RESEARCH PROJECT REPORT: RP3

PROCESSES CONTROLLING THE NATURAL ATTENUATION OF FUEL HYDROCARBONS AND MTBE IN THE UK CHALK AQUIFER

CONTAMINATED LAND: APPLICATIONS IN REAL ENVIRONMENTS

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Contaminated Land: Applications in Real Environments (CL:AIRE)

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Processes Controlling the Natural Attenuation of Fuel Hydrocarbons and MTBE in the UK Chalk Aquifer

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This is a CL:AIRE research project report. Publication of this report fulfils CL:AIRE's objective of disseminating and reporting on applied research. This report is a detailed description of processes that were controlling the natural attenuation of fuel hydrocarbons and MTBE in the UK Chalk aquifer. CL:AIRE strongly recommends that individuals/organisations interested in natural attenuation retain the services of experienced environmental professionals.

EXECUTIVE SUMMARY

This report summarises research completed from May 2001 to November 2004 to evaluate processes controlling the natural attenuation (NA) of petroleum hydrocarbons and methyl tertiary butyl ether (MTBE) in the Upper Chalk aquifer at the site of an unleaded fuel spill in St Albans, southeast England. The unsaturated zone and saturated zone of the aquifer are contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX), MTBE, tertiary amyl methyl ether (TAME) and tertiary-butyl alcohol (TBA). A mixed BTEX/MTBE/TAME/TBA plume extends 125 m from the site and <10 m below the water table, whereas a MTBE/TAME/TBA plume extends 220 m from the site and >15 m below the water table. The research was sponsored by EPSRC, Total UK and the Environment Agency and included field, laboratory and modelling studies. It was completed as a research project for CL:AIRE and hosted by the site owner.

MTBE can be biodegraded in the aquifer under aerobic conditions at concentrations up to 6 mg/L, with the production of TBA. Anaerobic degradation of MTBE is not significant, although the aquifer microorganisms have the potential for this. Measured first-order aerobic MTBE degradation rates obtained from uncontaminated aquifer microcosm experiments were 0.0074/day compared with 0.0025/day for plume microcosms. The presence of TBA as an impurity in MTBE and temporal variation in the release of TBA and MTBE from the source area, prevent the deduction of MTBE degradation at field scale from the distribution of TBA. Stable isotope compositions of MTBE in groundwater indicate that there has been no significant MTBE degradation in the plume, although the sensitivity of the technique will be low if isotope enrichment factors are small in this setting. Aerobic MTBE degradation may be inhibited by preferential aerobic degradation of BTEX or other more biodegradable hydrocarbon compounds in the groundwater. Aerobic MTBE degradation is unlikely to be an important process for MTBE attenuation *within the plume*, particularly in the presence of other hydrocarbons, but could be significant at the advancing plume fringe where O_2 is more available. Aerobic MTBE degradation should be considered in risk assessments for unleaded fuel releases at sites.

The more extensive migration of dissolved MTBE, TAME and TBA compared with BTEX in the aquifer reflects the relative proportions of the ether oxygenate compounds in the fuel mixture, their higher relative solubility and the greater potential for attenuation of BTEX by sorption and degradation. Biodegradation of BTEX occurs in the aquifer under aerobic and anaerobic conditions using dissolved oxidants (O_2, NO_3 and SO_4) in the groundwater and solid phase oxidants (Mn oxides and Fe oxides) on the aquifer matrix, creating a series of redox zones, which can be defined by the distribution of redox-sensitive chemical species and reaction products representing the different processes. Degradation of BTEX by methanogenesis occurs in the aquifer but is not quantitatively important. Stable isotope studies and a plume-scale mass balance incorporating probabilistic analysis with Monte Carlo methods, indicates that most BTEX degradation is from consumption of dissolved NO_3 and SO_4, with consumption of O_2, Mn-oxide, Fe-oxide and methanogenesis contributing the remainder. The dissolved O_2, NO_3 and SO_4 for degradation in the saturated zone are provided primarily by groundwater advection and diffusion from the aquifer matrix. Consumption of available O_2, NO_3 and SO_4 in groundwater by the biodegradation of more biodegradable hydrocarbons (e.g. ethylbenzene and toluene) in the plume may restrict benzene and MTBE degradation until these compounds have migrated downstream into zones where dissolved O_2 and NO_3 are available for degradation and other hydrocarbons are absent. First-order degradation rates of 0.14/day and 0.0108/day have been estimated for ethylbenzene and toluene degradation, respectively, from microcosm studies and isotope enrichment factors have been estimated for benzene degradation and SO_4-reduction. These parameters may be used to evaluate hydrocarbon attenuation at the field scale. Groundwater quality data indicate that the BTEX plume has probably reached a steady-state condition, where attenuation by biodegradation balances the flux of dissolved BTEX contaminants from the source.

Mass balance suggests that 65% of the original unleaded fuel released, exists as residual and free product trapped within the unsaturated and saturated zone, to provide a long-term source of dissolved contaminants to groundwater. Fluctuations in the water table result in periodic flushing of relatively high concentrations of contaminants from this source zone into groundwater, but over the last 4 years the contaminant flux into groundwater has decreased significantly. The source term composition has changed over this period and the contaminant flux into the plume is now dominated by BTEX rather than the ether oxygenates. In the longer term BTEX will be the main source term for the plume, but the aquifer has adequate capacity to attenuate this flux by degradation. Similar behaviour is expected for plumes at sites with other unleaded fuel releases.

The microbial ecology of the aquifer groundwater and matrix is similar, indicating that microbial populations responsible for hydrocarbon and MTBE degradation could exist within the Chalk matrix. Microbial colonisation of the aquifer matrix appears to occur via microfractures within larger matrix blocks, which provides an increased surface area for biofilm development. Pore throat diameters in the aquifer matrix vary from <1 µm to >1 µm with values <1 µm implying that typical bacteria may be physically excluded from colonising the matrix unless cell diameters are less than this. This may result in the spatial variability of degradation potential in the aquifer, according to whether (and the extent to which) the matrix and/or fracture surfaces support microbial colonisation. It is recommended that biodegradation is assumed to occur on the fracture surfaces only for the purposes of conservative risk assessment.

There is significant spatial variability in the distribution of aquifer hydraulic conductivity (K) at the site, with values changing by a factor of 10 for comparable depths along the plume flow path, but by a factor of 100 with depth over the 30 m thick plume section, where a hard band separates the aquifer into a “high” flow zone down to 33 m depth, and a “low” flow zone below this depth. The fracture network dominates groundwater flow and statistical analysis of fracture logs shows that the fracture spacing is skewed towards closely spaced fractures, with a mean separation of 0.22 m. The fracture spacing is statistically similar at locations across the site, but different with depth across the section of contaminated aquifer. The increased aquifer hydraulic conductivity and contaminant flux associated with the “high” flow zone is due to increased fracture aperture (wider fractures). Contaminant migration below 33 m depth is restricted by the hard band and the absence of a significant vertical hydraulic gradient in the aquifer. The study also showed that multilevel groundwater samplers (MLS) are a useful site investigation tool to reliably assess the plume geometry, contaminant distribution and aquifer fracture water and matrix water chemistry, indicating that the matrix is an important storage reservoir for contaminants and for electron acceptors required for degradation.

The effect of dual porosity on degradation and plume development is a function of the relative timescales of fracture vs diffusive transport, as controlled by the matrix properties (diffusion coefficients) and fracture properties (spacing and porosity). Modelling studies using representative aquifer properties and different scenarios for groundwater flow, matrix block size and fracture porosity showed that complete fracture-matrix equilibration of solutes by diffusion is achieved within one day, implying that contaminants migrating into the uncontaminated aquifer will be attenuated very quickly by diffusion. Contaminant pulses could also be completely attenuated by diffusion within 1 m of downgradient migration into the uncontaminated aquifer for typical conditions (groundwater velocity and aquifer properties), but that this distance would increase to 10 m for the maximum fracture porosity and groundwater velocity found at the site. Attenuation by diffusion was found to decrease as flow velocity, fracture porosity and matrix block size increase. Dual porosity transport has a significant effect on contaminant attenuation and degradation capacity in the aquifer, in that diffusion of dissolved electron acceptors from the matrix into fractures is fast and does not limit degradation, plume expansion is linked to the utilisation of a finite reservoir of dissolved oxidants in the matrix (supplied to fractures by diffusion), and back-diffusion of contaminants out of the matrix creates a secondary contaminant source for transport in the fractures after the primary contaminant source has decreased or been exhausted.

The conceptual model for NA of these contaminants in the Chalk aquifer at this site has been independently validated with a numerical dual porosity transport code, using parameter values for the relevant aquifer properties and experimental data obtained from the study. The model reproduced the main features of transient contaminant inputs, degradation processes and plume development. It established limits on the MTBE degradation rates at field scale, which were similar to laboratory-determined values and confirmed the significance of diffusion as a key process controlling contaminant migration and degradation in the aquifer. This analysis showed that MTBE concentrations in groundwater are affected more by variations in aquifer properties and hydrogeology, than degradation rate. Variations in MTBE concentration from dual-porosity transport may be greater than that from degradation. This may obscure the effect of MTBE degradation, i.e., changes in MTBE plume development caused by degradation may not be easily deduced at field scale from groundwater quality surveys. A key output from the study is the development of a simplified performance model to robustly predict the NA of petroleum hydrocarbons and MTBE in the Chalk aquifer using a subset of input parameters and more basic analytical models.

