

# Chlorobenzene compounds depletion in different groundwater contamination scenarios

Joana Gouveia Duarte

---

## Abstract

Groundwater is the main source of wetlands and rivers flow, representing 95% of freshwater available. Aquifer contamination is a serious issue, identified by several reports and European Directives, which establish a list of priority substances that, by 2025, must be eliminated from the environment. Among them, chlorobenzenes compounds and benzene are found and its movement and diminution in different groundwater contamination scenarios, as well as the efficacy of possible treatments to be applied, are the object of this study.

Visual MODFLOW<sup>®</sup> was applied to an accidental spill, using a 3D model. The influence of soil porosity ( $\phi$ ) and hydraulic conductivity ( $k$ ) in the plume volume and contaminants concentration were simulated for a saturated flow regime taking into account six scenarios. The plume volume decreases when  $\phi$  increases and  $k$  decreases for ranges of 0.1 to 0.6 for  $\phi$  and  $5 \times 10^{-7}$  to  $5 \times 10^{-4}$  for  $k$ .

Plume mitigation was studied through the simulation of different pumping tests, in order to optimize pumping conditions and wells network. Natural attenuation and permeable reactive barrier implementation efficacy were also analyzed. An optimized pumping system seems the best option to prevent, simultaneously, plume expansion and advance. Decontamination time ( $t_D$ ) for the implementation of a pump and treat treatment to each scenario for each soil layer, can varies from 3 to 14 years.

In these scenarios, a multivariate analysis demonstrates that the plume extension is larger for very low or high  $\phi$  and there is an optimal value for  $\phi$  that combines low capillary pressure with low gravity movement. For  $k$  the results demonstrate that for very low or high values, the time needed is lower, existing a critical value for which plume volume and plume resilience are at equilibrium. A sensitivity analysis of organic carbon ( $f_{OC}$ ) content in soil was made and demonstrates a high influence of this parameter in plume volume and contamination.

*Keywords:* Benzene, Chlorobenzenes, Groundwater, Natural attenuation, Pumping, Permeable hydraulic barrier

---

## 1. Introduction

Once groundwater is an important resource to be preserved, the WFWD (2000) states the Environmental Quality Standards (EQS) for water resources, defining the maximum concentration values for each pollutant. It also establishes a plan for monitoring thirty-three Priority Substances (PS), of which fourteen are classified as Priority Hazardous Substances (PHS) and imposes 2025 as the target date to have them eliminated from the environment. This work is, exclusively, concerned with a particular family of pollutants, which are addressed in the list of priority substances: benzene, 1,2,4-trichlorobenzene (1,2,4-TCB), trichlorobenzene, pentachlorobenzene and hexachlorobenzene (HCB). The presence in the environment of these compounds originates in different industry sources such as basic chemicals, polymers, other chemicals, fuel, paints, lacquers and varnish, pesticides, chloro-alkali, additive, preservatives, abrasives, pharmaceutical, intermediates and solvents (Pavlostathis and Prytula, 2000), (Hirano, *et al.*, 2007). The maximum allowed concentration, EQS, for benzene is 50  $\mu\text{g/L}$ , for HCB is 0.05  $\mu\text{g/l}$  and for the remaining chlorobenzenes are not, yet, set (Proposal Directive, 2000). The analysis of contaminants behaviour in groundwater and in soil is very complex, since any contaminant is subject to at least three types of mechanisms: transport, degradation and sorption, which are influenced by numerous factors.

### 1.1. Biodegradation paths and bioremediation

Natural attenuation (NA) is the result of eliminating contaminants from the environment through physical, chemical and biological processes (Azadpour-Keeley, *et al.*, 1999). The physical processes

comprise advection, dispersion, dilution, diffusion, volatilization, sorption and desorption (Zamfirescu and Grathwohl, 2001). The more frequent chemical reactions are ion exchange, complexation and abiotic transformation. The biological processes include aerobic and anaerobic biodegradation, plant and animal uptake. Biodegradation is based in complex oxidation/reduction reactions and the reduced electrons or equivalent have to be transferred to terminal electron acceptors. Aerobic, facultative and anaerobic bacteria can be involved in NA. Their presence and pollutant catabolism depends on the availability of molecular oxygen, nitrate and manganese or iron oxides, as it is shown in Table 1 for benzene degradation.

Aerobic degradation takes place mostly in the upper zone of the aquifer and in the boundaries of the contamination plume, while in the plume inner zone, the anaerobic pathways are responsible for the degradation process (Kao and Prosser, 2001) (Baldwin, *et al.*, 2008). The aerobic degradation of chlorobenzenes and benzene leads to the formation of catechol that is a less hazardous compound. Catechol may then be oxidized leading to compounds that can enter the citric acid cycle, such as succinate, acetyl-CoA and pyruvate (Vogt, *et al.*, 2004). On what concerns anaerobic degradation of chlorobenzenes, they tend to suffer reductive dechlorination, a process by which the chlorobenzenes will lose a chlorine ion, which will be replaced by an hydrogen atom (Pavlostathis and Prytula, 2000). Indeed chlorinated pesticides degradation, such as, hexachlorobenzene, occurs in anoxic environment (Madigan, *et al.*, 2000). It has also been reported that bacteria or anaerobic fungi can carry out benzene anaerobic degradation. (Johnson, *et al.*, 2003).

Table 1

Benzene microbial degradation pathways in different environments. Terminal electron acceptors are shown in bold. Adapted from Spence, *et al.*, 2005 and Kazumi, *et al.*, 1997.

Pathway	Microbial process	Degradation reactions for benzene (C <sub>6</sub> H <sub>6</sub> )
Aerobic	Aerobic degradation	$2C_6H_6 + 15 O_2 \rightarrow 12CO_2 + 6H_2O$
Anoxic	Denitrification	$2C_6H_6 + 12 NO_3^- \rightarrow 12HCO_3^- + 6N_2$
	Manganese (IV) reduction	$C_6H_6 + 15 MnO_2 + 24H^+ \rightarrow 6 HCO_3^- + 15Mn^{2+} + 12H_2O$
	Fe(III) reduction	$C_6H_6 + 30 FeOOH + 54H^+ \rightarrow 6 HCO_3^- + 30Fe^{2+} + 42H_2O$
	Sulphate reduction	$4C_6H_6 + 15 SO_4^{2-} + 12H_2O \rightarrow 24HCO_3^- + 7.5HS^- + 7.5H_2S + 1.5H^+$
Anaerobic	Methanogenesis	$4C_6H_6 + 18H_2O \rightarrow 9CO_2 + 15CH_4$

## 1.2. Remediation technologies

There are numerous technologies that can be used to clean-up contaminated soils and groundwater, and the best choice can vary in each stage of the decontamination process. Technologies can focus on the contaminant source or work throughout the plume, can contain or remove the contaminants, and can be done *in-situ* or *ex-situ*. Moreover, a good analysis of each process, as well as specific information and data of the results obtained in the field, is necessary to guaranty a cost-effective and sound investment decision (EPA, 2004).

