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CL:AIRE technical bulletins describe specific techniques, practices and methodologies currently being employed on sites in the UK within the scope of CL:AIRE technology demonstration and research projects. This Bulletin is the first of a series which supports an integrated approach to the investigation of NAPL contaminants in fractured rock systems.

Definitions of words written in bold type may be found in the Glossary of Terms within the Publications section of the CL:AIRE Web site at http://www.claire.co.uk

# INTRODUCTION TO AN INTEGRATED APPROACH TO THE INVESTIGATION OF FRACTURED ROCK AQUIFERS CONTAMINATED WITH NON-AQUEOUS PHASE LIQUIDS

## 1. INTRODUCTION

The UK and many other jurisdictions have adopted a risk-based approach to managing contaminated sites. In order to determine the risk that contamination may pose at a site, and to manage that risk, it is necessary to have a good understanding of the nature and distribution of contaminants in the subsurface and how the contaminant will behave within the soil and/or groundwater system.

Collecting environmental data is expensive. Owners of contaminated sites must balance costs against the need for adequate information about the subsurface conditions and contaminant distribution to be able to make informed decisions about whether the contamination represents a threat to human health or the environment.

Contamination of fractured rock **aquifers** by **non-aqueous phase liquids** (NAPLs) is a worldwide problem. The resulting groundwater contamination is difficult to manage, due in part to the problems associated with collecting the necessary data to understand contaminant behaviour within the system properly.

This technical bulletin is the first of a series which supports an integrated approach to the investigation of NAPL contaminants in fractured rock systems. It describes techniques and procedures for obtaining data to manage contaminated groundwater. Topics discussed in this series include multilevel sampling systems, hydraulic testing, groundwater sampling and borehole geophysics.

The purpose of this bulletin is to introduce some concepts and terminology to those who may have an interest in managing sites involving contamination in fractured rock systems. It is not the intention to provide an exhaustive treatment but rather to provide the reader with a general understanding of some of the issues and of the complexity of the problem. It is the intention that this publication will highlight the need for problem holders to acquire the necessary expertise to help them manage their problem.

## 2. PROBLEM DEFINITION

Management of NAPLs in fractured rock systems requires considerable knowledge and understanding of contaminant behaviour in the subsurface. This requires understanding of the physical and hydraulic characteristics of the fracture system, and the physical and chemical characteristics of the contaminant and its distribution within the system.

Obtaining the necessary site information involves a series of tests requiring specialised technologies and is generally expensive. Given the limited budgets of many contaminated site owners it is important that the characterisation of the site and the collection of environmental data is carried out in the most cost effective manner.

Site characterisation programmes must be well thought through to optimise data acquisition and to avoid creating additional problems at the site such as the inadvertent re-mobilisation of contaminants.
The following sections provide a background to understanding the basic processes of groundwater flow and contaminant transport.