Natural attenuation of BTEX and MTBE in the Chalk aquifer can be significant, although by different mechanisms. Sorption and biodegradation are more important for BTEX attenuation but physical processes such as diffusion are as important (or more so) than degradation, based on this study. NA can make an important contribution to the management strategy for unleaded fuel release sites on the Chalk aquifer and should be considered within risk assessments for such sites. A more detailed site investigation, using a wider range of techniques and more sophisticated monitoring networks with MLS will be required for this.

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ABBREVIATIONS

AIR	Atmospheric N_2 (International reference standard for nitrogen isotopic compositions)
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CFU	Colony Forming Units
CMT	Continuous Multichannel Tubing
CSIA	Compound-Specific Carbon Isotope Analysis
DEE	Diffusion Equilibrium Exchange
DO	Dissolved Oxygen
EA	Environment Agency
EC	Electrical Conductivity
Eh	Redox Potential
EPSRC	Engineering and Physical Sciences Research Council
ETBE	Ethyl Tertiary-Butyl Ether
f_{oc}	fraction of organic carbon
HDPE	High-Density Polyethylene
K	Hydraulic conductivity
LNAPL	Light Non-Aqueous Phase Liquid
mAOD	metres Above Ordnance Datum
mbgl	metres below groundlevel
mbfl	metres below forecourt level
MPN	Most Probable Number
MTBE	Methyl Tertiary Butyl Ether
MLS	Multilevel Samplers
MW	Monitoring Well
NA	Natural Attenuation
OPTV	Optical Televiewer
PTFE	Polytetrafluorethylene
SEM	Scanning Electron Microscope
SVE	Soil Vapour Extraction
T	Transmissivity
TAME	Tertiary Amyl Methyl Ether
TBA	Tertiary-Butyl Alcohol
TDIC	Total Dissolved Inorganic Carbon
TOC	Total Organic Carbon
V-CDT	Vienna-defined Canon Diablo Troilite (International reference standard for sulphur isotopic compositions)
V-PDB	Vienna-defined Peedee Belemnite (International reference standard for carbon isotopic compositions)
V-SMOW	Vienna-defined Standard Mean Ocean Water (International reference standard for oxygen isotopic compositions)
VFA	Volatile Fatty Acid

1. INTRODUCTION

1.1 BACKGROUND OF RESEARCH DEVELOPMENT

The research described in this report was undertaken between May 2001 and October 2004. It is focused on a retail filling station site in St Albans, contaminated with petroleum hydrocarbons containing benzene, toluene, ethylbenzene and xylenes (BTEX), and the ether oxygenate compounds, methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). The contamination has spread to the underlying Upper Chalk aquifer, creating a plume of dissolved hydrocarbon and ether oxygenate compounds in the saturated zone, sustained by residual phase product and free-product trapped within the unsaturated and saturated zones of the aquifer. The work described in this report was preceded by two phases of site investigation funded by the site owner, Total UK. This project was sponsored jointly by EPSRC, Total UK and the Environment Agency. It was completed as a research project for CL:AIRE and hosted by the site owner.

1.2 RESEARCH CONTEXT

Organic pollutants from industrial activities pose a risk to groundwater quality in UK aquifers. Recent attention has focused on the environmental fate of ether oxygenate compounds. These are added to petroleum fuels primarily to meet octane requirements without the use of lead, reduce the use of aromatic hydrocarbons such as benzene, and reduce atmospheric emissions for improved air quality (Environment Agency, 2000a; Schmidt *et al.,* 2004). The ether oxygenates most commonly added to petroleum fuel in the UK are MTBE, TAME and ethyl tertiary-butyl ether (ETBE), although MTBE is the most important and is generally used in concentrations of < 5% by volume (Environment Agency, 2000a). This contrasts with the USA, where MTBE concentrations in unleaded petroleum fuel are as high as 10-15% by volume (Fiorenza and Rifai, 2003). Tertiary-butyl alcohol (TBA) may also be present in unleaded petroleum fuels, as a by-product of the MTBE manufacture, or added intentionally, as an oxygenate compound, in some countries (Schmidt *et al.*, 2004). TBA is significant in this context in that it is an important breakdown product of aerobic MTBE biodegradation.

Global production of MTBE in 1999 was 21 Ma tonnes, of which 3.3 Ma tonnes were produced in the EU (Schmidt *et al.*, 2004). At the time this research was undertaken MTBE was found in 80% of oxygenated fuels used in the USA, where production had increased since the early 1980s to 7.7 Ma tonnes/year in the late 1990s when it was the most widely used and second most important manufactured chemical in the USA (Landmeyer *et al.*, 1998; Hanson *et al.*, 1999). Because of this widespread use, the frequency of MTBE detection in the environment has increased in recent years and after only a relatively short period MTBE has become one of the most commonly detected organic chemicals in groundwater in the USA (Schmidt *et al.,* 2004). MTBE most commonly enters groundwater via releases of ether oxygenate-amended petroleum fuel from failed seals in the pipeline infrastructure, leaking underground storage tanks, spillages at petroleum refineries and distribution facilities or increased vapour loss at the pump (Environment Agency, 2000a). Sites where releases have occurred are often located in heavily populated areas where pressures on groundwater resources are high. Studies completed in the late 1990s highlighted the occurrence of 3,000 MTBE plumes in California, USA, arising from these sources (Hanson *et al.,* 1999). There are particular management and remediation problems associated with such impacts. Because of its properties, remediation of MTBE in groundwater by traditional technologies used for the management of petroleum hydrocarbon contamination is less cost-effective. Although there are no proven human health issues related to the typical MTBE concentrations found in groundwater, there are taste and odour problems at very low concentrations (5-15 µg/L), which make drinking water unpalatable (Environment Agency, 2000a). The extent of groundwater contamination by MTBE and potential for attenuation during transport to a receptor is therefore often the main driver for risk assessments at sites contaminated with unleaded petroleum fuel containing MTBE.

These concerns have prompted a series of actions in North America and Europe with regard to MTBE. The chemical is being phased out of petroleum fuels in many states in the USA (to be replaced by alcohol oxygenates, such as ethanol), and in Denmark it is now mandatory to test groundwater near filling stations for MTBE (Anon, 2000; Fiorenza and Rifai, 2003). However, the situation in the UK is less pessimistic. A review by the Environment Agency and the Institute of Petroleum in 2000 demonstrated that the occurrence of MTBE in UK groundwater is low (Environment Agency, 2000a). In the study, which evaluated groundwater quality data from over 800 site investigations and 3000 samples from public supply and monitoring wells in England and Wales, MTBE was found above detection limits (0.1 µg/L) in only 13% of the monitoring locations considered, with the majority of MTBE concentrations being very low, typically < 1 µg/L. The study concluded that most of the sites where MTBE was detected in groundwater, present no risk to public supply boreholes and that ether oxygenates do not currently pose a major threat to groundwater resources in England and Wales. This is an important finding, compared with the situation in the USA, and is attributed to the lower MTBE content of UK petroleum fuels, combined with contrasting environmental conditions and different regulations and practices governing the manufacture, handling, distribution and use of ether oxygenates between the countries. However, the Environment Agency (2000a) review also noted that there was significant uncertainty in the (then) existing dataset on MTBE behaviour and fate in UK aquifers, with the recommendation that further research is undertaken to assess the potential for degradation (and by implication natural attenuation) of MTBE in groundwater as a measure to underpin future management strategies for MTBE-impacted sites.

Many of the perceived problems associated with MTBE and other ether oxygenate compounds in groundwater arise from the specific properties of these additives. In comparison with BTEX compounds, MTBE has much higher aqueous solubility (40-50,000 mg/L), is less volatile when dissolved in water, sorbs less to subsurface media and exhibits uncertain biodegradation potential (Environment Agency, 2000a; Schmidt *et al.,* 2004). However, laboratory studies show that MTBE and other ether oxygenate compounds can be biodegraded under aerobic conditions to TBA and other organic metabolites (Garnier *et al.,* 1999; Hanson *et al.*, 1999; Hyman and O'Reilly, 1999; Bradley *et al.*, 2001a; Kane *et al.*, 2001; Schirmer *et al.*, 2003). MTBE can be degraded as the sole carbon and energy source, and via cometabolism with other compounds found in petroleum hydrocarbon mixtures (Garnier *et al.*, 1999; Hanson *et al.*, 1999; Hyman and O'Reilly, 1999; Deeb *et al.*, 2000; Fiorenza and Rifai, 2003; Smith *et al.*, 2003; Schmidt *et al.*, 2004). In groundwater MTBE appears to degrade aerobically in the absence of BTEX compounds (Schirmer and Barker, 1998; Hurt *et al.*, 1999; Fiorenza and Rifai, 2003; Schmidt *et al.*, 2004). Several studies have also shown that MTBE and other ether oxygenates may be biodegraded under a variety of anaerobic conditions (Bradley *et al.*, 2001b; 2002; Somsamak *et al.*, 2001), although often this process is very slow compared with aerobic degradation and may not be environmentally significant at many contaminated sites (Yeh and Novak, 1994; Magar *et al.*, 2002; Fiorenza and Rifai, 2003). By contrast, BTEX compounds degrade readily under aerobic and anaerobic conditions at field scale and this feature is exploited in the management of BTEX-contaminated groundwater using natural attenuation (Wiedemeier *et al.*, 1999).