*In situ* treatment requires the application of different strategies to enhance contaminant desorption processes and oxidation. Air sparging or a pump and treatment (PAT) approach can be used (Kirtland and Aelion, 2000). *In situ* bioremediation consists in the enhancement of a site NA. Some examples of bioremediation technologies are bioventing, land farming, bioreactor, composting, in which bioaugmentation and biostimulation should take place. A permeable reactive barrier (PRB) is defined as an *in situ* method for remediating contaminated groundwater that combines a passive chemical or biological treatment zone with subsurface fluid flow management. It involves the construction of permanent, semi-permanent or replaceable units across the flow path of a dissolved phase contaminant plume (Guerin, *et al.*, 2002).

## 1.3. Soil characteristics

The impact of remediation technologies is highly dependent on the soil characteristics. In this study, the same methods will be simulated in six soils that differ in hydraulic conductivity, porosity, specific yield

and specific storage. Hydraulic conductivity ( $K$ ) is defined as the rate of movement of water through a porous medium such as a soil or aquifer. Porosity ( $\phi$ ) represents the ratio between the volume of void spaces and the total volume of the soil, which means the fraction of the total volume that is occupied by the porous media.  $\Phi$  depends on the particle size distribution, on the particle distribution and on the size and shape of the particles (Brusseau, 2005). Dispersivity is a measure of the spread of contaminant through all directions, due to concentration gradient. The Specific storage ( $S_s$ ) is the amount of water that an aquifer can release from storage, per unit of mass or volume of aquifer, per unit change in hydraulic head, while remaining fully saturated (Chiang and Kinzelbach, 1998). Finally specific yield ( $S_y$ ), is the volume of water per unit volume of the aquifer, a critical feature in water availability (Chiang and Kinzelbach, 1998).

#### 1.4. Site description

The site topography, spill and pumping and supply wells location can be found in Fig. 1.

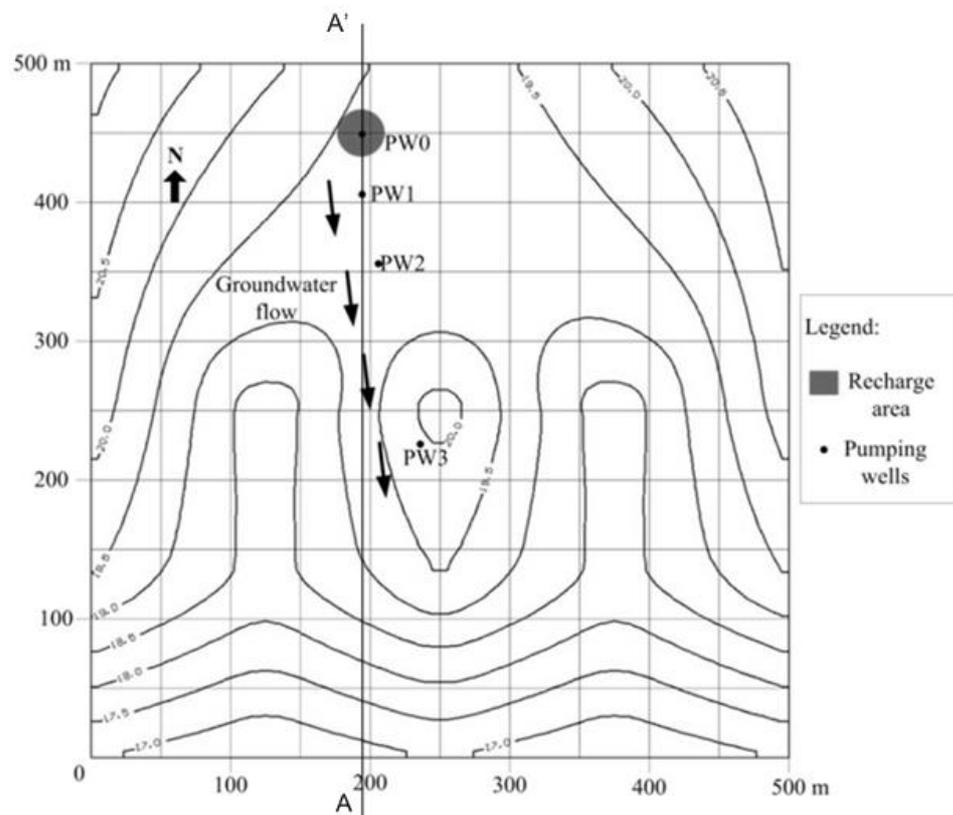


Fig. 1. Simulated spill site and topography. In grey the contamination recharge area. PW0 (185,450) is a pumping well located in the contamination source and PW1 (190,410), PW2 (202,354) and PW3 (228,235) are pumping wells at 40, 97 and 219 m from the source respectively.

Case study is based on a ten years leak of an old storage tank containing an aqueous phase saturated with benzene and other chlorobenzene compounds (Table 2).

The spill impact area extension was considered to be up to 25 hectares (500mx500m), as shown in Fig.1. The initial contamination area was assumed to be 10 m<sup>2</sup> (storage tank base area). Since the purpose was to study the impact of soil quality in the contaminant plume development, six different scenarios were established, Table 3. Soil characteristics are values set in bibliography with exception of  $S_s$  that was calculated from  $S_y$  and from the aquifer depth. Three different layers were considered. An upper unconfined aquifer as a top layer, followed by a middle aquitard and a lower confined aquifer (Fig.2). Contaminants degradation through anaerobic or aerobic paths was considered only in the saturated or unsaturated zone, respectively. With the characterization set described above it is possible to predict the size and shape of a contamination plume, after 10 years.

### 1.1. Parameters estimation

Biodegradation rates, in the adsorbed and mobile phases, were estimated for five contaminants (HCB, pentachlorobenzene, trichlorobenzenes, 1,2,4-TCB and benzene) based on bibliography data, as it is resumed in Table 4. It was considered that organic compounds degradation rates occur through pseudo first-order decay, so the half-life time is independent of the initial concentration. It was also assumed that site geochemistry assures that all the conditions for contaminant reduction (electron acceptors, pH, redox potential, etc.)

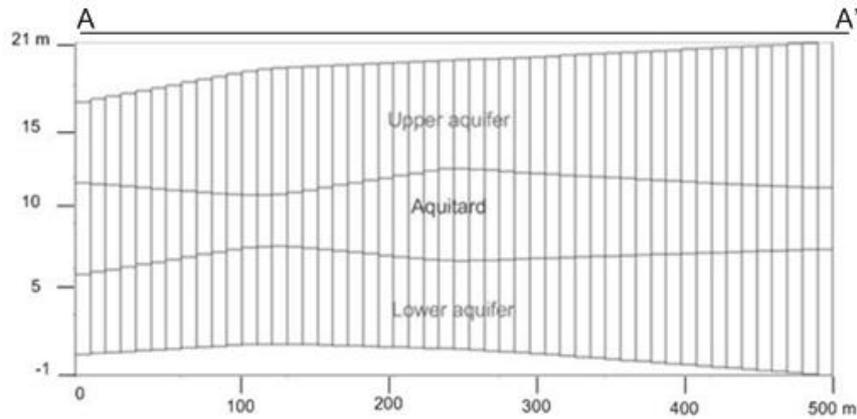


Fig. 2. Geological cut showing the three layers of soil, considered in the study.

Table 2  
Leak composition and contaminants CAS number and environmental quality standards.

