater; t is the time, D_h is the hydrodynamic dispersion tensor, \vec{u} is the unit flux, and n_s is the porosity of the site. The hydrodynamic dispersion tensor, D_h , is expressed as the sum of the tensor of mechanical dispersion, D , and the coefficient of molecular diffusion, D_{diff} , (a scalar), as better described by Konikow and Grove [42].

The unit flux vector \vec{u} can be determined by applying the Darcy equation, written as follows:

$$\vec{u} = K_s \cdot \nabla h \quad (3)$$

where K_s is the hydraulic conductivity and h is the hydraulic head.

The adsorption processes occurring in a PAB are usually described via the chemical reaction term (R) of Eq. (1), equal to:

$$R = -\frac{\rho_b}{n_b} \frac{\partial \omega}{\partial t} = k_c a [C - C^*(\omega)] \quad (4)$$

In Eq. (4), ρ_b is the adsorbing material bulk density, n_b is the barrier porosity, k_c is the mass transfer coefficient for adsorption reaction, a is the external specific surface area of adsorbent particles, and $C^*(\omega)$ is the pollutant concentration in the liquid phase at thermodynamic equilibrium with the concentration on the adsorbent solid. This is generally described via adsorption isotherms, e.g. expressed by a Langmuir model as follows:

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

where ω_{\max} and K are the Langmuir parameters, obtained experimentally.

3. PRB technology description

The design of both PAB-C and PAB-D is based on a preliminary characterization of the contaminated site aimed at identifying its hydraulic and geotechnical properties, and the type and extent of the contaminant plume. This preliminary phase is mandatory in order to determine the geometric dimensions of the barrier, allowing to capture the contaminant plume, and the most appropriate reactive barrier media. In Fig. 1, the main characteristics of both PAB-C (Fig. 1(a)) and PAB-D (Fig. 1(b)) are represented.

In order to correctly design a PAB-C (Fig. 1(a)), it is necessary to properly determine the position, the orientation (ε), the length (L), the height (H), the width (W), and the characteristics of the reactive material [13]. For a PAB-D (Fig. 1(b)) other variables must be considered, i.e. the well diameter (D_w), the well-to-well distance (I), the number of well lines in the grid (n_w) and the line-to-line distance (d_c) [21]. In order to find the optimal layout for both configurations, a heuristic procedure can be followed, as described by Di Nardo et al. [43]. A set of parameters (shape and features of the continuous wall or the wells grid) are tested so as to choose the layout and size that can assure a thorough pollutant capture during the whole PAB working time. For a PAB-D, the design procedure should account for its different spatial configuration (Fig. 1(b)) and for some other criteria aimed at its optimization. In particular: (i) the well barrier must be as close as possible to the pollutant plume for an immediate aquifer decontamination; (ii) each well line has to be orthogonal to the groundwater flow direction and the total dimensions (i.e. length, depth, and width) should allow for the capture of the whole contaminant plume; (iii) the number of lines has to be chosen by considering that the residence time of the

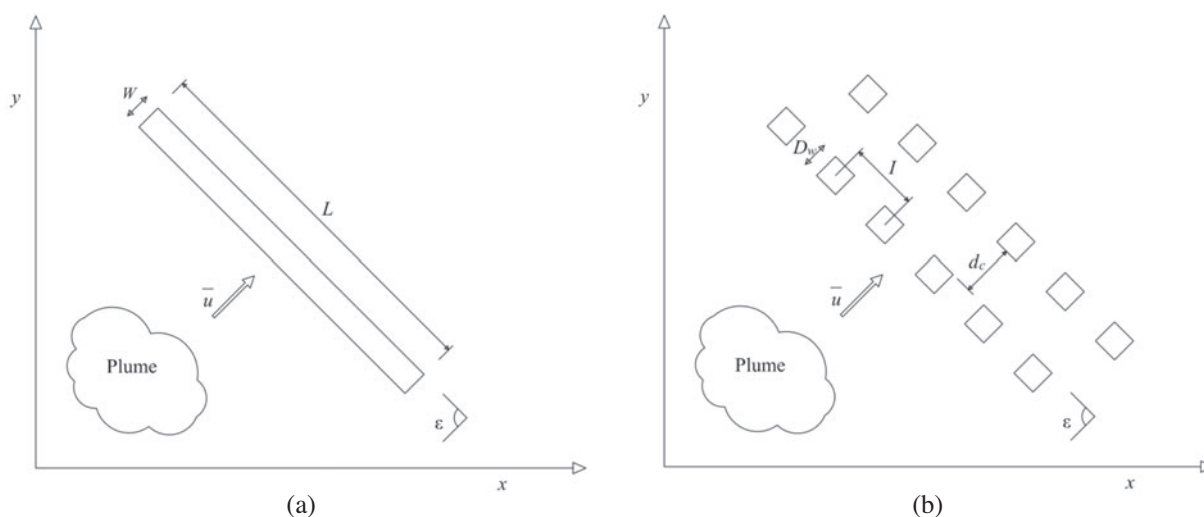


Fig. 1. (a) PAB-C and (b) PAB-D design conceptual model.

contaminated flow through the barrier needs to be long enough for adsorption processes to take place.