Natural attenuation (NA) is a management strategy for contaminated groundwater which uses a combination of dilution, biodegradation and abiotic reactions to reduce contaminant concentrations below risk-based values, which ensure protection to the environment and human health. It is an accepted approach for the remediation of aquifers contaminated with BTEX in the USA (Landmeyer *et al.*, 1998; Wiedemeier *et al.*, 1999). However, the presence of MTBE may restrict the use of NA at some petroleum-contaminated sites if the compound is not biodegradable within reasonable timescales (Schirmer and Barker, 1998).

The fate of petroleum hydrocarbons in the UK Cretaceous Chalk aquifer is poorly understood. This aquifer is the most important source of potable groundwater in the UK, yet published studies have focused on the behaviour of less soluble heavier petroleum hydrocarbons (Ashley *et al.*, 1994), rather than BTEX or MTBE. It is expected that the biodegradation potential of BTEX and MTBE in the Chalk aquifer and North America aquifers will be broadly similar. However, the Chalk is a deep dual-porosity aquifer, where fracture flow dominates groundwater transport. The aquifer has a large hydraulic storage capacity but groundwater travel times are fast. By contrast, North American aquifers in which the NA of BTEX plumes is well understood, are typically shallow sand and gravel systems, dominated by matrix porosity and intergranular flow. The geochemistry of the Chalk is also different from that of most North American aquifers. These fundamental differences in aquifer characteristics could result in significant differences in the capacity for NA of hydrocarbons and ether oxygenate compounds in unleaded petroleum fuel.

An additional imperative for this research is that U.S. technical protocols and guidance for applying NA may not be appropriate for MTBE risk assessments (Anthony *et al.*, 1999). The UK Environment Agency has published technical guidance for the use of NA at contaminated sites (Environment Agency, 2000b), but information on the NA of MTBE in UK aquifers is lacking. The research outlined in this report provided a unique opportunity to address these problems. The study examined the NA of petroleum hydrocarbons and ether oxygenate compounds in the Chalk aquifer, in light of the expected fate of these contaminants gained from experience in North America. However, this previous experience and knowledge base was used to compare the performance of NA for BTEX and MTBE contaminants, with respect to the unique properties of the Chalk aquifer.

1.3 RESEARCH OBJECTIVES AND SCOPE

The overall goal of this project was to develop a validated process-based model for the NA of dissolved petroleum hydrocarbons (e.g. BTEX) and ether oxygenate compounds (MTBE and TAME) in the Chalk aquifer. A process-based model incorporates a fundamental conceptual understanding of the transport and fate of these contaminants in this aquifer setting, with a quantitative analysis of the factors controlling the potential for NA. This includes the estimation of parameter values for the relevant processes and identification of aquifer properties which characterise the nature and extent of attenuation. In turn this information can be used to develop a generic performance model which can be used to make a robust prediction of petroleum hydrocarbon and ether oxygenate attenuation in the aquifer under these conditions. This goal was achieved using an integrated research programme that included field investigation of natural processes, laboratory studies to assess contaminant transport and degradation processes under controlled conditions for parameter estimation, and numerical modelling studies for validation and development of the performance model.

The project has delivered results on two levels. The results have a site-specific focus, with the research based on the Chalk aquifer looking at MTBE and TAME. However, the research has been undertaken in a way which ensures that the results have a more general application to predicting the transport and fate of petroleum hydrocarbons and ether oxygenates in UK dual-porosity aquifers. This is achieved by identifying the transferable concepts and quantitative analysis for similar contaminant settings and through the validation of a generic performance model for NA of these contaminants in these aquifers, as a tool for improved risk assessment. Based on the results of the site investigation which preceded this project and knowledge gaps identified from the literature review highlighted in the background section, the key objectives of the research were:

1. To determine if aerobic degradation is important for MTBE in the Chalk aquifer
2. To identify factors controlling degradation in the aquifer and estimate parameter values for processes
3. To identify whether degradation occurs in the fractures or matrix
4. To understand how dual porosity flow affects the potential for biodegradation
5. To demonstrate the validity of the conceptual model and parameter values

Particular focus was given to understanding the potential for NA of MTBE under various conditions identified in the aquifer. A range of hypotheses were formulated regarding the fate of MTBE in the aquifer, as follows:

1. MTBE is not degraded, with attenuation by physical processes (dual porosity transport) only
2. MTBE is degraded aerobically in the absence of other petroleum hydrocarbons
3. MTBE is degraded aerobically in the presence of other petroleum hydrocarbons
4. MTBE is degraded anaerobically
5. MTBE degradation is controlled by kinetics (slow/fast rates, short/long lag), also applies to 2, 3 and 4
6. MTBE degradation occurs on fractures or in the matrix, also applies to 2, 3 and 4

These hypotheses were evaluated using the laboratory and field studies developed within the research programme.

1.4 PROJECT OUTPUTS AND MILESTONES

The key outputs arising from the project are scientific advances in process understanding and parameterisation, improved site investigation methodologies and performance assessment approaches for interpreting NA of petroleum hydrocarbons and ether oxygenate compounds in the Chalk and other dual porosity aquifers. These are summarised below and explored in the subsequent sections, where achievements are described against the original project objectives. Transferable concepts and results, allowing application of the project outputs to similar settings are identified. The key science and technology advances made by the project are:

1. Development of a detailed process model describing the NA of petroleum hydrocarbons and MTBE in the Chalk aquifer, providing data on:
   - Physico-chemical properties and reactions which determine transport and attenuation capacity, with parameter values, including degradation rates for BTEX and MTBE under different redox and environmental conditions
   - Effect of environmental factors and contaminant interactions on degradation potential and rates
   - Contribution of dual-porosity transport and biodegradation in attenuation
2. Development of a new improved analytical method for the determination of ether oxygenate compounds, their metabolites and BTEX in petroleum fuel-contaminated groundwater, with superior performance to existing methods
3. Development of a novel method for the onsite sampling of pore water chemistry in contaminated consolidated aquifers
4. Development of a mass balance model as a spreadsheet-based, decision-making tool for the performance assessment of NA in dual-porosity aquifers, using typical site data and accounting for uncertainty in predictions with Monte Carlo analysis
5. Validation of conceptual model and parameters describing NA of petroleum hydrocarbons and MTBE in the Chalk aquifer, allied to the development of an advanced numerical code, with identification of dual-porosity effects and performance prediction for NA

The project milestones, allied to the scientific objectives and achieved through implementation of the project plan, were:

1. Approved project inception report and work plan, achieved via review of literature and previous investigations of the site

2. Profile of hydraulically active fractures and fracture properties, achieved via hydraulic and geophysical testing
3. Installation of multilevel groundwater samplers for monitoring of contaminant transport, achieved via review of site conceptual model
4. Understanding of spatial and temporal variation in contaminant distribution, redox processes and degradation, achieved via repeat groundwater quality surveys
5. Profile of aquifer geochemistry and microbiology with innocula for laboratory microcosms, achieved via rock coring at locations within contaminant plume and uncontaminated aquifer
6. Parameter values for processes and degradation potential, achieved via laboratory microcosm and diffusion studies developed from accumulated site data and conceptual model
7. Validated process model and predictions of contaminant fate, achieved via development of numerical dual-porosity transport code using site data and conceptual model to test research hypotheses for MTBE
8. Science and technology transfer to beneficiaries and end-users, achieved via dissemination of research outputs through conference presentations, seminars, publications and promotion using CL:AIRE

2. SITE DESCRIPTION

2.1 SITE CONDITIONS AND HISTORICAL INFORMATION

The research site is a retail filling station located in St Albans on the Upper Chalk aquifer in southeast England. The site is situated at the periphery of the city, but in a typical urban setting, surrounded by residential and commercial properties. It is adjacent to a busy trunk road servicing the various business concerns, residential and commuter traffic.

An accidental leakage of unleaded fuel from an underground storage tank was detected in February 1999. The subsequent audit showed that up to an estimated 55,000 litres of product had been lost, contaminating the aquifer with petroleum hydrocarbons, including BTEX, the oxygenate compounds MTBE, TAME and TBA, plus other aromatic organic compounds. MTBE and TAME are present in the unleaded fuel formulation at concentrations of 2.88% v/v and 1.65% v/v, respectively. TBA is present at trace levels, as an impurity in the ether oxygenate formulation. The unleaded fuel, termed light non-aqueous phase liquid (LNAPL), migrated through the unsaturated zone to the water table 20 m below ground. Dissolution of the LNAPL resulted in contamination of the groundwater with the organic compounds listed above. Treatment of the LNAPL source in the unsaturated zone was carried out from 1999 to 2002 using a soil vapour extraction (SVE) system. Low vapour yields eventually led to the decommissioning of the SVE system, although locally high BTEX and ether oxygenate concentrations in the unsaturated zone suggest that there is a residual contaminant source above the water table. In June 2002 the site was closed and in September 2002 six underground storage tanks were removed from the forecourt. This site is currently unused.