Substance	CAS	PHS	EQS $\mu\text{gL}^{-1}$	Leak composition	
				Concentration	Units
Benzene	71-43-2		50	$[\text{Benzene}]_{\text{aqueous}}$	$1.8^a$ $\text{gL}^{-1}$
Hexachlorobenzene (HCB)	118-74-1	X	0.05	$[\text{HCB}]_{\text{organic}}$	$31.6^a$ $\text{gL}^{-1}$
Pentachlorobenzene	608-93-5	X	*	$[\text{HCB}]_{\text{aqueous}}$	67.94 $\text{mgL}^{-1}$
Trichlorobenzenes	12002-481		*	$[\text{TCB}]_{\text{aqueous}}$	2.06 $\text{mgL}^{-1}$
1,2,4-trichlorobenzene (1,2,4-TCB)	120-82-1		*	$[\text{organic}]_{\text{aqueous}}$	1870 $\text{mgL}^{-1}$

<sup>a</sup> Government of Canada, 1993

Table 3  
Values of soil porosity and conductivity considered in each scenario.

Scenario	Soil type	Total Porosity (%) <sup>a</sup>	Effective Porosity (%) <sup>a</sup>	Conductivity $K_x$ and $K_y$ (m/s) <sup>a</sup>	Conductivity $K_z$ (m/s) <sup>a</sup>	$S_y$ <sup>(b)</sup>	$S_s$ (m <sup>-1</sup> )
1	Clay, sand and gravel mixes	60	45	$5 \times 10^{-4}$	$5 \times 10^{-5}$	0.07	$7 \times 10^{-3}$
2	Coarse sand	40	35	$5 \times 10^{-4}$	$5 \times 10^{-5}$	0.27	$2.7 \times 10^{-2}$
3	Clay	55	45	$1 \times 10^{-4}$	$1 \times 10^{-5}$	0.02	$2 \times 10^{-3}$
4	Gravel and sand	35	20	$1 \times 10^{-4}$	$5 \times 10^{-5}$	0.25	$2.5 \times 10^{-2}$
5	Silt	50	40	$1 \times 10^{-6}$	$5 \times 10^{-7}$	0.18	$1.8 \times 10^{-2}$
6	Sandstone	20	10	$5 \times 10^{-7}$	$5 \times 10^{-8}$	0.27	$2.7 \times 10^{-2}$

<sup>a</sup> Novotny and Olem, 1994; <sup>b</sup> Halford and Kuniansky, 2002

Table 4  
Half-life time for each compound for aerobic and anaerobic degradation paths

Path	Half-life time – $t_{1/2}$ (d)				
	HCB	Pentachlorobenzene	Trichlorobenzenes	1,2,4-TCB	Benzene
Aerobic	$80^a$	$270^a$	$365^a$	$320^a$	$16^a$
Anaerobic	$2.5^b$	$1.2^b$	$4.5^b$	$22.5^b$	$370^a$

<sup>a</sup> Government of Canada, 1993; <sup>b</sup> Pavlostathis and Prytula, 2000

### 1.1.1. Biodegradation rates calculation

A pseudo first-order decay is given by:

$$C_t = C_0 \times e^{-kt}, (1)$$

where  $C_t$  is the concentration at a certain time,  $C_0$  is the initial concentration,  $k$  is the degradation rate and  $t$  is the time.

Taking into account the compounds weathering along the plume and time, the least biodegradable compounds will be the limiting decontamination paths. This way it was assumed that trichlorobenzene should govern the degradation process in the aerobic zones while benzene degradation kinetics will be the limiting step in the anaerobic zone.

It was therefore assured that degradation kinetics values introduced in the model are the slowest ones, leading to a less effective NA assessment (Table 5). However it should be emphasized that abiotic factors were neglected and this can lead to significant errors.

Table 5  
Estimated overall aerobic and anaerobic decay.

Path	Limitant contaminant	$t_{1/2}$ (d)	$K$ ( $d^{-1}$ )
Aerobic	Trichlorobenzenes	365	$1.899 \times 10^{-3}$
Anaerobic	Benzene	370	$1.873 \times 10^{-3}$

In the capillary fringe a mean kinetics rate was set. In order to establish the plume volume and mass a plume contamination limit of  $0.05\mu\text{g/L}$  was established (Table 2), being confident that this value overestimates the plume volume and hazardousness.

### 1.1.2. Distribution coefficient

The distribution coefficient gives the amount of contaminant that is adsorbed by the soil particles. It can be calculated based on the partition coefficient. The partition coefficient ( $k_{oc}$ ) is the ratio of organic carbon sorbed and the amount of organic carbon in solution and it can be estimated using octanol-water coefficient ( $k_{ow}$ ), through an equation that has been successfully used to determine partition coefficients to chlorobenzenes (Schwarzenbach, 1981):

$$\log K_{OC} = 0.72 \times \log K_{OW} + 0.49, (3).$$

The distribution coefficient ( $K_d$ ) is calculated by:

$$k_d = \frac{[\text{organics}]_{\text{aqueous}}}{[\text{organics}]_{\text{sediment}}}, (4).$$

And is defined as the ratio between the amount of organic compounds in the aqueous phase and the amount of organic compounds in the sorbed phase, expressed by (L/kg). It can also be estimated by:

$$K_d = K_{OC} \times f_{oc}, (5)$$

$f_{oc}$  being the fraction of organic carbon. For groundwater aquifers  $f_{oc}$  usually varies between 0.001 and 0.01, (DERBCAP, 2001). So, the value of 0.005 will be assumed for all tests and a sensitivity analysis will be carried to evaluate the impact of this factor. Again the mixture distribution coefficient (Table 6) was considered as the limitant contaminant distribution coefficient. The remaining constant parameters that are common for each scenario, are compiled in Table 7.

Table 6  
Estimated aerobic and anaerobic distribution coefficients.

Path	Limiting contaminants	Log $k_{ow}$ <sup>a</sup>	Log $k_{oc}$	$f_{oc}$	$K_d$ (L/kg)
Aerobic	Trichlorobenzene	3.93	3.32	0.005	10.44
Anaerobic	Benzene	2.13	2.02	0.005	0.53

<sup>a</sup> Government of Canada, 1993

Table 7  
Assumptions introduced in the model, common to each scenario

Assumptions	Value	Units
Rain recharge	100	mm/year
Evapotranspiration	10	mm/year
Contaminant recharge	20	L/day
Contaminant recharge concentration	50	g/L
Longitudinal dispersivity	10	m
Horizontal/longitudinal dispersivity	0.1	-
Vertical/longitudinal dispersivity	0.01	-

The evolution of the groundwater contaminated plume was studied, in three stages: (1) Assessment of the size and shape of a plume for different types of soil and analysis of the risk of contamination of supply wells; (2) Assessment of the influence of the number of wells, locations and pumping rates in the decontamination efficiency of the groundwater plume; (3) PAT and PRB performance comparative analysis when applied to each plume and scenario.

### 1.2. Methods

Visual MODFLOW<sup>®</sup> is being applied since more than two decades with success and was the selected tool for this study. Soil characteristics (such as soil elevation, layer type and thickness, conductivity, porosity and dispersivity), hydraulic characteristics (recharge rate, evapotranspiration, storage and pumping rates) and contaminants degradation rates, sorption rate, and decay models are imposed, Fig.3.

The flow type considered the existence of a saturated area and the numeric engine that runs in this condition is the USGS MODFLOW 2000. The model considers that there is transport of contaminants.

