

case study bulletin

CL:AIRE case study bulletins provide a source of information on the characterisation and remediation of specific sites in the UK. This case study bulletin focuses on the characterisation of conditions within a fractured chalk aquifer contaminated with petroleum hydrocarbons and MTBE.

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>

Site Characterisation in Support of Monitored Natural Attenuation of Fuel Hydrocarbons and MTBE in a Chalk Aquifer in Southern England

1. INTRODUCTION

This Case Study Bulletin describes a research project, which was carried out to determine whether monitored natural attenuation was a viable option for managing fuel hydrocarbon contamination in a chalk aquifer in southern England. The research, which was carried out from February 2000 to March 2001, was undertaken by the University of Sheffield on behalf of TotalFinaElf at a petrol filling station site. The study was commissioned following the accidental release of approximately 55,000 L of unleaded petroleum from a ruptured underground storage tank in February 1999. The spilled petroleum fuel contained two ether oxygenates, methyl tertiary-butyl ether (MTBE) and tertiary methyl-amyl ether (TAME), at concentrations of 2.88 % v/v and 1.65 % v/v, respectively. As a result of the spill, the unsaturated zone beneath the site has been contaminated with petrol which belongs to a class of contaminants known as light non-aqueous phase liquids (LNAPL). The petrol has migrated below the water table at 20 m below ground level. Dissolution of the LNAPL has resulted in contamination of the saturated zone with a range of petroleum hydrocarbons that include diesel range hydrocarbons (DRHC); benzene, toluene, ethylbenzene, xylene (BTEX); MTBE; TAME, and other aromatic compounds.

2. AIMS AND APPROACH

The aims of the research were to i) assess the transport and fate of petroleum hydrocarbons in the Chalk aquifer beneath the site and ii) determine whether monitored natural attenuation was a viable means of managing the site. The focus of the study was the transport of dissolved phase contaminants in groundwater, but this also included an analysis of the controls on the distribution and migration of LNAPL in the fractured aquifers, which provides a source for groundwater contamination. Further emphasis is given to a comparison of the subsurface transport and fate of the ether oxygenates (MTBE and TAME), in the presence of other aromatic hydrocarbons and as an oxygenate only plume.

Like any other contaminated fractured rock system, chalk aquifers are difficult to remediate. Remediation techniques other than pump and treat are not often employed because of difficulties in resolving the extent and location of contamination or the prohibitive costs of conducting a clean up operation. These issues are discussed further in the CL:AIRE Technical Bulletin TB1. An alternative approach is to use natural attenuation processes occurring within the aquifer. Invoking natural attenuation requires adequate site characterisation of the fractured rock mass, the groundwater flow system and contaminant distribution and transport. This approach leads to the development of a conceptual site model, which can be modified and adapted as more site information is obtained. The conceptual model is an assemblage of simplifying assumptions about a complex real system, which underpins the development of a numerical or analytical model describing the key processes controlling the fate and transport of contaminants in the system.

In this study an initial site investigation was undertaken to define the likely nature and scale of contamination at the site. A number of conventional monitoring wells fitted with 10 m long screens were installed within the source zone, downgradient of the source in the dissolved phase plume, and transverse to the inferred axis of the dissolved phase plume. Additional data were sought in the literature regarding site geology, hydrogeology and hydrochemistry. These data were interpreted to derive a

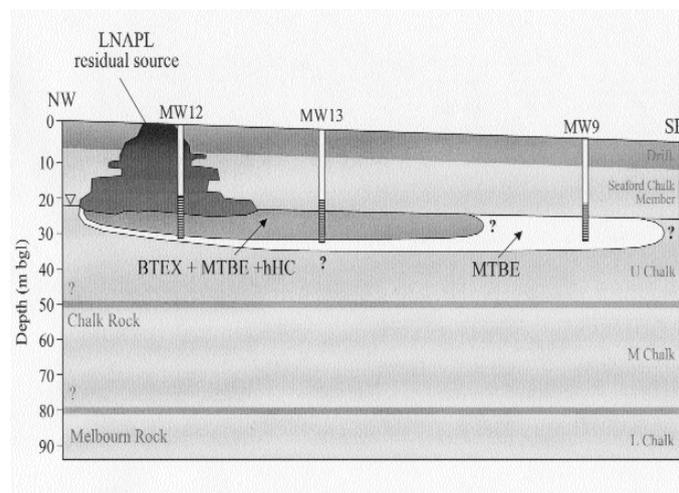


Figure 1: Initial conceptual model for the site.

