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## **Characterization of a contaminant plume and evaluation of decontaminating measures**

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## **Resumo**

A contaminação do freático é um tópico relevante, identificado em Directivas Europeias, que estabelecem a lista de substâncias prioritárias que devem ser eliminadas do ambiente. Os clorobenzenos e o benzeno são objecto deste estudo.

Visual MODFLOW® foi aplicado, a um derrame acidental usando um modelo 3D. A concentração dos contaminantes e o volume da pluma foram calculados, considerando seis cenários, com porosidades entre  $0,1 < \text{porosidade} < 0,6$  e condutividades hidráulicas entre  $5 \times 10^{-7} < k < 5 \times 10^{-4}$  m/s. O volume da pluma diminui com o aumento de porosidade e com a diminuição de k.

Analisou-se a mitigação da pluma por bombagem através da simulação de testes, visando a optimização da rede a implementar e as condições da bombagem. Foram avaliadas a atenuação natural e eficácia de uma barreira reactiva permeável, sendo o sistema de bombagem optimizado, o melhor processo por impedir simultaneamente a expansão e avanço da pluma. O tempo de descontaminação ( $t_D$ ) para cada cenário e por camada de solo é heterogéneo tendo-se obtido valores de 3 a 14 anos.

Uma análise multivariada de porosidade, k e  $t_D$  permite concluir que para porosidades muito baixas ou elevadas, o  $t_D$  aumenta, existindo uma porosidade<sub>óptimo</sub> que combina pressão capilar baixa com movimento vertical reduzido. Para a condutividade hidráulica, os resultados demonstram que para valores muito baixos ou elevados, o tempo necessário é menor, existindo um valor crítico no qual o volume e resiliência da pluma estão em equilíbrio. A análise de sensibilidade ao teor de matéria orgânica do solo demonstra o impacto deste na determinação do volume e contaminação da pluma.

### ***Palavras-chave***

Água subterrânea, Atenuação natural, Barreiras reactivas permeáveis, Benzeno, Bombagem, Clorobenzenos

## **Abstract**

Aquifer is one of the bases for wetlands and rivers flow, representing 95% of freshwater. Aquifer contamination is a serious issue, identified by European Directives, which establish a list of priority substances that must be eliminated from the environment. Chlorobenzenes and benzene are the object of this study.

Visual MODFLOW® was applied to an accidental spill, using a 3D model. Contaminants concentration and plume volume were calculated, considering six scenarios, with porosities between  $0.1 < \text{porosity} < 0.6$  and hydraulic conductivities between  $5 \times 10^{-7} < k < 5 \times 10^{-4}$  m/s. The plume volume decreases with porosity increase and with k decrease.

Plume mitigation was studied through the simulation of different pumping tests, with the purpose to optimize pumping conditions and network. Natural attenuation and permeable reactive barrier efficacy were also applied, showing the optimized pumping system as the best option to prevent, simultaneously, plume expansion and advance. The clean up time ( $t_D$ ) for each pumping scenario and each layer is heterogeneous. Values between 3 and 14 years were obtained for  $t_D$

A multivariate analysis of porosity, k and  $t_D$  demonstrates that for very low or high porosity,  $t_D$  is higher and that there is a porosity<sub>optimal</sub> that combines low capillary pressure with low gravity movement. The results also demonstrate that for very low or high k values,  $t_D$  is lower, existing a k critical value for which plume volume and plume resilience are at equilibrium. Sensitivity analysis of the mass fraction of organic natural carbon has shown a high influence of this parameter in plume volume and contamination.

## ***Keywords***

Benzene, Chlorobenzenes, Groundwater, Natural Attenuation, Permeable hydraulic barrier, Pumping

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# **Nomenclature**

## **Acronyms**

1,2,4-TCB	1,2,4 Trichlorobenzene
BTEX	Benzene, Toluene, Ethyl-benzene and Xylene isomers
CAS	Chemical Abstracts Service
DNAPL	Dense Non-Aqueous Phase Liquid
EQS	Environmental Quality Standards
EU	European Union
GD	Groundwater Directive
HCB	Hexachlorobenzene
LNAPL	Light Non-Aqueous Phase Liquid
MS	Member State
NA	Natural Attenuation
NAPL	Non-Aqueous Phase Liquid
PHS	Priority Hazardous Substances
PRB	Permeable Reactive Barrier
PS	Priority Substances
TEA	Terminal Electron-Acceptors
VOC	Volatile Organic Compounds
WFWD	Water Frame Work Directive

# **1. Introduction**

## **1.1. Objectives**

The objective of this thesis is to study the processes involved in the transport of contaminants, as well as their fate, in a groundwater aquifer, specially the role of natural attenuation (NA). The study will compare the results obtained, for six different types of aquifers using a mathematical model. The efficiency of two remediation processes (pumping system and Permeable Reactive Barrier (PRB)), will be also comparatively evaluated. The time required to remediate each type of aquifer will be estimated for the best technology.

## **1.2. Context**

This thesis started with the need to provide an efficient tool for the evaluation of groundwater resources contamination, since they are the main source of drinking water. Two European Directives were set with the purpose to protect groundwater resources. The Water Frame Work Directive (WFWD)<sup>1</sup>, clearly states, the objectives for the preservation and quality standards of all water resources and the Groundwater Directive<sup>2</sup> (GD), specifies some measures that must be applied to groundwater resources, for European Union (EU).

*“Groundwater is hidden from sight, yet it is an essential part of the water cycle. Over 95% of the world's freshwater, excluding glaciers and ice caps, is found underground. Groundwater provides the steady, base flow of rivers and wetlands. Maintaining its flow and keeping it free from pollution, is vital for surface water ecosystems”* (Water Note 3, 2008). Moreover, three of four European citizens use groundwater supply systems to provide drinking water and it is the main resource for industrial cooling and agricultural irrigation (GD, 2000).

For that reason, to ensure the protection of this resource, the WFWD (2000) establishes, that *“extraction of water from a groundwater body must not exceed the rate at which freshwater replenishes it. If it does, the clean groundwater from that body will become depleted.”*

The groundwater chemical quality standards are set by each Member State (MS), considering the approach and methods stated in GD (2006) taking into account the differences in geology, for instance. A good status can be achieved by complying with EU quality standards for nitrates (present in the Nitrates Directive<sup>3</sup> (1991)) and pesticides. To ensure a high quality of groundwater, the protection of surface waters and terrestrial ecosystems is required due to the connection between them, Figure 4 and 5.

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<sup>1</sup> Directive 2000/60/EC of the European Parliament and of the Council, of 23 October 2000

<sup>2</sup> Directive 2006/118/EC of the European Parliament and of the Council, of 12 December 2006

<sup>3</sup> Directive 91/676/EEC of the European Council, of 12 December 1991

By 2015, 30% of the groundwater resources will be at risk of not accomplishing a good status. Portugal is well placed, among the rest of the MS, since 80% of its groundwater bodies are expected to maintain or achieve a good status, by 2015 (WISE, 2008 (b)).

It is relevant to explain that groundwater body, which *“is a distinct volume of water in an aquifer where there are significant water flows or significant extraction of water”*, for the implementation of the WFWD (2000) *“a section of groundwater subject to significant pollution should be designated separately from neighbouring sections that do not.”* Furthermore distinct groundwater bodies can be considered, not only by the amount of pollution, but also by the human pressure imposed in a specific part of the water resource (WISE, 2008 (a), (b)).

The criteria used to define quality standards must consider the chemical status of groundwater bodies and if there is high naturally-occurring of substances or ions or their indicators, they must be taken into account when defining the quality standards (WFWD,2000).

The GD (2006) also enforces the need to make a distinction between hazardous substances and other pollutants, giving special attention to those present in the Annex II of WFWD (2000).

Concerning monitoring, the GD (2006) considers that *“reliable and comparable methods for groundwater monitoring are an important assessment of groundwater quality and also for choosing the most appropriate measures”*. Research is also identified as an important tool to provide better criteria for ensuring groundwater ecosystem quality and protection.

The WFWD (2000) states the environmental quality standards for water resources. The purpose is to define not only maximum concentration values for each pollutant, but also adapt these values to each type of surface or groundwater area. It also establishes a plan for environmental monitoring of thirty three priority substances (PS), of which fourteen are classified as priority hazardous substances (PHS) (Table 1), imposing 2025 as the target year, to eliminate these contaminants from the environment. The same document identifies these substances as a threat to the aquatic environment, leading to acute and chronic toxicity in aquatic organisms and accumulation in the ecosystem with losses of habitats and biodiversity, as well as threats to human health.

**Table 1** – List of Priority Hazardous Substances (PHS) with CAS number (Chemical Abstracts Service). Source: (Proposal Directive, 2006).

Substance	CAS	PHS	Substance	CAS	PHS
Alachor	15972-60-8		Mercury and its compounds	7439-97-6	X
Anthracene	120-12-7	X	Naphtalene	91-20-3	
Atrazine	1912-24-9		Nickel and its compounds	7440-02-0	
Benzene	71-43-2		Nonylphenol	25154-52-3	X
Brominated diphenylether		X	4-(para)nonylphenol	104-40-5	
Cadmium and its compounds	7440-43-9	X	Octyphenol	1806-26-4	
Chloroalkanes, C <sub>10-13</sub>	85535-84-8	X	(para-tert-octyphenol)	140-66-9	
Chlorfenvinphos	470-90-6		Pentachlorobezene	608-93-5	X
Chlorpyrifos	2921-88-2		Pentachlorophenol	87-86-5	
1,2-dichloroethane	107-06-2		Polyaromatic hydrocarbons		X
Dichloromethane	75-09-2		(Benzo (a) Pyrene)	50-32-8	
Di(2-ethylhexyl)phthalat (DEHP)	117-81-7		(Benzo(b)fluoranthene)	205-99-2	
Diuron	330-54-1		(Benzo (g,h,i)perylene)	191-24-2	
Endosulfan	115-29-7	X	(benzo(k)fluoranthene)	207-08-9	
(Alpha-endosulfan)	959-98-8		(indeno(1,2,3-cd)pyrene)	193-39-5	
Fluoranthene	206-44-0		Simazine	122-34-9	
Hexachlorobenzene	118-74-1	X	Tributyltin compounds	688-73-3	X
Hexachlorobutadiene	87-68-3	X	Tributyltin-cation	36643-28-4	
Hexachlorocyclohexane	608-73-1	X	Trichlorobenzenes	12002-48-1	
(gamma-isomer, Lindane)	58-89-9		(1,2,4-trichlorobenzene)	120-82-1	
Isoproturon	34123-59-6		Trichloromethane(chloroform)	67-66-3	
Lead and its compounds	7439-92-1		Trifluarin	1582-09-8	

For these substances it was established Environmental Quality Standards (EQS), which are listed in section 3.1, for the contaminants under study, based on both acute and chronic effects data, with the purpose of preventing chemical pollution in the short and long term (WFWD, 2000). So, there is a concerted effort to study the behaviour of these contaminants (migration rates, biodegrading paths) in water resources, to make an inventory of emission, discharges and losses, and to develop new treatment techniques (WFWD, 2000). The inventory must be done each year, in each river basin and must be compared to the reference period. In the case of PS, the concentration of the reference period is estimated as the average of the concentration of each pollutant, in each river basin, of the years 2007, 2008 and 2009 (WFWD, 2000). Despite the fact of 2025 was set as the target year, to eliminate these pollutants from the environment, by 2015 all water resources should achieve a good status. This implies that by the end of the 2009, every country should have not only identified the contaminated groundwater resources, but also have an overview of the technologies that must be applied in order to treat

and recover that resource, to guaranty that in the time frame of 6 years the groundwater quality has improved.

The WFWD (2000) specifies three types of monitoring, which are emphasized in the:

- **“Long-term surveillance monitoring** – which provides a broad understanding of the health of water bodies and tracks slow changes in trends such as those resulting from climate change.
- **Operational monitoring** – which focuses on water bodies which do not meet good status and on the main pressures they face – pollution where this is the main problem, water flow where extraction creates risks. Operational monitoring thus tracks the effectiveness of investments and other measures taken to improve the status of water bodies.
- **Investigative monitoring** which could also be undertaken by MS when further information is needed about surface water bodies that cannot be obtained via operational monitoring, including information on accidents.”

Besides the three types of monitoring, stated above, MS are obliged to achieve a more thorough analysis in order to protect drinking water or natural habitats and species (WISE, 2008 (c)).

The same monitoring principles must be applied to groundwater resources and an interaction between groundwater and surface water monitoring can be helpful, with the aim to protect each resource from contamination, since they are connected by the water cycle.

By March 2008, Europe had forty eight percent of the 105000 monitoring stations, dedicated to groundwater surveillance, evidencing the major effort in protecting this resource, since it is considered that groundwater resources are the key to reach the sustainability of resources. In Portugal there are at least 843 monitoring wells, belonging to a national monitoring net and the data obtained for each well can be followed on-line. Yet, it can only be monitored the groundwater level, which is considerably scarce, to monitor PS. (SNIRH, 2008).

Given the context of groundwater protection and the target dates that must be accomplished, it is urgent to identify:

- the contributors for groundwater contamination;
- the contaminants nature and hazardousness;
- mechanisms that allow the contamination movement and spreading;
- the parameters that influence the same mechanisms;
- treatment technologies that help to remediate the contamination.

### **1.3. Scope**

The scope of the present work is to identify, for a defined scenario, the main contributors to the depletion of pollutants in groundwater. The study of contaminants behaviour

in groundwater and in soil is very complex, since any contaminant experiences three types of mechanisms: transport, degradation and sorption, which are influenced by numerous factors.

Consequently this work lays, exclusively, on a particular family of pollutants, which are addressed in the list of priority substances: benzene and its derivatives (Table 2).

**Table 2** - List of the Priority Hazardous Substances object of this study. Adapted from Proposal Directive, 2006.

Substance	CAS	PHS
Benzene	71-43-2	
Hexachlorobenzene (HCB)	118-74-1	X
Pentachlorobezene	608-93-5	X
Trichlorobenzenes	12002-48-1	
1,2,4-trichlorobenzene (1,2,4-TCB)	120-82-1	

The production of these compounds crosses Europe. Benzene is produced in Belgium, Finland, France, Germany, Italy, Netherlands, Portugal, Spain, Sweden and United Kingdom. HCB is produced in Germany. There is not a list of the producers of pentachlorobenzene and 1,3,5-trichlorobenzene (1,3,5-TCB), in Europe. Trichlorobenzene is a high volume chemical produced in France and Germany. It comprises several isomers being 1,2,4-trichlorobenzene (1,2,4-TCB) the principal one (80-100%) (ESIS, 2000 (c)). 1,2,4-trichlorobenzene has an atmospheric half-life of 30 days and half life ranging from several weeks to a few months in soil and water. Bioaccumulation in aquatic life forms is high (EPA, 2006 (c))

Annually, over one million tonnes, of benzene, are produced, in Europe. Benzene is defined as a hazardous substance, since it is highly flammable, carcinogenic, and it is toxic through inhalation, contact with skin and if swallowed. In industry, benzene is used to produce basic chemicals, polymers, synthesise other chemicals, fuel, paints, lacquers and varnish. Moreover, it can also be used as fuel additive, pharmaceutical, intermediate, solvent, laboratory chemical, lubricant, etc. (Proposal Directive, 2006) (EPA, 2006 (a)).

The major use of 1,2,4-TCB is as a dye carrier. It is also used to make herbicides and other organic chemicals; as a solvent; in wood preservatives and in abrasives (ESIS, 2000 (c)). It was once used as a soil treatment for termite control.

HCB was used as a fungicide, until 1960s in United States and is still used in China, as well as in fireworks, ammunitions and synthetic rubber production, but the production ended in 1982 (Wu, *et al.*, 1997) (EPA, 2006 (b)) (Pavlostathis and Prytula, 2000). HCB is also, formed as a by-product during the manufacture of solvents, other chlorine-containing compounds and pesticides. Small amounts of HCB are produced during the incineration of municipal waste and are also found in the waste streams of Chloro-Alkali and wood-preserving plants (Hirano, *et al.*,

2007). HCB is known to be toxic, carcinogenic and is ecotoxic, since its bioaccumulation in aquatic species is high (ESIS, 2006 (b)).

Compounds like pentachlorobenzene, trichlorobenzene, 1,3,5-trichlorobenzene and 1,2,4-TCB are, also, by-products of the dechlorination mechanism of HCB in soil when its degradation process occurs by anaerobic via, Figure 3 (Kao and Prosser, 2001). The remediation of aromatic compounds in a subsurface water resource can be difficult, since these compounds tend to resist to biodegradation processes and when it happens, the metabolites produced, can be as hazardous as the initial compound.

To understand the fate of these contaminants, it is necessary to study its biodegradation paths and the remediation technologies that can enhance degradation kinetics. For that purpose, a full knowledge of the physical, chemical and biological interactions between soil, groundwater and contaminants is necessary, as they are the basis to establish models of transport and transformation (Table 3) (Kossom and Byrne, 1995).

**Table 3** – Information needed for prediction of organic contaminant movement and transformation in groundwater. Source: (Azadpour-Keeley, *et al.*,1999)

<b>BIOLOGICAL</b>	<b>Groundwater characteristics</b>	<b>Aquifer characteristics</b>	<b>Contaminant characteristics</b>
	Ionic strength pH Temperature Nutrients Substrate O <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> Macro (P, S, N) Trace Organism	Grain size Active bacteria number Monod rate-constant	Potential degradation products Toxicity Concentration
<b>CHEMICAL</b>	<b>Groundwater characteristics</b>	<b>Aquifer characteristics</b>	<b>Contaminant characteristics</b>
	Ionic strength pH Temperature O <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> Toxicants	Potential catalysts Metals, clays	Potential degradation products Concentration
<b>HYDRAULIC</b>	<b>Contamination source</b>	<b>Wells</b>	<b>Hydrogeologic environment</b>
	Location Amount Rate released	Location Amount Depth Pump rates	Extend of aquifer and aquitard Characteristics of aquifer hydraulic gradient Groundwater flow-rate
<b>SORPTION</b>	<b>Distribution coefficient</b>	<b>Sediment characteristics</b>	<b>Contaminant characteristics</b>
	Concentration Characteristics	Organic carbon content Clay content	Octanol/water partition coefficient Solubility

In the next chapters the degradation and transport mechanisms will be addressed.

## **1.4. Non-Aqueous Phase Liquid (NAPL) compounds**

The Non-Aqueous Phase Liquid (NAPL) compounds have none or little solubility in water (see Annex A, Table A.1), which means that they can create its own liquid phase, coexisting with water, in the soil pores. These compounds can be divided in two types:

- LNAPL – Light Non-Aqueous Phase Liquid compounds, which are lighter than water, such as benzene;
- DNAPL – Dense Non-Aqueous Phase Liquid compounds, which are heavier than water, such as HCB, pentachlorobenzene, trichlorobenzenes, 1,3,5-trichlorobenzene and 1,2,4-TCB.

The densities values are presented in Table A.1, in Annex A. Despite some concepts that can be applied to DNAPL and LNAPL, their behaviour will be very different when they reach the aquifer this subject will be further developed in section 2.1 and 2.2.

## **1.5. Biodegradation paths**

NA, also referred as natural assimilation, recuperation or passive remediation, 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. The more frequent chemical reactions are ion exchange, complexation and abiotic transformation. The biological processes include aerobic and anaerobic biodegradation, plant and animal uptake.

Whereas sorption processes reduce dissolved contaminant concentrations and retard contaminant migration relative to groundwater, biodegradation reduces total contaminant mass in the groundwater system. A plume is considered as a steady plume, when the rate of contaminant biodegradation in the groundwater equals its load rate. When the biodegradation rate is in excess, the plume undergoes a shrinking process. For this reason, it is important to understand the mechanisms and controls of biodegradation paths, in order to assess the aquifer capacity for NA (Spence, *et al.*, 2005).

NA demands in depth knowledge of the behaviour of each contaminant, due to its hazardous properties, to be considered an alternative to manage the risk associated with groundwater contamination. (Table A.1, Annex A)

In order to determine whether NA is occurring, a monitoring plan must be developed. To proceed with the monitoring, water must be sampled and some parameters must be analysed, at the time of the sample collection, such as: pH, redox potential, dissolved oxygen, electrical conductivity and temperature. In addition, the hydrocarbons (when a contamination occurs),

anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $NO_2^-$  and  $SO_4^{2-}$ ) and dissolved gases ( $CO_2$  and  $CH_4$ ) must be analysed with a method already stated, such as EPA's method (Azadpour-Keeley, et al., 1999).

The basis of NA states on the fact that the partition of chemicals into the aqueous phase reaches equilibrium with the biological transformation processes, at an acceptable distance and time from the source. (Azadpour-Keeley, et al., 1999) The contaminants biodegradation involves the production and the utilization of specific enzymes. Besides microbial degradation hydrogeochemical degradation can occur, when the environmental conditions allow the chemical reactions to take place. Nevertheless, the reactions are based in complex oxidation/reduction reactions and the reduced electrons or equivalent have to be transferred to a Terminal Electron-Acceptor (TEA). Numerous scientific publications support that biodegradation consists in series of microbial-mediated respiration reactions using different TEA in the aquifer. The sequence on which TEA are used is dictated by their relative energy yields per unit of organic carbon oxidized in the following order  $O_2$ ,  $NO_3^-$ , Mn(IV), Fe(III) and  $SO_4^{2-}$ , as shown in Table 4. However, the contribution of each TEA depends on its availability and on the ability of the indigenous microorganisms to use it (Spence, et al., 2005).