2.2 GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS

2.2.1 GEOLOGICAL CONDITIONS

This section describes the main lithological characteristics of the rocks beneath the research site to a depth of approximately 50 metres below ground level (mbgl), ca. 40 metres above ordnance datum (mAOD). The lithology immediately beneath the site is represented by up to 11 m of Quaternary drift deposits, which comprise clays (inferred as till) in the upper part with sands and gravels (inferred to be of glacio-fluvial origin) beneath. The upper section of the Quaternary sediments has been variably affected by urbanisation and up to 4 m of made ground may be present.

The Upper Chalk directly underlies the drift deposits. It is a very soft, structureless putty chalk, where the primary sedimentary fabric is absent and fractures cannot be resolved, to medium hard, rubbly to blocky chalk which is only slightly or moderately weathered. In general, the Chalk section beneath the site grades from a highly weathered, rubbly, weakly competent formation near the top of the section to a more competent rock at depth. Putty Chalk occurs adjacent to fractures and as fracture infill (Wealthall *et al.*, 2001). There are numerous sub-rounded to angular nodular flints throughout the sequence, often adjacent to fractures or voids in the rock, although the intensity decreases with depth. Few marl seams are present, although a prominent seam occurs at 38.86-38.96 mbgl. A layer of competent Chalk, interpreted to represent a Chalk rock hardground occurs ca. 45 mbgl. Marly, poorly consolidated Chalk occurs below this depth. Compositionally, the Upper Chalk is 99% $CaCO_3$, with very low mineral oxide (MnO_2, $Fe(OH)_3$) content.

A complex network of fractures dissects the Upper Chalk beneath the site. Fracture network characterisation has identified bedding-parallel fractures with a dominant ENE-WSW strike and dip of 2-29° to the SSE (Wealthall *et al.*, 2001; 2002). There is also a subordinate bedding-parallel fracture set with E-W strike and N dip of 10-30°. High-angled fractures include sets with an ENE-WSW or E-W trend and NNW dip of 30 to 80°, and sets with a NW-SE trend and NE dip of 35-75°. The mean fracture spacing for combined bedding-parallel and high-angled fractures was estimated from prior investigation at the site to be

0.23 m (Wealthall *et al.*, 2001; 2002). Fracture porosity is estimated as 1.1%, assuming three orthogonal fractures sets, a range of block sizes determined from this fracture spacing data and fracture aperture derived from ranges (see hydraulic properties below) obtained in the hydraulic tests. This porosity is similar to estimates from other studies (Barker, 1993).

2.2.2 HYDROGEOLOGICAL CONDITIONS

The aquifer is unconfined with an unsaturated zone thickness of ca. 20 m and the piezometric surface lies entirely within the Chalk (Wealthall *et al.*, 2001). Aquifer transmissivity determined from hydraulic (pumping and slug) tests varies significantly with depth beneath the site, with values from <1 to >300 m^2/day that are typical for the Chalk aquifer (Barker, 1993). In general, higher values of aquifer transmissivity occur between 20-30 m depth, decreasing by several orders of magnitude below this depth. However, localised zones of increased transmissivity, and therefore groundwater flow velocity, occur over a scale of a few metres within the upper 15 m of the saturated zone in the aquifer. These correspond to hydraulically active fractures and represent preferential pathways for contaminant migration. Groundwater velocity based on hydraulic tests, and assumed to reflect fracture flow, is 10^{-3} to 17 m/day. The horizontal hydraulic gradient, deduced from four surveys, varies from 0.0022 to 0.0031, with an arithmetic mean of 0.0024. There is no significant vertical hydraulic head gradient in the upper 20-45 m of the aquifer, indicating that there is no vertical flow component capable of inducing vertical migration of contaminants (Wealthall *et al.*, 2001; 2002). Below 45 m depth the hydraulic head profile is negative relative to the open borehole, indicating outflow in the open borehole (Wealthall *et al.,* 2001). This correlates with the inferred location of a hardground at ca. 45 metres below forecourt level (mbfl). An increase in transmissivity at this depth suggests that the hardground is a semi-confining layer, which limits vertical movement of groundwater, but still accommodates sub-horizontal movement of groundwater (Wealthall *et al.*, 2001). Another low permeability layer, probably representing a localised hard band, has also been identified in rock cores collected from the contaminant plume, where this feature has reduced the vertical migration of dissolved contaminants. Periodic monitoring shows that the water table elevation fluctuates by ca. 2 m (from 20-22 mbgl) and that the local groundwater flow direction (SSE) varies temporally by 10°.

The aquifer matrix has high porosity (ca. 30-45%) but low effective permeability, and the matrix pore water is essentially immobile. The fracture network contributes typically only 1% of the aquifer porosity, but has very high permeability and dominates groundwater flow in the system. The aquifer can be conceptualised as a dual-porosity system, with transport occurring primarily in fractures with high transmissivity and the bulk of groundwater being stored in the low transmissivity matrix.

2.3 DESCRIPTION OF ADDITIONAL SITE CHARACTERISATION STUDIES

Two phases of site characterisation were completed prior to the research described in this report. This previous work includes site investigation, monitoring and remediation activities (denoted “Phase 1”) undertaken by consultants since the fuel spill was identified (February 1999-to date), and also a one-year project (February 2000 to March 2001) completed by University of Sheffield (denoted “Phase 2”) immediately prior to the current study. The objectives and activities undertaken for these separate phases are outlined below.

2.3.1 PHASE 1 INVESTIGATION

The Phase 1 investigation commenced after the initial loss of unleaded fuel from the site. Environmental consultants commissioned by the site owner undertook onsite soil borings and installed a series of single-screen monitoring wells (MW7, MW9, MW10, MW11, MW13) within the source zone, downgradient of the source zone in the aquifer and transverse to the direction of the prevailing groundwater flow (Figure 2.1).

The monitoring wells were screened over 10 m across the zone of water table fluctuation. The key objectives of this work were:

- To ascertain the extent of subsurface contamination by free product and dissolved phase fuel hydrocarbons, MTBE and TAME
- To develop a groundwater monitoring well network to assess the behaviour of dissolved phase contaminants in the aquifer, and
- To design and implement an appropriate monitoring and remediation programme for the site

The SVE system was commissioned at this time for source management and routine groundwater monitoring surveys were undertaken at intervals of three weeks.

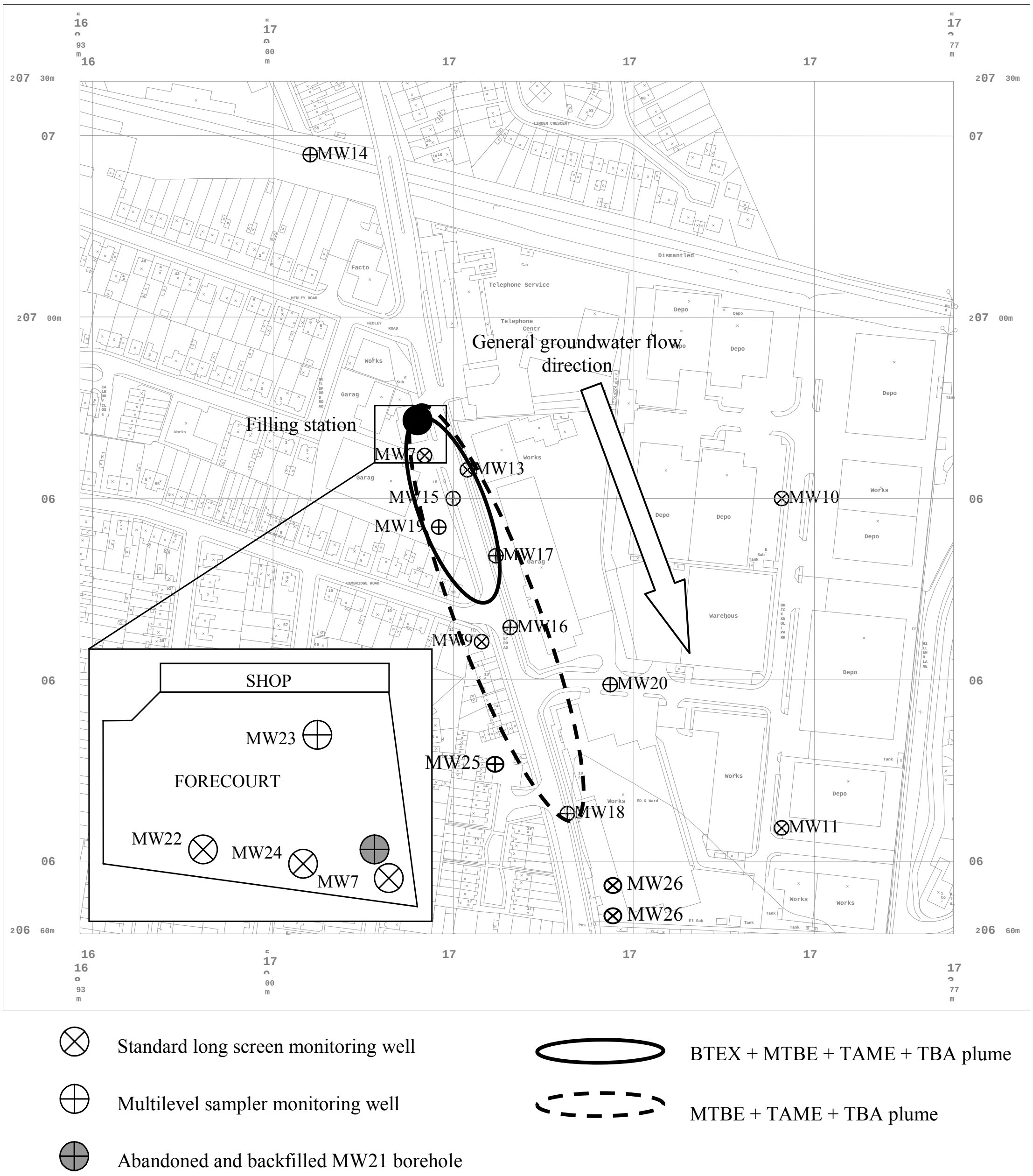

Figure 2.1: Location map for monitoring wells installed at the research site (grid squares are 100 m for scale)