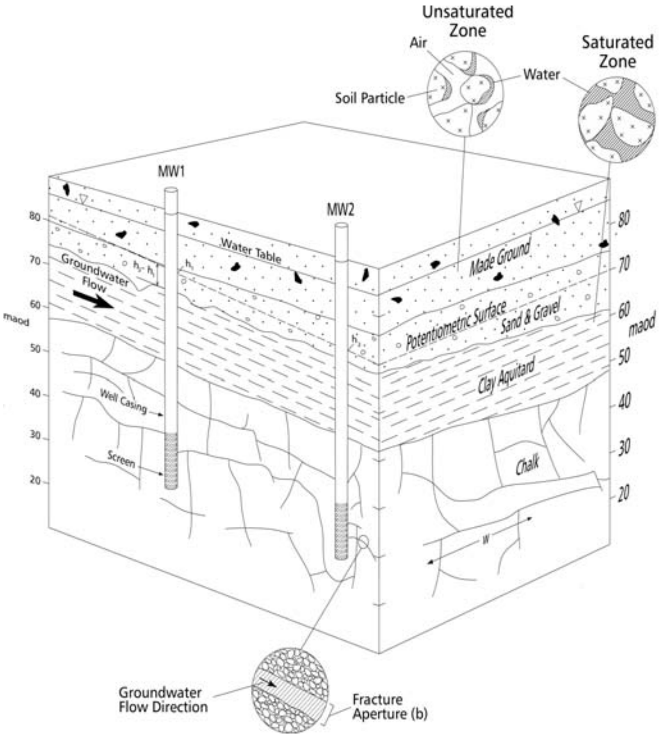

Figure 1: General view of aquifer conditions

### 2.1 Groundwater Flow

Many people are familiar with the **hydrologic cycle** which describes the distribution of water within the **biosphere**. Water evaporates from sources such as lakes and oceans and falls as precipitation. Rain falling on land is divided between surface water runoff, evaporation and **infiltration**. Some of the water that infiltrates, migrates under gravity through voids or pore spaces in the subsurface material, and eventually reaches the **water table**.

The degree of interconnectivity of the subsurface void or pore space is referred to as **permeability**. The greater the permeability or interconnectedness, the greater the volume of water that can infiltrate and be transmitted in a given time.

The water table marks the approximate location of the interface between the overlying **unsaturated** zone and the underlying **saturated** zone (Figure 1). The unsaturated zone is characterised by pore space which is partially filled with water. The water is held by capillary forces by soil/rock particles, and is under negative pressure. This water will not flow under the influence of gravity. In the saturated zone, where the pore space is completely water filled, water is under positive pressure and will flow under the influence of gravity and in response to natural differences in fluid pressure. There is a narrow zone between the unsaturated zone and the saturated zone which is called the **capillary fringe**, in which the pore space is completely

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saturated, but the fluid pressure is negative due to capillary forces. The location of the water table is measured in monitoring wells often as an elevation relative to a defined datum such as ordnance datum (od) or a local datum.

Aquifers are portions of the saturated zone which yield useful volumes of water such as drinking water or industrial process water. A zone which does not yield useful quantities of water is termed an **aquitard**. Aquifers can comprise **consolidated** rock or bedrock such as chalk, limestone or sandstone or **unconsolidated** materials such as sands and gravels. In the UK, chalk is considered to be the most important aquifer.

In unconsolidated sand and gravel aquifers, the volume of groundwater flowing through the formation is calculated by a simple equation known as **Darcy's Law** (Equation 1):

$$Q = -K\,iA \qquad \text{(Eqn 1)}$$

Where Q = the volume of groundwater flow ($l^3/t$)
K = hydraulic conductivity (l/t)
i = hydraulic gradient (l/l)
= $(h_2-h_1)/d$
h = head, or the elevation of water in a well above a defined datum
d = horizontal distance between head measurements
A = cross sectional area of the aquifer
= thickness multiplied by width ($l^2$)

**Hydraulic conductivity** refers to the ease with which water flows through the aquifer and is directly related to permeability. It can be measured in the field using a variety of tests (see TB3) and has units of length divided by time. **Hydraulic gradient** is the driving force of groundwater flow and since groundwater flow is three dimensional, it has both horizontal and vertical components. It is calculated by dividing the difference in **head** between two measured points by the horizontal or vertical distance between them. Head is the level to which water will rise in a well, measured in units of length as an elevation. Water flows in the direction of greatest head to lowest head. Head measurements as water levels are a standard field determination.

The cross sectional area of an aquifer is estimated from the knowledge of the local geology, taken from boreholes, and requires estimates of the aquifer width and thickness.

Two dimensional horizontal groundwater flow in unconsolidated aquifer materials is illustrated in Figure 2. The cross-sectional area of the aquifer is estimated as the thickness of the aquifer (see ht in Figure 2) multiplied by the width or lateral extent of the aquifer which is perpendicular to the plane of the page.