When selecting the engine to perform transport and considering the data available, it was selected DoD MT3DMS 5.1 that allows modelling the reactive transport. In this model, to characterize the plume total mass of contaminants present is considered. For this reason, it is not necessary to implement a reactive multispecies analysis. The type of run was chosen to be a steady-state flow, which means that the conductivity and pressure are constant. To simulate sorption, the model chosen was linear isotherm, since the information related with contamination sorption process, used in this study, considered this type of model.

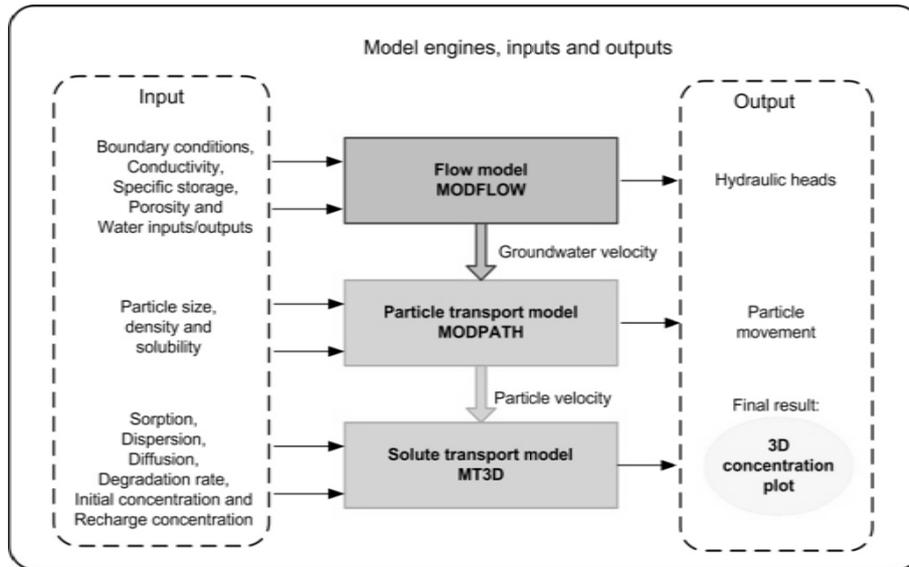


Fig. 3. Flux diagram between model engines, parameters inputs and the 3D outputs.

A pseudo first-order decay was used to run the reaction model. Nevertheless, other models, more complex, are available, but need more information. Beyer, *et al.*, (2006) identified Michaelis-Menten, as a good degradation kinetics model, as the error associated with the possibility to underestimate the plume is low. However, Pavlostathis and Prytula (2000) were able to estimate better pseudo first order decay than Michaelis-Menten degradation rates for chlorobenzenes (lower standard error).

### 1.2.1. Selecting the best pumping system

The plume from scenario 1 (Fig.4) was selected to establish the best pumping system, since it is the largest and the longest one, taking into account that after contamination had been found and stopped, treatment technologies should recover the aquifer in 16 years, since by 2025 the groundwater resources must be cleaned. Three wells positions (PW1, PW2 and PW3) were selected and PAT efficiency for different pumping wells network at different pumping rates was analyzed (Table 8). Negative values imply pumping water, while positive values stand for aquifer recharge, in order to prevent abrupt changes in the aquifer water level.

Table 8  
Pumping rates applied in each well and test.

Test	PW1 (m <sup>3</sup> /d)	PW2 (m <sup>3</sup> /d)	PW3 (m <sup>3</sup> /d)
1	-1000	0	0
2	0	-1000	0
3	0	0	-1000
4	-1000	-1000	0
5	0	-1000	-1000
6	-1000	0	-1000
7	-1000	-1000	-1000
8	-1000	1000	-1000
9	-1100	-1100	-1100
10	-1100	-1100	0
11	-750	-750	-750
12	-750	-750	0

The implementation of a PAT system includes, necessarily, a treatment unit. For low concentration of chlorobenzenes in pumped groundwater, phytoremediation can be an option (Nasir and Batarseh, 2008). For high amounts of chlorobenzenes, in-situ incineration is considered the best option (MAFRTR, 1998). For comparative analysis it was assumed that treatment efficiencies are similar in any case.

### 1.2.2. Establishing PRB treatment

Another subject of analysis is the assessment of a PRB efficiency. A barrier with 15 m thickness, 100 m long settled in front of PW1 well was chosen. The purpose of this barrier is to prevent the plume advection and to recover part of the pollution. For that the conductivity inside the barrier is low,  $1 \times 10^{-12}$  m/s and with a contaminant recovery of 70% (Guerin, *et al.*, 2002). The PRB are only applied to those scenarios for which plume spreading were detected. The simulation time was also 16 years.

### 1.2.3. Sensitivity analysis of $f_{oc}$

A sensitivity analysis of soil organic carbon content in the plume volume and total mass of contaminant during the contamination process (10 years) and the NA phase (16 years) was carried out for scenario 1, Table 9.

Table 9

Values of  $f_{oc}$  simulated in each test and respective distribution coefficient in saturated and non saturated region, for scenario 1.

Test	$f_{oc}$	Kd (L/mg)	
		Non-saturated	Saturated
A	0.001	$4.58 \times 10^{-9}$	$9.04 \times 10^{-8}$
B	0.00125	$5.72 \times 10^{-9}$	$1.13 \times 10^{-7}$
C	0.0025	$1.14 \times 10^{-8}$	$2.26 \times 10^{-7}$
D	0.005	$2.29 \times 10^{-8}$	$4.52 \times 10^{-7}$
E	0.0075	$3.43 \times 10^{-8}$	$6.78 \times 10^{-7}$
F	0.01	$4.58 \times 10^{-8}$	$9.04 \times 10^{-7}$

## 2. Results

### 2.1. Influence of porosity and hydraulic conductivity in plume volume and total mass of contaminant

The assessment of the size and shape of contaminant plumes for scenario 1 and 5, when contamination was stopped (day 3650) are shown.

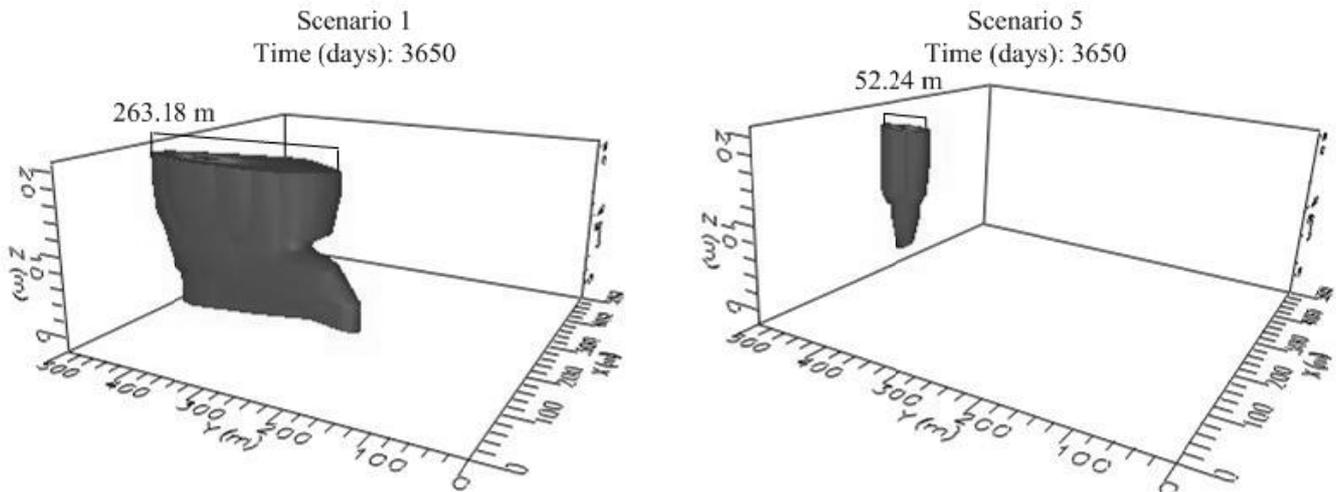


Fig. 4 Plumes 3-D shape for scenario 1 (clay, sand and gravel mixes) and 5 (silty soil) when contamination was stopped.