2.3.2 PHASE 2 INVESTIGATION

The Phase 2 investigation was undertaken between February 2000 and March 2001 by the University of Sheffield, on behalf of the site owner. This work involved an integrated field investigation, groundwater monitoring and modelling study of the transport of dissolved contaminants in the Chalk aquifer beneath the site. The study also included an analysis of controls on the distribution and migration of LNAPL in the unsaturated and saturated zone, which provides a source for groundwater contamination. Further emphasis was given to a comparison of the subsurface transport and fate of BTEX, MTBE and TAME in the fuel mixture, since the ether oxygenate compounds are considered to be the primary risk driver in relation to groundwater contamination at the site. The site investigation included the drilling of three cored boreholes (locations of MW14, MW15 and MW16 in Figure 2.1), downhole geophysical testing, hydraulic testing, installation of commercial multilevel groundwater samplers (MLS) equipped with seven sample ports (Einarson and Cherry, 2002) in MW14-16, groundwater quality monitoring of all site monitoring wells at intervals of three weeks and 1-D transport modelling, to interpret the following:

- Site geology and hydrogeology
- Fracture network properties
- Dissolved phase contaminant distribution and transport
- Natural attenuation processes and performance
- Predictions of MTBE transport and attenuation under different boundary conditions

2.3.3 ONGOING INVESTIGATION

The research described in this report commenced in May 2001 after the Phase 2 study and was completed in October 2004. During this period, a further five MLS monitoring wells (MW17, MW18, MW19, MW20, MW23) and two single-screen monitoring wells (MW22, MW24) were installed at locations in the source area and downgradient of the source in the aquifer (Figure 2.1). Cored boreholes were also drilled at locations in the uncontaminated aquifer (MW20), downgradient contaminant plume (MW17) and source zone (MW22 and MW23) at this time. The results of this activity and analysis of rock cores are discussed in Chapter 5. In August 2004, an additional phase of investigation was undertaken by the site owner to further understand the downgradient migration of the plume and lateral extent of dissolved hydrocarbon and oxygenate contamination in the aquifer. This work included the installation of a nested piezometer (MW26) and single screen monitoring well (MW26A) for cross-borehole tracer tests and hydraulic tests, plus three additional MLS monitoring wells (MW25, MW27, MW28) used to define the plume flow path and migration. The locations of MW25, MW26 and MW26A are shown on Figure 2.1, but MW27 and MW28, which are further downgradient of MW26, are not shown on the map. A summary of the location (as of July 2004) and function of monitoring wells installed at the site, relative to the plume source area, is given in Table 2.1.

Table 2.1: Location and function of monitoring wells installed at the research site

Monitoring well	Distance from plume source area (m)	Function	Installation date
MW7 *	16	Defining mass flux from source area	1999
MW9 *	129	Defining plume flowpath	1999
MW13 *	26	Defining plume flowpath	1999
MW14	143	Upstream of site, background reference	July 2000
MW15	46	Defining plume flowpath	Oct 2000
MW16	125	Defining plume flowpath	Oct 2000
MW17	76	Defining plume flowpath	Jan 2002
MW18	220	Defining plume flowpath, downstream sentinel well	Dec 2001
MW19	65	Defining plume flowpath, transverse to flowline	April 2002
MW20	152	Defining plume flowpath, transverse to flowline	Dec 2001
MW22	13	Defining mass flux from source area	Dec 2002
MW23	0	Assumed source area	Dec 2002
MW24	15	Defining mass flux from source area	Dec 2002

Note: * Monitoring well screened over 10 m; all other monitoring wells are multilevel groundwater samplers fitted with seven monitoring points (Einarson and Cherry, 2002)

The monitoring well network is aligned approximately parallel with the plume flow path. This network provides information on the spatial distribution of dissolved contaminants across a monitored interval of 25 m in the saturated zone, over a distance of >300 m from the site and transverse to the plume flow path. MW23 represents the source area and all other monitoring well locations are referenced relative to this datum, including the depth below ground level, which is expressed as mbfl relative to the elevation of this monitoring well, in some presented data. This data excludes the offsite monitoring wells, MW10 and MW11.

There has been ongoing groundwater quality monitoring at the site during the period of this research. This parallel activity relates to the monitoring plan agreed between the site owner and the Environment Agency and is undertaken by environmental consultants. In this activity, the groundwater quality monitoring has focused on selected monitoring wells and depths, identified as important flow paths for contaminant migration. The objective is to understand the temporal variation in contaminant concentrations in relation to water table fluctuations and changes in the plume source term and how this affects the long term plume development, with respect to compliance criteria agreed with the regulator. The research programme described in this report has been carefully co-ordinated with the various additional phases of site investigation and routine groundwater quality monitoring undertaken by the site owner as part of this ongoing work.

2.4 NATURE AND EXTENT OF CONTAMINATION

The unsaturated and saturated zones of the Chalk aquifer beneath the site are contaminated with hydrocarbon and oxygenate compounds derived from the petroleum fuel. However, the total contaminant levels and relative proportions of specific compounds distributed between the unsaturated and saturated zones are significantly different.

Analyses of the pore water chemistry in core samples (MW23) collected from the source area, using the method of Spence *et al.*, (2005a) show that there is contamination of the unsaturated zone down to the water table. Concentrations of dissolved BTEX, MTBE, TAME and TBA reach mg/L values in the unsaturated zone pore water, suggesting the presence of residual product trapped in the pore spaces and/or fractures above the water table.

There is a peak in these contaminant concentrations at 10 mbgl in the source area (MW23), which is close to the base of the Quaternary drift deposits underneath the location of the former leaking underground storage tank. A further peak in contaminant concentration occurs close to the water table at 20-22 mbgl. This is attributed to dissolution of product close to the water table or drainage of contaminated infiltration from higher levels in the profile. No other dissolved fuel compounds were detected in the unsaturated zone by this method (Spence *et al.*, 2005a) of pore water analysis. However, it is likely that higher molecular weight hydrocarbon compounds are present, possibly adsorbed onto the Chalk matrix. In addition, a thin layer (1 cm) of product was found on the water table when coring MW23. In combination with the analysis of the pore water chemistry, these results indicate that there are free phase and probably residual phase organic contaminants trapped in the unsaturated zone beneath the site.

The routine groundwater quality monitoring has detected a wide range of dissolved hydrocarbons and ether oxygenate compounds in the saturated zone, including BTEX, MTBE, TAME, TBA, isopropylbenzene, propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, sec-butylbenzene, tert-butylbenzene and naphthalene. However, the majority of these dissolved contaminants occur at low concentration in groundwater close to the site (MW7 and MW13) and most of the larger scale contamination is contributed by BTEX, MTBE, TAME and TBA. In general, two overlapping plumes of contaminants can be identified from the distribution of dissolved hydrocarbons and ether oxygenate compounds in groundwater beneath the site. These are a mixed plume of BTEX, MTBE, TAME and TBA extending approximately 125 m downgradient of the site and a plume of MTBE, TAME and TBA extending approximately 220 m downgradient of the site. This basic distribution is illustrated in Figure 2.1. Dissolved phase ether oxygenate contamination also extends between 20-30 m depth in the saturated zone, from immediately beneath the source area near MW15, to the downgradient monitoring well MW18. However, the dissolved phase hydrocarbon (e.g. BTEX) contamination is present over this depth interval but extends downgradient only as far as MW16. The reasons for this distribution are explained in Chapter 5. This idealised contaminant distribution reflects the status of the respective mixed BTEX / ether oxygenate and ether oxygenate-only plumes when this research was completed in October 2004.

3. RESEARCH SUPPORT ISSUES

3.1 HEALTH AND SAFETY

The health and safety issues in this project are those applicable to the investigation of contaminated sites. No special procedures were required, other than adherence to proper practice for this type of work. A site safety plan was developed and agreed prior to commencement of each phase of site investigation, taking account of known or expected hazards and risks from the contaminants and intended operations, with appropriate preventative or remedial action identified. Key identified hazards included potential exposure of site workers and the public to contaminated groundwater and sediments during the drilling and groundwater sampling activities. This safety plan was co-ordinated with all parties (contractors, consultants and researchers) involved in the drilling work.

Appropriate personal protection equipment was provided and used where necessary for the drilling and groundwater sampling activities. This included provision of hard hats, high-visibility jackets, overalls, safety glasses, safety boots, gloves and medical accessories.