In this study, the design of the PAB-D was performed via COMSOL Multi-physics simulations and an optimization procedure was adopted [42]. This procedure aims at identifying the minimum number of well lines, n_c , and the minimum length of each well line (i.e. corresponding to the minimum number of wells per line) to reduce the adsorbent material required and the overall intervention size. The final target of the procedure was to assure that the benzene concentrations were lower than the regulatory limit, throughout the whole domain downstream the barrier.

4. Case study

The case study deals with an area of 2.25 km² in Giugliano in Campania, in the metropolitan area north of Naples (Italy), where many solid waste landfills are located. The groundwater aquifer, located at a depth of 35–40 m from the land surface and confined by an aquitard (50 m), is contaminated by a large number of pollutants, both inorganic and organic [27]. In particular, benzene was detected at concentrations significantly higher than the corresponding Italian regulatory limit for groundwater quality (C_{lim}), set at 1 $\mu\text{g L}^{-1}$, with a peak value close to 8 $\mu\text{g L}^{-1}$. The main characteristics of the aquifer are presented in Table 1. A single layer consisting in Neapolitan yellow tuff was assumed to be representative of the groundwater soil composition, whose hydraulic conductivity (K_s) and longitudinal dispersivity (α_x) ranged between

2×10^{-5} – $1 \times 10^{-4} \text{ m s}^{-1}$ and 0.5–4 m, respectively. The transverse dispersivity (α_y) was estimated using equation as follows [44]:

$$\alpha_y = \alpha_x/10 \quad (6)$$

An activated carbon (AC) obtained from the stems of *Arundo Donax* by H_3PO_4 acid activation was chosen as adsorbent material. Its benzene adsorption capacity was studied by Basso and Cukierman [37]; in particular, the adsorption isotherm is described by the Langmuir model, expressed by Eq. (5), and the Langmuir parameters are $\omega_{max} = 35.1 \text{ mg g}^{-1}$ and $K = 0.0577 \text{ L mg}^{-1}$ [37].

The transport equations, Eqs. (1)–(5), assumed to design both PABs, were solved via a finite element software (COMSOL Multi-physics[®]), using the following initial and boundary conditions:

$$C = 0 \quad \begin{cases} x = 0 & \forall y \forall t \\ y = 0 & \forall x \forall t \\ y = Y & \forall x \forall t \end{cases} \quad (7)$$

$$\frac{\partial C}{\partial t} + \frac{\vec{u} \cdot \nabla C}{n_s} - \nabla \cdot (D_h \nabla C) = 0 \quad x = X \quad \forall y \forall t$$

In particular, a reference frame coinciding with the boundary of the domain—where $X = 1,100 \text{ m}$ and $Y = 990 \text{ m}$ are the size of the domain in the x - and y -directions, respectively—and a constant porosity in all the domain was assumed.

The initial concentration of the contaminant in the liquid phase is reported in Fig. 2, assuming that

Table 1

Case study: aquifer characteristic

Aquifer characteristic	
Polluted area total extent, A	0.225 km ²
Aquifer average piezometric level, H_w	8 m
Piezometric gradient, J	0.01 m m ⁻¹
Porosity, n_s	0.25
Dry soil bulk density, ρ_s	1,400 kg m ⁻³
Hydraulic conductivity, K_s	2×10^{-5} , 5×10^{-5} , 1×10^{-4} m s ⁻¹
Longitudinal dispersivity, α_x	0.5, 1, 4 m
Transverse dispersivity, α_y	0.05, 0.1, 0.4 m
Molecular diffusion coefficient, D_{diff}	10^{-8} m ² s ⁻¹