Two different plumes were achieved. For scenario 1 the plume moves downward due to the strong advection component, in direction to the supply wells. Some dispersion in the opposite direction to groundwater flow can also be noticed. This type of plume was also observed for scenario 2. The plume found for scenario 5 is characterized by some dispersion and very slow or none movement in the groundwater direction flow, as in scenarios 3, 4, and 6. The plumes volume and mass of contaminant obtained at day 3650, can be observed in Table 10.

Table 10

Plume volume and total mass of contaminant obtained, considering the porosity and conductivity of each scenario (day 3650).

Scenario	Plume volume (m <sup>3</sup> )	Contaminant mass within the plume (g)
1	141040	151
2	104601	106
3	14767	33
4	10025	25
5	1416	3.6
6	1133	3.8

Through the application of multivariate analysis, a non-linear regression was applied to study the evolution of the plume volume with soil porosity and conductivity. A linear regression could not be applied, since the plume volume is not the only dependent variable. Hydraulic conductivity is a result of porosity and other soil characteristics, such as grain size, grain size distribution and hydraulic heads. Despite the accuracy of the regression ( $V = -3.79 \times 10^4 + 1.96 \times 10^5 \varphi - 8.77 \times 10^8 K + 1.63 \times 10^6 \varphi^2 + 1.71 \times 10^{12} K^2$ ;  $R^2=0.91$ ), it should be emphasized that it was obtained from the previous simulated results. Although, based on the equation, resulting from the application of multivariate analysis, it was possible to draw a graphic representation of the volume plume evolution with porosity and hydraulic conductivity, as it can be seen in Fig. 5. It is possible to display, clearly the relation between porosity and hydraulic conductivity with plume size.

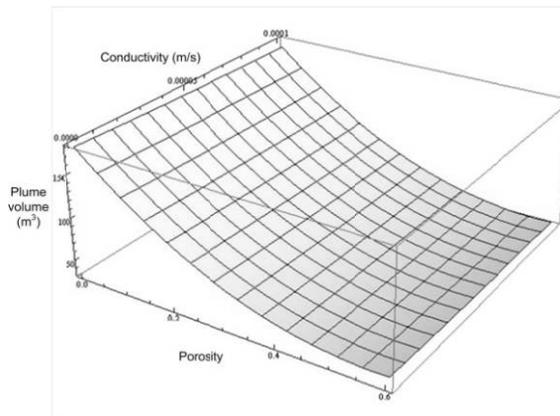


Fig. 5. Variation of plume volume with porosity and hydraulic conductivity.

It can be concluded that for soils with the same porosity, the soil with higher hydraulic conductivity leads to higher plume volumes and mass of contaminant. It also confirms that for soils with same hydraulic conductivity, the one that has higher porosity has the lower plume volume and the higher mass of contaminant.

## 2.2. NA influence in contaminant plume remediation

To better understand the impact of NA, the model was run, for each scenario, considering that the source of contamination had stopped and no treatment was applied, during the next 16 years. Based on the results, it was possible to analyse the influence of natural attenuation in each scenario (Table 11). Actually, plumes were all decontaminated by the end of 2025, but to understand the influence of porosity and conductivity on NA for the same geochemistry conditions, it is necessary to evaluate the time needed in each scenario to reach a total decontamination (Table 11).

Table 11

Time necessary to decontaminate the plumes present in each scenario, by layer.

Scenario	Decrease after 8 years (%)		Time to decontaminate by NA (years)		
	Total Volume	Total Mass	Layer 1	Layer 2	Layer 3
1	71	99	10	9	4
2	75	99	10	9	5
3	68	99	13	12	4
4	63	99	13	12	4
5	67	99	14	11	N.c.
6	67	99	14	12	N.c.

N.c.-Not contaminated (< 0.05 µg/L)

The time necessary to decontaminate is dependent on the plume volume. Regardless of the porosity, scenarios with the same hydraulic conductivity take the same time to decontaminate, such as scenario 1 and 2. When the hydraulic conductivity is low, the risk of lower layers contamination is reduced (scenario 3 and 6). In all scenarios, after 8 years, plume volume decreases, meaning that the velocity of the plume movement is not high enough to compensate the loss through degradation. When considering the total contaminant mass within the plume, one can observe that NA could be responsible for an almost total degradation of contaminant mass, if site geochemistry assures the right conditions.

*Plume evolution during NA process*

In order to understand the movement of the contaminant plume, the evolution of the plumes generated in each scenario is presented (Fig. 6).