The bacteria involved in NA can be divided in three groups:

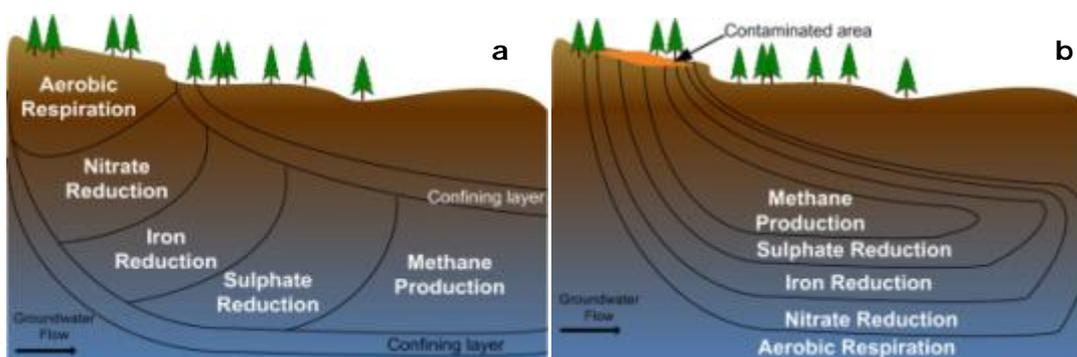
- Aerobes – which use only oxygen molecules as TEA
- Facultative aerobes/anaerobes – they use molecular oxygen, but in its absence or in very low concentrations, they are able to use nitrate, manganese and iron oxides;
- Anaerobes – which are unable to use oxygen, since it is toxic for them. Can use all the TEA described in Table 4, but the most common are sulphate and carbon dioxide.

**Table 4** – Bacteria aerobic and anaerobic pathway for the degradation of benzene. The electron acceptors are shown in bold. Adapted from Spence, et al., 2005 and Kazumi, et al., 1997.

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

The distribution of the TEA reactions in an aquifer is dictated by several factors, including the relative abundance of the various electron acceptors, the amount and availability of the electron supply and the nature and rate of groundwater flow.

The amount of oxygen decreases with the depth of the soil. In the saturated aquifer zone, there is no interaction with air, leading to small or null amounts of oxygen. When an aquifer is highly contaminated the amount of oxygen, in the inner plume tends to vanish quite rapidly. Consequently, the aerobic degradation only takes place in the upper zone of the aquifer, or in the boundaries of the contamination plume, while in the plume inner zone, the anaerobic pathways are responsible for the degradation process (Corseuil, *et al.*, 1997) (Kao and Prosser, 2001) (Baldwin, *et al.*, 2008) (Hurst, *et al.*, 1997). Nevertheless, two types of distributions can be presented, according to the scale of energy yield, as shown in Figure 1.



**Figure 1** – Idealized diagrams of sequential succession of electron-accepting reactions. In a) the limiting factor for natural attenuation are the electron donors. In b) the limiting factor are the electron acceptors. Adapted from Hurst, *et al.*, 1997.

In Figure 1 a) it can be observed the sequential reaction occurring when the electron donor is the limiting factor. In this case, the amount of organic matter is not abundant, which will limit the flow of carbon and energy through the microbial food chain. The sequence of reactions occurs according to Table 4 and the thickness of each reaction zone, according with the direction of the groundwater, depends on the amount of TEA present in that area. Figure 1 b) reflects plume conditions when electron acceptor is the limiting factor. This is the case when a large contamination with organic compounds takes place. The available TEA are rapidly consumed creating a methanogenic zone. As the organic compounds are transported and diluted in the groundwater a point is reached where the TEA can be present and the electron-acceptor reactions can take place. (Hurst, *et al.*, 1997)

Despite the similitude between Figure 1 b) and a situation of groundwater contamination, other factors influence the plume giving it a different shape. At first the soil is not homogeneous, the TEA are not equally distributed in the soil, hydrogeochemical factors can induce some reactions, or retard others, and geochemical gradients may arise.

If a contaminant is the only source of carbon and energy, the pH, redox potential and temperature conditions have to be between certain limits, so the degradation can take place.

Despite limiting factors such as hydrogeologic complexity, microbial toxicity – induced by the contaminants, chemical, biological and physical factors – most organic compounds can be degraded in the soil, by the indigenous microorganisms.

Small amounts of petroleum hydrocarbons, such as benzene, released into aquifers, can lead to concentrations of dissolved hydrocarbons far in excess of regulatory limits. In addition, conventional approaches to groundwater remediation can be extremely costly, especially when one considers small or diffuse groundwater contamination plumes (Spence, *et al.*, 2005).

Besides the high amount of scientific publications found concerning benzene, the study of its biodegradation, in soil, is highly connected with the other components of BTEX (Benzene, Toluene, Ethyl-benzene and Xylene isomers), that represent an important fraction of contamination from a gasoline spill. So, the degradation rates reported, for benzene, are measured in the presence of other contaminants and, since benzene usually degrades after the toluene and one of the xylene isomers degradation, its degradation rate is slower than if benzene was the only contaminant (Kao and Prosser, 2001) (Baun, *et al.*, 2003) (Zamfirescu and Grathwohl, 2001). For this reason, present study will only take into account biodegradation rates that consider the contaminants present in this study, by themselves or all together. The scientific publications that were consulted during the course of this study are present in Table 5.

### **1.5.1. Aerobic path**

For the most part of bacteria, utilization of aliphatic hydrocarbons is an aerobic process: in the absence of oxygen, saturated hydrocarbons are virtually unaffected by microorganisms (Madigan, *et al.*, 2000 (a)).

In order to saturate aliphatic hydrocarbon, the initial step involves molecular oxygen, as a reactant, being incorporated into the oxidized hydrocarbon. The reaction can be carried out by a monooxygenase or dioxygenase. The end product of the reaction sequence is acetyl-CoA, or pyruvate that is later transformed in acetyl-CoA (Madigan, *et al.*, 2000 (a)). *Pseudomonas sp.* have been identified as, bacteria that are capable of degrade, aerobically, benzene and chlorobenzenes after oxygenation of the compounds (Werlen, *et al.*, 1996).

The aerobic degradation of chlorobenzenes and benzene leads to the formation of catechol that is less hazardous<sup>4</sup>. Single-ring compounds, such as the compounds subject of the present study, are referred as starting substrates, because the oxidative catabolism only starts after they are converted to simpler forms. Catechol may then degrade to compounds that can enter the Cytric Acid Cycle, such as succinate, acetyl-CoA and pyruvate (Aronson and Howard, 1997). The benzene degradation process is exemplified in Figure 2.

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<sup>4</sup> The concentration limit to be harmless is 20%, while for benzene is 0.1% and for the other chlorobenzenes is 0.25% (ESIS, 2000 (a))

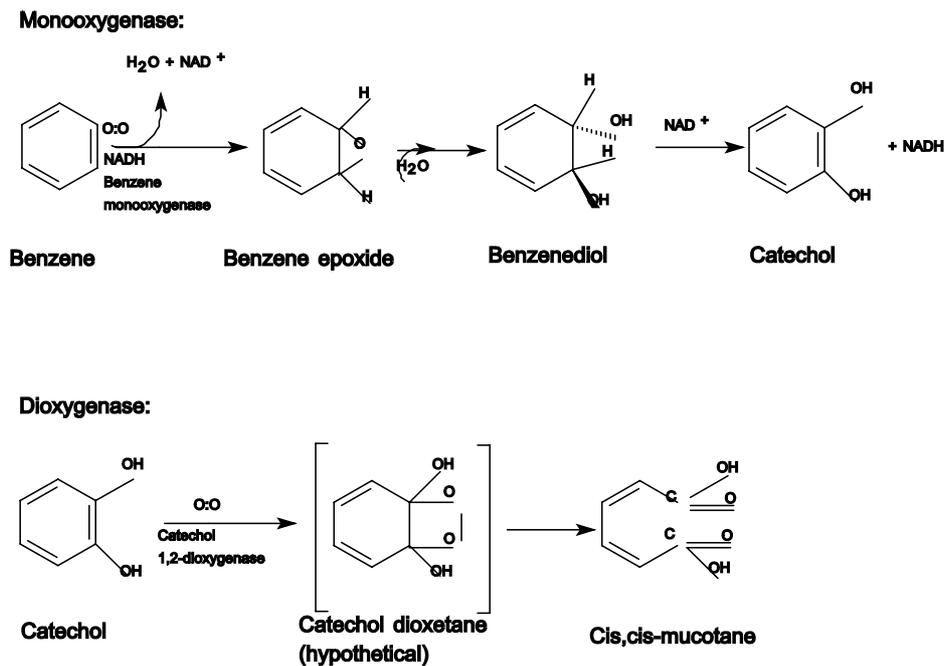
**Table 5** - Scientific publications consulted during the course of this study.

Author	Date	Subject	Method	Results
Mascolo <i>et al.</i>	2007	Advanced Oxidation Process (AOP)	The tests were realised in hard water. (AOP) – medium pressure UV, UV/H <sub>2</sub> O <sub>2</sub> , and UV/TiO <sub>2</sub>	Considering 1 ppm of benzene as initial concentration, 100% removal can be achieved for all processes, with exception of UV. Best technique was UV/ H <sub>2</sub> O <sub>2</sub>
Kao <i>et al.</i>	2007	Air sparging	Application of air sparging in a soil manly composed by sands and silty sands	Benzene concentration reduces, with biosparging, from 10 mg/l to 0.1 in one year. The technique induces an increase in heterotrophs, decrease in anaerobes, but methanogens increase.
Murray <i>et al.</i>	2000		The soil was mainly silty sands	Benzene aerobic degradation rate of 0.272 kg/day
Kirtland and Aelion	1999		Application of the techniques in sand, coarse and clay soils.	Silt and clay soils are not recommended for AS/SVE, since the mass removal decreases with the elevation of the groundwater level.
Johnston <i>et al.</i>	1998		Study of the importance of biodegradation and volatilisation in Aeolian and littoral calcareous sand	Elimination in 16 days ( initial concentration (20 mg/l) another well(always a residue of concentration) Estimated of 135 g of benzene volatilise Degradation order is a crescent scale of Henry's law constant
Küster <i>et al.</i>	2004	Biomonitoring	The use of biomonitors in a Quaternary aquifer	States the advantages of real monitoring, by bioluminescence using <i>Vibrio fischeri</i> .
Davis <i>et al.</i>	1998	Bioremediation	Sulphate reduction	The differences in the groundwater contents (low inorganic contents except HCO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , and H <sub>2</sub> S and negative Eh) between uncontaminated and contaminated. Sometimes de concentration increases due the liberation of benzene that was adsorbed, when the water table fluctuates. The half time life was between 120 to 230 days.
Gersberg <i>et al.</i>	1994		Adding nutrients with potassium nitrate and ammonium polyphosphate. Infiltration of the groundwater in the system again	Soil remediated after 3 months, with 83% benzene removal. The Bacteria <i>Ceriodaphnia dubia</i> was identified as the main actor of the bioremediation process.
Kommalapati <i>et al.</i>	1997	Dispersion	Removing by dispersion in sandy loam with clay	The solubility increases with the addition of natural surfactant (90%) and increases the desorption (only 10% remains due to irreversible adsorption) increases the long term cumulative removal
Booty <i>et al.</i>	1994	Modelling		Properties good scheme of transport of contaminants
Prince <i>et al.</i>	2008	Natural attenuation		No aerobic degradation of HCB
Adebusoye <i>et al.</i>	2007		Soil with lack o mineral nutrients	Proved aerobic degradation of chlorobenzenes
Baldwin <i>et al.</i>	2007		Soil composition: Silty clay, fine to medium sand, gravel	Benzene was suffered aerobic degradation, but it was limited by the high concentrations. In 2 years the concentration increases from 5 to 1700 µg/L. The author use Mann-Kendall analysis

Author	Date	Subject	Method	Results
Dou <i>et al.</i>	2007	Natural attenuation		Lower degradation rates in the presence of sulphates than in the presence of nitrates. The use of substrates increases the degradation rate, till a maximum. The nitrates are reduced to nitrites.
Junfeng <i>et al.</i>	2007		The soil is composed by silty clay soil. NA can be enhanced by bioaugmentation	Anaerobic BTEX-degrading Bacteria can reach in 60 days to none detectable levels of benzene, with an initial concentration of 100 mg/l. Using other hydrocarbons as coadjutants the degradation rate decreases. The rates can be enhanced with sodium acetate or with nitrate.
Matamoros <i>et al.</i>	2007		Biodegradation and plant uptake in gravel	90% removed of pentachlorobenzene in 21 days
Mckelvie <i>et al.</i>	2007		Biodegradation in the presence of ethanol	The soil was thin sand layers with less permeable silts and clayey silts. Ethanol enhanced benzene degradation
Wang <i>et al.</i>	2007			58% removal in 30 days in a stabilized Bacteria media
Hirano <i>et al.</i>	2007		Study in sediments	HCB is highly hydrophobic and strongly associated with the organic carbon, clay and silt that comprise the anaerobic regions of sediments. The degradation rates after 20 days improved to 59.4% from 80% in none sterile soil, considering a initial concentration of 0.5 mg.
McKelvie <i>et al.</i>	2005			No biodegradation of benzene. The soils are alluvial sediments (silty sand and gravel).
Spence <i>et al.</i>	2005		The aquifer was composed by deep fractured bedrocks aquifer	Proved aerobic and Anaerobic degradation (tested in the presence of sulphate and nitrate). Benzene was oxidized in nitrate presence, after all the TEX was exhausted
Borghini <i>et al.</i>	2004			Proves that there is a correlation between temperature and concentration of HCB and pentachlorobenzene
Baun, A. <i>et al.</i>	2003		Chloride was used as a tracer, in a field experience that lasted 10 years	Anaerobic conditions, within the first 150 m of the plume, induced organic compounds degradation, with exception for benzene
Johnson, S.J., <i>et al.</i>	2003		Review of anaerobic degradation and TEA used	Two strains of <i>Dechloromonas</i> are able to degrade benzene using nitrate as the only TEA. Proved degradation on iron, sulphate presence, but combined with methanogenesis
Lovanh <i>et al.</i>	2002		Effects of ethanol in biodegradation rates	At low concentrations of ethanol the inhibition can be offset by the use of fortuitous growth of specific degraders of ethanol. <i>P. putida</i> (mt-2 and F1), <i>P. Mendocina</i> (KR1), <i>Burkholderia pickettii</i> (PKO1)
Bockelmann <i>et al.</i>	2001		shallow Quaternary gravels with locally embedded sand, silt and loamy clay	
Chen <i>et al.</i>	2001		review	There have been reports of HCB dechlorination to monochlorobenzene (MCB) or even to benzene by adapted mixed cultures (Ramanand <i>et al.</i> , 1993; Nowak <i>et al.</i> , 1996). lactate enhanced dechlorination more than pyruvate or acetate Similar dechlorination rates were observed under both conditions during initial culture transfers (days 12 to 24). In second (day 24 to day 36) and third (day 36 to day 50) transferred cultures, treatment with lactate resulted in a longer lag phase. Better results in a environment rich in nitrates

Author	Date	Subject	Method	Results											
Zamfirescu and Grathwohl	2001	Natural attenuation	The aquifer was a quaternary aquifer (sand and gravel)	Only anaerobic degradation and benzene has a half life that corresponds in distance to 20 m from the plume source											
Kao and Prosser	2000		The soil composition was of holocene sands and humic soils and thick-bedded, light-coloured sands and clays, with local clay-clast conglomerates	Methanogenesis was the dominant degradation path (within plume). At the edges of the plume, the degradation was mainly by aerobic path. The benzene degradation was afterwards toluene and xylene and of approximately 88 mg/day. The mass balance of the contaminants is present											
Pavlostathis <i>et al.</i>	2000		Evaluation of HCB degradation in sediments with enriched culture	Methanogenesis anaerobic degradation. The application of the Michaelis-Menten equation shows that low presence of 1,2,3,4 tetra and 1,2,3 tri and states that dechlorination is the dominant process, of chlorobenzene degradation											
Schirmer <i>et al.</i>	1998			First order aerobic degradation rate of 0.03/day It was needed 40.3 years to benzene reach 5 µg/l by dispersion and with degradation only 3.3 years											
Corseuil <i>et al.</i>	1997		Degradation pathways in sandy soils	After 10 days the benzene concentration was none, considering an initial concentration of 25mg/l, in the presence of ethanol. With more than 300 mg/l the environment was anoxic before the degradation of benzene could even start. Without amends with inorganic nutrients the efficiency is lower. The only pathway proved to happen was aerobic degradation.											
Polese	1997	Sampling preparation	Extracting for sampling from sand soils.	The method recovers between 89-100% with a fortification level of 0.5. when the fortification levels rises to 20 the recovery decreases for 86 to 93%. Using n-hexane and dichloromethane to extract Study points out that there is a proportion between the concentration and the distance to the dumping site											
Lee	2007	Sorption		Modelling alcohol with BTEX as they are cosolvent (miscible with NAPL and with water) and up to 30% of the benzene is in the cosolvent phase.											
Nascimento <i>et al.</i>	2004		Contaminant distribution in sandy soils	The vertical and horizontal distribution patterns indicate that the soil waters acts as a vector of the pollutant throughout the landscape. The dispersion of HCB is probably a result of complexation and transport with dissolved organic matter.											
Dentel <i>et al.</i>	1998		Sorption in clay soils	1,2,4-TCB has no tendency to sorption											
Santos <i>et al.</i>	1997		Sorption in sandy soil	Water is the better element to desorbs chlorobenzenes											
Gabelish <i>et al.</i>	1996		Simulation	Extractant for HCB and tetrachlorobenzene is hexane											
Wu <i>et al.</i>	1996		Identifying techniques applied to transition soil	Identification techniques to HCB and pentachlorobenzene											
Gray <i>et al.</i>	1994		Study of partition coefficients in loamy sand and silty loamy	Results for partition coefficients <table border="1" data-bbox="1025 1219 1839 1335"> <thead> <tr> <th>Contaminant</th> <th>Loamy sand</th> <th>Silty loam</th> </tr> </thead> <tbody> <tr> <td>Tetrachlorobenzene</td> <td>1.9 ± 0.89</td> <td>3.5 ± 1.5</td> </tr> <tr> <td>Trichlorobenzene</td> <td>2.0 ± 0.90</td> <td>3.6 ± 1.2</td> </tr> <tr> <td>Pentachlorobenzene</td> <td>1.7 ± 0.75</td> <td>2.5 ± 1.1</td> </tr> </tbody> </table>	Contaminant	Loamy sand	Silty loam	Tetrachlorobenzene	1.9 ± 0.89	3.5 ± 1.5	Trichlorobenzene	2.0 ± 0.90	3.6 ± 1.2	Pentachlorobenzene	1.7 ± 0.75
Contaminant	Loamy sand	Silty loam													
Tetrachlorobenzene	1.9 ± 0.89	3.5 ± 1.5													
Trichlorobenzene	2.0 ± 0.90	3.6 ± 1.2													
Pentachlorobenzene	1.7 ± 0.75	2.5 ± 1.1													

<b>Author</b>	<b>Date</b>	<b>Subject/Results</b>
Guerin, <i>et al.</i>	2001	Study with MODFLOW <sup>®</sup> , that evaluates the efficiency of the implementation of funnel and gate technology. Not specific for benzene but good to the application in the model, with specific changes
Booji <i>et al.</i>	2000	Semi permeable membrane devices to study concentration proves that HCB over saturates rapidly in atmosphere (8 times higher than in soil) - high volatilisation.
Zhang <i>et al.</i>	2002	HCB model predicting fate and transport. Prediction points that 78% of all HCB is adsorbed into soil



**Figure 2** – Hydroxylation of benzene to catechol by a monooxygenase and cleavage of catechol to *cis,cis*-muconate by a dioxygenase. Source: (Madigan, *et al.*, 2000 (a)).

Halophilic and halotolerant bacteria, in larger communities in which *Marinobacter spp.* was the dominant bacteria, showed very good results, using only benzene as an energy source (Nicholson and Fathepure, 2003). Nevertheless, high amounts of contaminants may inhibit aerobic degradation, as can be also toxic to microorganisms present in the soil (Baldwin, *et al.*, 2008).

### 1.5.2. Anaerobic path

Chlorobenzene anoxic degradation can also occur, but the catabolism occurs by anaerobic microbial consortia to methanogenesis (Madigan, *et al.*, 2000 (b)).