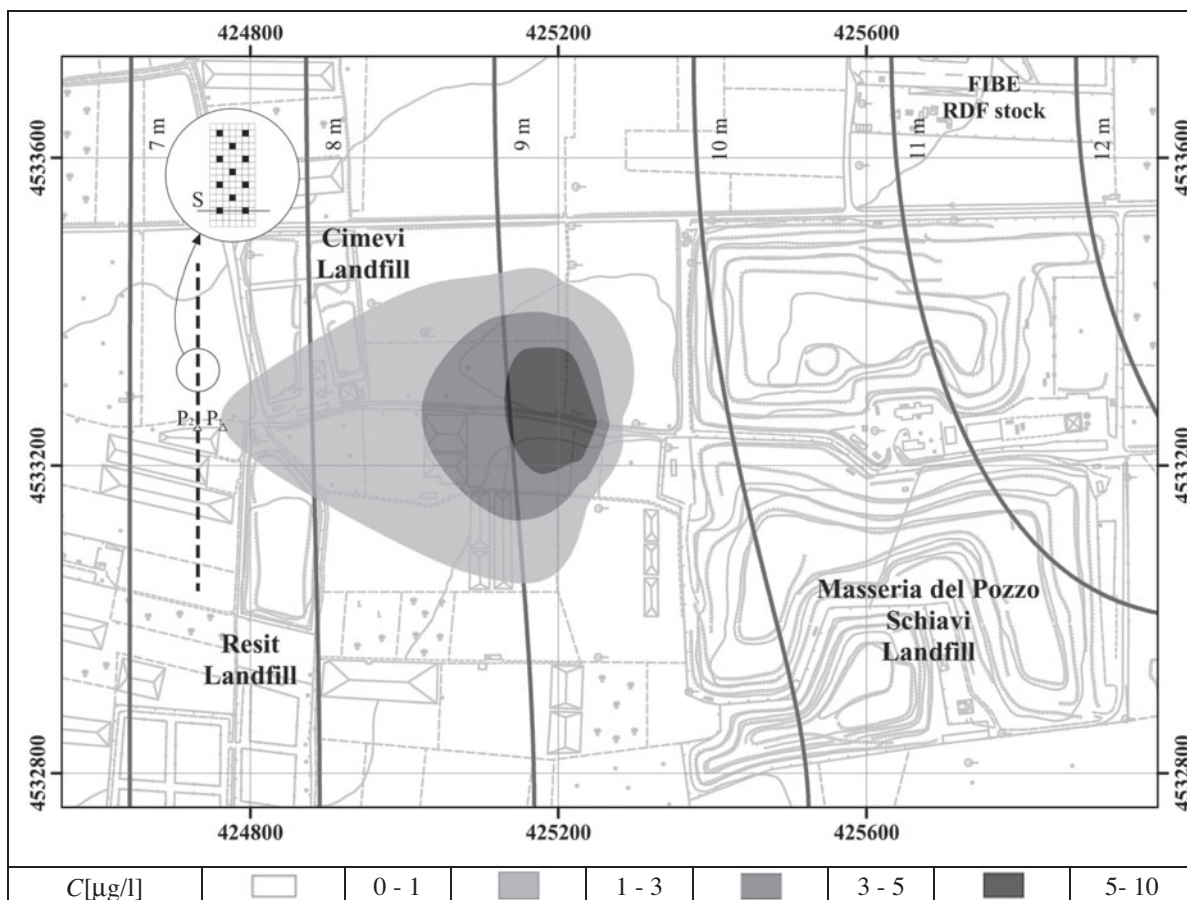


Fig. 2. Benzene iso-concentration contours at initial condition, piezometric levels and PAB-D configuration with the focus zone.

the initial pollutant concentration on the adsorbing material of the PAB is equal to zero.

The main hydraulic and material parameters used for the PAB design are reported in Table 2.

A preliminary evaluation of the groundwater average velocity was made by comparing the time profiles of the benzene concentration, calculated assuming $K_s = 5 \times 10^{-4}$, $\alpha_x = 1$ and $\alpha_y = 0.1$, in two different

points of the domain. The first point (P_1) is on the boundary of the pollutant plume and the second (P_2) is on the upstream of the PAB-D; the distance between these two points, $\overline{P_1P_2}$, is 10 m. As it is possible to observe in Fig. 3, these profiles are quite similar but the peaks are time-shifted by approximately 120 d. A groundwater average velocity of about 30 m/year can be estimated as the ratio between the distance

Table 2
PAB parameters

PAB characteristics	
Porosity, n_b	0.45
ACs bulk density, ρ_b	520 kg m^{-3}
Hydraulic conductivity, K_{PAB}	10^{-3} m s^{-1}
Longitudinal dispersivity, $\alpha_{x\text{PAB}}$	0.05 m
Transverse dispersivity, $\alpha_{y\text{PAB}}$	0.005 m
Molecular diffusion coefficient, D_{diff}	$10^{-8} \text{ m}^2 \text{ s}^{-1}$
AC BET surface area, S_{bet}	$1.116 \text{ m}^2 \text{ g}^{-1}$
AC average pore diameter, d_{pore}	233.5 nm

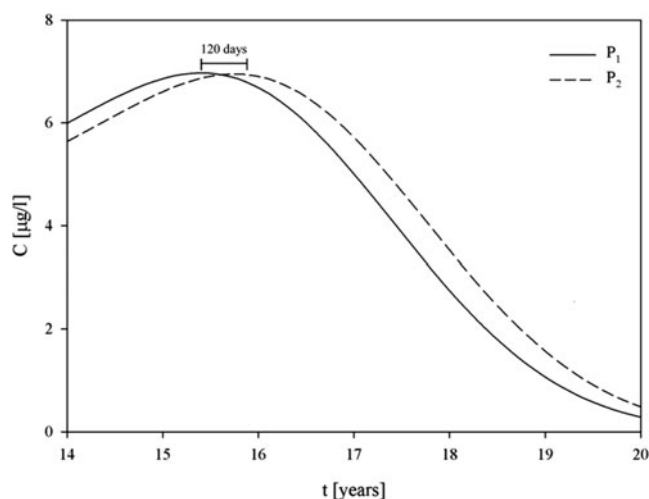


Fig. 3. Breakthrough curves for benzene concentration in correspondence of the probe points P_1 and P_2 .

between the two points, $\overline{P_1P_2} = 10 \text{ m}$, and the time shift of the two concentration profile peaks, which is equal to 120 d.