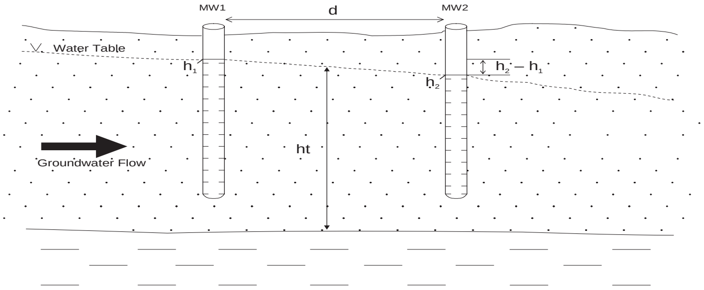

**Figure 2: Groundwater flow in unconsolidated materials.**

The volume of groundwater flowing through fractured rock can be calculated in two ways. If the system is sufficiently fractured, it can be considered to behave like an unconsolidated aquifer system or a uniform porous medium, and groundwater flow can be estimated using Darcy's Law. If the system is not well fractured or it is not considered appropriate to treat the system as a uniform porous medium, then groundwater flow can be calculated in individual fractures by the following equation (Equation 2):

$$Q = \frac{b^3}{12\mu}\, w\triangle h \qquad \text{(Eqn 2)}$$

Where Q = volume of groundwater flow through the fracture ($l^3/t$)
b = fracture aperture (l)
μ = fluid dynamic viscosity (m/lt)
w = fracture width (l)
$\triangle h = h_2 - h_1$ (head difference)

The **aperture** of the fracture is the distance between its two walls and is typically fractions of a millimetre to several millimetres. The width of the fracture is its lateral extent and can be estimated from regional fracture mapping at surface outcrops and from borehole information. The dynamic viscosity of water in the aquifer at a given temperature has a constant value.

The equation governing groundwater flow in fractures is known as the "**cubic law**" and shows that only a slight increase in fracture aperture can result in significantly higher volumes of groundwater flow. If the aperture is doubled, the amount of groundwater flow through the fracture is increased by a factor of eight.

Fractures in rock may account for only about 1% of the total aquifer volume, but they accommodate most of the groundwater flow. In some rock types, such as chalk and sandstone, significant volumes of water are tied up between the grains which make up the matrix of the rock mass, but because the permeability of the matrix is so low, the rate of groundwater flow within it is very small compared to the rate of flow through the fractures.

Groundwater flow in a fractured rock system which is overlain by an aquitard is shown in Figure 1. The aquitard acts as a **confining layer** above the aquifer. If monitoring wells are completed in the aquifer, the level to which water rises in the well will be above the top of the aquifer formation. This equilibrium level is termed a **potentiometric surface** rather than a water table, and is a characteristic of **confined aquifers**. If the potentiometric surface extends above the ground surface, the well will flow under natural conditions and is termed an **artesian well**.

## 2.2 Contaminants

Non-aqueous phase liquids (NAPLs) is a term given to several chemical groups of contaminants which maintain a separate phase when they come into contact with water.

Environmental practitioners distinguish between two types of NAPL - **LNAPLs** and **DNAPLs**. LNAPLs are lighter or less dense than water (e.g. petroleum products such as petrol and lube oil) and will form a separate phase on the surface of the water table and commonly depress it. DNAPLs are more dense than water and will sink through the water column until they reach an impermeable boundary and form a separate phase along this interface. Examples of DNAPLs are coal oil, and chlorinated solvents such as **trichloroethene** (TCE), a degreasing agent which was in common industrial use during the 1950s to 70s.

Whilst NAPLs in sufficient volume form a separate phase with water, a small percentage of the NAPL will dissolve. The degree to which a NAPL dissolves in water is termed its **solubility** and is measured in terms of mass of substance per unit volume of water for a given water temperature. Whereas in chemical terms the solubility of NAPLs is quite low, in human health and environmental terms, it can be very significant because of the extreme toxicity of some NAPL compounds.