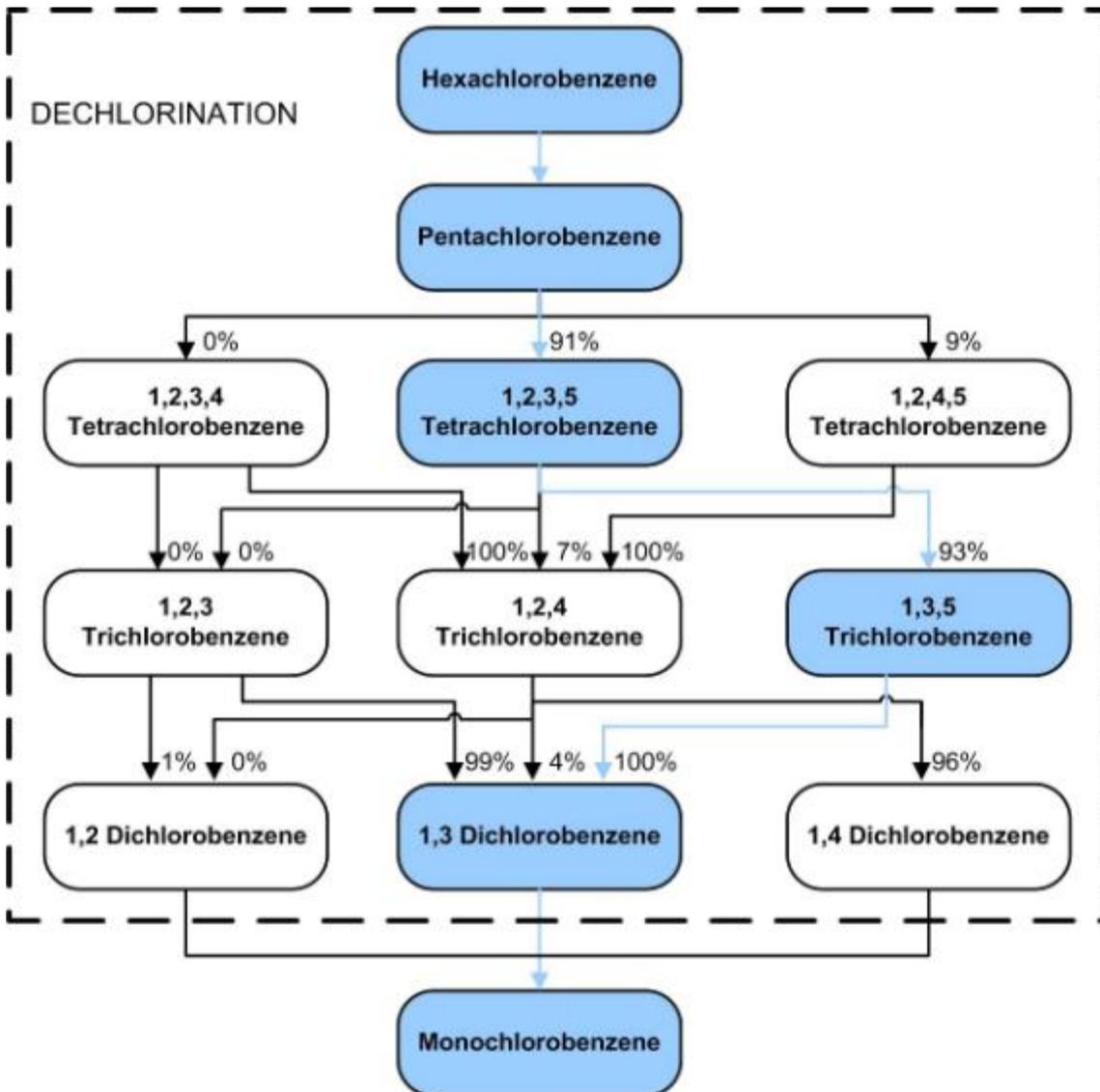
On what concerns the chlorobenzenes, under anaerobic conditions, they tend to suffer reductive dechlorination, a process by which the chlorobenzenes will lose a Chlorine, which will be substituted by a Hydrogen atom. Since it is a decay chain reaction, each time there is a leak of HCB, is possible to have pentachlorobenzene, tetrachlorobenzene and trichlorobenzenes (Figure 3) (Pavlostathis and Prytula, 2000). Actually, degradation of significant chlorinated pesticide, such as, HCB, occurs in anoxic environment, since it is linked to dechlorination and the sub-products formed are less toxic, than the original chlorinated molecule (Madigan *et al.*, 2000(b)). In Table 6 some of the bacteria that are able to degrade this type of compounds by an anoxic or anaerobic path are listed.

It has been showed that no single microbial species are able to degrade completely the compound under anaerobic conditions, although stable benzene-degrading enrichment cultures

were known. The only organisms known to degrade benzene anaerobically are bacteria, but it is suggested that the currently poorly studied anaerobic fungi might prove to be involved (Johnson, *et al.*, 2003). When no other electron acceptors are present, benzene can degrade to CO<sub>2</sub> and methane. Yet, in this situation, the total mineralisation of benzene is not possible. In the absence of another TEA this form of degradation might take an important role in limiting the extent of the contaminant plume (Johnson, *et al.*, 2003). Benzene degradation via benzoate was proved (Chaudhuri and Wiesmann, 1995). A sulphate-reducing consortium was found to remain relatively complex despite the culture's long exposure to benzene as the only carbon and energy source and repeated dilutions of the original enrichment.

**Table 6** – Families of Bacteria that are able to degrade chlorinated compounds. Source: (Madigan, *et al.*, 2000 (b)).

Bacteria	Electron donors
<i>Dehalobacter</i>	H <sub>2</sub>
<i>Desulfomonile</i>	H <sub>2</sub> , formate, pyruvate, lactate and benzoate
<i>Desulfitobacterium</i>	H <sub>2</sub> , formate, pyruvate and lactate
<i>Dehalospirillum</i>	H <sub>2</sub> , formate, pyruvate, lactate and benzoate
<i>Dehalococcoides</i>	H <sub>2</sub> and lactate
<i>Dehalobacterium</i>	Dichloromethane, lactate, ethanol and glycerol



**Figure 3** – Microbial dechlorination pathway of hexachlorobenzene under anaerobic conditions. Source: (Pavlostathis and Prytula, 2000).

An important aspect to take into account in anoxic degradation is the presence of humic substances. They are complex of high-molecular-weight organic materials, derived from the plant, animal and microorganisms remains and are generally resistant to microbial metabolism. Although an exact redox potential cannot be measured, because of its complex composition, model low-molecular-weight compounds, such as fulvic acid, have positive redox potential, showing that they are good electron acceptors (Madigan, *et al.*, 2000(c)).

## 1.6. Remediation technologies

There are numerous technologies that can be used to clean-up soils and groundwater from contamination and in each stage, of the contaminant removal, the best technology that can be applied can vary. The technologies can focus on the source of the contamination or work

throughout the plume, can contain or remove the contamination and can be done *in-situ* or *ex-situ*, as can be seen in Table 7. 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).

As a complementary measure, surfactant solutions can be added to soil, in order to enhance HCB solubility in water. This action improves contaminant recovery from groundwater by pumping systems and by natural attenuation. The use of natural surfactants is preferred, since the fate of some commercial surfactants is still unknown (Kommolapati, *et al.*, 1997).

**Table 7** – Treatment technologies to decontaminate groundwater. Source: (EPA, 2004).

<p><b>Source Control Treatment Technologies</b></p> <ul style="list-style-type: none"> <li>• Bioremediation</li> <li>• Chemical Treatment</li> <li>• Electrokinetics</li> <li>• Flushing</li> <li>• Incineration (on-site and off-site)</li> <li>• Mechanical Soil Aeration</li> <li>• Multi-Phase Extraction</li> <li>• Neutralization</li> <li>• Open Burn (OB) and Open Detonation (OD)</li> <li>• Physical Separation</li> <li>• Phytoremediation</li> <li>• Soil Vapor Extraction</li> <li>• Soil Washing</li> <li>• Solidification/Stabilization</li> <li>• Solvent Extraction</li> <li>• Thermal Desorption</li> <li>• Thermally Enhanced Recovery</li> <li>• Vitrification</li> </ul>	<p><b>Pump-and-treat Technologies (Ex-Situ Treatment)</b></p> <ul style="list-style-type: none"> <li>• Adsorption</li> <li>• Air Stripping (also a source control technology)</li> <li>• Bioremediation</li> <li>• Chemical Treatment (also a source control technology)</li> <li>• Filtration</li> <li>• Ion Exchange</li> <li>• Metals Precipitation</li> <li>• Membrane Filtration</li> </ul>
<p><b>In-situ Groundwater Treatment Technologies</b></p> <ul style="list-style-type: none"> <li>• Air Sparging</li> <li>• Bioremediation (also a source control technology)</li> <li>• Chemical Treatment (also a source control Technology)</li> <li>• Electrokinetics (also a source control technology)</li> <li>• Flushing (also a source control Technology)</li> <li>• In-well Air Stripping</li> <li>• Multi-phase Extraction</li> <li>• Permeable Reactive Barriers (PRB)</li> <li>• Phytoremediation (also a source control technology)</li> <li>• Thermally Enhanced Recovery (also a source control technology)</li> </ul>	<p><b>Monitored Natural Attenuation for Groundwater</b></p> <p>• Includes a variety of physical, chemical, or biological processes, such as biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.</p> <hr/> <p><b>In-situ Groundwater Containment</b></p> <ul style="list-style-type: none"> <li>• Vertical engineered subsurface impermeable barrier</li> <li>• Hydraulic Barrier created by pumping</li> </ul> <hr/> <p><b>Other Groundwater</b></p> <ul style="list-style-type: none"> <li>• Groundwater Use Restrictions</li> <li>• Alternative Water Supply</li> <li>• Groundwater remedies that do not fall into above categories</li> </ul>

This study will focus on part of the treatments listed above that can be applied in-situ: air sparging, bioremediation and permeable hydraulic barrier.

### 1.6.1. Air sparging

Air sparging consists on the application of the same concepts that are in the basis of air stripping, but it is an *in-situ* technique.

In air stripping the water containing contaminants is distributed at the column's top and flows downward through the packing material. Simultaneously, the air is introduced in a counter current flow, at the bottom of the column and flowing upward through the packing. The packing extends the surface contact area between the two fluids and retards the flow of both fluids, increasing the contact time. During the contact the contaminants move from water to the air. The water leaves the column with less or almost none contaminants and the air is then subject of another treatment to meet emissions levels limits (CPEO, 2002).

To apply this technique to groundwater remediation, it is necessary to create a complementary system to pump the water from the aquifer to the treatment facility (Kirtland and Aelion, 2000).

This technique, not only enhances the volatilisation of the contaminants, but also increases the biodegradation rate, in the soil, by increasing the amount of oxygen introduced in the system. To enhance biodegradation, there are different approaches for air sparging:

- Cometabolic – propane is injected with air, in order to provide another nutrient for microorganisms (CPEO, 2002);
- Bio-SpargeSM<sup>®</sup> – induces desorption. It is used in a pump-and-treat system and consists in pumping the contaminated groundwater to the surface and pulling the groundwater through a “cone of depression”. It is in the capillary fringe that most of the contaminant remain, so, after the pumping ends, the groundwater returns to the former level, being re-contaminated by the sorbed materials. The injection of air is coupled with water, nutrients and Bacteria in order to induce the desorption within the capillary zone. Since the system is a closed loop, there are no emissions, and for that purpose, there is no need for a off-gas treatment (CPEO, 2002);
- C-Sparge<sup>®</sup> – periodically injects an ozone/air mixture combined with pulsing pump. It is a two-phase process in which at first the bubbles extract the Volatile Organic Compounds (VOC) out of contaminated groundwater and in the second stage the ozone reacts with VOCs forming end products, such as carbon dioxide, diluting hydrochloric acid and water (Kerfoot Technologies, 2008).

Air sparging is recommended for VOCs and fuels in groundwater. Nevertheless, there are some limitations, since the air flow may not be uniform through the saturated zone, which can be amplified by the soil heterogeneity and specific geology. There are emissions to the atmosphere and uncontrolled movement of dangerous vapours that must be controlled.

### 1.6.2. Bioremediation

Bioremediation consists in enhancing the NA of a site, already explained in topic 1.5. It can be done by addition of well adapted microorganisms that are fit to degrade the contaminant present in the soil. It also can be achieved by adding nutrients, in order to develop the indigene community in the soil and decrease the amount of toxic compounds that are in touch with the microbial community. Adding TEA can also increase the rate of degradation, when the soil is poor in oxygen or in another TEA. Nevertheless, the soil and groundwater must be subject of a complete analysis, with the purpose of understanding which are the needs of the microbial community, to have a better performance on NA (Bockelmann, *et al.*, 2001).

Generally, bioremediation technologies can be classified as *in situ* or *ex situ*. *In situ* bioremediation involves treating the contaminated material at the site while *ex situ* involves the removal of the contaminated material to be treated elsewhere. Some examples of bioremediation technologies are bioventing, land farming, bioreactor, composting, bioaugmentation and biostimulation.

### 1.6.3. Permeable reactive barrier

A PRB is defined as an *in situ* method for remediating contaminated groundwater that combines a chemical or biological treatment zone with subsurface fluid flow management (EPA, 2008) and involves the construction of permanent, semi-permanent or replaceable units across the flow path of a dissolved phase contaminant plume (Guerin, *et al.*, 2002).

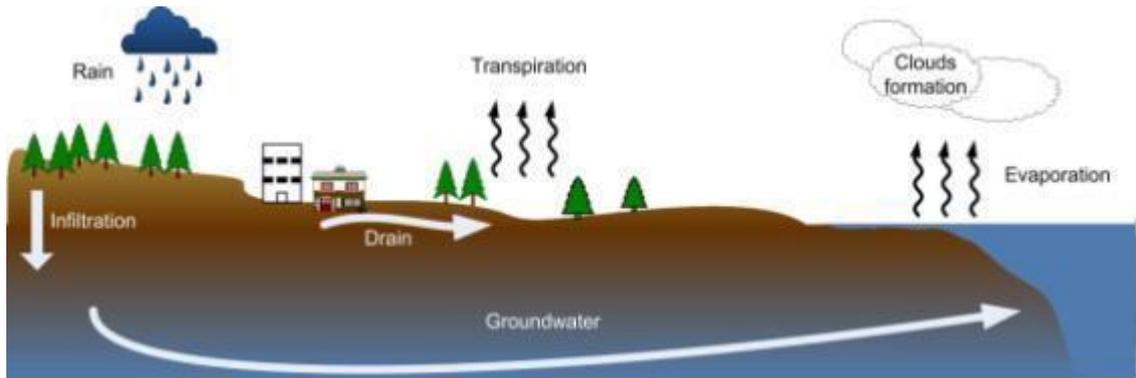
Treatment media may include zero-valent iron, chelators, sorbents, and microbes to address a wide variety of groundwater contaminants, such as chlorinated solvents, other organics, metals, inorganics and radionuclides. The contaminants are concentrated and either degraded or retained in the barrier material, which may need to be replaced periodically.

As the contaminated groundwater moves naturally through the treatment wall, contaminants are removed by physical, chemical and/or biological processes, including precipitation, sorption, oxidation/ reduction, fixation, or degradation. These barriers may contain agents that are placed either in the path of contaminant plumes to prevent further migration or immediately downgradient of the contaminant source to prevent plume formation.

The funnel and gate system is one application of a PRB for *in situ* treatment of dissolved phase contamination. Such systems consist of low hydraulic conductivity cut-off walls (e.g.,  $1 \times 10^{-6}$  cm/s) with one or more gaps that contain permeable reaction zones. Cut-off walls (the funnel) modify flow patterns so that groundwater primarily flows through high conductivity gaps (the gates). The type of cut-off walls commonly used are slurry walls, sheet piles, or soil admixtures applied by soil mixing or jet grouting (Guerin, *et al.*, 2002).

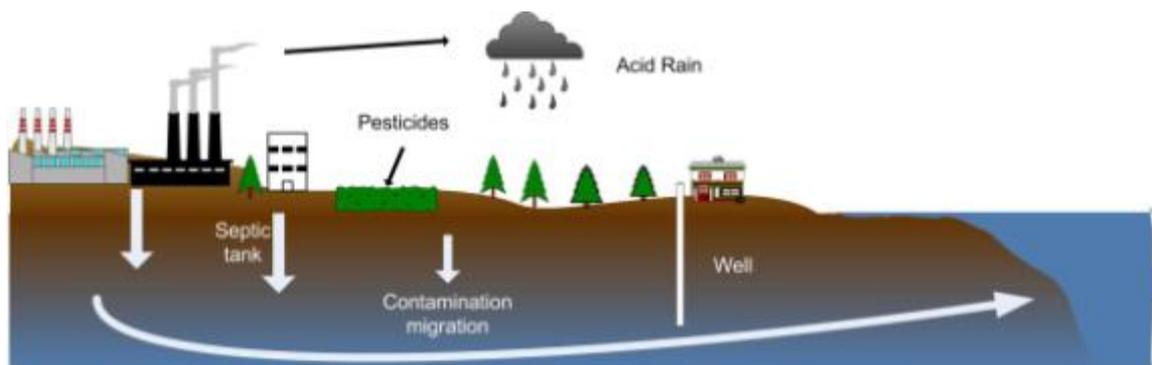
## 2. Modelling concepts

The water cycle consists in the trade and movement of water between different physical states (Figure 4). The Sun has a major role in the cycle, since it provides the energy used to evaporate water. After accumulating in the atmosphere, the water falls, as rain, and travels on the soil, through water lines and rivers until it reaches the ocean or it infiltrates through the soil until arrive at the groundwater aquifer.



**Figure 4** – Water cycle.

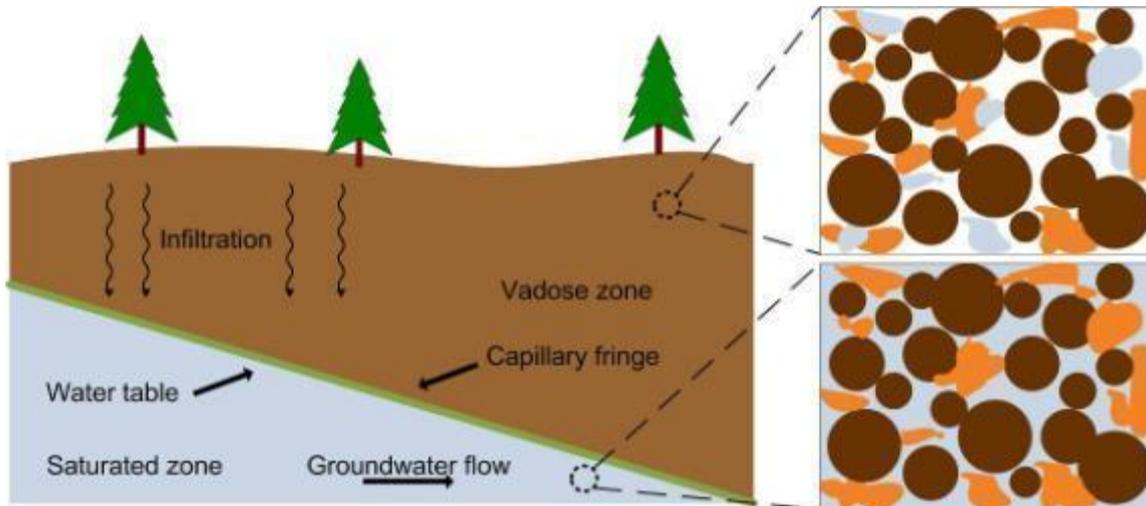
When a leak or spill takes place and a contaminant enters in this cycle, it can at first be volatilised to the air. The high values of the contaminants vapour pressure indicate that they are able to easily volatilise. When the contaminant infiltrates into the soil, it can be adsorbed to the soil particles, be degraded, or reach the groundwater basin (Figure 5).



**Figure 5** – Sources of contamination and its path in the environment.

Precipitated water drags the contaminants through the vadose zone (zone of none or partial saturation above the aquifer) till it reaches the zone of saturation, where groundwater flows occurs. The rate of infiltration is a function of soil type, rock type, antecedent water and time. The porous media is filled with water and air. In the end of this zone lays the capillary

fringe, which is partially saturated with water that rises from the saturated zone by capillary forces (Figure 6).



**Figure 6** – Vadose and saturated zone. Representation of the different liquid and gas phases present in each zone (the orange spots represent LNAPL, the blue symbolizes water and the white area refers to air).

## **2.1. LNAPL behaviour in soil**

As the LNAPL infiltrates into the soil, it will start to substitute the air in the porous media. While migrating through the vadose zone, it can be caught by capillary forces. Actually, if the amount of LNAPL released is small, it can be trapped only in the vadose zone, but if the amount is high it can migrate completely and be restrained in the saturated zone.

When it reaches the capillary zone, the LNAPL substitutes the water in the pores, becoming an enduring source of groundwater pollution to the dissolved plume.

In the 80's decade, it was thought that LNAPL behaviour would consist on floating above the water, replacing all water and air in the porous media (pancake model). When the water infiltration occurs only the water layer thickness would be transformed. Despite well observations denoting that the thickness of LNAPL layer was not homogeneous, only later, tools to assess other model types, would be developed.

With basis on information retrieved since early 30's, by several American Universities, it was possible to determine the capillary forces effect in the subsuperficial layers, which allowed a development of conductivity based models, for petroleum recuperation from reservoirs (Brusseau, 2005).

In the 90's, through a serial of scientific studies, it was possible to verify that water and LNAPL can coexist. The determination of LNAPL saturation depends on the lithology, capillary forces, fluid properties and amount of LNAPL spill. The LNAPL doesn't fill all the pore capacity

and the LNAPL saturation decreases with depth, until water fills all the porous. The variation of the LNAPL amount, through soil, can be determined, if the subsuperficial layer, fluid and thickness properties are known. Theories from Farr, Lenhard, McWhorten and Parker allow, with basis on several measures throughout the plume, to the quantification of contaminant total volume, migration profile and recovery potential (API, 2006).

The dissolution model for LNAPL shows that the maximization of hydraulic recovery, does not reduce the risk of contaminating the aquifer, but reduces the time of that risk.

## ***2.2. DNAPL behaviour in soil***

When a spill of DNAPL occurs it is necessary to promptly identify the source, the characteristics of the contaminant and from the local, in order to assess if the contaminant remediation is beneficial. As it is not possible to recover all the contaminant, the contaminant remediation applied on field, will only be partial.

The DNAPL will tend to migrate through the porous media of the vadose zone, into the aquifer and if the contamination amount is significant, it will spread throughout the soil layers beneath the aquifer, since it's denser than water.

One may think that the vadose zone would be less contaminated during a DNAPL spill than during a LNAPL spill, due to its density. Nevertheless, the vadose zone is heavily contaminated, since not only the contaminant density influences the velocity and path of migration, but also the pore size. If the pore size is too small, the contaminant will be trapped. For this reason DNAPL contamination will affect the layers beneath the aquifer, which can be very difficult to recover. To remove these contaminants, it is necessary that the capillary pressure is enough to push them out of the pores, and, sometimes, it is not feasible through pump-and-treat technologies (Brusseau, 2007).

## ***2.3. Parameters to equation on modelling***

As it was already stated in Table 3 there are abiotic and biotic factors that influence the mechanisms of depletion and transport. The biological and chemical influence on these mechanisms has already been overviewed. This chapter synthesizes some of the parameters that influence transport (by hydraulic and sorption mechanisms) which are porosity, saturation, capillary pressure, specific volume and dispersion.

### ***2.3.1. Sorption***

Sorption consists in a chemical bond between the soil particles and contaminant. It can be done by covalent or ionic bond. Sorption will discontinue the migration process of

contaminants. By one hand it will diminish the plume spread and avoids the contamination to reach other areas – very important, when the aquifer is not completely confined. On the other hand, it will block the possibility of recover the contaminant, since some of these bonds are irreversible, or reversible only in very specific conditions (Brusseau, 2007).