5. Simulation results

The simulation results led to a PAB-D located at a distance equal to 10 m from the pollutant plume, with a north direction orientation (ε), indicated in Fig. 2 as a dotted line. The well configuration is qualitatively reported in the zoomed zone of Fig. 2. A constant well diameter, D_w , equal to 0.5 m, and a constant line-to-line distance, d_c , equal to 0.5 m, were determined as appropriate for the case study. The well-to-well distance, I , was set equal to four times the well diameter ($I = 4D_w$).

5.1. Sensitive analysis

A sensitivity analysis was performed to ascertain the effect on PAB-D design parameters of some

aquifer characteristics, whose values are not well established and consequently uncertainty still exists. For this aim, the PAB-D design procedure was repeated by changing hydraulic conductivity (K_s) and the longitudinal and transversal dispersivities (α_x , α_y). Following an approach adopted in previous works [26], nine different cases were considered, corresponding to the combination of several investigated parameter values, as indicated in Table 3.

For all the nine cases reported in Table 3, the same number of well lines (i.e. $n_c = 3$) but a slightly different number of wells per line was determined, confirming the role of the parameters investigated, as expected. In Table 4, the geometrical characteristics of the PAB-D, the total number of wells, n_w , and the contribution of each well line are reported for all the nine cases of the sensitive analysis.

Starting from the well diameter and the total number of wells, the length of the PAB-D (not including the well-to-well distance, I) and the PAB-D volume (V_{ad}) were determined. The sensitivity analysis shows that the number of wells is nonmonotonically influenced by the hydraulic conductivity, while a reduction of this was observed by increasing the dispersivity components. By varying the hydraulic conductivity and dispersivity components by one order of magnitude, the maximum variation observed was of about 10% from 464 wells (case 7) to 418 wells (case 3). Therefore, also the PAB-D volume V_{ad} , varied only between 928 m^3 (case 7) and 836 m^3 (case 3). Such a small variation does not justify any further effort to accurately evaluate these parameters through expensive and time-consuming on-site tests. However, it is worth observing that K_s , α_x and α_y have a significant influence on both the dynamics of the aquifer and the performances of the PAB-D, through the modification of the motion field. Indeed, the adsorption kinetics is strictly dependent on the groundwater flow rate and pollutant residence time

Table 3
Run plan of the sensitivity analysis [26]

	$K_S \text{ (m s}^{-1}\text{)}$	$\alpha_x \text{ (m)}$	$\alpha_y \text{ (m)}$
Case 1	2×10^{-5}	0.5	0.05
Case 2	2×10^{-5}	1	0.1
Case 3	2×10^{-5}	4	0.4
Case 4	5×10^{-5}	0.5	0.05
Case 5	5×10^{-5}	1	0.1
Case 6	5×10^{-5}	4	0.4
Case 7	1×10^{-4}	0.5	0.05
Case 8	1×10^{-4}	1	0.1
Case 9	1×10^{-4}	4	0.4

Table 4
PAB-C [26] and PAB-D [this study] dimensions and absorbent material amount

	PAB	n_c			n_w	H (m)	W (m)	L (m)	V_{ad} (m ³)	ΔV (%)
		Line 1	Line 2	Line 3						
Case 1	PAB-C					8	0.567	400	1,814.40	
	PAB-D	206	149	99	454	8	0.5	454 × 0.5	908	50
Case 2	PAB-C					8	0.564	400	1,804.80	
	PAB-D	206	134	95	435	8	0.5	435 × 0.5	870	52
Case 3	PAB-C					8	0.554	390	1,728.48	
	PAB-D	206	132	80	418	8	0.5	418 × 0.5	836	52
Case 4	PAB-C					8	0.568	400	1,817.60	
	PAB-D	206	135	91	432	8	0.5	432 × 0.5	864	52
Case 5	PAB-C					8	0.570	400	1,824.00	
	PAB-D	206	133	86	425	8	0.5	425 × 0.5	850	53
Case 6	PAB-C					8	0.556	390	1,734.72	
	PAB-D	206	146	81	433	8	0.5	433 × 0.5	866	50
Case 7	PAB-C					8	0.604	400	1,932.80	
	PAB-D	206	167	91	464	8	0.5	464 × 0.5	928	52
Case 8	PAB-C					8	0.6043	400	1,933.76	
	PAB-D	206	148	81	435	8	0.5	435 × 0.5	870	55
Case 9	PAB-C					8	0.595	390	1,856.40	
	PAB-D	206	134	81	421	8	0.5	421 × 0.5	842	55

inside the barrier, which can modify the mass transfer coefficient (see Eq. (4)). In order to investigate this point in detail, the inlet and outlet PAB-D benzene concentrations were determined in correspondence of the most critical PAB-D section, S , as a function of the simulation time. The most critical section was identified in every case as the one in which the highest benzene inlet concentration was expected. The results in terms of inlet and outlet benzene concentrations are reported in Figs. 4 and 5, respectively.