**Benzene** is a component of petrol. Benzene in pure product form and petrol are both LNAPLs. Benzene is an EEC Class 1 carcinogen (EEC, 1967). Its European Drinking Water Standard is 1 μg/L (microgram per litre) or 0.000001 grams of benzene for each litre of water. While its solubility is low by chemical standards at 1,750 mg/L (milligrams per litre) or 1.75 grams per litre of water (at 25 °C) (USEPA, 1990), it exceeds the safe drinking water limit by approximately 1.8 million times. Likewise, TCE, a Category 3 carcinogen (EEC, 1980), has a European Drinking Water Standard (EEC, 1998) of 10 μg/L* but a solubility of 1,400 mg/L (at 25 °C) (USEPA, 1990), which as a minimum is approximately 140,000 times the safe drinking water limit.

Highly toxic NAPLs form some of the commonest chemical compounds currently in use today and in the recent past, and are commonly stored on site. Spillage and leakage of these compounds over time can cause significant impacts to soil and groundwater. Whilst there is growing awareness of the potential problems with careless management of these chemicals today, many of the problems that have arisen are associated with past activities when the environmental cost of such lack of care was not considered.

When a NAPL leaks from a storage tank or it is spilled on the ground, it begins to infiltrate the subsurface both downward under the influence of gravity and laterally. The NAPL will continue to migrate through the unsaturated zone displacing the air that is in the pore spaces. Provided there is sufficient volume in the source, the NAPL will continue downward until it reaches the water table.

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* European Drinking Water Standard of 10 μg/L includes both TCE and PCE.

If the NAPL is a DNAPL, it will continue to penetrate the saturated zone moving through fractures, displacing water, and continuing downward. The connected DNAPL which occupies the pore space in the unsaturated zone and the fractures in the saturated zone, forms a vertical column of higher density liquid which generates sufficient downward pressure to displace water in the lower fractures. This displacement will continue as long as the pressure of the DNAPL "column" exceeds the displacement pressure of the water in the fracture. Consequently, DNAPLs can migrate to significant depths in fractured rock. A DNAPL spill is shown in Figure 3.

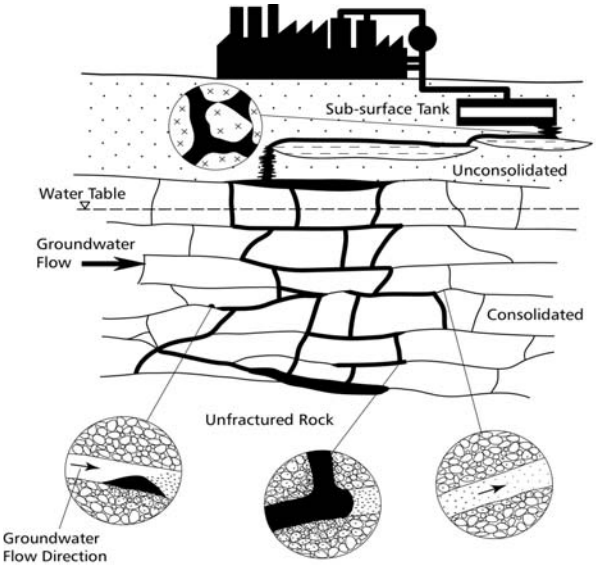

Figure 3: Diagram of DNAPL spill (adapted from Pankow and Cherry, 1996 and Jackson *et al*., 1992)

LNAPLs, on the other hand, will typically resist migration below the water table because of the buoyancy effects arising from their lower density, and will tend to migrate laterally across the top of the water table. In the case of large spills, the weight of the LNAPL can depress the water table. Theoretical calculations and field studies have shown that where there is a sufficient "column" of LNAPL, it will penetrate below the water table to a limited extent when the pressure exerted by the column exceeds the displacement pressure of the water in the fractures (Figure 4).

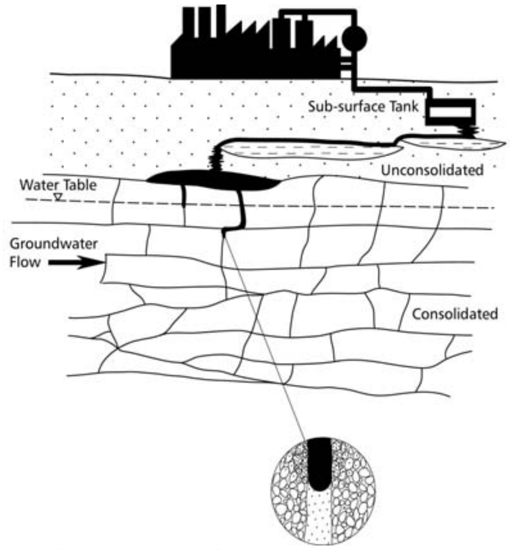

Figure 4: Diagram of LNAPL spill (adapted from Pankow and Cherry, 1996 and Jackson *et al*., 1992).