Many models already assess sorption processes. The adsorption equilibrium is given by Langmuir and Freundlich isotherm, equation 1 and 2, and by the linear isotherm, equation 3 (Brusseau, 2005).

**Langmuir isotherm:**

$$q = \frac{bc}{1 + bc} q_{\max} , (1)$$

Where q is the amount of contaminant adsorbed, c the concentration of contaminant in the fluid, the coefficient b represents the Langmuir coefficient,  $q_{\max}$  the maximum amount of adsorbed component at a given temperature.

**Freundlich isotherm:**

$$q = K_f c^{n_f} , (2)$$

Where  $K_f$  is the Freundlich constant and  $n_f$  is the Freundlich power, for each component.

**Linear Isotherm:**

$$q = Kc , (3)$$

Where K is the linear isotherm slope.

### **2.3.2. Porosity**

Porosity 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. Porosity depends on the particle size distribution, on the particle distribution and on the size and shape of the particles.

In clay soils the total porosity can be denominated by as primary porosity, since another type of porosity arises due to the clay fraction, induced by worms and plant roots. This last type is called secondary porosity. Although, secondary porosity represents a small fraction of total

porosity and capillary pressure is reduced through these pores, in clay soils they have a significant role in the movement of particles by gravity migration (Brusseau, 2005).

### **2.3.3. Saturation**

Saturation is the fraction of void space volume that is occupied by a certain fluid. Saturation is represented by a fraction or percentage, since the pores can be filled by different immiscible fluids – water, DNAPL, LNAPL and air. A soil is considered saturated, by a certain fluid, when that fluid is the only one present (Brusseau, 2005).

### **2.3.4. Capillary pressure**

The capillary pressure is defined as the ratio between the non-liquid phase pressure and the liquid phase pressure. Between the saturated zone and the non-saturated zone lays the capillary fringe. The capillary fringe is due to the contact tension between two immiscible phases. In soil the water will rise throughout this contact zone. Besides the contact tension, contact angle and pore diameter are also factors that influence capillary pressure (Brusseau, 2007).

In soils with low porosity, the capillary pressure is high, inducing a higher water level. This concept explains why coarse sand and gravel don't retain much water in comparison with clay soils that remain humid for a long period of time. The capillary pressure is deeply related to saturation, since high capillary pressures induce fast soil saturation.

The same principle that is applied to water/air contact is applied to NAPL/air or NAPL/water. Nevertheless, other factors contribute to capillary pressure, such as the compound density. In this case, the contaminant elevation extent depends on equilibrium between capillary pressure and gravity (Brusseau, 2005).

In a NAPL/water system, the water represents the "wet phase", since the NAPL has higher capacity to adsorb to soil particles. In a NAPL/air system, the NAPL represents the "wet phase", since it has a higher density. However, the elevation extent will not be as high as in a water/air system, since the superficial tension is lower.

### **2.3.5. Specific volume**

Through NAPL saturation and saturation distribution is possible to calculate the volume of NAPL in soil (Brusseau, 2007). The integration of the distribution curve represents the specific volume, which is expressed in  $m^3/m^2$ . In a well, the calculated specific volume is less than the NAPL layer thickness. In order to be applied in a model, three considerations have to be attended:

- The fluids are in a vertical equilibrium, which means that the water table has to be stable;
- Only one capillary pressure curve is applied;
- The soil is homogeneous.

### **2.3.6. Dispersion**

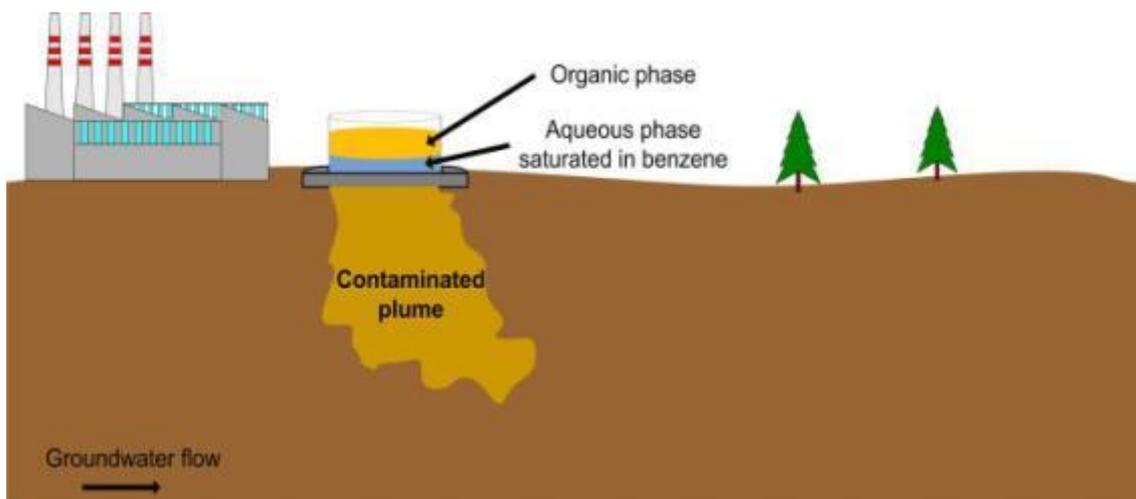
Dispersion is a physical process that tends to 'disperse', or spread, the contaminant mass in the X, Y and Z directions along the advective path of the plume, and acts to reduce the solute concentration. Dispersion is caused by the tortuosity of the flow paths of the groundwater as it travels through the interconnected pores of the soil (Waterloo Hydrogeologic, Inc., 2008).

### 3. Materials and Methods

Since the contaminants behaviour is associated with the complex mechanisms, explained in the last chapters, the use of modelling mechanisms is required, to fully understand the contamination plume. In order to evaluate the importance of each parameter, tools based on specific software, developed for the study of groundwater contamination are commonly used..

#### 3.1. *Case study*

In a hypothetical scenario a reservoir leak has conducted to a soil and groundwater contamination during 10 years. The leak was originated from storage tank, with a bottom area of 10 m<sup>2</sup>, in which there was benzene and an aqueous solution of benzene and other organic contaminants. Since benzene is a LNAPL, the bottom of the storage tank consisted in the aqueous solution. It was this solution that was released from the leak. A representation of the storage tank leak is present in Figure 7.



**Figure 7** – Storage tank leak of the aqueous phase and contaminated plume.

The solution was saturated on benzene and the organic phase of this solution was saturated on HCB. Pentachlorobenzene, trichlorobenzenes and 1,2,4 trichlorobenzene were also, present in the organic phase. All the data related with the leak composition is present in Table 8.

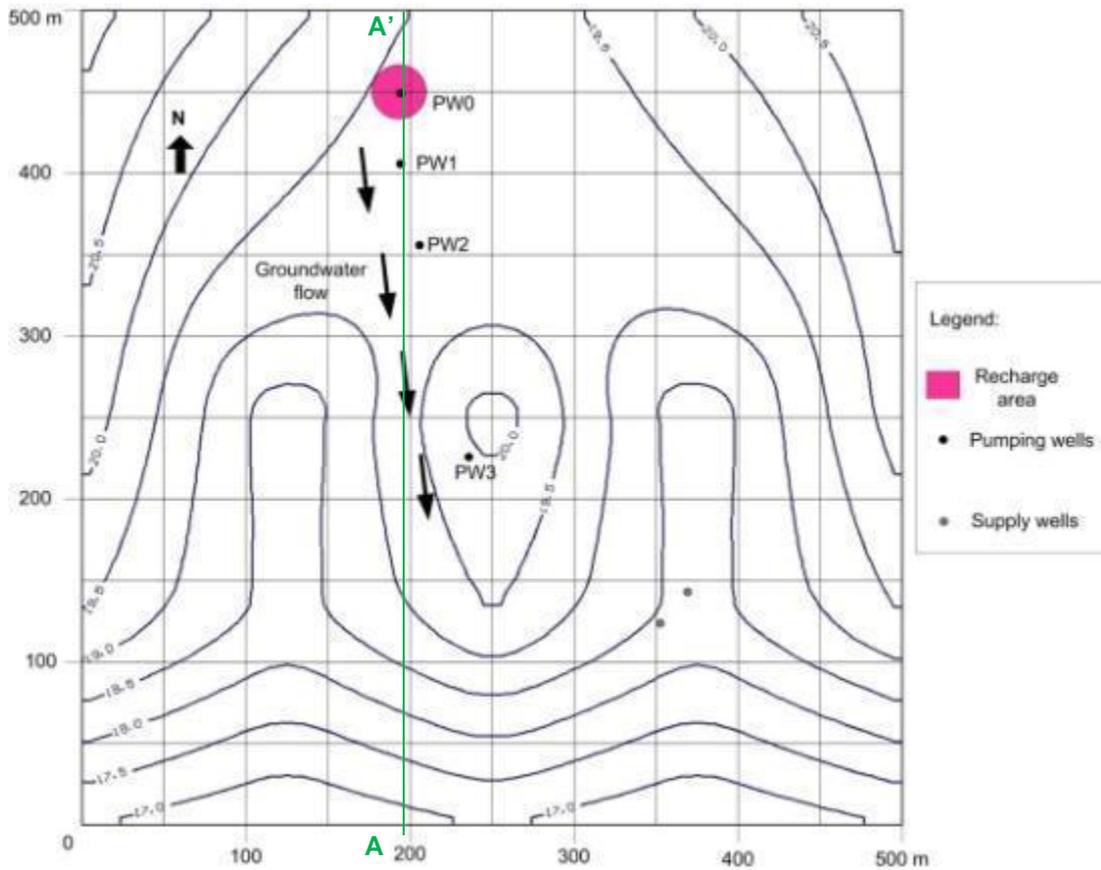
**Table 8** - Leak discharge rate and contaminants concentration.

Leak characteristics	Value	Units
Recharge area	10	m <sup>2</sup>
Discharge rate	20	L/d
[Benzene] <sub>aqueous</sub>	1.8	g/L
[HCB] <sub>organic</sub>	31.6	g/L
[HCB] <sub>aqueous</sub>	67.94	mg/L
[TCB] <sub>aqueous</sub>	32.06	mg/L
[organic] <sub>aqueous</sub>	1870	mg/L

The leak had on average a discharge rate of 20 L/d and with a concentration of benzene in aqueous phase of 1.8 g/L. The organic phase is saturated in HCB, which means that is in a concentration of 31.6 g/L. The organics total concentration in the aqueous phase is of 1870 mg/L.

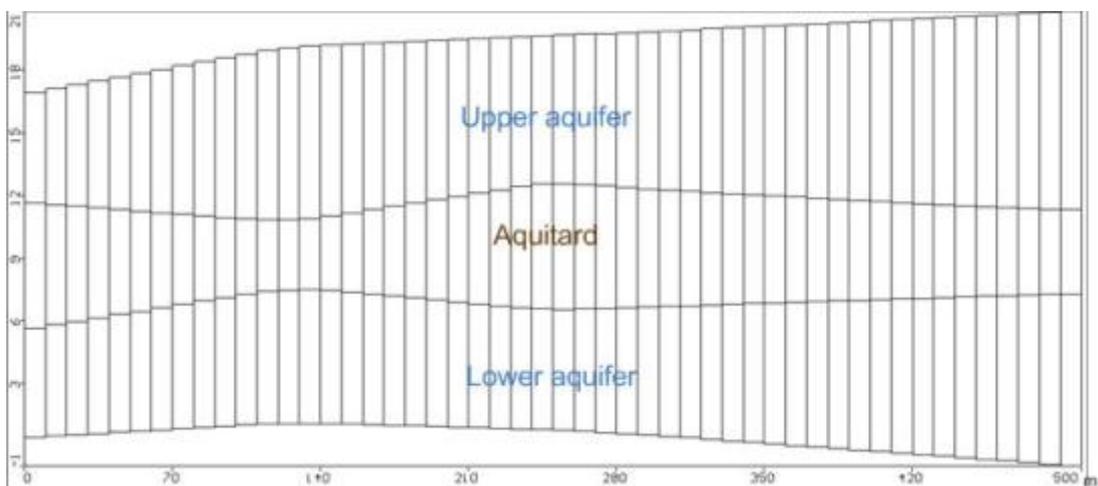
### 3.1.1. Site description

Hypothetical site characterization are described Figure 8, being the extension of the site study area approximately 250000 m<sup>2</sup> (500x500).



**Figure 8** - Area of the site under study. In pink the contamination recharge area. PW0, PW1, PW2 and PW3 are the pumping wells and the supply wells are presented in the lower right side. The line AA' represents a cross section that will be used in results.

Since the purpose was to study the impact of the soil type in the plume development, only parameters like porosity and conductivity should be object of study, and the remain parameters have to be constant in each scenario. The site geography is composed by three layers (Figure 9). The top layer represents an upper unconfined aquifer, the second layer an intervening middle aquitard and the last, a lower confined aquifer.



**Figure 9** – Geological cut showing the three layers of soil, considered in the study.

### 3.2. Soil characteristics

To study the behaviour of the contaminants leak in different soils, six scenarios were established based on the porosity, conductivity and specific volume storage. The topography of the site remained the same.

#### 3.2.1. Establishing porosity, conductivity and specific volume storage for each scenario

The different scenarios are based in the typology of soil used. In Table 9, the 6 scenarios used, are shown and the parameters in which they differ.

**Table 9** – Values of porosity and conductivity considered in each scenario.

Scenario	Soil type	Effective Porosity (%) *	Total Porosity (%) *	Conductivity Kx and Ky (m/s) *	Conductivity Kz (m/s) *
1	Clay, sand and gravel mixes	45	60	$5 \times 10^{-4}$	$5 \times 10^{-5}$
2	Coarse sand	35	40	$5 \times 10^{-4}$	$5 \times 10^{-5}$
3	Clay	45	55	$1 \times 10^{-4}$	$1 \times 10^{-5}$
4	Gravel and sand	20	35	$1 \times 10^{-4}$	$5 \times 10^{-5}$
5	Silt	40	50	$1 \times 10^{-6}$	$5 \times 10^{-7}$
6	Sandstone	10	20	$5 \times 10^{-7}$	$5 \times 10^{-8}$

\*Novotny and Olem, 1994

In section 2.1.3 it was referred the importance of specific volume storage due to its relation with saturation. In the model two parameters are introduced to characterize saturation, specific yield ( $S_y$ ) and specific storage volume ( $S_s$ ). The average values of  $S_y$  can be found in Table 10, for each type of soil.  $S_s$  can be calculated by multiplying  $S_y$ , by the aquifer depth, 10 m, in this case.

**Table 10** – Specific yield ( $S_y$ ) and specific storage ( $S_s$ ) values for each scenario.

Scenario	Soil type	$S_y^{(a)}$	$S_s (m^{-1})$
1	Clay, sand and gravel mixes	0.07	$7 \times 10^{-3}$
2	Coarse sand	0.27	$2.7 \times 10^{-2}$
3	Clay	0.02	$2 \times 10^{-3}$
4	Gravel and sand	0.25	$2.5 \times 10^{-2}$
5	Silt	0.18	$1.8 \times 10^{-2}$
6	Sandstone	0.27	$2.7 \times 10^{-2}$

<sup>a</sup> Halford and Kuniansky, 2002

With the characterization set above it is possible to predict the size and shape of a contamination plume, originated from an unknown leak, after 10 years.

### **3.3. Parameters estimation**

Biodegradation rates, in the sorbed and mobile phase, were calculated for a mix of the six contaminants (HCB, pentachlorobenzene, trichlorobenzenes, 1,2,4-TCB and benzene) based on data retrieved from bibliography, as can be seen in Table 11. Instead of introducing concentration recharge value for each contaminant and monitoring each contaminant, this study takes only into account the total mass of contaminants by volume. The analysis will be more limited, since it does not allow studying the evolution of each contaminant. Plus, since these scenarios are hypothetical, there is no data to compare with model results, which would not support the study of the evolution of each contaminant. The same method is applied in several examples to BTEX and Visual MODFLOW<sup>®</sup> has, in fact, a specific reaction model engine design to study the overall behaviour of BTEX mass.

In this study is only evaluated the biodegradation path. As, already, been referred on chapter 1.5, hydrogeochemical degradation, can also occur, but will not be the focus of the present work.

#### **3.3.1. Decay kinetics**

In Table 11 is present the half-life time, of each contaminant, present in the leak solution, for aerobic and anaerobic paths.

**Table 11**– Half-life time for each compound in aerobic and anaerobic degradation path.

Path	Half-life time – $t_{1/2}$ (d)				
	HCB	Pentachlorobenzene	Trichlorobenzenes	1,2,4-TCB	Benzene
Aerobic	80.00 <sup>a</sup>	270.00 <sup>a</sup>	365.00 <sup>a</sup>	320.00 <sup>a</sup>	16.00 <sup>a</sup>
Anaerobic	2.50 <sup>b</sup>	1.20 <sup>b</sup>	4.48 <sup>b</sup>	22.48 <sup>b</sup>	370.00 <sup>a</sup>

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

It was considered, in the model, that organic compounds degradation rates occurs through pseudo first-order decay kinetic, so the half-life time is independent of the initial concentration.

#### Biodegradation rates calculation

A kinetic of pseudo first-order decay considers the mass balance of the system, where there are no entries or outputs and is given by:

$$\frac{dC}{dt} = \text{Input} - \text{Output} - \text{Transformation}, (4)$$

When Input = Output = 0, leads to the following equation:

$$C_t = C_o \times e^{-kt}, (5)$$

Where  $C_t$  is the concentration at each time,  $C_o$  is the initial concentration,  $k$  is the degradation rate and  $t$  is the time. The equation is only valid in closed systems, which is not the case present in this study, but it will be used to determine the degradation rate. Once the degradation rate is independent of the initial concentration, it can be applied in the model, where is considered that there is inputs to the system. To calculate  $t_{1/2}$ ,  $C_t = C_o/2$ , which leads to:

$$\frac{C_o}{2} = C_o \times e^{-kt_{1/2}} \leftrightarrow \frac{1}{2} = e^{-kt_{1/2}} \leftrightarrow \ln(2) = kt_{1/2}, (6)$$

Knowing the  $t_{1/2}$  of each contaminant it is possible to determine its degradation rate by:

$$k = \frac{\ln(2)}{t_{1/2}}, (7)$$

Nevertheless, the degradation rate of the contaminants mixture should be determined experimentally. Since it was not possible to carry out this determination it will be considered that the degradation rate of the mixture will be the degradation rate of the worst case scenario of degradation. If considering that the trichlorobenzenes degrade aerobically, but when the degradation of benzene occurs, the contaminant has already travelled to the anaerobic zone, the scenario represents, the worst degrading case, where the degradation path is the slowest. When considering this scenario, the degradation kinetics introduced in the model, are the slowest, which allows analysing the less effective NA. If NA still proves to fit the aquifer needs for remediation, it is known that, in a real scenario, NA would be, even, more effective.

The degradation rate applied is actually the limitant path. Taking into account Table 11 and equation 15, it is possible to determine the limitant degradation rate for each path. For the aerobic path it is the rate estimated, considering that the limitant contaminant are trichlorobenzenes and for the anaerobic path is benzene. The results of the application of this equation are present in Table 12.

**Table 12** – Estimated aerobic and anaerobic limitant degradation rates.

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

### 3.3.2. Implementation of degradation rates to capillary fringe and to saturated and unsaturated zone

For the saturated zone is considered that only anaerobic degradation occurs and in the unsaturated zone only aerobic degradation occurs. For the capillary fringe the two types of reaction can take place, so the degradation rate considered is the average of the degradation rates for the two types of path. In the capillary fringe it is considered an average value of the aerobic and anaerobic degradation rate.

Concerning the rates for the adsorbed phase, it is considered that the rates are slower since the amount of TEA that are in contact with the contaminants are lower, it was considered for each zone the lowest rate. The degradation rates resulted are present in Table 13.

**Table 13** – Estimated degradation rates of the plume to each zone.

Zone	Degradation rate (d <sup>-1</sup> )	
	First-order reaction for the solved phase	First-order reaction for the sorbed phase
Unsaturated zone	1.899 x10 <sup>-3</sup>	1.873 x10 <sup>-3</sup>
Capillary fringe	1.886 x10 <sup>-3</sup>	1.873 x10 <sup>-3</sup>
Saturated zone	1.873 x10 <sup>-3</sup>	1.873 x10 <sup>-3</sup>

The maximum allowed concentration, by the EQS, for benzene is 50 µg/L, for HCB is 0.05 µg/l and for pentachlorobenzene and trichlorobenzenes are not, yet, set (Proposal Directive, 2006). For the present study the plume limit is considered to be at 0.05 µg/L, since a concentration of organics lower than this, would never have a contaminant in a concentration that could be hazardous. This value is important to establish the plume volume and mass and to determine the decontamination efficacy. Again, it is considered a value that overestimates the plume volume and hazardousness.

### 3.3.3. 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 with the amount of organic carbon in solution and it can be estimated using octanol-water coefficient ( $K_{OW}$ ) through three types of models (Boguslavsky, 2000):

$$\log K_{OC} = 0.82 \times \log K_{OW} + 0.44, (8)$$

$$\log K_{OC} = 0.72 \times \log K_{OW} + 0.49, (9)$$

$$\log K_{OC} = \log K_{OW} - 0.21, (10)$$

Equation (9) will be used, since it has been used successfully to determine partition coefficients to chlorobenzenes (Schwarzenbach, 1981). The distribution coefficient ( $K_d$ ) is calculated by:

$$k_d = \frac{[organics]_{aqueous}}{[organics]_{sediment}}, (11)$$

As the ratio between the organic concentration in the aqueous phase and in the sorbed phase, expressed by (L/kg), but it can also be calculated by:

$$K_d = K_{OC} \times f_{OC}, (12)$$

In which  $f_{oc}$  is the fraction of organic carbon. Since it is not possible to determine this parameter and since it is usually between 0.001 and 0.01 (DERBCAP, 2001), for groundwater aquifers, it will be assumed the value of 0.005 and a sensitivity analysis will be carried to evaluate the impact of this factor.