From Figs. 4 and 5, the effect of K_s , α_x and α_y on the patterns of inlet and outlet benzene concentrations is clearly visible. Low values of α_x and α_y resulted in a higher benzene inlet concentration, while K_s seems to exert a high effect on the time at which the concentration peak is verified. In fact, the lower the hydraulic conductivity, the higher the time required for the benzene concentration peak to reach the barrier, while the higher the dispersivity, the lower the concentration peak, keeping K_s constant. It can be observed that a higher hydraulic conductivity allowed for a shorter remediation time as the pollutant moves more rapidly to the barrier to be captured. In particular, when $K_s = 1 \times 10^{-4}$ a remediation time of about 10 years was required, while with $K_s = 2 \times 10^{-5}$ the value arises to about 50 years (Fig. 4). These results are in agreement with the findings reported in our previous study in which a Continuous PAB (PAB-C) was studied [26].

Similar considerations can be made for the benzene outlet concentrations, for which the highest benzene

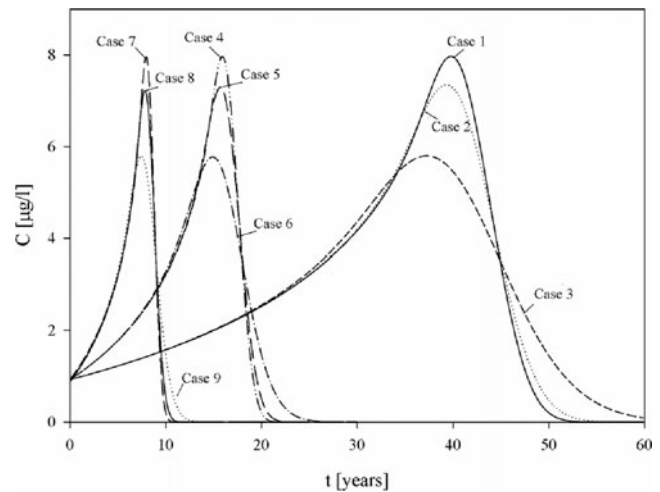


Fig. 4. Inlet concentration of benzene in the PAB-D across section S .

concentration peak is shifted in time by reducing the hydraulic conductivity. An increase in the dispersivity determines a light shift of the highest peak and a simultaneous decrease in its magnitude. However, for all the investigated scenarios, the outlet concentrations of benzene are lower than the regulatory limit (set at $1 \mu\text{g L}^{-1}$), also accounting for the possible occurrence of desorption phenomena, thus confirming the effectiveness of the PAB-D for the remediation of the aquifer.

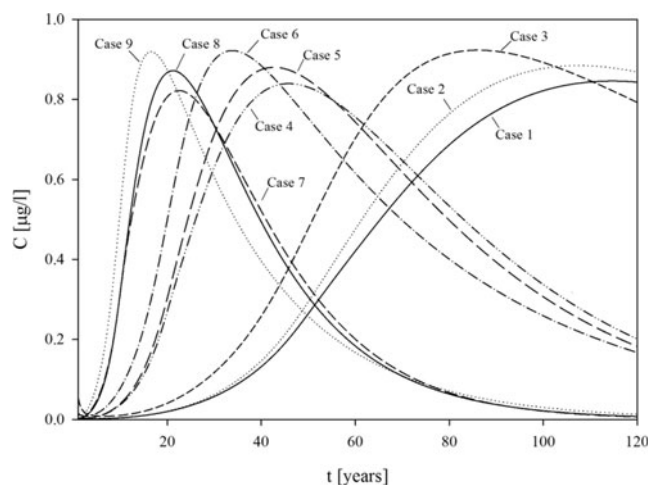


Fig. 5. Outlet concentration of benzene from the PAB-D across section S.

5.2. PAB-D and PAB-C comparison

Once the performances of the PAB-D were assessed, a comparison between PAB-D (this study) and PAB-C ([26]) for the remediation of the same case study and via considering the same hypotheses was completed. In Table 4, the design values for the PAB-C for all the nine scenarios considered are reported, together with the corresponding values of the PAB-D, for an equal comparison. In particular, the comparison was made in terms of both the volume of adsorbent material (V_{ad}) needed for the site remediation and ΔV , i.e. the % reduction of adsorbent material needed to build the PAB-D respect to the PAB-C.

It can be observed that, whatever is the scenario considered, a ΔV ranging between 50 and 55% was determined, hence showing a significant saving of building material and, consequently, a reduction of economic resources in the case of PAB-D application.