If the supply of NAPL in the spill is terminated, the NAPL will continue to drain from pore spaces under gravity. However, a small amount of NAPL will be left in the pores which will not drain and is held by capillary pressure within the soil particles or in fractures. The NAPL that remains is termed "residual". If the **residual NAPL** becomes disconnected it forms discrete NAPL "fingers" called **ganglia**. Residual NAPL remains a long term continuous source of contamination as it is dissolved gradually by infiltrating precipitation in the unsaturated zone or by flowing groundwater in the saturated zone. The portion of the subsurface containing NAPL is called the **source zone**.

In situations of fluctuating water levels where the water table rises and falls in response to infiltration and discharge, LNAPL on the water table will fall when the water table falls. When the water table rises, some of the LNAPL can remain trapped as residual below the water table and is not displaced from the fractures by the rising groundwater.

Once NAPL- forming compounds are dissolved in water it is no longer proper to use the term NAPL because the liquid is no longer a separate phase. Instead, the contaminant should be identified as being in the dissolved phase (eg dissolved phase TCE or TCE in solution). Dissolved phase contaminants are found downgradient of the source zone. This zone of contamination is termed a **plume**.

Residual NAPL in a chalk aquifer can be depleted by several processes. Dissolved in groundwater a contaminant such as TCE will be carried along by the moving groundwater. This process is termed **convection** and comprises **advection** which is the movement by water, and **dispersion** which is the spreading of the contaminant due to the **tortuosity** or the convoluted pathway that the groundwater takes due to variations in direction of the pore space or orientation of the fractures. Dispersion can occur both laterally and vertically. The migrating TCE forms a contaminant plume which is defined by the extent of measurable concentrations of TCE within the groundwater. Concentrations of TCE in the plume will be higher near the source of the dissolved contaminant and lower further away from the source.

Residual NAPL in a chalk aquifer can also partition to the matrix or the main mass of the chalk by a process of **diffusion**. Diffusion is controlled by chemical gradients, and is much slower than advection. Over time, however, a considerable mass of contaminant can be transferred from fractures to the chalk matrix. If the contaminant is removed from the fracture by a remedial programme involving pumping, so that the fracture contains uncontaminated groundwater, then the chemical gradient between the fracture and the matrix will be reversed, and a portion of the contaminant within the matrix will diffuse back into the fracture, contaminating the groundwater again. This phenomenon is often observed where pump and treat systems have been installed. During pumping, groundwater in the fracture shows a rapid decrease in the concentration of the contaminant to the clean up level. Once the clean up level is reached the pumps are shut off. But gradually the contaminant level in the fracture builds up as the contaminant diffuses from the matrix back into the fracture.

There are a number of processes which occur naturally and which can reduce the concentration of the contaminant. The most common include: **dilution**, **sorption**, **volatilisation**, and **biodegradation**. Dilution is the reduction in contaminant concentration due to mixing with a higher proportion of less or non-contaminated groundwater. Sorption is a surface effect whereby the contaminant is attracted to and adheres to the surface of the solid particles which make up the aquifer matrix. Volatilisation represents a phase change from a liquid to a gas. Both benzene and TCE are volatile organic compounds (**VOCs**) and can migrate naturally from the aqueous phase at the top of the saturated zone into a gaseous phase in the unsaturated zone. Biodegradation is the breakdown of the contaminant by microbes such as bacteria and fungi. Most contaminated sites contain large numbers of naturally occurring microbes which have adapted to the site conditions and can degrade or partially degrade certain contaminants.