Source: University of Sheffield

conceptual site model (Figure 1). A number of uncertainties still existed in this initial model, however, and these formed the basis for further investigation. These uncertainties included:

- The physical composition and spatial distribution of the source term;
- The depth of the base of the plume;
- The leading edge of the proximal (MTBE, BTEX and higher hydrocarbons) plume;
- The leading edge of the distal (MTBE only) plume;
- The spatial variation in aquifer properties, and;
- The presence of hardgrounds, which could influence the hydrogeology and contaminant migration.

3. SITE CHARACTERISATION

The site characterisation programme involved borehole drilling, testing and instrumentation at three locations in order to:

- Describe the aquifer lithology and fracture characteristics in core samples;
- Measure the hydraulic properties of the Chalk aquifer using packer testing;
- Characterise the intensity, orientation and style of fracturing using downhole geophysical logging;
- Discriminate the vertical distribution of contaminants at the site during drilling to determine the location of monitoring intervals for the multilevel sampler (MLS) wells;
- Provide level-specific monitoring points for the sampling and analysis of groundwater for geochemical parameters, and indicators of biodegradation processes for the hydrocarbon compounds.

The field activities were staged in two phases, to allow data interpretation, equipment modification (where necessary) and consideration of the lessons learned in the early phase (Phase I) to be incorporated into the later phase (Phase II) activities.

Given the uncertainties in the aquifer system (identified from the site conceptual model) and the unknown depth of the contaminant plume, it was decided during Phase I to drill and complete one borehole upgradient of the site and two boreholes downgradient of the site.

3.1 Drilling

The borehole drilling programme at the site needed to fulfil a number of rigorous criteria which included: recovery of undisturbed rock samples to describe the aquifer lithology and nature and frequency of fracturing; minimise disturbance of the borehole wall to allow subsequent hydraulic characterisation using inflatable borehole packers; and maintain borehole stability (where possible) to allow in-situ testing, geophysical logging and completion of the borehole with a MLS system.

Previous site experience indicated that drilling using cable-tool percussion techniques would be suitable to satisfy the above criteria. This technique was used in the Phase I upgradient borehole. Sample recovery was adequate in the unsaturated zone, but extremely low in the saturated zone of the Chalk. The borehole diameter was variable throughout the depth of the borehole, which resulted in poor packer seals in the upper section of the saturated zone. A review of drilling techniques was undertaken for the downgradient plume wells based on the drilling criteria from Phase I. A rotary water flush coring method was selected which utilised the GeoBore system, a wireline coring approach with the potential to recover undisturbed samples by removing only the inner barrel thereby causing minimal disturbance to the borehole wall. This method has a number of advantages over the cable tool percussion approach including:

- Recovery of 1.5 m samples in a clear liner which, in the absence of smearing, allowed visual inspection of the intact core, and preserved the intensely fractured rock core for detailed lithological and fracture logging;
- Less uncertainty in depth recording for individual core-runs;
- Less disturbance to the borehole wall as the cutting tool was not removed from the borehole at the end of each core run;
- Efficient recovery of drilling induced fines from the water flush when recirculation was possible.

3.2 Geology

The primary aims of the geological characterisation were to i) identify gross lithological variations, which may influence hydrogeology at the local (10s metres) to intermediate (100s metres) scales, and ii) record the location, type (bedding parallel or high angled) and characteristics of fractures.