Based on these assumptions it is possible to calculate the distribution coefficient for each contaminant, but for the contaminants mixture it had to be determined experimentally. Again it was considered the limitant contaminant distribution coefficient as the mixture distribution coefficient, as seen in Table 14.

**Table 14**– Estimated aerobic and anaerobic limitant distribution coefficients.

Path	Limitant contaminant	Log $K_{ow}$	Log $K_{oc}$	$K_{oc}$	$f_{oc}$	Kd(L/kg)	Kd(L/mg)
Aerobic	Trichlorobenzene	3.93	3.32	2087.37	0.005	10.44	$1.04 \times 10^{-5}$
Anaerobic	Benzene	2.13	2.02	105.58	0.005	0.53	$5.28 \times 10^{-7}$

The remaining constant parameters that are common for each scenario, introduced in the model are present in Table 15.

**Table 15** - Characteristics introduced in the model, common to each scenario.

Characteristics	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 values for dispersivity allow determining the plume dispersion and are default values for an alluvial sediment aquifer (Novotny and Olem, 1994).

In order to evaluate the evolution of a groundwater contaminated plume in three phases, this software was used. The phases are:

- Evaluation of the size and shape of a plume in different types of soil and analysis of the risk of contamination of supply wells;
- Evaluation of different pumping rates, locations and number of pump wells in decontaminating a groundwater plume;
- Identification of the best approach to decontaminate each plume generated in each scenario.

### 3.4. Methods

Visual MODFLOW<sup>®</sup> was the selected software, since allows the user to input the soil characteristics (such as soil elevation, layer type and thickness, conductivity, porosity and dispersivity), hydraulic characteristics (recharge rate, evapotranspiration, storage and pumping wells) and contaminant characteristics (degradation rate, degradation path, sorption rate, degradation models).

Visual MODFLOW<sup>®</sup> consents the use of different transport, sorption and degradation mechanisms, in order to evaluate which fits better with monitoring data retrieved. In Table 16 is present a summary of the mechanisms selected to generate the model.

**Table 16** - Mechanisms used in the software and models applied to each mechanism.

Mechanism	Model
Flow Type	Saturated USGS MODFLOW 2000
Advective transport model	MODPATH
Solute transport model	MT3DMS 5.1
Run type	Steady-state flow
Sorption model	Linear isotherm
Reaction model	First-order irreversible decay

The type of run was chosen to be a steady-state flow, which means that the conductivity and pressure are constant.

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 numeric engine determines the

groundwater flow through an aquifer, by advection, based on the partial differential equation (13):

$$\frac{\partial}{\partial x} \left[ K_{xx} \frac{\partial h}{\partial x} \right] + \frac{\partial}{\partial y} \left[ K_{yy} \frac{\partial h}{\partial y} \right] + \frac{\partial}{\partial z} \left[ K_{zz} \frac{\partial h}{\partial z} \right] + W = S_s \frac{\partial h}{\partial t}, \quad (13)$$

Where  $K_{xx}$ ,  $K_{yy}$  and  $K_{zz}$  are the values for hydraulic conductivity along the three coordinates(m/s),  $h$  is the potentiometric head (m),  $W$  is the volumetric flux (1/d) that stand for all the inputs or/and outputs of water from the system,  $S_s$  is the specific storage of the soil (1/m) and  $t$  is time. The equation 13 is solved by the method of the finite differences. When applying this running engine the velocity of the fluid can be calculated (Chiang and Kinzelbach, 1996 (b)).

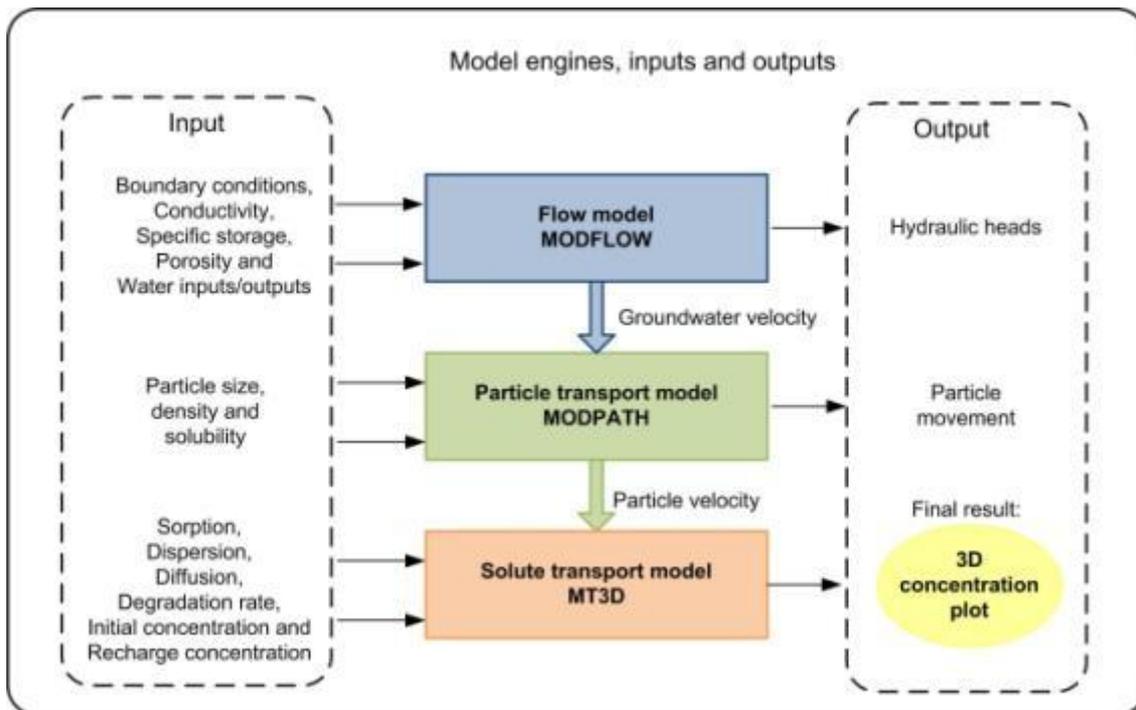
To calculate the advection transport of a particle, the engine used was MODPATH (Chiang and Kinzelbach, 1996 (a)). This engine will calculate the transport of a particle in the fluid. If the fluid had no movement, the particle would still move due to dispersion. The equation that is the basis of this engine is given by:

$$v \cdot \nabla = u \frac{\partial h}{\partial x} + v \frac{\partial h}{\partial y} + w \frac{\partial h}{\partial z}, \quad (14)$$

Where  $v \cdot \nabla$  is the velocity vector and  $u, v$  and  $w$  are the velocities in  $x, y$  and  $z$  directions, respectively (Chiang and Kinzelbach, 1996 (b)).

When selecting the engine to perform the solute transport and considering the data available, it was selected DoD MT3DMS 5.1 that allows modelling the reactive transport. As it was explained before, in this model, to characterize the plume it is considered the total mass of contaminants present. For this reason, it is not necessary to implement a reactive multispecies analysis. This engine will calculate the solute transport based on the physical, chemical and biological processes involved in the porous media. Through this engine the effect of dispersivity, sorption and biodegradation will be evaluated (Chiang and Kinzelbach, 1996 (a)). To simulate sorption, between the models presented in section 2.1.3, the model chosen was linear isotherm, since the data recovered and introduced in the model, considered this type of model. The same approach was used to select the reaction model, using the equations and parameters set on section 3.3. Nevertheless, other models, more complex, are available, yet more information is needed. Beyer, *et al.*, (2006) identified Michaelis-Menten, as a better 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 pseudo first order decay and Michaelis-Menten degradation rates for chlorobenzenes dechlorination and identified that the pseudo first order decay degradation rate had lower standard error.

In Figure 10 the interaction between the different engines is present.



**Figure 10** – Diagram of the interaction between model engines, the necessary parameters inputs and the 3D outputs.

### 3.4.1. Assumptions and corrective measures applied to the model

As it was explained before the values of distribution coefficient and degradation rate estimated considered the worst case scenario. Taking these considerations into account the technologies will be tested in the worst conditions.

Nevertheless, 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), explained in chapter 2. The model considers that the contaminant is either adsorbed or in solution with water. However, every substance as limit solubility in water, so part of the contaminant should be in the organic phase, with a slower movement, towards the groundwater flow.

In this particular case, with exception to benzene, HCB has very low solubility and pentachlorobenzene, trichlorobenzenes and 1,2,4 TCB are insoluble in water ( see Table A.1, Annex 1). 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.

In this study it is assumed the soil composition to be homogeneous. In a real scenario the heterogeneity of the soil might not substantiate the results obtained. Beyer, *et al.*, (2006) showed that the uncertainty induced by soil heterogeneity, can lead to underestimated plumes length, with an error of about 50%, despite the kinetic model used, in a 2D model.

### **3.4.2. Volume and mass of contaminant calculation**

The volume and mass of contaminant are calculated based on the data recovered from the model that gives the concentration of contaminant in each cell.

The plume volume is calculated considering the volume of each cell that has a concentration greater than 0.05 µg/L, which is the limit concentration of the plume. The volume of each cell is calculated based on the grid set, the depth of the cell (equal to the thickness of each layer) and considering the porosity of the soil, since the groundwater can only flow through the soil pores. The plume volume calculated is estimated in excess, since it is considered that the soil is saturated in water. Although, this assumption is true for the deepest layers, it is false for the top layer. Since it was not possible to determine, the amount of air present in the top layer pores, the plume volume calculated is overestimated.

The amount of contaminant present in the plume is calculated considering the concentration in each cell and each cells volume. To guarantee the liability of the calculations made, it is determined, for the time studied, 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.

### **3.4.3. Selecting the best pumping system**

After generating all the plumes, for each scenario, a plume is selected to establish the best pumping system to a well developed plume. The plume selected is from scenario 1, since it is the largest and longest plume. Considering that by 2009, the hypothetic contamination had been found and stopped, the simulation time, for the application of treatment technologies, is of 16 years, since by 2025 the groundwater resources must be cleaned.

Three wells positions (PW1, PW2 and PW3) are selected and its efficiency is evaluated along with the efficiency of the combined action of more than one well and different pumping rates. The wells position is identified on Figure 8 and Table 17 along with the different tests performed on the wells. The wells are positioned along the direction of groundwater flow, considering the source zone.

Negative values imply pumping water, while positive values stand for aquifer recharge. The aquifer recharge is done, in test 7, in order to test if it forces the water to the pumping wells, to help to dissolve remain contaminants and to introduce more oxygen into the soil, providing better degradation rates. Also, allows the aquifer not to enter in great water level disequilibrium.

**Table 17** – 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 pump-and-treat technology include, necessarily, a treatment unit. The treatment technology implemented will not be a subject of this study. 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 (Member Agencies of the Federal Remediation Technologies Roundtable, 1998).

#### **3.4.4. Establishing PRB treatment**

Another subject of analysis is the estimation of the efficacy of PRB. The applied barrier has 15 m thickness, 100 m long and is settled in front of PW1 well. The purpose of the barrier is to prevent the plume dispersion 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 that have a possibility of a spreading plume. The simulation time is also of 16 years.

### 3.4.5. Determining the best performance treatment technology

In this stage the results of the application of PRB, pumping system and NA are evaluated, to each scenario, in order to assess the best performance, for the time frame set. The best pumping rate test, evaluate in section 3.2.2, is applied to scenarios which have a similar contamination plumes, either in shape and volume. To the plumes which have different shapes a different pumping system is applied. The time necessary to treat the plumes generated in each scenario was estimated.

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

An analysis is set to evaluate of  $f_{oc}$  impact in the plume volume and total mass of contaminant during the contamination process (10 years) and during the NA process (16 years). The analysis is made to scenario 1 and the data set is present in Table 18.

**Table 18** – Values of  $f_{oc}$  applied to each test and resulting distribution coefficient for aerobic and anaerobic path, in scenario 1.

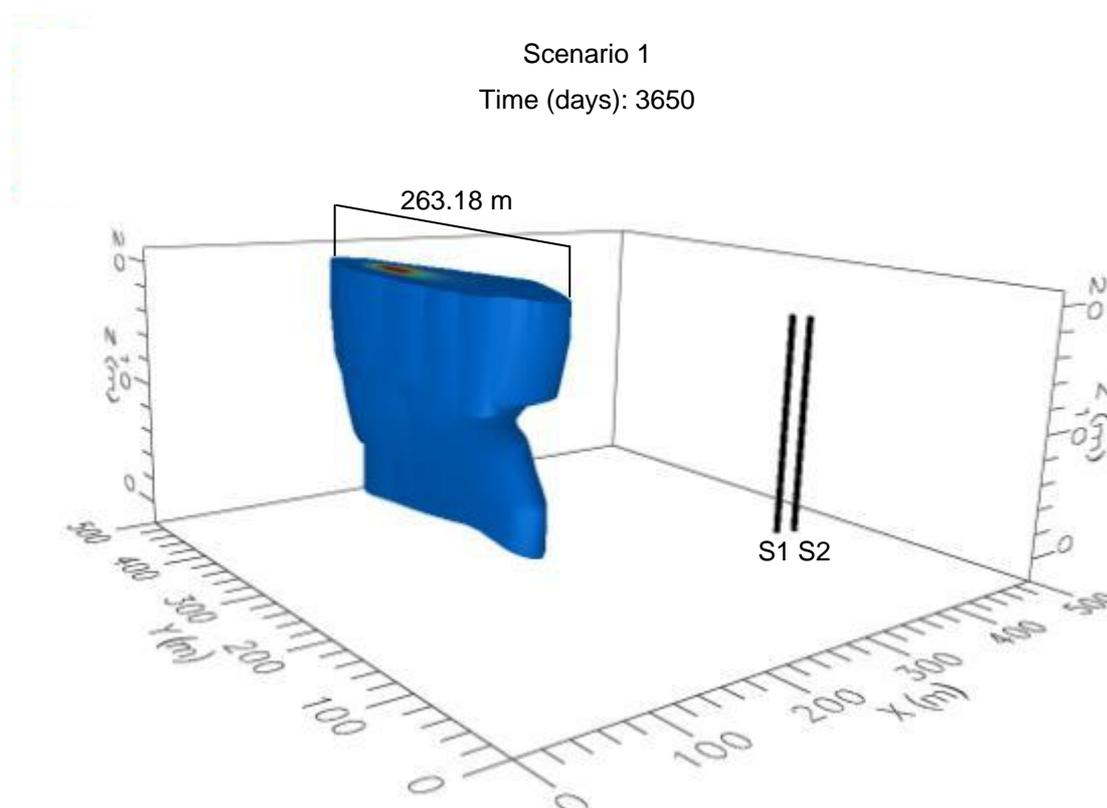
Test	$f_{oc}$	Kd(L/mg)	
		Aerobic	Anaerobic
A	0.001	$4.58 \times 10^{-9}$	$9.04 \times 10^{-8}$
B	0.00125	$5.72 \times 10^{-9}$	$1.13 \times 10^{-7}$
C	0.0025	$1.14 \times 10^{-8}$	$2.26 \times 10^{-7}$
D	0.005	$2.29 \times 10^{-8}$	$4.52 \times 10^{-7}$
E	0.0075	$3.43 \times 10^{-8}$	$6.78 \times 10^{-7}$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

## 4. Results

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

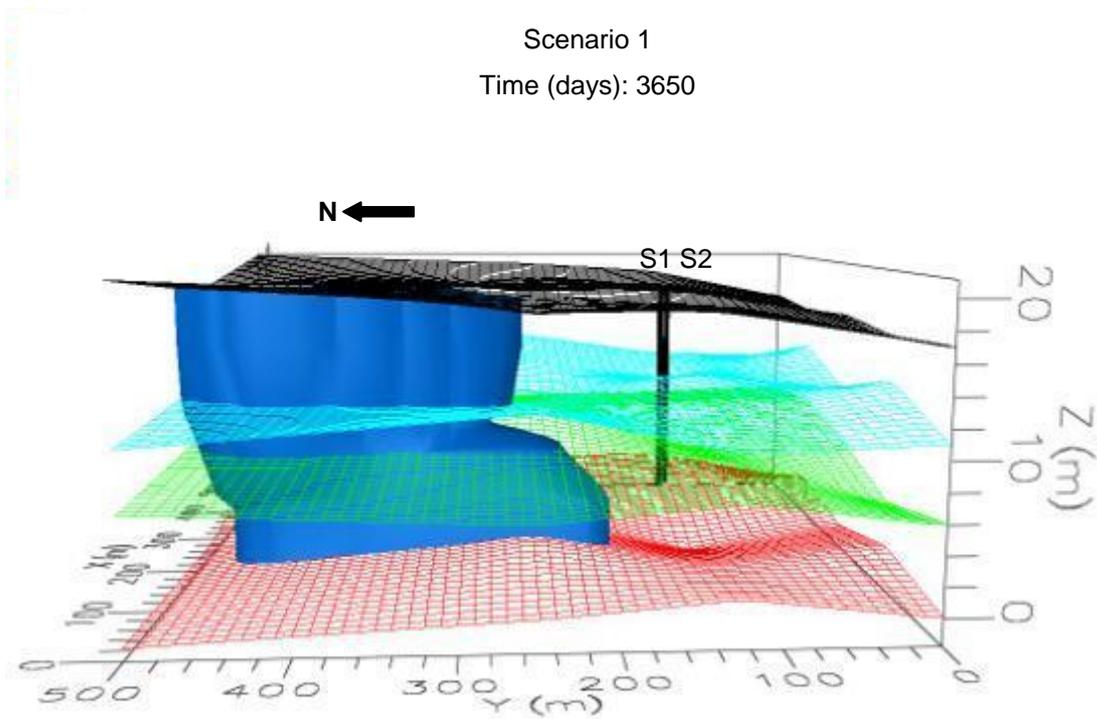
The results from setting the scenarios show two different types of contaminant plumes, regarding the influence of the advection component.

#### 4.1.1. Plume with strong advection influence.



**Figure 11** – Result of a contaminant plume, with strong advection component, when applying scenario 1 parameters (clay, sand and gravel mixes soil, with high hydraulic conductivity). S1 and S2 are the supply wells.

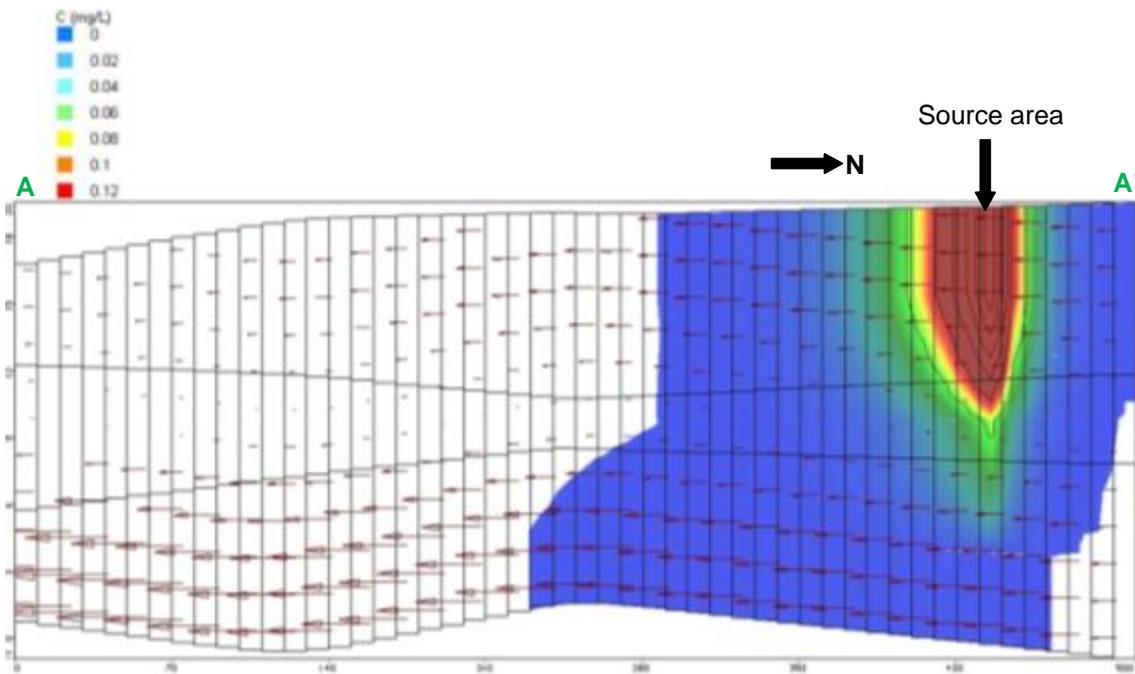
The first type, as can be seen in Figure 11, moves downward due to the strong advection component, in direction to the supply wells. It can also be denoted some dispersion in the opposite direction to groundwater flow. The contaminant concentration decreases, in part due to volatilization, biodegradation and also dilution caused by the high contaminant movement giving a false illusion of a rapid contaminant loss. This type of plume is generated in scenarios 1 and 2.



**Figure 12** – Result of a contaminant plume, in each layer, with strong advection component, when applying scenario 1 parameters (clay, sand and gravel mixes soil, with high hydraulic conductivity). S1 and S2 are the supply wells.

As can be seen in Figure 12, in the top and bottom layer the advection component is very strong. In the middle layer, the aquitard, the advection component is not so strong and main factor for transport of contaminant is in the vertical component. In the aquitard zone the contaminant does not suffer the effect of advection, since there is no groundwater movement. The vertical movement is due to migration by gravity.

Figure 13 is the result of a slice of the plume, generated in scenario 1, across the line AA', identified in Figure 8.