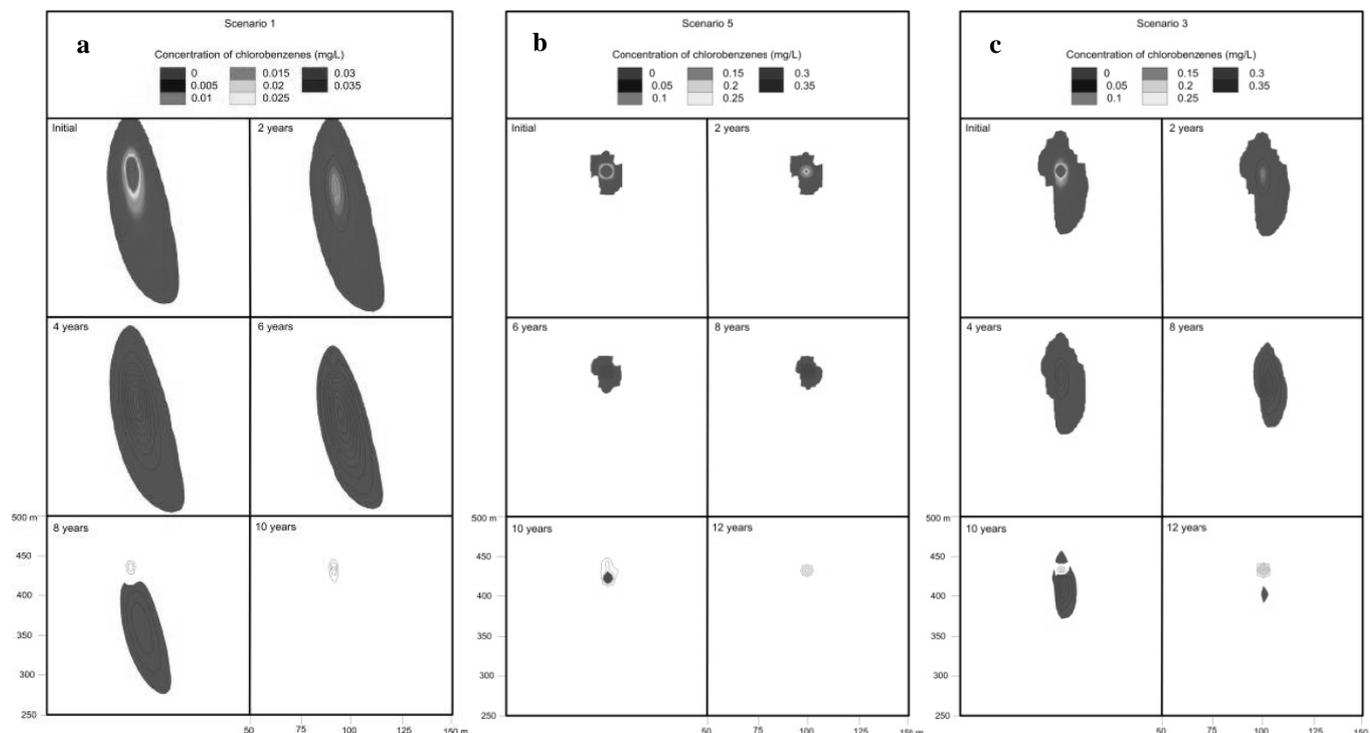


Fig. 6 Evolution of the contaminant plume generated in scenario 1 a), 5 b) and 3 c), during 10 years.

Scenario 1 shows a well developed plume, as can be seen in Fig.6a). Actually, after the end of the contaminant recharge, the plume still grows. The advection forces lead to the increase of the plume. The amount of contaminant within the plume guarantees the recharge of the plume while it expands. This way the concentration of contaminant is still high enough to be detected. The biodegradation effort is not strong

enough to compensate the plume advance. However the amount of contaminant near the source decreases due, mainly, to biodegradation. After 4 years, the plume starts to lose volume, since the amount of contaminant that moves, per unit of time, is less than the amount that is degraded.

After 8 years, it is possible to verify that the plume centre has moved downward, in groundwater flow direction, and that the source is already decontaminated. After 10 years the contaminants concentration has reached a level of security. Scenario 2 had a similar plume evolution.

In Fig.6b) the observed plume is very distinct from that in Fig.6a). The advection influence is very low, leading to no increase of volume. The main drive present is biodegradation, which induces the loss of contaminant concentration and a loss of volume, after 6 years. This plume is more difficult to decontaminate, taking more time to reach the security levels established. Scenario 6 led to similar results.

In scenario 3, (Fig.6c)), the plume has a higher advection component than the one in Fig.6b) but not enough to allow the contaminants movement, after the end of the discharge, as in Fig.6a). There is a balance between the action of biodegradation, advection and dispersion, since it is not possible to determine which one has a dominant effect, in this scenario. In this scenario the separation of the plume does not last long, although this could represent a bigger effort, when applying a treatment technology. Scenario 5 led to the same type of evolution as scenario 4.

### 2.3. Influence of pumping rate and number of wells in the plume extension

Plume mitigation through PAP for scenario 1 was addressed. The different pumping tests described in Table 8 were simulated (Table 12).

Table 12

Plume volume and mass for each test after the implementation of a pumping system, after 8 years and time necessary to decontaminate each layer.

Test	Time to decontaminate by layer (years)			After 8 years			
	1	2	3	Plume volume (m <sup>3</sup> )	Volume decrease (%)	Contaminant mass within the plume (g) Mass	decrease (%)
0	10	9	4	40357		3.9	
1	8	8	3	10986	73	0.03	99
2	9	9	4	32438	19	0.4	90
3	10	9	4	44443	-10	1.2	69
4	8	8	3	0	100	0	100
5	9	8	4	0	100	0	100
6	8	8	3	0	100	0	100
7	7	8	3	0	100	0	100
8	8	8	3	0	100	0	100
9	7	8	3	0	100	0	100
10	7	8	3	0	100	0	100
11	8	8	3	0	100	0	100
12	8	8	3	0	100	0	100

The results demonstrate that every pumping system could obtain good results in reducing the contaminant mass from scenario 1, when compared with the results obtained if no remediation technology was implemented. When considering volume decrease the results are also very good, with exception for test 3, in which the pumping system induces the advection component of the plume movement.

The wells position has an important role in the decontaminating process of the plume, as can be seen when comparing the results of test 1, 2 and 3. Combining more than one pumping well, the results achieved are better and it is possible to reach a total removal, even with lower pumping rates, see test 11 and 12 (Table 12); The higher the pumping rate, the higher will be the efficiency in the first layer (tests 9 and 11 e 10 and 12). However in the end it does not make any difference, since for the second layer a

longer time is still necessary. Recharging of the aquifer, does not allow a better performance, when compared to test 7, in fact it slows the recovering rate. Also, it is possible to identify tests, in which different pumping rates accomplish the same results, for example test 7, 9 and 10. Test 9 is a more expensive system to implement and achieve similar results, in the same time frame, as test 7. The same type of approach, to establish a pump-and-treat system was applied in a study developed by Baú and Mayer (2008).

#### 2.4. Influence of pumping wells in the plume shape and on creating a diving plume

The location and pumping rate applied to a plume can change the shape of a plume, since the groundwater flow, near the well, changes of direction. This process can originate hidden plumes, either because part of the plume is outside the well influence (as in Fig. 7), or due to differences in soil composition, which demands a too high pumping effort, to achieve a full recover.

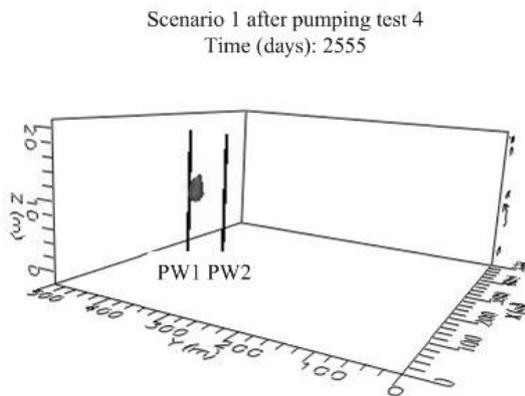


Fig. 7. Scenario 1, after 8 years of PAT, test 4.

In scenario 4 Fig. 6, the pumping system did not allow the recovery of part of the plume that was between the two wells, in the middle layer. In fact, in all tests, the aquitard zone, was the most difficult to recuperate, since the capillary pressure necessary to recover a contaminant is very high. These observations are of extreme importance since if the pumping wells were the only wells available to monitor the aquifer; the plume could not be identified. As a result, modelling an aquifer not only allows estimating the efficiency and procedures of treatment technologies, but also identifies problems and flaws resulting from its application.

#### 2.5. Efficiency of pump-and-treat and PRB technology

Using the results of the tests performed in scenario 1, the pumping test with a good performance and lower pumping rates, test 7, was applied to all the scenarios. The results were not good, when the pumping test was applied to scenarios with low advection movement as it was expected. In those cases, a pumping well was set in the middle of the source area. The well position (PW0) can be seen in Fig.1. The application of PRB technology was only possible in scenarios that had a major direction movement, which was the case of scenarios 1 and 2. For this reason, the technology was not applied to scenarios 3, 4, 5 and 6, since the low plume dispersion and movement did not substantiate the use of such technology. The results of the efficiency from the application of a PAT and PRB, after 8 years, are present in Table 13.