A geotechnical description of chalk was used which describes the rock in terms of hardness, extent of weathering and intensity of discontinuities. A fracture log recorded the position and type of fractures. The dip angles of the majority of bedding parallel fractures were less than 30° and it was proposed to categorise high angled fractures as those with a dip greater than 30° from horizontal. This criterion was applied irrespective of fracture origin.

3.3 Geophysical Techniques

The study recovered undisturbed core samples for detailed fracture logging supported by geophysical fracture detection methods. These independent methods were used to characterise the spatial distribution of fractures in the Chalk aquifer, including fracture intensity, fracture orientation and fracture type. Recent advances in fracture characterisation methods have allowed the accurate representation of subsurface features by optical and acoustic methods for imaging the borehole wall. The image of inclined fractures (see Figure 2a) is represented as an ellipse intersecting the borehole wall, and may be 'unwrapped' (see Figure 2c) to present a sinusoidal shaped image of the fracture, which can be analysed for dip and dip azimuth.

The Acoustic TeleViewer (ATV) scans the borehole wall using a transducer to emit and receive ultrasonic signals. The reflected signal is represented as a false-colour image based on the intensity of reflection. The image may be interpreted from either the amplitude of the reflected signal or the travel time of the ultrasonic pulse.

The OPTical TeleViewer (OPTV) provides one of the most effective borehole imaging tools for detecting fractures and lithology. The technique provides high resolution, optical, true-colour images of the borehole wall. The borehole wall is illuminated by

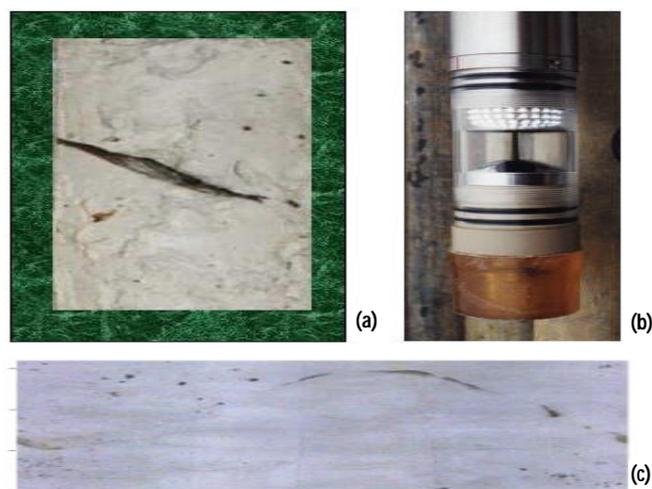


Figure 2: Optical TeleViewer tool.

Source: University of Sheffield

a white light source and the tool records images from a rotating mirror/optical lens and photoelectric transformer (see Figure 2b).

The analysis of fracturing from core and geophysical logs has provided an important insight into the spatial distribution and characteristics of the fracture network and in predicting the potential influences of the fracture system on the distribution of contaminants at the site. Combined fracture orientation plots for both low angled, bedding plane fractures (see Figure 3a) and high angled fractures (see Figure 3b) are illustrated for three boreholes (MWS14, 15 and 16). The figures comprise two components. The upper rose diagram shows the number of fracture measurements and the orientation or strike of the fracture while the lower stereonet diagram plots the pole to the plane of the fracture which depicts the dip and dip azimuth of the fracture.