6. Conclusions

In this study, a discontinuous permeable adsorptive barrier (PAB-D) was designed for the remediation of a benzene-contaminated site in the area north of Naples (Italy), where several solid waste landfills exist. The pollutant transport in the aquifer and the adsorption on the PAB were described via a 2D numerical model, implemented in COMSOL Multiphysics and using a finite-element model.

The simulation results showed that for each investigated scenario the PAB-D can be efficiently used for the remediation of the aquifer, as the outlet benzene concentrations are lower than the corresponding regulatory limit throughout the whole domain.

A sensitivity analysis was performed also to evaluate the effects that uncertainties in the values chosen for hydraulic conductivity (K_s) and longitudinal and transversal dispersivities (α_x , α_y) have on the PAB-D design. The analysis confirmed that the hydraulic conductivity plays a major role in determining the time at which the highest benzene concentration reaches the barrier and the time at which it flows out. Consequently, it was observed that a higher hydraulic conductivity significantly enhances the process, reducing the total remediation time. In addition, the dispersivity influences the magnitude of the highest concentration peak, and in particular the higher the dispersivity, the lower are the concentration peaks, keeping K_s constant. At the same time, the sensitivity analysis showed that a simultaneous change in these parameters of an order of magnitude affects the barrier dimension only of 10%. This result suggests that any expensive and uncertain on-site measurement of these parameters is not worth performing.

A comparison was also made between a PAB-D and a continuous barrier (PAB-C) applied to the same aquifer, based on the results reported in our previous studies. To this aim, the adsorbent material volume (V_{ad}) needed for the remediation of the site and the ΔV , i.e. the % reduction of adsorbent material needed to build the PAB-D compared to the PAB-C were determined. The results showed that the PAB-D can dramatically reduce the total volume of building material up to 55%, with an expected significant saving of economic resources. The use of a PAB-D for the remediation of the aquifer studied is preferable due to a lower amount of building material needed, which also determines a lower extent of the intervention on the site. Moreover, it is interesting observing that a constant value of the well diameter (i.e. $D_w = 0.5$ m) allows a significant simplification of the realization of the barrier, in comparison to the PAB-C and hypothesizing to adopt the traditional excavation techniques, in particular for groundwater flowing at great depth like in the case analyzed.

List of symbols

a	— external specific surface area of adsorbing material ($\text{m}^2 \text{m}^{-3}$)
C	— liquid concentration of the pollutant ($\mu\text{g L}^{-1}$)
C^*	— equilibrium liquid concentration ($\mu\text{g L}^{-1}$)
C_{lim}	— pollutant regulatory limit value ($\mu\text{g L}^{-1}$)
d_c	— column-to-column distance
D	— tensor of mechanical dispersion
D_{diff}	— molecular diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_h	— tensor of hydrodynamic dispersion
X	— distance between barrier and western boundary of the domain (m)
D_w	— well diameter (m)

Y	— extension domain in y direction
H	— barrier height (m)
h	— hydraulic head (m)
I	— well-to-well distance (m)
K	— Langmuir constant ($l \text{ mol}^{-1}$)
k_s	— hydraulic conductivity (m s^{-1})
K_s	— barrier hydraulic conductivity (m s^{-1})
k_c	— overall mass transfer coefficient for adsorption reaction (m s^{-1})
L	— barrier length (m)
n_b	— barrier porosity
n_s	— soil porosity
n_c	— number of wells per line
n_w	— number of well lines
t	— time
u, v	— groundwater flow velocity along (x and y) (m s^{-1})
W	— barrier width (m)
V_{ad}	— barrier adsorbing volume (m^3)
ε	— barrier orientation ($^\circ$)
α_x	— longitudinal dispersivity (m)
α_y	— transversal dispersivity (m)
$\alpha_{x\text{PAB}}$	— barrier longitudinal dispersivity (m)
$\alpha_{y\text{PAB}}$	— barrier transversal dispersivity (m)
ρ_b	— adsorbing material bulk density (kg m^{-3})
ρ_s	— dry soil bulk density (kg m^{-3})
ω	— activated carbon adsorption capacity (mg g^{-1})
ω_{max}	— maximum carbon adsorption capacity (mg g^{-1})
d_{pore}	— activated carbon average pore diameter (nm)
S_{bet}	— activated carbon BET surface area ($\text{m}^2 \text{g}^{-1}$)