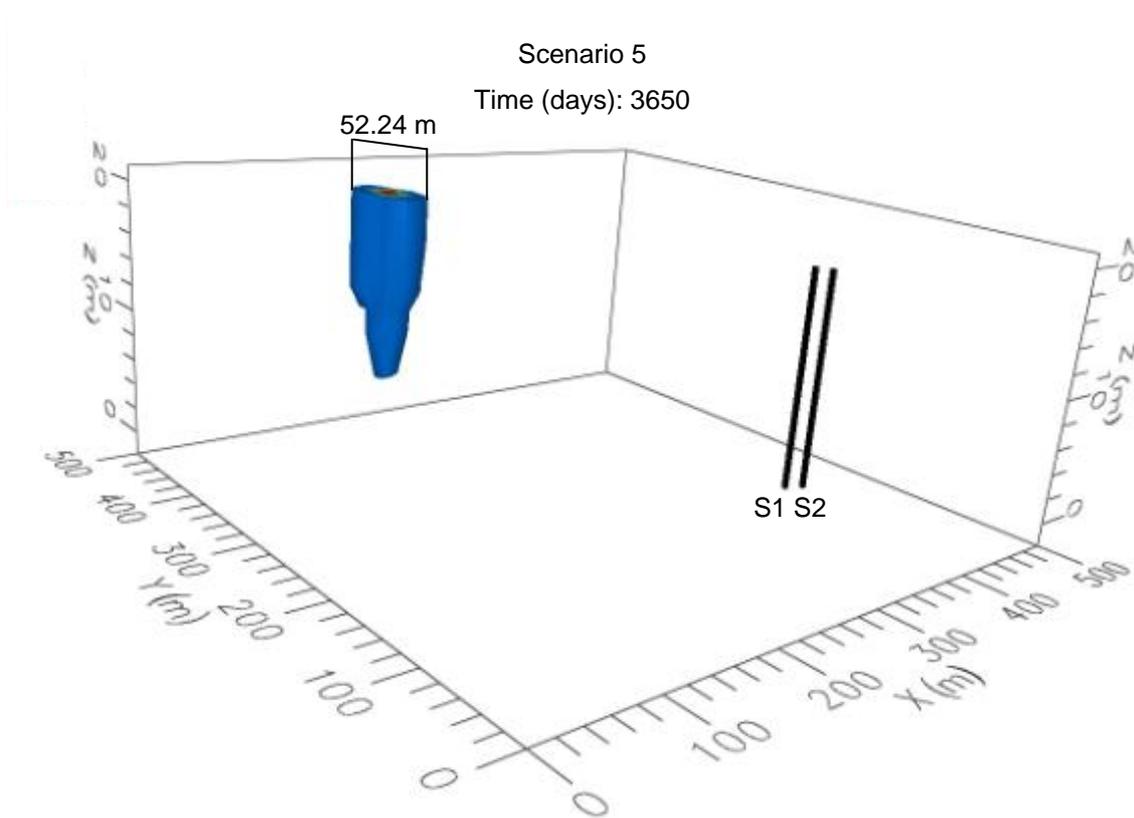
**Figure 13** – Results for groundwater velocity, in each layer of scenario1.

In Figure 13 the groundwater velocity vectors are shown. It can be observed that in the aquitard zone, middle layer, the velocity is very slow, towards the groundwater flow direction. It is in the bottom layer where the velocity is higher, due to the pressure of the upper layers. Since in the aquitard zone, the movement is, practically, through gravity, the plume remains, almost, with the same shape as in the top layer.

The higher movement in the bottom layer, in the direction of the groundwater flow, reduces the influence of dispersion, leading to a plume shrink in the area behind the source zone. As the plume goes forward, there is some dispersion influence the plume shape in the aquitard zone.

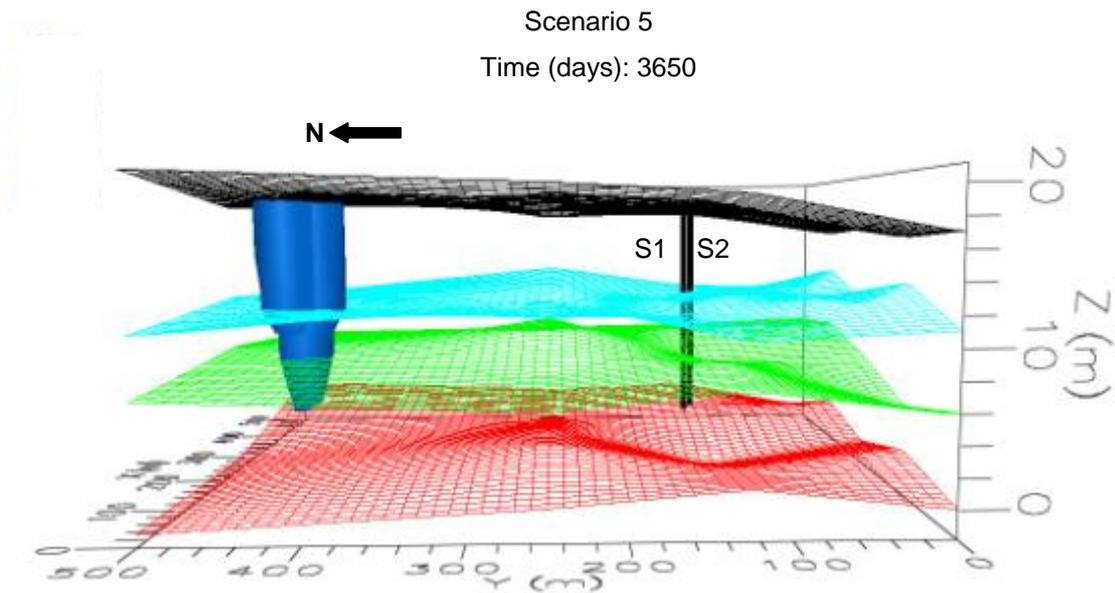
The higher concentrations of contaminant remain, essentially, in the top layer, due to the strong advection influence.

#### 4.1.2. Plume with low advection influence.



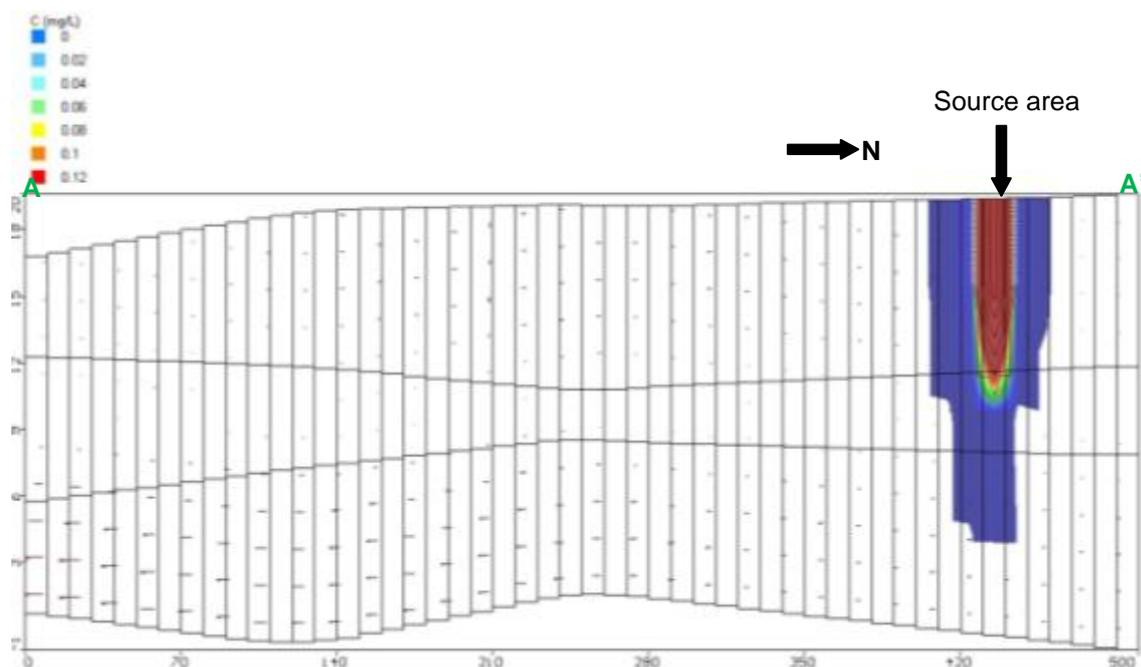
**Figure 14** – Result of a contaminant plume, with low advection component, when applying scenario 5 parameters (silty soil, with low hydraulic conductivity). S1 and S2 are the supply wells.

As can be seen in Figure 14, the type of plume is characterised by some dispersion and very slow or none movement in the groundwater direction flow, due to low advection. In fact the plume length is, in this case, is 20% of the length of the plume from scenario1. Scenarios 3, 4, 5 and 6 show this type of plume.



**Figure 15** – Result of a contaminant plume, in each layer, with strong advection component, when applying scenario 5 parameters (silty soil, with low hydraulic conductivity). S1 and S2 are the supply wells.

As can be seen in Figure 15, in the advection component is very low. In the middle layer, the aquitard, there is a decrease in the plume thickness, due to lower dispersion movement, and main factor for transport of contaminant is in the vertical component. The bottom layer has low contamination, since the amount of contaminant that is trapped in the above layers. Figure 16 is the result of a slice of the plume, generated in scenario 5, across the line AA', identified in Figure 8.



**Figure 16** – Results for groundwater velocity, in each layer of scenario 5.

In Figure 16 the groundwater velocity vectors are shown. It can be observed that the velocity is lower than in Scenario 1. As before, it is in the bottom layer where the velocity is higher, due to the pressure of the upper layers. The main factor influencing the contaminant movement is dispersion, since there is almost as plume thickness, from the source, in both south and north directions. Considering that the groundwater flow direction is NO→SE, if advection had some influence, there would be considerable contamination in the area south of the source area. On the aquitard zone, the lower dispersion leads to a plume loss of thickness that is reflected in the bottom layer.

The higher concentrations of contaminant remain, essentially, in the top layer, due to low ability for the contaminants to move.

In a real site, the amount of sources zones and different contaminants plumes would disturb the concentration gradients, in groundwater flow. In these cases the study of the overall plume gives little information and the study of each contaminant plume done separately, can be, in some cases impossible (Bockelmann, *et al.*, 2003).

#### 4.1.3. Data analysis of porosity and hydraulic conductivity influence in plume volume and mass of contaminant

The plumes sizes and mass of contaminant can be observed in Table 19.

**Table 19** – Values obtained for plume volume and total mass of contaminant, considering the porosity and conductivity of each scenario.

Scenario	Porosity (%)	Conductivity (m/s)	Plume volume(m <sup>3</sup> )	Contaminant mass within the plume (g)
1	60	5x10 <sup>-4</sup>	141040	151.26
2	40	5x10 <sup>-4</sup>	104602	106.19
3	55	1 x10 <sup>-4</sup>	14768	33.14
4	35	1 x10 <sup>-4</sup>	10025	25.69
5	50	1 x10 <sup>-6</sup>	1417	3.56
6	20	5 x10 <sup>-7</sup>	1133	3.76

It can be observed that for soils with the same hydraulic conductivity (scenario 1, 2 and scenarios 3 and 4), as porosity decreases, the plume volume increases. The same analysis is valid for total contaminant mass within the plume. None of the plumes reaches the supply wells, although the plume from scenario 2 is close, which means that by now they are not at risk.

Through the application of multivariate analysis, using XLSTAT® 2008 a non linear regression was applied, to study the evolution of the plume volume with 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. Two types of non linear regression were applied:

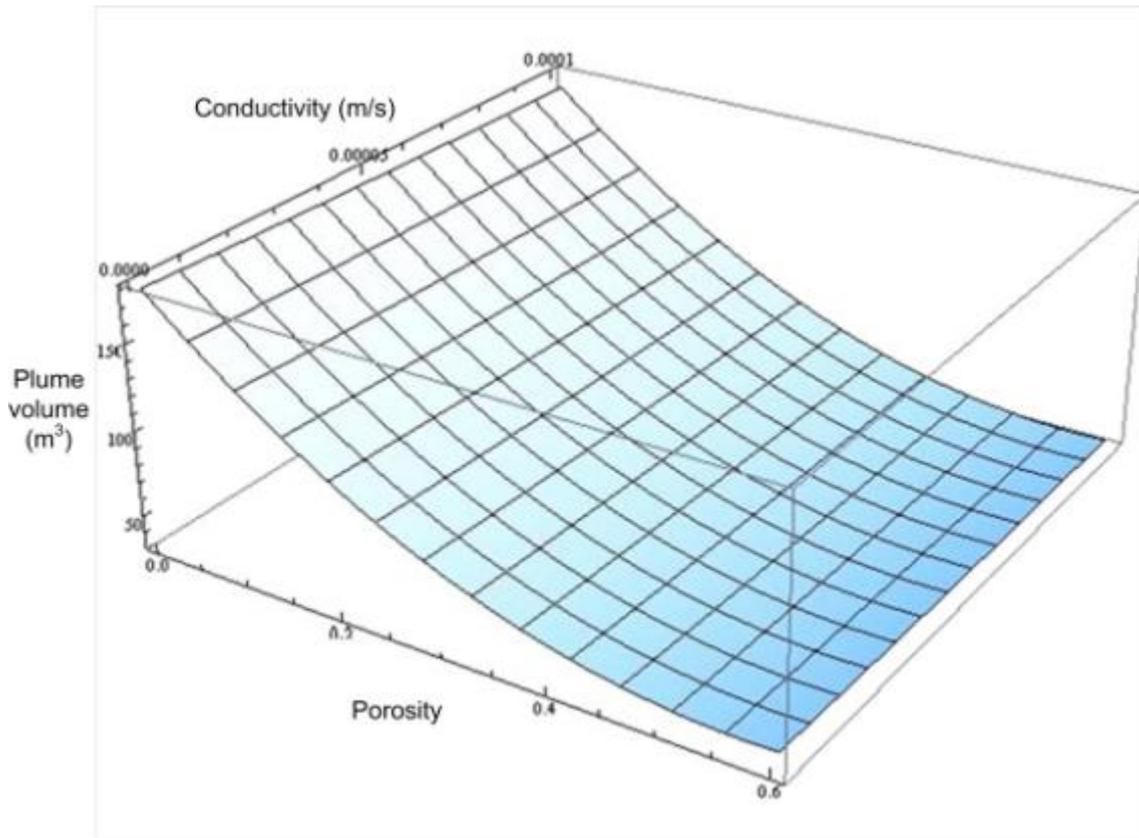
- $V = pr1 + pr2 \cdot X_1 + pr3 \cdot X_2 + pr4 \cdot X_1^2 + pr5 \cdot X_2^2$  (15)
- $V = pr1 + pr2 \cdot X_1 + pr3 \cdot X_2 + pr4 \cdot X_1^2 + pr5 \cdot X_2^2 + pr6 \cdot X_1 \cdot X_2$  (16)

In which V stands for plume volume,  $X_1$  for porosity and  $X_2$  for conductivity. The second type (equation 16) introduces another factor that links the two variables. The best results, presented in Table 20, were obtained with the first approach (equation 15), probably due to the fact that there were only 6 scenarios and a better performance to the second type could only be obtained if more data was available. Nevertheless, the accuracy of the regression is very good, since  $R^2$  is 0.91.

**Table 20** – Non linear regression parameters to the plume size for each scenario.

Parameters	Value
pr1	$-3.79 \times 10^4$
pr2	$1.96 \times 10^5$
pr3	$-8.77 \times 10^8$
pr4	$1.63 \times 10^6$
pr5	$1.71 \times 10^{12}$
$R^2$	0.91

Based on the equation it was possible to draw a graphic representation of the volume plume evolution with porosity and hydraulic conductivity, as seen in Figure 17, as it is possible to demonstrate, clearly the relation between porosity and hydraulic conductivity with plume size.



**Figure 17** – Variation of plume volume with porosity and hydraulic conductivity.

The graphic representation shows that for soils with the same porosity, the soil with higher hydraulic conductivity leads to higher plume volumes. Also confirms that for soils with same hydraulic conductivity, the one that has higher porosity has the lower plume volume. The same result was obtained for 2D model by Graf and Therrien (2007).

For contaminant mass plume it was not possible to apply the same type of regression analysis, with good results.

#### **4.2. NA influence in contaminant plume recover**

To understand the impact that a treatment technology could have in decontaminating, it was necessary to run the model, for each scenario, considering that the source of contamination had stopped and no treatment was applied, during 16 years. Based on these plumes and on the resulting plumes from the contamination, it is possible to analyse the influence of NA in each scenario.

Actually, all the plumes were decontaminated by the end of 2025, but to understand the influence of porosity and conductivity on NA, it is necessary to evaluate the time needed in each scenario to reach a total decontamination (Table 21).

**Table 21** – Time necessary to decontaminate the plumes present in each scenario, by layer.

Scenario	Porosity (%)	Conductivity (m/s)	Initial plume (m <sup>3</sup> )	Time to decontaminate by NA (y)		
				Layer 1	Layer 2	Layer 3
1	60	5x10 <sup>-4</sup>	141041	10	9	4
2	40	5x10 <sup>-4</sup>	104602	10	9	5
3	55	1 x10 <sup>-4</sup>	14768	13	12	4
4	35	1 x10 <sup>-4</sup>	10025	13	12	4
5	50	1 x10 <sup>-6</sup>	1417	14	11	Not contaminated
6	20	5 x10 <sup>-7</sup>	1133	14	12	Not contaminated

First, it has to be taken into account that the time necessary to decontaminate is independent of the plume volume, since scenarios with larger plume volumes (such as scenario 1 is easier to decontaminate than scenario 6, which has a lower plume volume). Regardless the porosity, scenarios with the same hydraulic conductivity, takes the same time to decontaminate, such as scenario 1 and 2 and scenarios 3 and 4. When the hydraulic conductivity is low, the risk of contaminating the lower layers is reduced. In scenario 5 and 6 the contamination never reached layer 3, despite the high porosity of scenario 5.

To fully understand the mechanism beyond the NA impact on plume volume and mass of contaminant, it is necessary to evaluate the behaviour of the six plumes during the decontamination process. For that, the plume volume and mass of contaminant were calculated, after 8 years, where NA was the only remediation technology applied. The results are present in Table 22.

**Table 22** – Plume volume and mass of contaminant for the initial plume and 8 years after of NA, for each scenario.

Scenario	Plume volume (m <sup>3</sup> )			Contaminant mass within the plume (g)		
	Initial plume	After 8 years	Volume decrease (%)	Initial plume	After 8 years	Mass decrease (%)
1	141041	40357	71.4	151.3	3.9	99.6
2	104602	26517	74.7	106.2	2.7	99.6
3	14768	4776	67.7	33.1	0.9	99.3
4	10025	3727	62.8	25.7	0.7	99.3
5	1417	473	66.6	3.6	0.1	99.3
6	1133	379	66.6	3.8	0.1	99.0

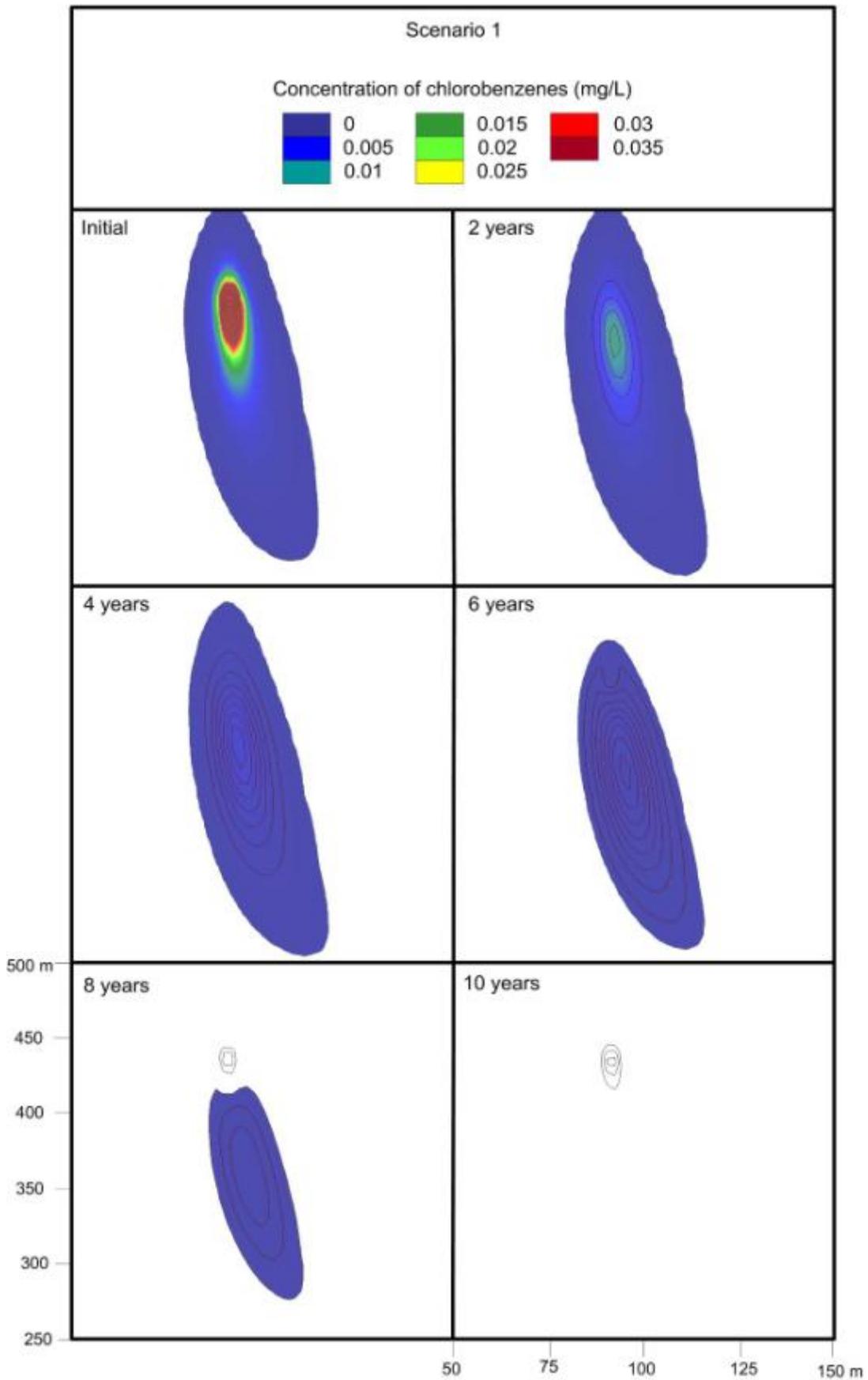
On what concerns plume volume, in all scenarios, it decreases, meaning that the velocity of the plume movement is not higher enough to compensate the loss through degradation. The degradation rate is strong enough to sustain the plume dispersion and advection. For scenarios with the same hydraulic conductivity (scenarios 1 and 2 and scenarios 3 and 4), when porosity is higher, the volume decrease is faster. When considering the total contaminant mass within the plume, one can observe that NA is responsible for more than 99% reduction of contaminant mass, which represents a high decontamination achievement.