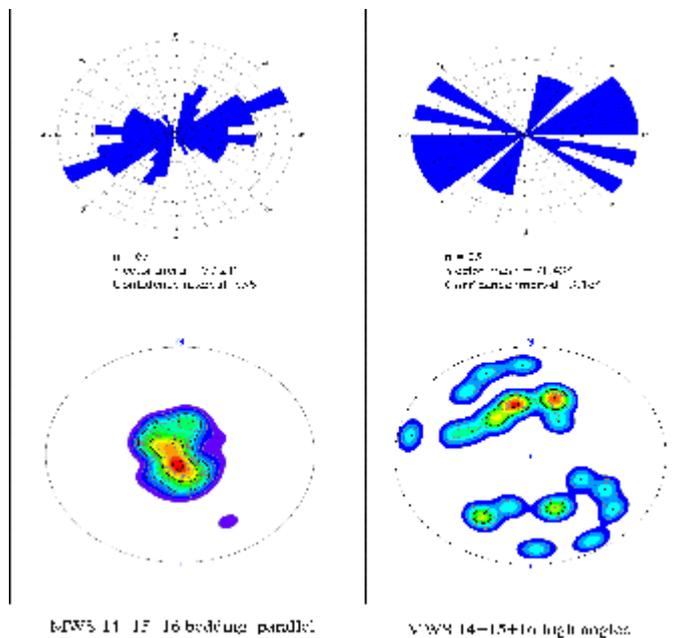


Figure 3a,b: Fracture orientation plots for the global unrefined fracture dataset (MWS14, 15, 16).

Source: University of Sheffield

3.4 Hydrogeology

Hydrogeology describes the physical and chemical conditions of the fluids within the aquifer system and this is used to develop an understanding of groundwater flow, transport and fate of contaminants.

3.4.1 Hydraulic properties

Pumping tests were used to measure hydraulic properties in the higher permeability test zones. The residual drawdown data were analysed using an automated curve fitting software programme. Residual drawdown data are often more reliable than pumping test drawdown data due to the irregular responses in the drawdown limb,

including removal of drilling induced fines from fractures (small-scale well development). Falling head slug tests were used to determine hydraulic conductivity in the less permeable test zones.

Hydraulic testing was undertaken in MWS14 between core runs using a single packer system whereas a double-packer system was used to characterise the hydraulic properties of the rock mass in MWS15 and 16. The latter were developed for approximately 2 hours using a submersible pump at a flow rate of approximately 150 L/min (ca. 9 m³/hr).

Hydraulic tests proceeded in three main phases:

1. Equilibration period where transient effects - resulting from packer inflation and head equilibration in the test zone - were allowed to dissipate;
2. Diagnostic and Main Phase where i) the order of magnitude of response was observed, allowing selection of an appropriate hydraulic test type, ii) the hydraulic response was monitored for boundary effects (including fracture development from the removal of drilling induced fines) until quasi equilibrium conditions were achieved, and iii) where the groundwater sample may be collected;
3. Recovery Phase where the flow field was reversed and residual drawdown data was collected.

Figure 4 plots hydraulic head versus elapsed time in MWS14 over the depth interval from 30.04 to 34.34 m bgl (metres below ground level). The uppermost line of data labelled ATZ show stable head conditions above the test zone during the test. The second line of data labelled TZ show head response in the test zone due to pumping during the shut-in period, from 1500 to 3600 seconds, when the packers are inflated. At 1500 seconds when the packers are inflated, the head drops by almost 1 metre and then reaches quasi-equilibrium during the test. At 3500 seconds, the pump is turned off, the packers are deflated, and the head recovers. The lack of response in the ATZ during the test shows that the zone above the test is hydraulically independent from the test zone.

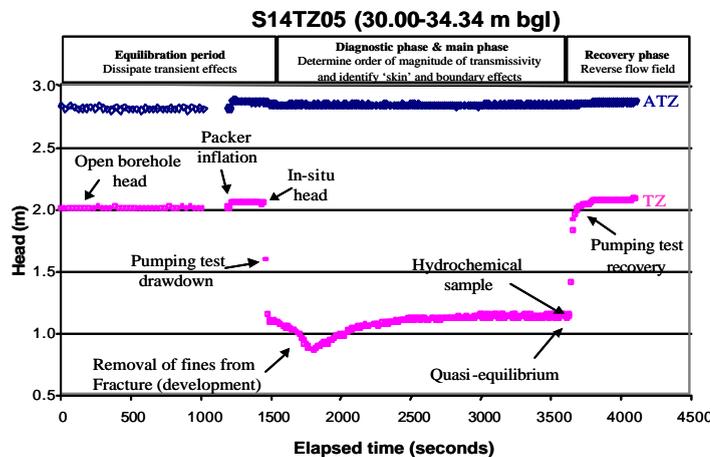


Figure 4: Typical responses during a pumping test.