References

- [1] M. Rizzo, G.K. Druschel, S.E. Morales, N. Hayden, P. O'Grady, L. Stevens, Enhanced detection of groundwater contamination from a leaking waste disposal site by microbial community profiles, *Wat. Resour. Res.* 46 (2010) 1–12.
- [2] R.M. Cohen, J.W. Mercer, R.M. Greenwald, EPA Groundwater Issue, Design Guidelines for Conventional Pump-and-Treat Systems, EPA, 1998, 540/S-97/504. Available from: <<http://www.epa.gov/ada/is sue.html>>.
- [3] US EPA, Pump-and-Treat ground-Water Remediation, US Environmental Protection Agency, EPA/625/R-95/005, United States of America, Washington, DC, 1996.
- [4] I. Bortone, S. Chianese, A. Di Nardo, M. Di Natale, A. Erto, D. Musmarra, G.F. Santonastaso, A Comparison between pump & treat technique and permeable reactive barriers for the remediation of groundwater contaminated by chlorinated organic compounds, *Chem. Eng. Trans.* 32 (2013) 31–36.
- [5] US EPA, Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers, EPA, 1999, 542-R-99-002. Available from: <<http://www.clu-in.org>>.
- [6] R.D. Wilson, D.M. Mackay, J.A. Cherry, Arrays of unpumped wells for plume migration control by semi-passive in situ remediation, *Ground Water Monit. Rem.* 17 (1997) 185–193.
- [7] Y. Park, W.S. Shin, S. Choi, Sorptive removal of cobalt, strontium and cesium onto manganese and iron oxide-coated montmorillonite from groundwater, *J. Radioanal. Nucl. Chem.* 292 (2012) 837–852.
- [8] F. Di Natale, M. Di Natale, R. Greco, A. Lancia, C. Laudante, D. Musmarra, Groundwater protection from cadmium contamination by permeable reactive barriers, *J. Hazard. Mater.* 160 (2008) 428–434.
- [9] D. Jun, Z. Yongsheng, Z. Weihong, H. Mei, Laboratory study on sequenced permeable reactive barrier remediation for landfill leachate-contaminated groundwater, *J. Hazard. Mater.* 161 (2009) 224–230.
- [10] Y. Han, T.J. Gallegos, A.H. Demond, K.F. Hayes, FeS-coated sand for removal of arsenic(III) under anaerobic conditions in permeable reactive barriers, *Water Res.* 45 (2011) 593–604.
- [11] H. Lorbeer, H.S. Starke, M. Gozan, A. Tiehm, P. Werner, Bioremediation of Chlorobenzene-contaminated groundwater on granular activated carbon barriers, *Water Air Soil Pollut. Focus* 2 (2002) 183–193.
- [12] C.L. Ake, M.C. Wiles, H.J. Huebner, T.J. McDonald, D. Cosgriff, M.B. Richardson, K.C. Donnelly, T.D. Phillips, Porous organoclay composite for the sorption of polycyclic aromatic hydrocarbons and pentachlorophenol from groundwater, *Chemosphere* 51 (2003) 835–844.
- [13] A. Erto, A. Lancia, I. Bortone, A. Di Nardo, M. Di Natale, D. Musmarra, A procedure to design a permeable adsorptive barrier (PAB) for contaminated groundwater remediation, *J. Environ. Manage.* 92 (2011) 23–30.
- [14] K.D. Warren, R.G. Arnold, T.L. Bishop, L.C. Lindholm, E.A. Betterton, Kinetics and mechanism of reductive dehalogenation of carbon tetrachloride using zero-valence metals, *J. Hazard. Mater.* 41 (1995) 217–227.
- [15] S.F. O'Hannesin, R.W. Gillham, Long-term performance of an *in situ* "iron wall" for remediation of VOCs, *Ground Water* 36 (1998) 164–170.
- [16] B.D.M. Painter, Reactive barriers: Hydraulic performance and design enhancements, *Ground Water* 42 (2004) 609–617.
- [17] M. Prisciandaro, A. Lancia, D. Musmarra, Calcium sulphate dihydrate nucleation in the presence of calcium and sodium chloride salts, *Ind. Eng. Chem. Res.* 40 (2001) 2335–2339.
- [18] B. Courcelles, Guidelines for Preliminary Design of Funnel-and-gate Reactive Barriers, Proceedings of the 4th International Conference on Environmental Pollution and Remediation Prague, Czech Republic, August 11–13, 2014.
- [19] Environment Agency UK, Smith, Guidance on the use of permeable reactive barriers for remediating contaminated groundwater, 2002, Environment Agency NC/01/51, 146 pp.
- [20] S. Liu, X. Li, H. Wang, Hydraulics analysis for groundwater flow through permeable reactive barriers, *Environ. Model. Assess.* 16 (2011) 591–598.
- [21] I. Bortone, A. Di Nardo, M. Di Natale, A. Erto, D. Musmarra, G.F. Santonastaso, Remediation of an aquifer polluted with dissolved tetrachloroethylene by an array of wells filled with activated carbon, *J. Hazard. Mater.* 260 (2013) 914–920.
- [22] S. Canzano, S. Capasso, M. Di Natale, A. Erto, P. Iovino, D. Musmarra, Remediation of groundwater polluted by aromatic compounds by means of adsorption, *Sustainability* 6 (2014) 4807–4822.