3.2 PROJECT WORK PLAN

The original project work plan developed to achieve the research objectives identified in section 1.3 included the following key activities and provisional timescales:

- Project mobilisation (3 months)
  - Literature review
  - Design of field and laboratory studies
  - Preparation of inception report

- Borehole testing of drilled boreholes (3 months)
  - Geophysical testing
  - Hydraulic tests
  - Data review against previous work

- Multilevel groundwater sampler installation (1 month)
  - Installation of 1 commercial device
  - Development for sampling

- Groundwater quality monitoring (6 months)
  - Analysis for hydrochemistry, microbiology and stable isotopes
  - Three annual surveys

- Collection of rock cores (1 month)
  - Anaerobic drilling of two cores with geological and fracture logging
  - Samples for porewater and solid phase analysis and laboratory microcosms
  - Analysis for hydrochemistry, microbiology and stable isotopes

- Laboratory microcosm and diffusion studies (30 months in total)
  - Degradation of BTEX and MTBE under different redox conditions
  - Evaluation of environmental factors on degradation potential
  - Degradation potential in ^{14}C-MTBE, ^{14}C-phenol and ^{14}C-toluene labelled systems
  - Molecular-genetic analysis of ^{14}C-MTBE-labelled systems
  - Diffusion properties for different chemical species and Chalk samples
  - Analysis for hydrochemistry, microbiology and stable isotopes

- Modelling (6 months)
  - Literature review of analytical closed form models
  - Testing research hypotheses with laboratory and field data

  - Evaluation of parameter sensitivity and upscaling
  - Validation of process-based conceptual model and development of performance model

- Reporting and dissemination (5 months)
  - Preparation of progress reports
  - Biannual review by project steering committee
  - Final reporting and preparation of publications

This work plan was subsequently modified as the project developed, to accommodate advances in knowledge and revised priorities as data was collected, and also to incorporate the site investigation undertaken in parallel with this study by the site owner. The latter provided the opportunity to achieve substantial gearing up in the science and technology outputs from the project, for the benefit of all parties involved. The key modifications made to the original project work plan include:

- Collection of six rock cores (compared with two planned) and installation of seven multilevel groundwater samplers (compared with one planned), plus the related borehole investigations and groundwater sampling. The majority of this additional activity was sponsored by the site owner and undertaken jointly with the research team.

- Development of a numerical dual-porosity reactive transport code to underpin and upgrade the modelling efforts, providing the opportunity to pursue the interpretation beyond that originally anticipated. This work was included within the project through an externally funded PhD study and undertaken jointly with the University of Vancouver, Canada.

3.3 DESCRIPTION OF SAMPLING PLAN

3.3.1 GROUNDWATER SAMPLING PLAN

Groundwater samples were collected from different aquifer horizons during hydraulic testing of drilled boreholes and from all the monitoring wells during routine groundwater quality surveys. The purpose of this activity was to provide samples for the analysis of groundwater hydrochemistry, dissolved gas composition, microbiology and stable isotope composition of selected dissolved chemical species. The procedures used to collect the groundwater samples for the range of analyses required are summarised in Figure 3.1.

3.3.2 METHODS AND DATA QC/QA PROCEDURES FOR HYDROCHEMICAL ANALYSIS OF GROUNDWATER SAMPLES

Procedures were used which ensured the collection of representative groundwater samples for chemical and microbiological analysis. Dedicated sampling tubes were used in each monitoring well to minimise cross-contamination of samples. A purpose built groundwater sample processing rig was constructed and used for each survey. An inlet line to this rig was connected directly to the dedicated inertial lift pump in each MLS monitoring well to form a closed circuit, allowing individual monitoring levels to be purged and samples to be collected and processed without exposure to the atmosphere. This procedure minimised changes in sample chemistry that can occur when anaerobic groundwater samples are exposed to the atmosphere. Filtration of samples was also completed on-site with this apparatus, using N_2 gas. This rig was used to collect all samples from the MLS boreholes, but could not be used for sampling the single screen monitoring wells (MW7, MW9, MW13, MW22 and MW24) due to excessive agitation of the pump tubing during pumping. These monitoring wells were sampled by filling all containers directly from the inertial lift pump discharge line.

Each monitoring well was purged prior to sampling to remove approximately three bore volumes of groundwater. The purging protocol takes account of the volume of each chamber in the MLS monitoring well. It is assumed that groundwater passes through the full section of the sand pack at each monitoring point. Time series sampling of individual levels in the monitoring wells has confirmed that sample chemistry rapidly stabilises within the purging time used and provides reproducible samples. The purging and sample processing procedures used ensured that the collected groundwater samples were representative of the section of aquifer sampled by each monitoring well.

The samples collected for hydrochemical analysis included the following (Figure 3.1):

- Well head parameters (pH, Eh, electrical conductivity (EC), temperature, dissolved oxygen (DO)) measured onsite in unfiltered samples using an in-line flowcell
- Alkalinity (as mg/l $CaCO_3$) measured by titration onsite in samples 0.45 µm Nylon-filtered to remove interference (over estimation) from particulate $CaCO_3$ in analyses
- VOCs (BTEX, MTBE, TAME, TBA) and volatile fatty acids measured in unfiltered, unpreserved samples
- Total organic carbon (TOC) measured in unfiltered, unpreserved samples
- Total dissolved inorganic carbon (TDIC) measured in unfiltered samples collected for carbon isotope analysis
- Anions (F, Br, NO_3, NO_2, PO_4, Cl, SO_4) measured in filtered, unpreserved samples
- Cations (Ca, Mg, K, Na, Mn(II), Fe(II), Li, Si, total S, heavy metals) measured in filtered and preserved (HNO_3 <pH 1) samples
- Dissolved gases (CO_2, CH_4, H_2) measured in duplicate gas samples which were collected as described in Thornton *et al.,* (2001)

All groundwater samples were transferred directly to appropriate sample bottles (containing preservatives as necessary), which were filled completely to leave no headspace. These procedures ensured that samples were quickly processed onsite, to minimise contact with the atmosphere and to stabilise the concentrations of reactive species. All groundwater samples were stored in an onsite chest chiller cabinet at 4°C. A summary of the methods used for the hydrochemical analysis of groundwater samples is given in Table 3.1.

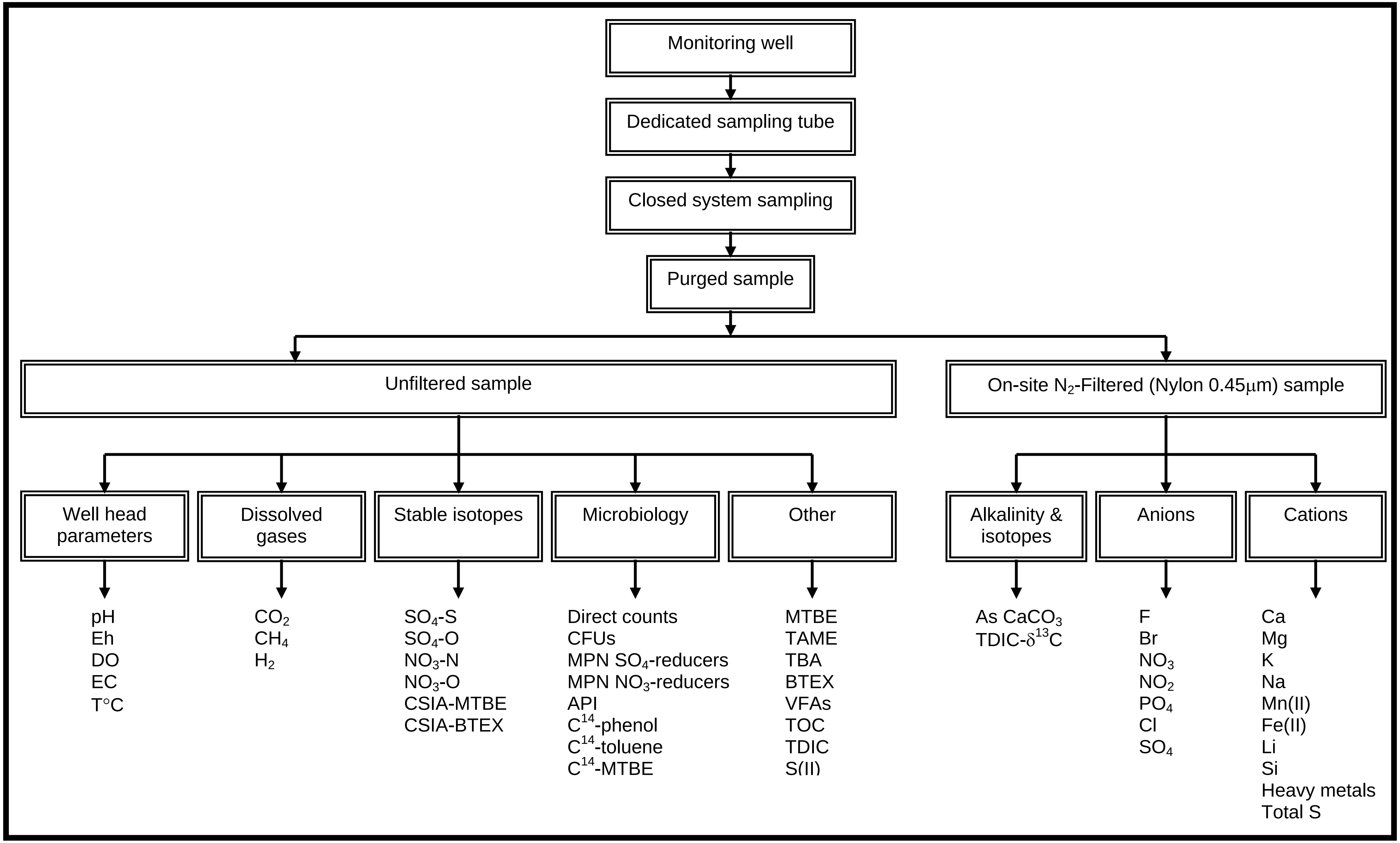

Figure 3.1: Summary of processing procedures for groundwater samples

Table 3.1: Summary of methods used for the hydrochemical analysis of groundwater samples