Source: University of Sheffield

The hydraulic test data were analysed for:

- Transmissivity: Two estimates of transmissivity were resolved. Firstly a 'test zone' transmissivity was determined from the contribution of all of the fractures in the test zone, and secondly an 'individual' transmissivity was calculated, assuming an equal contribution from all fractures in the test zone, by dividing 'test zone' transmissivity by the number of fractures in the test zone.
- Equivalent (hydraulic) aperture: Aperture values were estimated using the cubic law approach for both 'test zone' and 'individual' transmissivities. A spreadsheet-based analysis package was developed to calculate hydraulic apertures.
- Hydraulic head: expressed as head change in the shut-in test zone relative to the open borehole pressure.

3.4.2 Groundwater velocity estimates

The upper and lower values of transmissivity from MWS15 and 16 have been used to estimate the potential range of average linear velocities. The estimates assumed a fracture porosity of 0.0108 and hydraulic gradient of 0.0022. The results are

summarised in Table 1.

Table 1: Average linear velocity estimates.

Source: University of Sheffield

Velocity (m d ⁻¹)	MWS15	MWS16
Upper limit	70.3	100.7
Lower limit	9.19x10 ⁻³	1.53x10 ⁻²

The values of average linear velocity from MWS15 and 16 compare favourably. The upper and lower limits reflect the heterogeneity expected in the Chalk aquifer. The calculation of average linear velocity assumes constant porosity and hydraulic gradient, therefore, local variations in hydraulic gradient and porosity may also vary the velocity term.

3.4.3 Groundwater gradient

Determination of the horizontal component of hydraulic gradient may be used to predict groundwater flow direction and plume orientation. This information was obtained from analysis of the water table elevation in the long screen monitoring wells at the site. Flow direction varied by 10° over successive surveys, but generally trended SSE, sub-parallel to the regional groundwater flow direction.

3.5 Well Completion

The boreholes were completed using the Continuous Multichannel Tubing (CMT) system (further details on this system are given in CL:AIRE Technical Bulletin TB2). This system allows seven sampling intervals to be installed in a single well of approximately 150 mm diameter. The individual sampling intervals were completed with inert graded sand (0.5-1 mm diameter) and sealed from above and below the sampling interval by bentonite seals. All sand packs and bentonite seals were installed to a tolerance of ±2 cm.

The location of the MLS intervals were determined by analysis of:

- Key plume indicator parameters including organic vapour analysis, dissolved oxygen, Eh and pH, determined onsite using rock core and groundwater samples;
- Relative transmissivity, determined from the flow rate and relative drawdown during pumping tests;
- Fracture intensity, derived from core and geophysical logs, including the presence of any prominent fractures/fracture zones;
- Lithology, in particular the presence of putty chalk and/or marls and hardgrounds.
- Caliper log to identify major fractures and wash-out zones

4 GROUNDWATER QUALITY MONITORING AND DATA COLLECTION

A groundwater sampling protocol was adopted for the study which took into account the hydrogeology of the site, the properties of the key contaminants, the nature of analytes to be measured and the monitoring well network and design. These factors were considered in terms of implementing an appropriate groundwater sampling schedule and sample collection procedure.

Groundwater samples were collected at intervals of three weeks from the long screen and MLS monitoring wells installed during the study. Solute distributions were determined during the packered pumping tests of the MLS to assist the determination of monitoring zones. A sample collection and onsite processing protocol was developed and implemented to obtain representative samples and to maintain sample quality prior to laboratory analysis. All the groundwater monitoring wells were completed with dedicated inertial lift pumps to avoid cross-contamination of samples and monitored intervals.

All groundwater samples were analysed for petroleum hydrocarbons, MTBE, TAME and known organic degradation products, major cations and anions, redox-sensitive species and a variety of field determinands. Laboratory measurements of these field determinands were performed where it was not possible to do this onsite.