NA has proved to have an important role in groundwater plume attenuation. However, Chapman *et al.*, (2007) demonstrate that, if the site study would be set in a zone near the connection between the aquifer and surface water, the major source of groundwater plume depletion would be the transport to the surface water.

Monitored NA has been developed, in recent years, has a treatment remediation technology. Witt *et al.*, (2002) have proved its efficiency in reducing the amount of chlorinated compounds, in Dover Air Force Base, despite the half-time lives of the compounds in study were very high. Davis *et al.*, (2002), in a parallel investigation, were able not only to identify the gene sequence used by the microbial community, in this site area, but also to support the theory that both anaerobic and aerobic reaction were occurring and the half-time lives considered by Witt *et al.*, (2002).

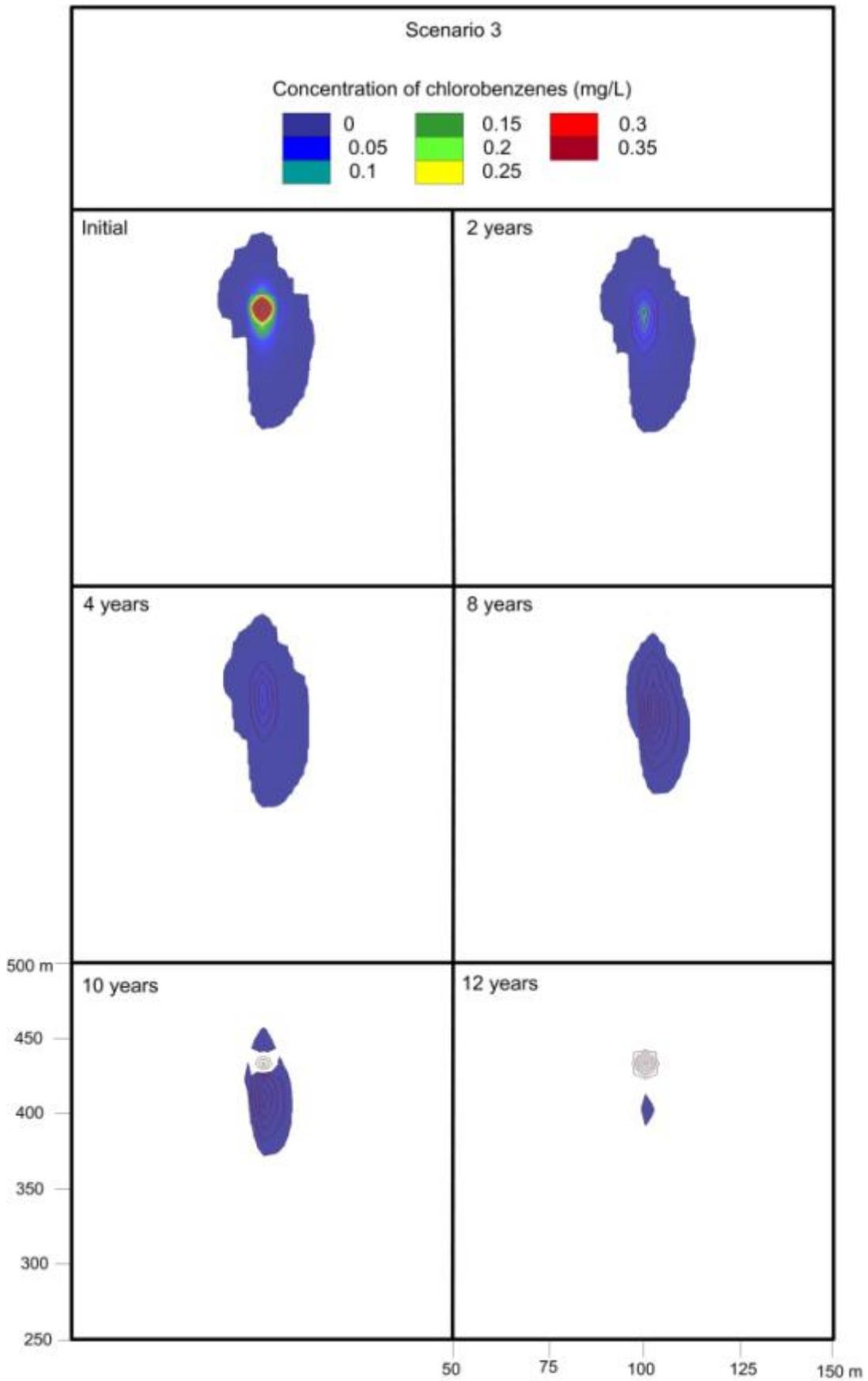
### **4.3. Plume evolution during NA process**

With the intention of understanding the movement and of a contaminant plume, in Figure 14, 15 and 16, the evolution of the plumes generated in each scenario are displaced.



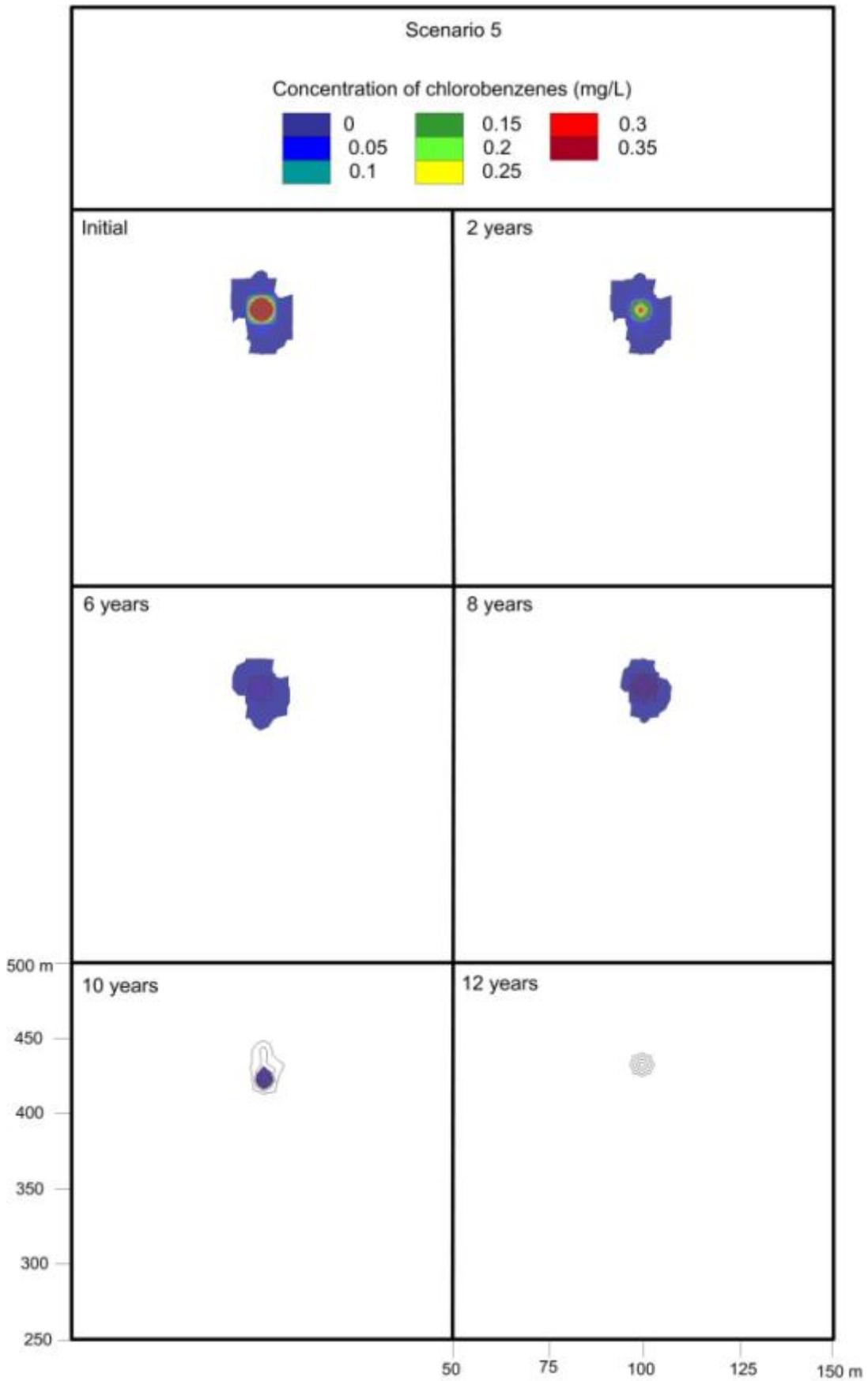
**Figure 18** – Evolution of the contaminant plume, generated in scenario 1, during 10 years.

Scenario 1 shows a well developed plume, as can be seen in Figure 18. Actually, after the end of the contaminant recharge, the plume still grows. This effect is a result of special circumstances that take place in the plume frontiers. The advection forces lead to the increase of the plume and the amount of contaminant within the plume guarantees a recharge that as the plume grows the concentration of contaminant is high enough to be detected. The biodegradation effort is not strong enough to compensate the plume advance. The amounts of contaminants near the source, mainly, to biodegradation. After 4 years, the plume starts to loose volume, since the amount of contaminant that moves, per unit of time, is less than the amount that is degrade. After 10 years the contaminants concentration has reached a level of security. When analysing the plume 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. Scenario 2 had a similar plume evolution.



**Figure 19** - Evolution of the contaminant plume, generated in scenario 3, during 12 years.

In scenario 4, as can be observed in Figure 19, it can be found a plume that establishes a compromise between the two types observed in Figure 18 and Figure 20. The plume has strong advection, but not enough to allow the contaminants movement, after the end of the discharge, as in scenario 1. There is a balance between the action of biodegradation, advection and dispersion, since it is not possible to determine which as a dominant effect, in this scenario. After 10 years, the plume centre is also translocated downward and the plume suffers a separation. In this scenario the separation of the plume does not last long, however this could represent a bigger effort, when applying a treatment technology. Scenario 4 shows the same type of evolution as scenario 3.



**Figure 20** - Evolution of the contaminant plume, generated in scenario 5, during 14 years.

In Figure 20 it can be observed a plume very distinct from the one observed in Figure 18. The advection influence is very low, leading to none increase of volume. The main force 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 is represented by a plume with the same type of evolution.

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

The results are based in the application of different pumping rates applied to one or more pumping wells, with different distances from the contamination source, to scenario 1. Since all scenarios could be decontaminated after 16 years, by NA, to evaluate the efficacy of a remediation technology it is necessary to guarantee that it is able to decontaminate in less time. With this purpose the data was retrieved considering that the technology was applied during 8 years. This data must be compared to the size and contaminant total mass, after the same time, if one considered that no remediation technology was applied. The plume volume and mass results are present in Table 23.

**Table 23** – Plume volume and mass for each test, 16 years after the implementation of a pumping system.

Test	PW1 (m <sup>3</sup> /d)	PW2 (m <sup>3</sup> /d)	PW3 (m <sup>3</sup> /d)	Plume volume (m <sup>3</sup> )	Volume decrease (%)	Contaminant mass within the plume (g)	Mass decrease (%)
0	0	0	0	26517		2.65	
1	-1000	0	0	1610	72.8	0.09	99.3
2	0	-1000	0	2473	19.6	0.13	90.2
3	0	0	-1000	12453	-10.1	0.75	68.8
4	-1000	-1000	0	0	100	0	100
5	0	-1000	-1000	0	100	0	100
6	-1000	0	-1000	0	100	0	100
7	-1000	-1000	-1000	0	100	0	100
8	-1000	1000	-1000	0	100	0	100
9	-1100	-1100	-1100	0	100	0	100
10	-1100	-1100	0	0	100	0	100
11	-750	-750	-750	0	100	0	100
12	-750	-750	0	0	100	0	100

The results demonstrate, clearly, 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 decontaminating the plume, as can be seen when comparing the results of tests 1, 2 and 3. When combining more than one pumping well, the results achieved are better (test 4 versus tests 1, 2 and 3); nevertheless the wells proximity to the plume controls the efficiency, since test 5 as worse results than test 1, in reducing the plume volume, but better results in recovering the mass of contaminant. The higher the pumping rate, the higher the efficiency (test 1 versus tests 8 and 10), however the wells position as a bigger impact, since tests 8 and 9, with lower pumping rates show higher efficiency than tests 2 and 3, and tests 9 and 11 are better than test 5.

Test 7 shows that the recharging of the aquifer, does not allow a better performance, when compared to test 6, in fact it slows the recovering rate.

Again it was applied multivariate analysis, but this time for the study of the importance of wells rate pump and position, to the plume volume and the contaminant total mass. The same two types of non linear regression were applied:

- $V = pr1 + pr2*X_1 + pr3*X_2 + pr4*X_3 + pr5*X_1^2 + pr6*X_2^2 + pr7*X_3^2$  (17)
- $V = pr1 + pr2*X_1 + pr3*X_2 + pr4*X_3 + pr5*X_1^2 + pr6*X_2^2 + pr7*X_3^2 + pr8*X_1*X_2 + pr9*X_1*X_3 + pr10*X_2*X_3$  (18)

This time V stands for plume volume, but  $X_1$ ,  $X_2$ , and  $X_3$  are, respectively wells PW1, PW2 and PW3. As before, on what concerns the plume volume, the best results were obtained with the first regression function (equation 17) and the accuracy was not good,  $R^2$  0.62. Also, It was not possible to obtain a good regression for the contaminant total mass within the plume, since  $R^2$  was 0.43.

To proceed with the analyses of the best pumping system, one must look into the time needed to decontaminate each layer of the plume, as in Table 24.

**Table 24** - Time needed to decontaminate each layer of the plume, for each pumping test system.

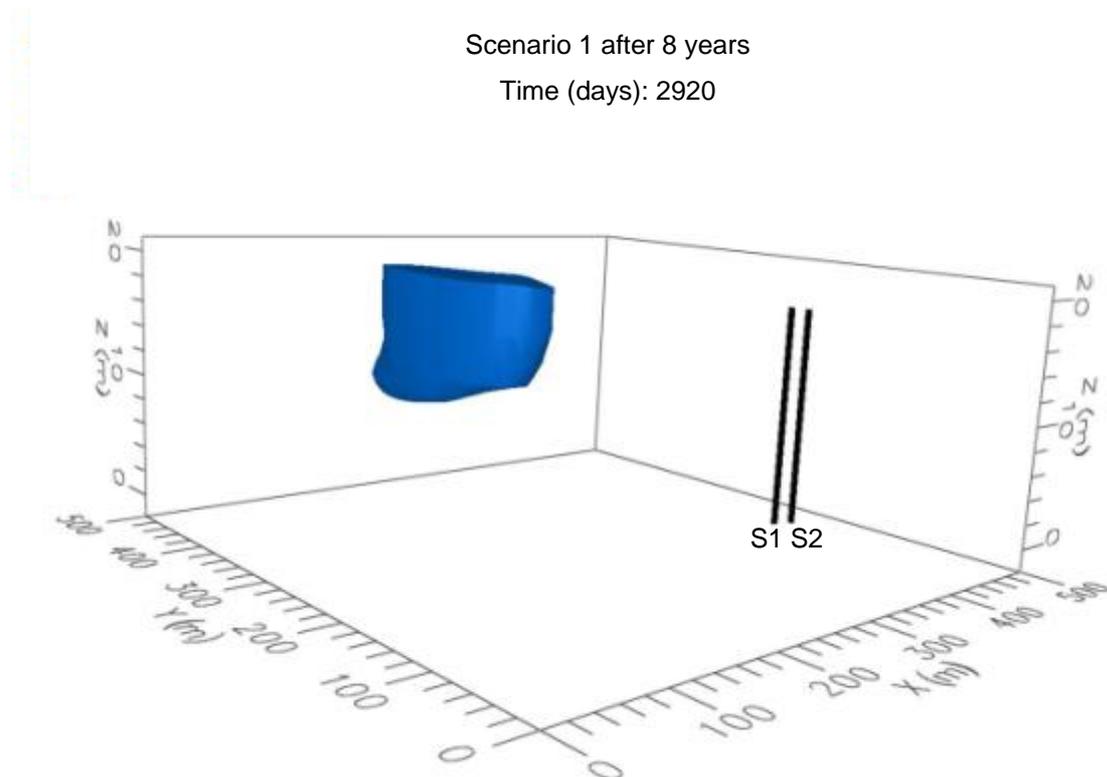
Test	PW1 (m <sup>3</sup> /d)	PW2 (m <sup>3</sup> /d)	PW3 (m <sup>3</sup> /d)	Layer 1	Layer 2	Layer 3
0	0	0	0	10	9	4
1	-1000	0	0	8	8	3
2	0	-1000	0	9	9	4
3	0	0	-1000	10	9	4
4	-1000	-1000	0	8	8	3
5	0	-1000	-1000	9	8	4
6	-1000	0	-1000	8	8	3
7	-1000	-1000	-1000	7	8	3
8	-1000	1000	-1000	8	8	3
9	-1100	-1100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

It is possible to understand that to eliminate with efficacy the contaminant plume, it is always necessary to pump in well PW1. Well PW2 can be a important in order to reduce the pumping rates established, but as test 1 and 4, when PW1 pumping rate is high, PW2 is unnecessary. The same consideration can be done to well PW3, however as it is more distant to the source of contamination, its impact is less evident.

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 costive system to implement and achieve the similar results in the same time frame than test 7, that implies less pumping rate, or test 10, that only uses two wells. The same type of approach, to establish a pump-and-treat system was applied in a study developed by Baú and Mayer (2008).

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

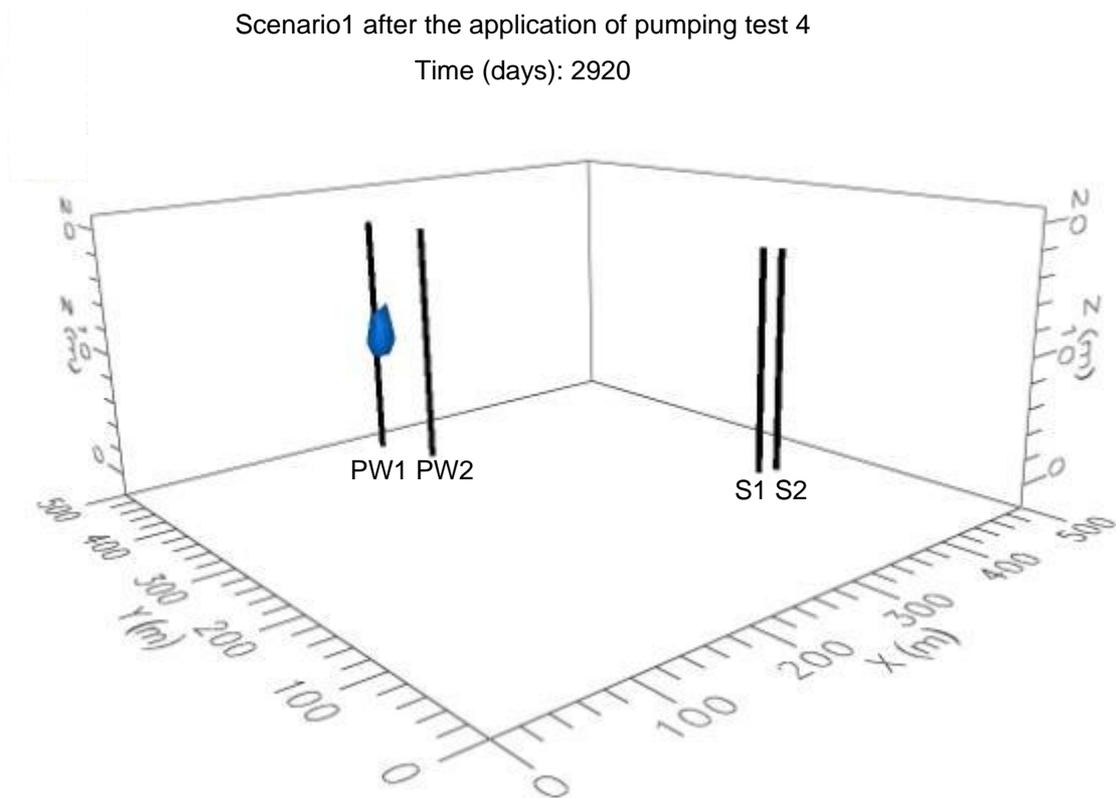
The location and pumping rate applied to a plume can change the shape of a plume, since the groundwater flow, near the well, changes of direction. This process can originate hidden plumes, because part of the plume is outside the well influence, or due to differences in soil composition, which makes the necessary pumping effort too high, to achieve a full recover. In Figure 21 the plume resulting from scenario 1 is showed, after 8 years, during which the source of contamination was found and stopped and no treatment technology was applied.



**Figure 21** – Evolution of scenario 1 after 8 years without any kind of treatment applied. S1 and S2 are the supply wells.

As it can be seen, when comparing Figure 11 and Figure 21, the plume suffered a change on the shape and size. The plume has narrowed in the groundwater flow direction and in the opposite direction of the flow, due to action of NA.

In every pumping test applied, to scenario 1, it was observed that the most difficult area to decontaminate was the aquitard zone. Two examples of the resulting plumes of the application of pumping tests to scenario 1 are present in Figure 22 and Figure 23.