These naturally occurring processes may, in some circumstances, provide an acceptable means of managing a contaminated site, although sufficient characterisation and monitoring are required to demonstrate that these processes are occurring and are adequate. This management technique is called **monitored natural attenuation**.

## 3. AN INTEGRATED APPROACH TO THE INVESTIGATION OF FRACTURED ROCK AQUIFERS

Spills of NAPL require immediate action, but the migration of NAPLs into the subsurface, particularly DNAPLs, is an extremely complex process and difficult to predict.

In a typical contaminated site scenario, the first consideration is to identify and remove the mobile portion of the source if possible, to prevent it from spreading and acting as a long term source of contamination. The site investigation, is carried out to characterise the subsurface conditions in an attempt to assess the potential impact of the contaminant release. An initial **conceptual model** of the site is developed from existing information. It is important at this stage, and particularly with DNAPL sources, that the site characterisation programme is thought through carefully to avoid exacerbating the problem. Drilling in the middle of a DNAPL source can open up new pathways for DNAPL migration and cause the spread of the contaminant, making remediation more difficult and more expensive. In complex situations the site characterisation process may be carried out in stages, where investigation starts around the periphery of the source to develop an understanding of the subsurface conditions and groundwater flow system and to improve the conceptual model. New information to fill gaps in knowledge about the ground conditions at the site, and the nature and distribution of the contaminants is needed to update the conceptual model. The revised model is used to develop a long term management plan for the site. A variety of numerical models are applied to the field data to represent and predict the fate of contaminants within the aquifer.

The detailed conceptual model shown below (Figure 5) was developed from the results from two phases of investigation, carried out by University of Sheffield and funded by TotalFinaElf, at an active petrol station where approximately 55,000 litres of petrol had leaked from underground storage tanks. The data collected was used to provide an improved understanding of the groundwater flow system, the distribution of contaminants, geochemical conditions and the microbial ecology in the aquifer and to model the fate and transport of petrol contaminants within the source zone and downgradient of the source zone in the dissolved phase plume.

The illustrated model shows the residual source zone in dark grey shading occupying vertical and horizontal fractures in the area around monitoring well MW7. A plume comprised of diesel range hydrocarbons (DRHC), benzene, toluene, ethylbenzene and xylene (BTEX), methyl tertiary-butyl ether (MTBE) and tertiary methyl-amyl ether (TAME) is shown in lighter grey shading extending approximately 30 m downgradient to MWS15. The MTBE and TAME plume shown in white extends approximately 155 m downgradient to MWS16.

The model depicts a rapid decrease in the effective solubility of MTBE in the source zone compared to benzene, indicating that MTBE will be dissolved out of the source zone area in considerably shorter time than benzene. This implies that benzene will continue to act as a contaminant source to groundwater for some time after the MTBE has been removed. Contaminants, as a dissolved phase in groundwater, are transported by the process of advection via fractures. Some of the source zone contamination will migrate from fractures into the chalk matrix via diffusion. Over time, as the contaminant concentration in the source term is depleted, and the dissolved phase contaminant concentration in the fractures decreases, contaminants within the matrix will diffuse back into the fractures and continue to contaminate groundwater in low concentrations.

Evidence for the natural biodegradation of BTEX within the plume area is inferred from a reduction in BTEX concentrations and changes in **redox** conditions whereby dissolved oxidants such as $O_2$, $NO_3^-$ and $SO_4^{2-}$, and mineral oxidants such as $MnO_2$ and $Fe(OH)_3$ become depleted in favour of reduced species.

The conceptual model is used to argue that natural attenuation processes are taking place within the aquifer, and that natural attenuation is a potentially viable approach to the management of the site, and demonstrates how a well planned, integrated, and phased approach to site characterisation can optimise cost effective, high quality data retrieval and build confidence in developing a preferred management option for a contaminated site.

Such information is obtained through a variety of integrated techniques which require planning by a team with relevant expertise to ensure the cost effective acquisition of good quality data on which to develop a management plan. Techniques used to obtain the data which led to the conceptual model shown in Figure 5 included multilevel sampling systems, hydraulic testing, groundwater sampling and borehole geophysics. These are described in detail in CL:AIRE Technical Bulletins 2-5 respectively.