Species	Analytical method	Method detection limit	Precision
Wellhead parameters			
pH Eh DO EC Temperature	Flowcell with dedicated probes	0.1 pH units 1 mV 0.1 mg/L D.O. 1 µS/cm 0.1°C	Recorded value represents stable reading on meter during sampling. Meters were calibrated prior to use using certified standards
Dissolved hydrocarbons			
BTEX	EPA 624/8260 using mass-sensitive detection	1 ppb	5% RSD
Dissolved ether oxygenates			
MTBE, TAME, TBA	EPA 624/8260 using mass-sensitive detection	1 ppb	5% RSD
Anions			
F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}	Ion chromatography (Dionex DX 120 system)	0.05 mg/L	5% RSD
Dissolved gases			
CO_2 CH_4	Collected by equilibration with an N_2 bubble in a gas flowcell (Thornton *et al.*, 2001).	1 µg/L	Recorded value is average of duplicate analyses
Sulphide			
HS^-	Determined by nitrogen sparging of 20L of acidified groundwater and quantitative recovery as Ag_2S	1 µg/L	Not applicable
TDIC			
Expressed as mg/L C	Determined quantitatively via CO_2 yield from $SrCO_3$ precipitate formed on addition of excess $SrCl_2$	1 mg/L	Not applicable
Transition metals			
Mn^{2+}, Fe^{2+}	ICP-AES	0.01 mg/L	5% RSD

3.3.3 METHODS AND DATA QC/QA PROCEDURES FOR ISOTOPE ANALYSIS OF GROUNDWATER SAMPLES

Groundwater samples for the analysis of dissolved total inorganic carbon (CO_3^{2-} + HCO_3^- + H_2CO_3 + $CO_{2\ (aq)}$) (TDIC) and $\delta^{13}C$-TDIC were collected in 0.5 L airtight HDPE bottles and fixed as $SrCO_3$ by the addition of $SrCl_2$ and ammonia (Bishop, 1990). The impure $SrCO_3$ precipitate was recovered on a 0.45 µm cellulose nitrate membrane and dried at 50°C. The total precipitate mass was noted and a sub-sample taken for conversion to CO_2 in a high vacuum line. The CO_2 yield from this process was then used to calculate the groundwater TDIC from the precipitate mass. CO_2 gas for isotopic analysis was produced from organic compounds by combustion in sealed quartz tubes (Louie *et al.*, 1993). $\delta^{13}C$ analyses on samples of CO_2 gas were done using a VG Sira-10 gas source mass spectrometer and the data corrected using standard procedures. Precision is better than 0.05‰.

Samples for isotopic analysis of SO_4-S ($\delta^{34}S$-SO_4) and SO_4-O ($\delta^{18}O$-SO_4) were collected in 0.5 L dark glass bottles containing 1 g/L sodium azide to limit microbial activity. The bottles were filled completely with groundwater, sealed with PTFE-lined caps and stored in the dark at 4°C prior to analysis. These samples were acidified to pH 2.0-2.5 and heated to ~ 80°C on a hot plate. A volume of 100 g/L $BaCl_2$ solution equal to 10% of the sample volume was then added and the $BaSO_4$ precipitate left to cool and coarsen overnight. $BaSO_4$ precipitates were recovered on 0.45 µm cellulose nitrate membranes and washed with deionised water prior to drying at 50°C.

Groundwater samples for S(II)-S ($\delta^{34}S-HS^-$) isotopic analysis were collected in the field using twin 20 L barrels to increase the rate of sample collection / recovery. One barrel was filled with groundwater while the other full barrel was sparged with N_2 to extract dissolved H_2S. The barrels were flushed with N_2 for 5 minutes prior to the gas stream being reduced and diverted through acid vapour filters and bubble traps. After a further 5 minutes of N_2 flushing, filling with groundwater commenced at ~ 200 mL/min. During barrel filling a slow stream of N_2 was passed through the sparging line to reduce the impact of O_2 incursion. The lines to the sulphide traps were open so that H_2S exsolved from the groundwater during pumping did not escape. The collection of 20 L of groundwater required approximately 1.5 hours, although in several cases 5 L of water was sufficient for high sulphide concentrations. After filling, approximately 240 mL of concentrated HCl was added to the barrels to reduce the pH to 1. The sparge rate was then increased to a flow rate of ~2000 mL/minute for approximately 80 minutes to exsolve aqueous H_2S. This was collected as a black silver sulphide precipitate in a glass measuring cylinder containing buffered silver nitrate solution. This precipitate was recovered by filtration onto a pre-weighed 0.45 µm cellulose nitrate membrane. Filter membranes and precipitates were stored in the dark at 4°C in glass vials to limit oxidation prior to analysis.

Nitrate in groundwater was collected as pure $AgNO_3$ for the determination of $\delta^{15}N-NO_3$ and $\delta^{18}O-NO_3$ following the method of Silva *et al.,* (2000). Anion exchange columns were used to recover NO_3 from 500 mL of pre-filtered groundwater using the onsite sample processing rig. Groundwater was first transferred to a 1 L holding vessel, which was then pressurised to 2 atmospheres and the outlet connected to a filter cartridge containing a 0.4 µm polycarbonate membrane, fixed in line with the anion exchange column. This greatly increased the sample filtration rate. The anion exchange columns were capped after use and stored in the dark at 5°C prior to processing.

Nitrate and sulphur isotopic analyses were performed on a Micromass Isoprime continuous flow mass spectrometer coupled to a Eurovector Elemental Analyser using standard methods. Method precision is better then 0.3 ‰ for $\delta^{34}S$ and better than 0.2‰ for $\delta^{15}N$ and $\delta^{18}O$ in nitrate. The analysis of $\delta^{18}O$ in sulphate was achieved by converting SO_4 to CO_2 by reaction with graphite as described by McCarthy *et al.,* (1998), with a precision of ± 0.4 ‰. $\delta^{18}O$ analyses were done using a VG Sira-10 gas source mass spectrometer and the data corrected using standard procedures (Craig, 1957).

Samples for compound-specific carbon isotope analysis (CSIA) of benzene and MTBE were collected in 125 mL glass crimp vials containing 35 g of Analar sodium chloride, which were filled and sealed in the field, leaving a 2 mL headspace. Polytetrafluorethylene (PTFE) faced butyl rubber septa were used to prevent analyte loss by sorption into the septum. The samples were stored inverted at 5°C, prior to analysis. Carbon isotope ratios in benzene and MTBE were determined using an Agilent 6890A gas chromatograph coupled through a combustion interface and water trap to a Finnigan MAT 252 continuous flow irMS. Repeat analyses of headspace gas yielded an analytical precision (95% confidence interval) of ±0.6‰ for benzene and ±0.3‰ for MTBE. The detection limit of the technique was ~ 1 µg/L for benzene and ~ 10 µg/L for MTBE.

Sulphur, carbon, nitrogen and oxygen isotope data are reported using the standard δ-notation (Eq. 1), relative to the V-CDT, V-PDB, AIR and V-SMOW standards, respectively:

$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] .10^3 \ (‰) \qquad \text{(Eq. 1)}$$

where R_{sample} and R_{standard} are the isotopic ratio in sample and standard, respectively.

3.3.4 METHODS AND DATA QC/QA PROCEDURES FOR MICROBIOLOGICAL ANALYSIS OF GROUNDWATER SAMPLES

Groundwater samples for microbiological analysis were collected using the purpose-built sample processing rig described in section 3.3.2. These samples were collected in sterilised amber glass 500 mL bottles, which were pre-flushed with N_2 gas. The bottles were filled completely and stored at 4°C in an onsite chiller cabinet. These samples were analysed for the range of microbiological determinands outlined in Figure 3.1 using standard methods.

3.3.5 ROCK CORE SAMPLING PLAN

Rock cores were collected from different locations at the site to support the other field and laboratory investigations. The rock cores were obtained from boreholes which were then subjected to geophysical and hydraulic testing, followed in some cases by the installation of an MLS for the collection of groundwater samples from different aquifer horizons. The primary purpose of collecting rock cores was to provide samples of matrix pore water for chemical and stable isotope analysis and to estimate the matrix porosity in vertical profiles from uncontaminated and contaminated locations in the aquifer. In addition, Chalk matrix samples were collected for laboratory microcosm and diffusion studies and for the analysis of microbiological determinands, geochemical properties and mineralogical composition.