Table 13

Efficiency of the application of a pumping system and PRB, to each scenario, in reducing plume volume and contamination, after 8 years.

Scenario	Pumping system	Plume volume decrease (%)		Contaminant mass decrease (%)	
		PAT	PRB	PAT	PRB
1	PW1 and PW2	100	99	100	99
2	PW1 and PW2	100	100	100	100
3	PW0	99	n.a.	99	n.a.
4	PW0	99	n.a.	99	n.a.
5	PW0	73	n.a.	87	n.a.
6	PW0	89	n.a.	97	n.a.

With exception of scenario 1 and 2, in the remaining scenarios it was not possible to choose a pumping system that would fit to decontaminate the aquifer. However, when analysing the plume dimension, it is visible that besides the varied plumes dimension, within the time frame, the system obtains good results. Despite having the smaller plume volume, in scenario 5, it was not possible to remove all contaminant from the plume, because part of the contaminant stayed trapped within the soil pores and the pressure required to release it is very high.

In what concerns the application of PRB, the results are good, since at least the plume dimension suffers a reduction of 99% and the total mass of contaminant is practically recovered. Comparing with the results where no technology was applied, the plume dimension does not reach values so high as if no technology was applied. When compared with the results of the pumping system, the pumping system proves to be a better treatment technology, as it allows a total recover and within the time frame set. Since the barrier, in PRB, is not as wide as it should be, comparing to the plume wideness, it was not possible to restrain the plume better.

## 2.6. Time necessary to recover the plume resulting from each scenario

The next step was to evaluate the relation between porosity, hydraulic conductivity and time needed to decontaminate the plume. In Fig. 8 the graphic presented results from the application of a nonlinear regression based on the time needed to decontaminate the plume in function of soil porosity and hydraulic conductivity.

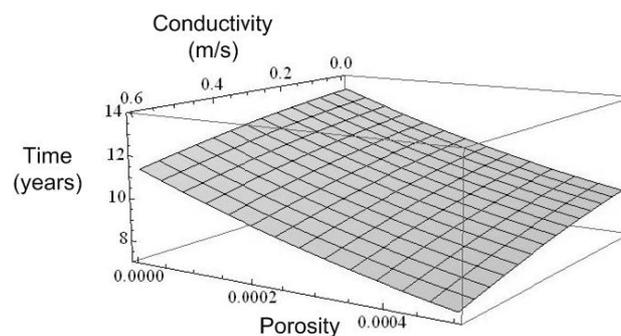


Fig. 8. Time needed to decontaminate a plume in function of soil porosity and hydraulic conductivity.

In fact, at first, for soils with the same hydraulic conductivity, the time to decontaminate decreases with the increase of soil porosity, until soil porosity reaches a certain value. From that value on, as porosity raises, the time to decontaminate increases.

When fixing porosity, the behaviour is similar, but instead of a minimum, it reaches a maximum time to decontaminate. The turning point for porosity is at 50%, where there is equilibrium between the contaminant depth and capillary pressure of plume dimension and plume resilience, which is the worst scenario for contaminant removal. The critical hydraulic conductivity of  $1.02 \times 10^{-2}$  m/s is due to equilibrium between plume volume and resilience.

## 2.7. Sensitivity analysis of $f_{OC}$ results

A sensitivity analysis was made in order to evaluate if assuming a  $f_{OC}$  value, between the ranges of default values, would induce severe changes in the plume volume and concentration. The results of the sensitivity analysis of  $f_{OC}$  are present in Table 14. The value used to the remaining simulations was of 0.005.

Table 14  
Results of  $f_{OC}$  sensitivity analysis to scenario 1

Test	$f_{OC}$	Volume (m <sup>3</sup> )		
		(Day 3650)	(Day 6570)	Volume decrease (%)
A	$1 \times 10^{-3}$	403551	0	100
B	$1.25 \times 10^{-3}$	349182	0	100
C	$2.5 \times 10^{-3}$	225779	75050	67
D	$5 \times 10^{-3}$	141040	40357	71
E	$7.5 \times 10^{-3}$	70936	9124	87
F	$1 \times 10^{-2}$	35247	7135	79

During the contamination years, it is possible to observe that, when the  $f_{OC}$  increases, the plume volume decreases, while the amount of contaminant within the plume increases. Since high values of  $f_{OC}$ , induces a higher distribution coefficient, the amount of contaminant that is adsorbed is higher, taking longer to degrade. When analysing the behaviour of plume volume during the period when only NA occurs, for very low amounts of organic carbon the decontamination is complete after 8 years, since the amount of contaminant adsorbed is low, leading to lower degradation rates. Yet, for a certain value of  $f_{OC}$ , the analyses change. As  $f_{OC}$  increases, the amount of trapped contaminant is higher, leading to a slower advection and dispersion movement increasing the efficacy of recover. The rates of volume decrease and mass decrease, indicate, that the amount of organic carbon in soil has a strong impact in recovering a plume by NA. When analysing the time required to decontaminate each plume layer for the six  $f_{OC}$  applied, the results confirm the analysis made. As  $f_{OC}$  is used to determine the distribution coefficient, in a real site study the determination of the real  $f_{OC}$  is essential to estimate the contaminants dissolution. When well determined it can estimate the contaminants movement within the plume with good accuracy, otherwise it normally will overestimate the plume (Fraser *et al.*, 2008).

## Conclusions

NA has proved to be effective in the reduction of mass of contaminant, but in terms of plume volume decrease it can be enhanced by the use of an additional treatment technology. Pump-and-treat systems can be more adaptable.  $f_{OC}$  has proven to be an important parameter to be quantified, since it can substantially influence the precision of the modelling results.

The model does not take into account the solubility of the contaminants and neither the three phases of the mobile phase in soil (water, organic, air). It considers that the contaminant is either adsorbed or in solution with water. However, with exception to benzene, HCB has very low solubility and the other species are insoluble in water (Government of Canada, 1993). But since the model cannot introduce this factor, the plume extent will be higher than what is expected in a real scenario to happen, representing the worst scenario of plume dispersion. On one hand, this will increase the extent of volume to recover; on the other hand the amount of contaminant found in the source area will be reduced. The plume volume calculated is estimated in excess, since it is considered that the soil is saturated in water. Yet, this assumption is false for the top layer. The amount of contaminant present in the plume is calculated considering the plume volume and it is compared with the amount of contaminant degraded and adsorbed, in order to confirm if the results are compatible with the amount of contaminant introduced in the soil. The amount of contaminant is also overestimated for the top layer, since it is calculated based on the plume volume.