A series of quality control (QC) checks were completed to validate the procedures used for sample analysis, including an interlaboratory comparison.

Groundwater quality data were obtained using the above procedures and were evaluated in the form of solute concentration profiles versus depth below ground level for the MLS wells and solute concentration profiles versus distance from the site

for the standard monitoring wells. The results from the groundwater quality surveys were used to construct a revised conceptual model for the site.

5 DESIGN OF A REVISED CONCEPTUAL SITE MODEL

The overall aim of this study was to understand the subsurface transport and fate of contaminants at the site. This was achieved by focusing on the immediate needs of the existing site characterisation and remediation programme, considering possible impacts on downgradient receptors and the identification of appropriate remediation strategies, based on technical feasibility.

After the assimilation and interpretation of the site characterisation and groundwater chemistry data, a revised conceptual model describing natural attenuation of the fuel hydrocarbons was devised and is presented in Figure 5. The model considers different aquifer characteristics, contaminant properties and processes that control the distribution, transport and fate of contaminant groups in the hydrocarbon mixture. A key aspect of this model is that degradation of BTEX will occur rapidly, close to the site, but that MTBE degradation may only occur after the MTBE has migrated downstream of the BTEX.

Geological structures, aquifer hydrogeology, contaminant properties and groundwater chemistry control contaminant fate and transport at this site. Groundwater quality data, a negligible vertical groundwater head gradient, and theoretical calculations suggest that LNAPL has penetrated along vertical fractures to a depth of at least 16 m below the water table, to produce the current dissolved phase plume. Lateral migration of product, transverse to the dissolved plume orientation may have occurred along dominant NE-SW to E-W trending high angled fractures. Both features imply a more widely dispersed distribution of LNAPL and dissolved phase contaminants than previously thought. The plume of dissolved phase contaminants is sinking with increasing downgradient transport due to migration along horizontal bedding fractures (greater than or equal to 3° dip).

Contaminants are distributed over 20 m depth in the aquifer. A mixed plume of diesel range hydrocarbons, BTEX compounds, MTBE and TAME extends from the site to

30 m downgradient and a MTBE/TAME plume extends from 30 to 115 m downgradient. This distribution reflects the early release of the more soluble oxygenates from the LNAPL. Temporal variations in contaminant flux arise from water table fluctuations in the source area. Contaminant concentrations and variations in contaminant flux are higher in fractures with higher transmissivity. Approximately 7% of the dissolved BTEX mass has been degraded using naturally occurring dissolved O₂, NO₃⁻ and SO₄²⁻, and Mn(IV) and Fe(III) oxides present in the aquifer. It is possible that MTBE can aerobically degrade to tertiary butyl alcohol (TBA). However, it is difficult to deduce the occurrence of this process at fieldscale due to the presence of TBA as an impurity in the LNAPL source. Analysis of organic tracers indicates that dilution of the contaminants by transport in the fractures and from diffusion into the chalk matrix is significant. A mass balance for the dissolved phase contaminants suggest that >90% of the contaminant mass could be present, dissolved or sorbed within the aquifer matrix, under worst case conditions. Transport modelling also confirmed the importance of diffusion and degradation in the fate of contaminants. However, the modelling approach was limited by difficulties in representing heterogeneity in the source term flux and aquifer properties.

In the absence of natural attenuation (other than dilution), contaminants could have migrated over 2000 m from the site based on measured groundwater velocities. However, the contaminant plume has migrated <150 m from the site based on the present monitoring network, indicating that natural attenuation has been effective in reducing contaminant flux and groundwater concentrations. The results suggest that monitored natural attenuation is a potentially viable means of managing contamination at the site.

Acknowledgement: This work was carried out by Dr Steve Thornton and Mr Gary Wealhall at the Groundwater Protection and Restoration Group, Department of Civil and Structural Engineering, University of Sheffield on behalf of TotalFinaElf.