- [23] A. Erto, R. Andreozzi, F. Di Natale, A. Lancia, D. Musmarra, Experimental and statistical analysis of trichloroethylene adsorption onto activated carbon, *Chem. Eng. J.* 156 (2010) 353–359.
- [24] A. Erto, A. Lancia, D. Musmarra, A modelling analysis of PCE/TCE mixture adsorption based on ideal adsorbed solution theory, *Sep. Purif. Technol.* 80 (1) (2011) 140–147.
- [25] A. Molino, A. Erto, F. Natale, A. Donatelli, P. Iovane, D. Musmarra, Gasification of granulated scrap tires for the production of syn-gas and a low cost adsorbent for Cd(II) removal from waste waters, *Ind. Eng. Chem. Res.* 52(34) (2013) 12154–12160.
- [26] D. Karatza, A. Lancia, D. Musmarra, F. PEPE, G. Volpicelli, Removal of mercuric chloride from flue gas by sulfur impregnated activated carbon, *Hazard. Waste Hazard. Mater.* 13(1) (1996) 95–105.
- [27] I. Bortone, A. Erto, G. Santonastaso, A. Di Nardo, M. Di Natale, D. Musmarra, Design of permeable adsorptive barriers (PABs) for groundwater remediation by COMSOL Multi-physics simulations, *Desalin. Water Treat.* 55(12) (2015) 3231–3240.
- [28] A. Erto, I. Bortone, A. Di Nardo, M. Di Natale, D. Musmarra, Permeable Adsorptive Barrier (PAB) for the remediation of groundwater simultaneously contaminated by some chlorinated organic compounds, *J. Environ. Manage.* 140 (2014) 111–119.
- [29] I. Bortone, A. Erto, A. Di Nardo, M. Di Natale, G. Santonastaso, D. Musmarra, Design of permeable adsorbing barriers for groundwater protection: Optimization of the intervention, *Chem. Eng. Trans.* 32 (2013) 31–36.
- [30] C.A. Staples, A.F. Werner, T.J. Hoogheem, Assessment of priority pollutant concentrations in the United States using storet database, *Environ. Toxicol. Chem.* 4 (1985) 131–142.
- [31] IPCS, Benzene, Environmental Health Criteria 150, World Health Organization/International Programme on Chemical Safety, Geneva, 1993. Available from: <<http://www.inchem.org/documents/ehc/ehc/ehc150.htm>>.
- [32] ATSDR, Toxicological Profile for Benzene, Agency for Toxic Substances and Disease Registry, Atlanta, GA, 2007, 438 pp.
- [33] J. Carratalá-Abril, M.A. Lillo-Ródenas, A. Linares-Solano, D. Cazorla-Amorós, Activated carbons for the removal of low-concentration gaseous toluene at the semipilot, *Ind. Eng. Chem. Res.* 48 (2009) 2066–2075.
- [34] M.A. Lillo-Ródenas, A.J. Fletcher, K.M. Thomas, D. Cazorla-Amorós, A. Linares-Solano, Competitive adsorption of a benzene–toluene mixture on activated carbons at low concentration, *Carbon* 44 (2006) 1455–1463.
- [35] F.J. Maldonado-Hódar, C. Moreno-Castilla, F. Carrasco-Marín, A.F. Pérez-Cadenas, Reversible toluene adsorption on monolithic carbon aerogels, *J. Hazard. Mater.* 148 (2007) 548–552.
- [36] J. Carratalá-Abril, M.A. Lillo-Ródenas, A. Linares-Solano, D. Cazorla-Amorós, Regeneration of activated carbons saturated with benzene or toluene using an oxygen-containing atmosphere, *Chem. Eng. Sci.* 65 (2010) 2190–2198.
- [37] M.C. Basso, A.L. Cukierman, Arundo donax-based activated carbons for aqueous-phase adsorption of volatile organic compounds, *Ind. Eng. Chem. Res.* 44 (2005) 2091–2100.
- [38] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations, *Carbon* 43 (2005) 1758–1767.
- [39] C. Liang, Y.-J. Chen, Evaluation of activated carbon for remediating benzene contamination: Adsorption and oxidative regeneration, *J. Hazard. Mater.* 182 (2010) 544–551.
- [40] V. Plagentz, M. Ebert, A. Dahmke, Remediation of ground water containing chlorinated and brominated hydrocarbons, benzene and chromate by sequential treatment using ZVI and GAC, *Environ. Geol.* 49 (2006) 684–695.
- [41] J. Bear, *Hydraulics of Groundwater*, McGraw-Hill, New York, 1979.
- [42] L.F. Konikow, D.B. Grove, Derivation of equations describing solute transport in ground water. US Geological Survey Water Resources Investigations, 1977, 30 pp.
- [43] A. Di Nardo, I. Bortone, M. Di Natale, A. Erto, D. Musmarra, A heuristic procedure to optimize the design of a permeable reactive barrier for in situ groundwater remediation, *Adsorpt. Sci. Technol.* 32 (2014) 125–140.
- [44] L.W. Gelhar, C. Welty, K.R. Rehfeldt, A critical review of data on field-scale dispersion in aquifers, *Water Resour. Res.* 28 (1992) 1955–1974.