## References

- Al Nasir, F. and Batarseh, M. I., 2008. Agricultural reuse of reclaimed water and uptake of organic compounds: Pilot study at Mutah University wastewater treatment plant, Jordan. *Chemosphere*, 72, 1203-1214.
- Azadpour-Keeley, A., Russell, H. H., and Sewell, G. W., 1999. Microbial processes affecting monitored natural attenuation of contaminants in the subsurface. *Groundwater Issue*, EPA.
- Baldwin, B. R., Nakatsu, C. H., and Nies, L., 2008. Enumeration of aromatic oxygenase genes to evaluate monitored natural attenuation at gasoline-contaminated sites. *Water Research*, 42, 723-731.
- Baú, D. A. and Mayer, A. S., 2008. Optimal design of pump-and-treat systems under uncertain hydraulic conductivity and plume distribution. *Journal of Contaminant Hydrology*, 100, 30 – 46.
- Beyer, C., Bauer, S. and Kolditz, O., 2006. Uncertainty assessment of contaminant plume length estimates in heterogeneous aquifers. *Journal of Contaminant Hydrology*, 87, 73-95.
- Boguslavsky, S., 2000. Organic Sorption and Cation Exchange Capacity of Glacial Sand, Long Island – Master Thesis, State University of New York At Stony Brook, [http://www.geo.sunysb.edu/reports/boguslavsky/chapter\\_3.htm](http://www.geo.sunysb.edu/reports/boguslavsky/chapter_3.htm) (accessed 15-08-2008).
- Brusseau, M. L., 2005. Understanding the behaviour of Light Non-Aqueous Phase Liquid (LNAPL) in the subsurface. University of Arizona. [http://www.clu-in.org/conf/tio/lnaplsbasics\\_121205/download.cfm](http://www.clu-in.org/conf/tio/lnaplsbasics_121205/download.cfm) (accessed 8-05-2008).
- Chiang, W-H. and Kinzelbach, W., 1998. Processing Modflow, A Simulation System for Modeling Groundwater Flow and Pollution. Springer-Verlag Berlin and Heidelberg GmbH & Co. K. pp 79.
- Council Directive 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Union, L 327, 0001-0072.
- DERBCAP, 2001. Delaware's ONLINE Risk-Based Corrective Action Program. Delaware Department of Natural Resources and Environmental Control [http://www.dnrec.state.de.us/dnrec2000/divisions/awm/ust/tgm/d\\_cap/Section4.html](http://www.dnrec.state.de.us/dnrec2000/divisions/awm/ust/tgm/d_cap/Section4.html) (accessed 21-08-2008).
- EPA, 2004. Cleaning Up the Nation's Waste Sites: Markets and Technology Trends" Environmental Protection Agency. <http://www.clu-in.org/download/market/2004market.pdf> (accessed 10-06-2007).
- Fraser, M., Barker, J. F., Butler, B., Blaine, F., Joseph, S. and Cooke, C., 2008. Natural attenuation of a plume from an emplaced coal tar creosote source over 14 years. *Journal of Contaminant Hydrology*, 100, 101-115.
- Government of Canada, 1993. Environment Canada and Health Canada, Priority Substances List Assessment Report. Canadian Environmental Protection Act, Minister of Supply and Services Canada,
- (a) [http://www.hc-sc.gc.ca/ewh-semt/alt\\_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/benzene/benzene-eng.pdf](http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/benzene/benzene-eng.pdf) (accessed 07-05-2008).
- (b) [http://www.hc-sc.gc.ca/ewh-semt/alt\\_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/hexachlorobenzene/hexachlorobenzene-eng.pdf](http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/hexachlorobenzene/hexachlorobenzene-eng.pdf) (accessed 07-05-2008).
- (c) [http://www.hc-sc.gc.ca/ewh-semt/alt\\_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/pentachlorobenzene/pentachlorobenzene-eng.pdf](http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/pentachlorobenzene/pentachlorobenzene-eng.pdf) (accessed 07-05-2008).
- (d) [http://www.hc-sc.gc.ca/ewh-semt/alt\\_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/trichlorobenzenes/trichlorobenzenes-eng.pdf](http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/trichlorobenzenes/trichlorobenzenes-eng.pdf) (accessed 07-05-2008).
- Guerin, T. F., Horner, S., McGovern, T., and Davey, B., 2002. An application of permeable reactive barrier technology to petroleum hydrocarbon contaminated groundwater. *Water Research*, 36, 15–24.
- Halford, K. J. and Kuniansky, E. L., 2002. Documentation of Spreadsheets for the Analysis of Aquifer-Test and Slug-Test Data. U.S. Geological Survey, Carson City, Nevada, US. <http://pubs.usgs.gov/of/2002/ofr02197/documentation.pdf> (accessed 19-06-2008).
- Hirano, T., Ishida, T., Oh, K., and Sudo, R., 2007. Biodegradation of chlordane and hexachlorobenzenes in river sediment. *Chemosphere*, 67, 428 - 434.
- Johnson, S.J., Woolhouse, K.J., Prommera, H., Barrya, J. D. A., and Christofib, N., 2003. Contribution of anaerobic microbial activity to natural attenuation of benzene in groundwater. *Engineering Geology*, 70, 343–349.
- Kao, C.M., and Prosser, J., 2001. Evaluation of natural attenuation rate at a gasoline spill. *J. Hazard. Mater.*, 82, 275 – 289.
- Kazumi, J., Caldwell, M. E., Sulfita, J. M., Lovley, D. R. And Young, L.Y., 1997. Anaerobic degradation of benzene in diverse anoxic environments. *Environmental Science and Technology*, 31, 813-818.
- Kirtland, B. C., and Aelion, C. M., 2000. Petroleum mass removal from low permeability sediment using air sparging/soil vapor extraction: impact of continuous or pulsed operation. *Journal of Contaminant Hydrology*, 41, 367-383.
- Madigan, M. T., Martinko, J. M., and Parker, J., 2000. Brock - Biology of Microorganisms. New Jersey: Prentice Hall, (a) – 633-634, (b) - 626, (c) – 619.
- Member Agencies of the Federal Remediation Technologies Roundtable, 1998. Abstracts of Remediation Case Studies, Volume 3. U.S. Environmental Protection Agency. <http://www.fitr.gov/pdf/abstractsvol3.pdf> (accessed 21-09-2008).
- Novotny, N., and Olem, H., 1994. Water quality prevention, identification and management of diffuse pollution. Von Nostrand Reinhold, 395-404.
- Pavlostathis, S., and Prytula, M., 2000. Kinetics of the sequential microbial reductive dechlorination of hexachlorobenzene. *Environmental Science and Technology*, 34, 4001-4009.

- Proposal for a Directive of the European Parliament and of the council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC”, 2006.
- Schwarzenbach, R. P. and Westallt, J., 1981. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies. *Environmental Science and Technology*, 15, 1360 – 1367.
- Spence, M. J., Bottrell, S. H., Thornton, S. H., Richnow, H. H. and Spence, K. H., 2005. Hydrochemical and isotopic effects associated with petroleum fuel biodegradation pathways in a chalk aquifer. *Journal of Contaminant Hydrology*, 79, 67-88.
- Vogt, C., Alfreider, A., Lorbeer, H., Hoffmann, D., Wuensche, L. and Babela, W., 2004. Bioremediation of chlorobenzene-contaminated ground water in an in situ reactor mediated by hydrogen peroxide. *Journal of Contaminant Hydrology*, 68, 121-141.
- Zamfirescu, D., and Grathwohl, P., 2001. Occurrence and attenuation of specific organic compounds in the groundwater plume at a former gasworks site. *Journal of Contaminant Hydrology*, 53, 407 – 427.