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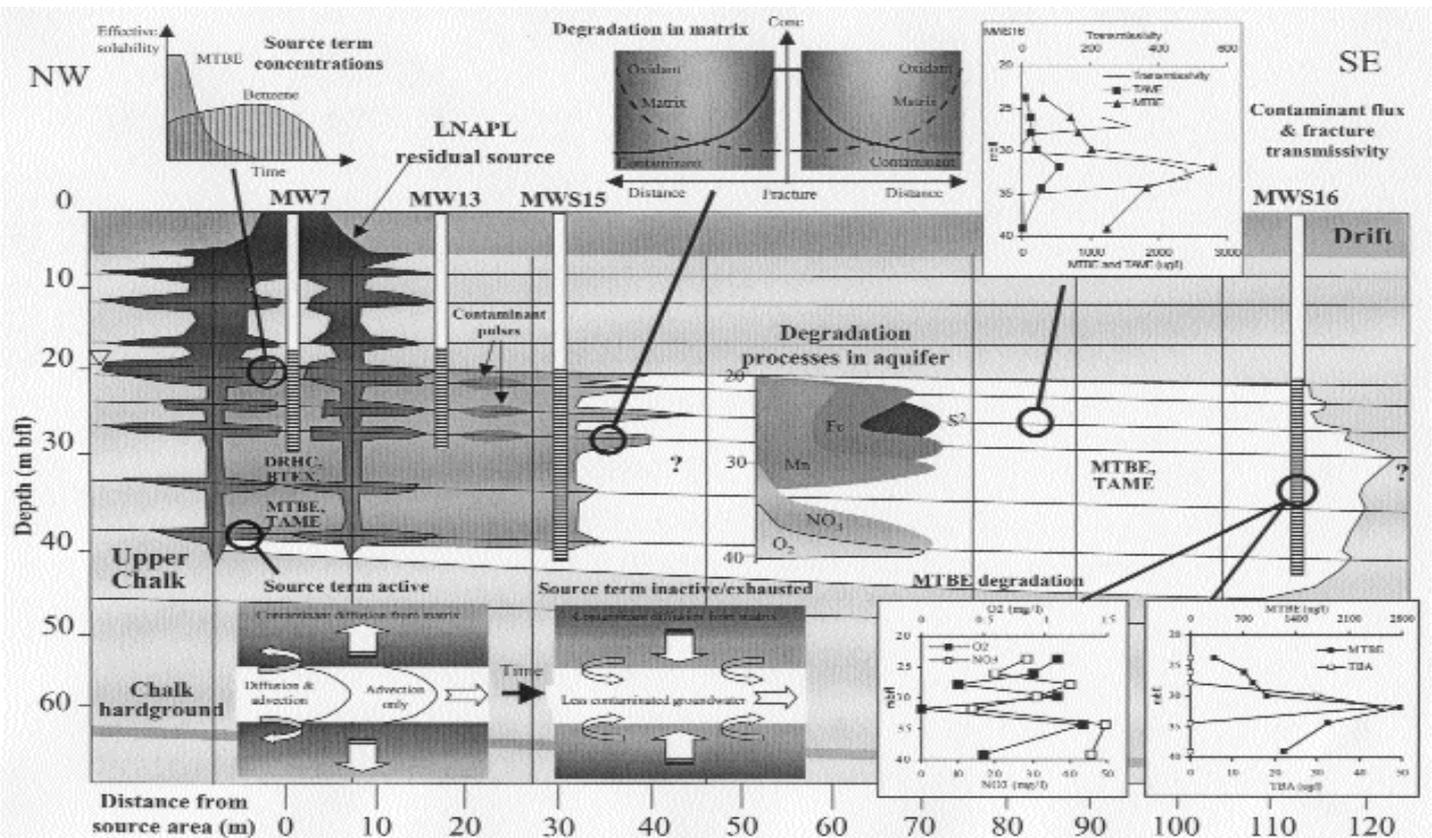


Figure 5: Revised conceptual model of the site.

Source: University of Sheffield