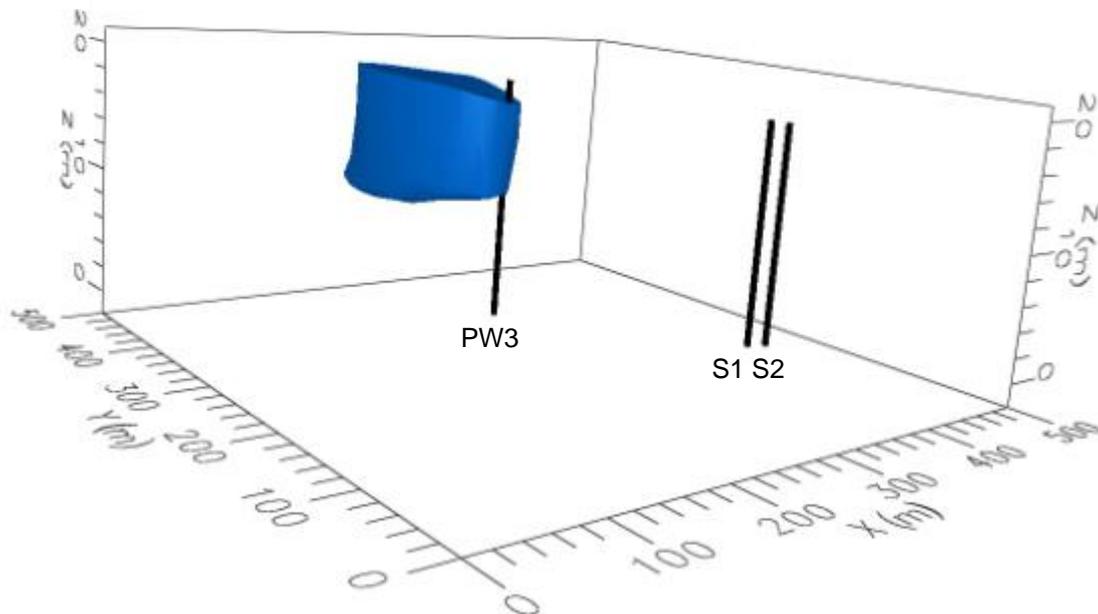


**Figure 22** – Hidden plume that is not detected by observation wells, resulting from the application of test 4, in well PW1 and PW2, in scenario 1. S1 and S2 are the supply wells.

In test 4, pumping from well PW1 and PW2 did not allow recovering part of the plume that was between the two wells (see Figure 22), in the middle layer. In fact, in all tests, this zone, the aquitard zone, was the most difficult to recover, since the capillary pressure necessary to recover a contaminant is very high.

Scenario 1 after the application of pumping test 3

Time (days): 2920



**Figure 23** - Hidden plume, not detected by observation wells, resulting from the application of test 3, in well PW3, in scenario 1. S1 and S2 are the supply wells.

In test 3, as seen in Figure 23, the pumping well that was operating in this test, was PW3. The plume remains in the upper layer and a small part of the plume is, behind PW1 since, part of the contaminant travels outside the groundwater flow direction, due to dispersion. These observations are of extreme importance since if the pumping wells were the only wells available to monitor the aquifer, the two plumes could not be identified if:

- in test 3 part of the plume was outside the wells domain;
- in test 4, if the sampling in well PW1 and PW2 was only made in the first layer.

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.

#### **4.6. Efficiency of pump-and-treat 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 plumes with low advection movement. In those cases, a pumping well was set in the middle of the source area. The well

position (PW0) can be seen in Figure 8. The results from the application of a pumping system are present in Table 25.

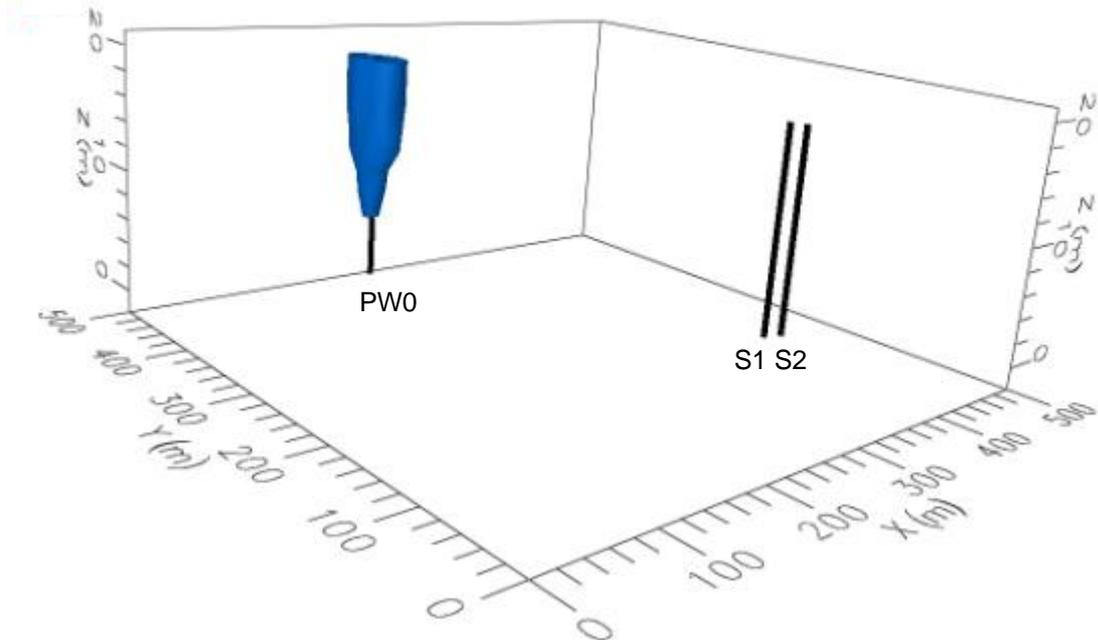
**Table 25** – Plume volume and contaminant mass, within the plume, resulting from the application of a pumping system to each scenario.

Scenario	Pumping system	Plume volume (m <sup>3</sup> )		Contaminant mass within the plume (g)	
		After 8 years	With pumping	After 8 years	With pumping
1	PW1 and PW2	40357	0	3.98	0
2	PW1 and PW2	26512	0	2.65	0
3	PW0	4776	21.1	0.85	0.001
4	PW0	3727	13.4	0.65	0.001
5	PW0	473	126	0.12	0.015
6	PW0	379	38.1	0.12	0.003

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. The plume that results from the pumping, in scenario 5, can be observed in Figure 24.

Scenario 5 after pumping

Time (days): 2920



**Figure 24** – Plume that remains after the application of pumping wells in scenario 5. S1 and S2 are the supply wells.

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. To recover all the contaminant more time would be needed. A similar observation was made in Figure 22.

The plume, remains in the aquitard zone, behind all the wells, which does not allow its detection. Although there is a dominant flow direction, part of the contaminants travelled through dispersion, in the opposite way, outside the reach of the pumping well. The part of the plume that obeyed to the dominant groundwater movement flow was recovered.

#### **4.7. Efficiency of the implementation of PRB technology**

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 movement did not substantiated the use of such technology. The obtained results for the application of a PRB are showed in Table 26.

**Table 26** – Plume volume and contaminant mass, within the plume, resulting from the application of a PRB system to each scenario.

Scenario	Plume volume (m <sup>3</sup> )			Contaminant mass within the plume (g)		
	After 8 years	With barrier	Volume decrease (%)	After 8 years	With barrier	Mass decrease (%)
1	40357	789	99.4	3.98	0.05	99.9
2	26517	0	100	2.65	0	100

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 (Table 21); 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 better the plume. A bigger barrier was not tested, since no scientific source was identified using a bigger barrier.

Vogt *et al.*, (2004) proved the efficiency of the application of PRB, *in situ*, in the presence of oxygen and nitrate and were able to isolate the strains of bacteria responsible for the degradation process. Most of the strains identified were Pseudomonads and Rhodococci.

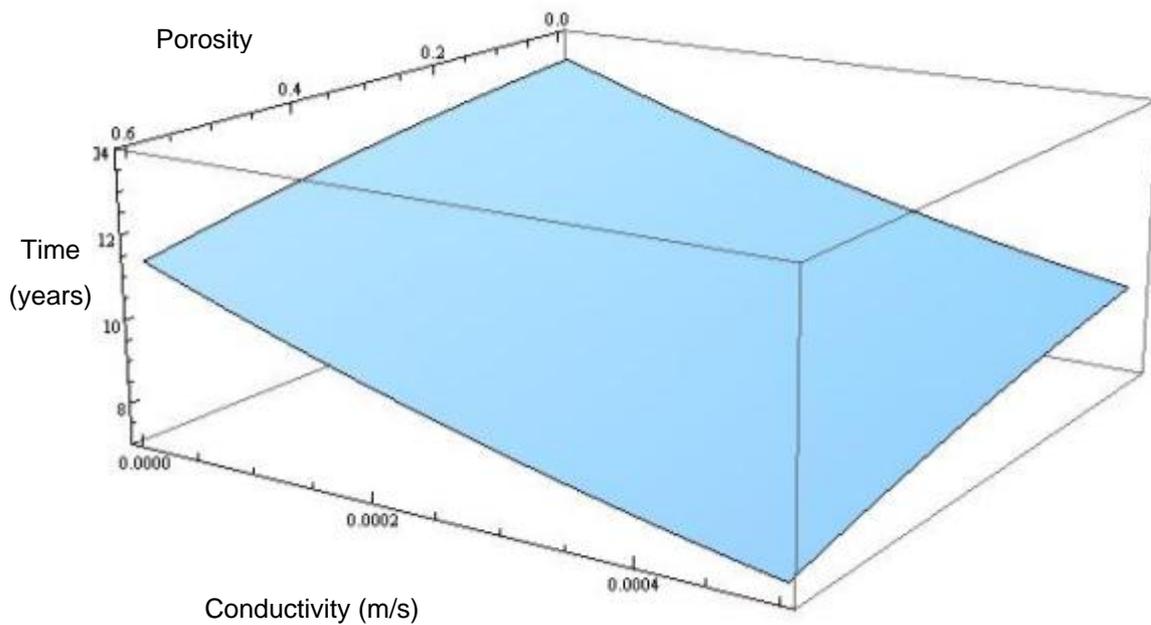
#### **4.8. Time necessary to recover the plume resulting from each scenario**

The next step was to evaluate which scenario had been decontaminated faster and the results are showed in Table 27.

**Table 27** – Time necessary for the contaminant removal in each layer, when a treatment technology is applied.

Scenario	Pumping system	Time to decontaminate (years)		
		Layer 1	Layer 2	Layer 3
1	PW1 and PW2	7	8	3
2	PW1 and PW2	7	8	3
3	PW0	11	9	1
4	PW0	11	9	1
5	PW0	12	11	Not contaminated
6	PW0	12	12	Not contaminated

At first, when comparing scenarios 1, 2 and scenarios 3 and 4, one can conclude that for equal or similar conductivities (see Table 9), despite the porosity, the time needed to decontaminate is the equal. Another important observation is that as conductivity increases the contaminants travel to the lower layers, making those layers harder to remediate. However the upper layers become more easily recovered. In Figure 25, it is presented the graphic resulting from the application of a non linear regression based on the time needed to decontaminate the plume in function of soil porosity and hydraulic conductivity.



**Figure 25** – 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% and for hydraulic conductivity is  $1.02 \times 10^{-2}$  m/s. These values can be calculated by applying a partial derivate to the equation obtained, by non-linear regression, and equalling the result equations to zero.

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

A sensitivity analysis was made in order to evaluate if assuming a  $f_{OC}$  value, between the range 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 28.

**Table 28** - Results of  $f_{OC}$  sensitivity analysis.

Test	$f_{OC}$	Volume (m <sup>3</sup> )			Contaminant mass (g)		
		Initial plume	After 8 years	Volume decrease (%)	Initial plume	After 8 years	Mass decrease (%)
A	$1 \times 10^{-3}$	403552	0	100	49	0	100
B	$1.25 \times 10^{-3}$	349182	0	100	78	0	100
C	$2.5 \times 10^{-3}$	225779	75050	66.8	151	4.67	98.7
D	$5 \times 10^{-3}$	141041	40357	71.4	358	3.98	97.4
E	$7.5 \times 10^{-3}$	70936	9124	87.1	779	0.75	99.0
F	$1 \times 10^{-2}$	35248	7135	79.8	980	0.59	98.8

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 (equation 12), the amount of contaminant that is adsorbed is higher, taking more time to degrade.

When analysing the behaviour of plume volume and mass of contaminant during the period when only NA occurs, the results are quite different. 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. Due to this fact it is expected that as  $f_{OC}$  increases the plume volume and mass of contaminant increases. Yet, for a certain value of  $f_{OC}$ , the analyses change. As  $f_{OC}$  increases, the amount of trapped contaminant is higher, leading to 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 set in the previous paragraph.

**Table 29** – Time required decontaminating each layer considering different values of  $f_{OC}$ .

Test	$f_{OC}$	Layer 1	Layer 2	Layer 3
A	$1 \times 10^{-3}$	8	8	9
B	$1.25 \times 10^{-3}$	9	9	9
C	$2.5 \times 10^{-3}$	10	9	8
D	$5 \times 10^{-3}$	10	9	5
E	$7.5 \times 10^{-3}$	10	10	4
F	$1 \times 10^{-2}$	10	10	4

For layer 1 and 2 as the amount of organic carbon is higher, the time needed to remediate the layer is longer. Since the contaminant stays trapped, the plume volume can be small, yet it has a high concentration of contaminant. When analysing layer 3, for small amounts of organic carbon, the layer takes more time to decontaminate. In fact, as the most part of the contaminant travels through the soil, without being adsorbed, it reaches the lower layers.

As  $f_{OC}$  is used to determine the distribution coefficient, in a real site study, determining 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).

## 5. Conclusions

Groundwater contamination by chlorobenzenes can be a serious issue, due do the contaminants hazardous properties. European legislation has already stated limit values, and target dates in order to access quality and define recovery objectives for the next few years.

An important analysis of the factors that influence the plume size, concentration and distribution was made. The plume size increases with low hydraulic conductivities and low porosities. The same observation can be made for the evolution of the total mass within the plume. Since the contaminants velocity is a function of these factors, these results were expected. As porosity and hydraulic conductivity increases the three types of mechanism take place that induce a reduction on plume value:

- The advection component is higher, leading to higher plume volume and dilution and lower levels of contaminants within the plume;
- There is a bigger surface area, allowing degradation to be more effective;
- The concentration decreases within the plume, reducing the levels of toxicity to bacteria, improving degradation.

The last mechanism could not be evaluated in this study, since the degradation model was of first order decay.

NA has proved to be an effective way to reduce the mass of contamination. Nevertheless, it has small effect on reducing the plume size. Besides, in none of the scenarios, the supply wells were at risk of being contaminated, a technology that could reduce the plume size would be more adequate, in order to prevent the contamination spreading.

Hydraulic conductivity has an important influence in NA. The results showed that for scenarios with the same or similar hydraulic conductivity, the movement and loss of the contaminant plume was similar. Scenarios 4 and 5, for instances, had very distinct porosities, and, yet, its behaviour was similar. As a result, hydraulic conductivity has proved to be the main factor influencing the plume movement, shape and loss by NA, for the conditions tested in this model.

The results obtained with the pumping tests application revealed that this option can represent an interesting approach. Besides achieving a simple graphic that allows identifying varied possibilities to remove the contamination, also proves that a multiple pump systems can offer better results than a single and well located well. Another important point that was observed in this stage was the possibility of pumping systems, enhance the formation of hidden plumes or, in some cases, diving plumes. Diving plumes allow chemicals to migrate bellow the observation wells, becoming undetected. This matter is well characterized in API (2006), which attent to the diving plumes issue, risk factors and methods to assess the dive. In order to

identify the possibility of a diving plume to occur and to rapidly detect its development, modelling is an essential tool as well as monitoring wells at different depths.

The pump-and-treat technology did allowed a full recovery in all scenarios. Nevertheless, in the second layer of scenario 5 and 6 it did not induced a faster removal. In fact it induced the formation of hidden plumes. To enhance the treatment efforts, a higher pumping rate should be applied, or a removal of part of the contaminated soil.

The results with PRB were, almost, as good as the pumping system results. Even so, in order to have good performance results, it can only be applied to plumes, well developed through, groundwater direction flow. Soils that induce little plume movement are faster to treat by pumping system and will not have good results with PRB. Soils that allow plume migration are better recovered with pumping system, but the possibility to combine the two technologies would bring better results.

When analysing the time needed to treat the plume evidences show that very low or very high hydraulic conductivities lead to faster decontamination rates. In the first case low conductivities result in smaller plumes, which allow a rapid contaminant recovery, when a pump well is settled, if the pumping rate is high. In the second case, besides high hydraulic conductivities provoke a wider plume, when the pumping rate is stronger, it inverts the groundwater movement towards the well, in a high velocity, allowing a rapid recovery. When hydraulic conductivity is  $1.02 \times 10^{-2}$  m/s, the equilibrium between plume dimension and plume resilience is achieved, which is the worst scenario for contaminant removal.

On what concerns porosity, the time needed to treat the plume shows that for very low or very high soil porosity, the decontamination rates are higher. When porosity is low, the contaminants stay trapped in the soil pores, and the pressure necessary to remove them is so high that it would be required a very high pumping rate. When porosity is very high, the contaminants tend to travel faster, within the soil, especially by gravity, being more difficult to recover and requiring a higher pumping rate. If porosity is of 50%, 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 sensitivity analysis of  $f_{OC}$  shows that this factor has a major impact on the resulting plume volume and mass. In this study it was not possible to determine an exact value for  $f_{OC}$ , since the scenarios are hypothetical, in a real site study, the experimental determination of this parameter, distribution coefficient and degradation rate should be realized.

Despite, the fact that this study was made considering one specific topography and geochemical distribution, the same principles can be applied in different soil geologies. However the values and equations are not applicable. The software used proved to be an important tool

to evaluate groundwater contamination, efficacy of the treatment technologies that can be applied and the possible problems resulting from its application. However, it is necessary to take into account the assumptions and corrective measures applied and the error associated with these actions. Software can only predict the most probable mechanisms that would occur, but since soil and groundwater are interactive, it cannot consider specific mechanisms that act in each part of the system in study.

## **6. Future work**

A real contaminated site could not be the basis of this study, since the contaminated sites location is still being evaluated, in Portugal.

For future work, it would be of the best interest, to develop a connection between the work developed, in this study, and a contaminated site, in order to enhance groundwater characterization and treatment. It would also, allow determining some of the parameters introduced in the model, with more accuracy (such as degradation rate, distribution coefficient, porosity, hydraulic conductivity), which is of the most importance, considering the varied values determined, for each type of soil, at a laboratory scale, published in scientific journals.

The experimental determination of these parameters would improve, considerably, the software ability to predict the need to implement treatment technologies and the outcome of its application.

Also, the same type of approach can be done to industrial sites, where the model could be applied as a risk assessment tool and part of the emergency plan. Since the model could predict the plume resulting from a spill and could help establishing the measures that could be taken, in order to minimize the effects of the accident.

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## **Annex A – Chemical, physical and hazardous properties for the compounds in study**

**Table A. 1** – Physical and chemical properties of the compounds under study.

<b>Properties</b>	<b>Benzene</b>	<b>Hexachlorobenzene</b>	<b>Pentachlorobenzene</b>	<b>Trichlorobenzenes</b>	<b>1,2,4-Trichlorobenzene</b>
CAS number	71-43-2	118-74-1	608-93-5	87-61-6	120-82-1
Melting point (°C)	5.5	231.8	86	64	17
Boiling Point (°C at 1013.25 hPa)	80	325	277	220.5	213.5
Molar weight (g mol <sup>-1</sup> )	78	285	250.5	181.5	181.5
Density (g/cm <sup>3</sup> at 20 °C)	2.04	1.21	1.8	1.69	1.46
Vapour pressure (hPa at 20 °C)	0.0983962	0.1399796	0.00101	0.458	0.46
Partition Coefficient (log Kow at 25 °C)	2.13	5.73	5.17	3.93	4.02
Water solubility (mg/l at 25°C)	1.79	0.0062	none	none	none
Henry's law constant (atm m <sup>3</sup> /mole at 25 °C)	0.00555	0.0017	0.000703	0.00365	0.00142
Atmospheric OH rate constant (cm <sup>3</sup> /molecule-sec at 25 °C)	1.23 x10 <sup>-12</sup>	2.7 x10 <sup>-14</sup>	5.79 x10 <sup>-14</sup>	6.79x10 <sup>-13</sup>	5.5 x10 <sup>-13</sup>
Risk phrases	R11, R45, R46, R48/23/24/25, R65, R36/38	R45, R48/25, R50-53	R11, R22, R50-53	R22, R50-53	R22, R38, R50-53

Source: (ESIS, 2000 (a), (b) and (c)), (ATSDR, 2002 (a) and (b)), (Government of Canada, 1993 (a), (b), (c) and (d)).

**Table A. 2** - Hazardous properties for the compounds under study and concentrations limits.

<b>Code</b>	<b>Hazardous</b>	<b>Risk Phrases</b>	<b>Limit Concentrations</b>	<b>Substances</b>
H3A/H3B	Highly Flammable/Flammable	R11	<21°C	Pentachlorobenzene and Benzene
H4/H8	Irritant/Corrosive	R36/38 R38	<20%	Benzene and 1,2,4-Trichlorobenzene
H5/H6	Harmful/Toxic	R22 R48/25 R48/23/24/25 R65	R22<25%	Pentachlorobenzene, Trichlorobenzenes and 1,2,4-Trichlorobenzene
			R48/23/24/25 R48/25 R65 <3%	Hexachlorobenzene and Benzene
H7	Carcinogenic	R 45	<0.1%	Hexachlorobenzene and Benzene
H11	Mutagenic	R46	<0.1%	Benzene
H14	Ecotoxic	R50/53	<0.25%	Hexachlorobenzene, Pentachlorobenzene, Trichlorobenzenes and 1,2,4-Trichlorobenzene

Source: (ESIS, 2000 (a), (b) and (c)), (EA, 2006).