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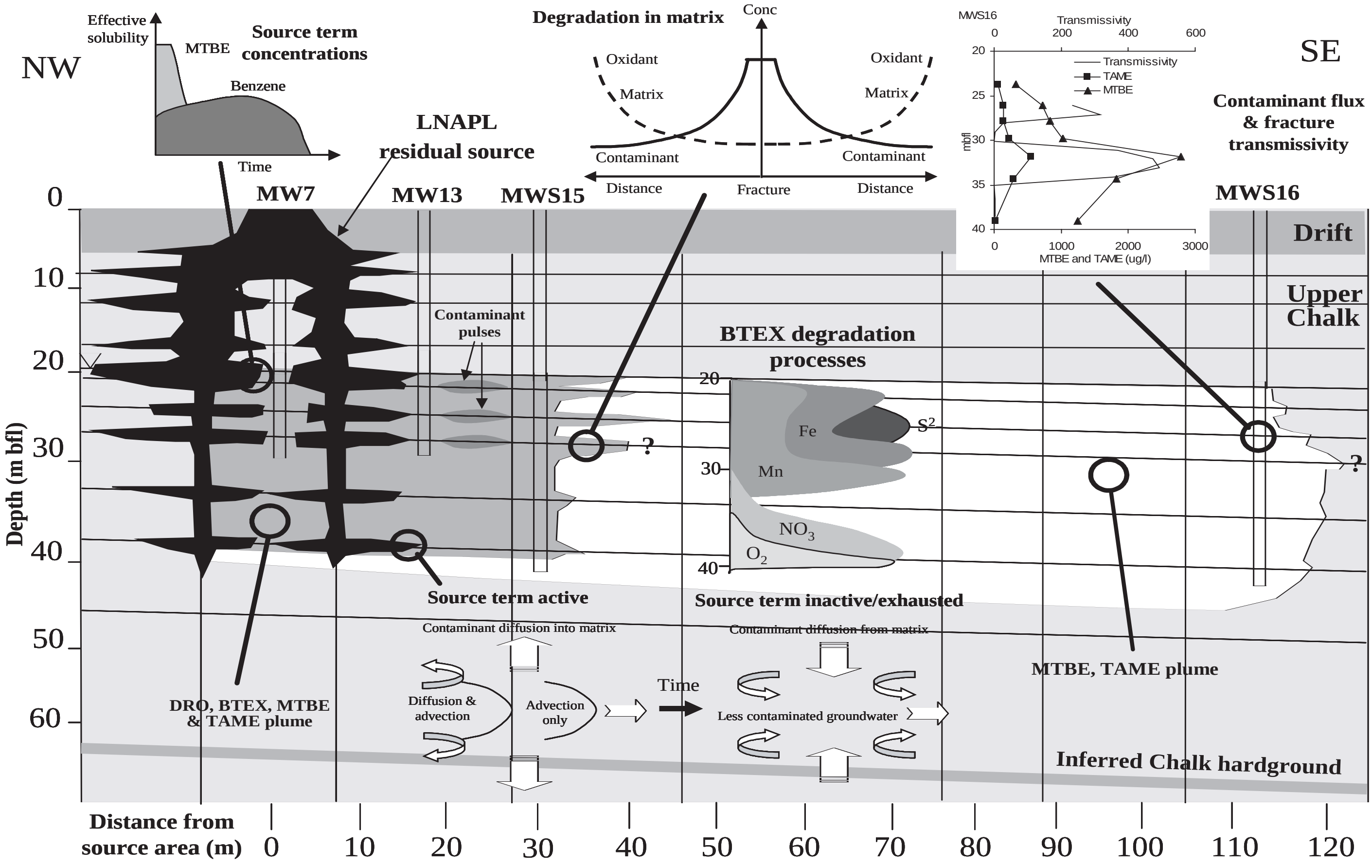

Figure 5: Conceptual Site Model (modified from Wealthall *et al*., 2001)

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