3.3.6 METHODS AND DATA QC/QA PROCEDURES FOR THE COLLECTION OF ROCK CORES

3.3.6.1 Sampling of Matrix Pore Water Chemistry

With respect to the sampling of the matrix pore water chemistry, the key data quality issues identified for the collection of rock cores were:

- Contamination of pore water samples with drilling fluid during core recovery
- Minimisation of changes in pore water chemistry due to exposure of core and groundwater samples to the atmosphere after collection and prior to analysis

The matrix pore water chemistry may be changed by contamination with drilling fluid during the collection of the rock core. This occurs because water is commonly used as the drilling fluid in this process. The drilling fluid may have a different chemistry to that of the pore water contained within the Chalk matrix, and may also be oxygenated. Contamination of the (potentially anaerobic) matrix pore water with such a drilling fluid may therefore change the chemical composition of the sample and result in oxidation of reduced (organic and inorganic) chemical species. Secondary contamination of pore water samples by exposure to the atmosphere may occur when the rock core is subsequently processed after collection. This exposure can result in loss of volatile components (organic compounds and dissolved gases) and oxidation of reduced organic and inorganic chemical species in pore water samples, prior to analysis. Procedures were therefore developed and used which ensured the collection of representative pore water samples from rock cores for chemical and stable isotope analysis. These procedures included the adoption of innovative methods to minimise the sampling artefacts discussed above and to provide all the necessary information for the combined determination of the matrix pore water chemistry and porosity by a novel onsite rock core processing methodology. This methodology involves the sampling of the matrix pore water chemistry and porosity using diffusion equilibrium exchange (DEE) and its application at the research site is described in Spence *et al.,* (2005a). The steps required to process rock core and determine the pore water chemistry in samples using this newly developed DEE methodology are summarised in Figure 3.2. The rock sampling strategy adopted for this study is outlined below.

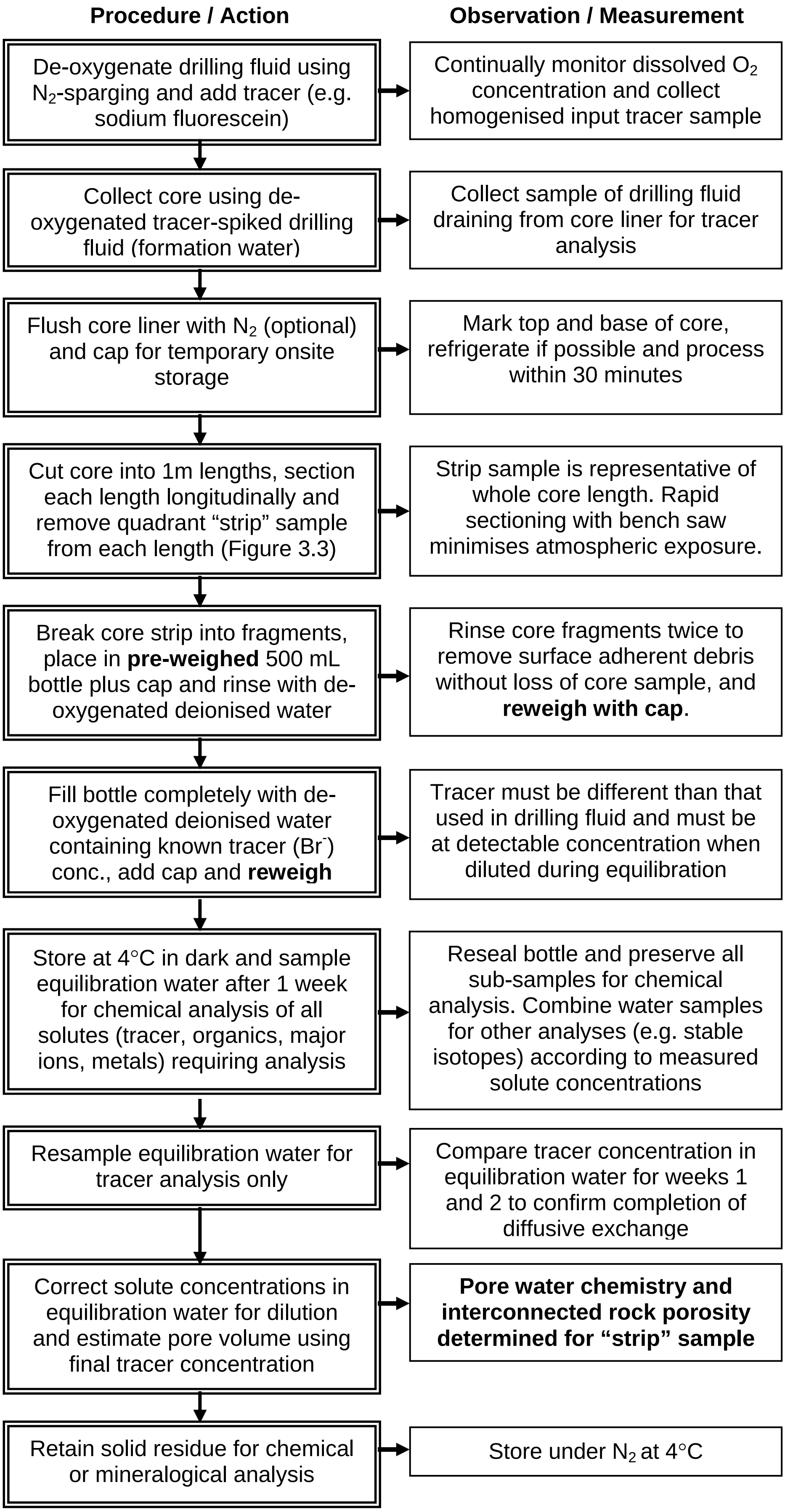

Figure 3.2: Summary of procedure for the extraction of pore water samples from Chalk rock core using the DEE methodology

Cored boreholes were completed from 1-2 m above the rest water table to final depth in each borehole (ca. 45 m in most locations but up to 55 m in MW20, giving a nominal 35 m of core). Rotary drilling with a wireline geobore coring device was used to collect the rock cores in 3 m runs. Clean groundwater from a roadside hydrant was used as the drilling fluid in all cases. Attempts were made to recover the rock cores from contaminated locations in the plume anaerobically, by continually sparging the drilling fluid aggressively with N_2 during the drilling of each 3 m core run. This was achieved by submerging a purpose-built finely perforated gas sparging device in the drill rig re-circulation tanks. This procedure was implemented to preserve the anaerobic quality (redox status, microbial ecology) of the recovered core, prior to analysis. It was not considered necessary to use this de-oxygenation procedure for the collection of rock cores from uncontaminated locations, which were therefore unlikely to be significantly affected by contact with the oxygenated groundwater used as the drilling fluid.

Sodium fluorescein was added to the groundwater in the drill rig re-circulation tanks, as a conservative tracer to determine the extent of invasion of the rock core matrix by drilling fluid. It is important to understand the extent of drilling fluid contamination when sampling the rock core for laboratory microcosms and interpreting matrix pore water chemistry. Fresh stock solutions of Na-fluorescein were added to the re-circulation tanks prior to each core run. At the end of each core run a sample of the drilling fluid containing the diluted Na-fluorescein tracer in contact with the core was collected from the core liner for analysis. The Na-fluorescein concentration in the drilling fluid from individual core runs and subsequent matrix pore water samples were used to assess the extent of contamination of the latter by the drilling fluid. Appropriate corrections were made to the chemical analyses of the matrix pore water samples, based on this degree of drilling fluid contamination and the composition of the drilling fluid. In most cases, the extent of drilling fluid contamination of the matrix pore water was less than 5% and did not significantly affect the measured pore water composition.

Rock cores were sampled in two ways, summarised below and illustrated in Figure 3.3.

- **Samples cut as a series of sections in each run.** These were selected to evaluate pore water solute gradients in the matrix in a profile away from individual fracture sets. For some of these samples, the matrix block either side of the selected fracture (i.e. above and below) was sampled. The number and location of these samples was determined largely by the clear identification of natural fractures (as opposed to drilling induced fractures) and the availability of adjacent matrix blocks of sufficient thickness for the collection of gradient samples. Gradients in the matrix pore water composition are best obtained in large (1.5 m) matrix blocks where long diffusion paths are expected to result in clearly defined solute profiles away from fractures. Matrix blocks for these samples were collected at intervals of 0-20 cm away from the fracture and then at 50-60 cm and 1-1.1 m, where possible. The 20 cm blocks recovered adjacent to fractures were subdivided at a later stage in an anaerobic cabinet. Attempts were also made to sample unfractured matrix blocks down the entire length of the core to provide a representative estimate of the matrix pore water composition.

- **Samples cut as parallel sections in each core run**. These were selected to determine vertical profiles of matrix pore water chemistry. In this case, the objective was to obtain a sample which was integrated over the depth of each core run, rather than an isolated sample from different depths, (which can bias results in a profile). These were obtained by cutting the rock core along its length on a table with a tile saw, to produce a quadrant section. The outer 1.5 cm layer of this quadrant was removed leaving an intact triangular section from the centre of the core. This was then broken up and placed in clean pre-weighed 500 mL Duran bottles. Each bottle and sample was then gently rinsed three times with de-oxygenated deionised water to remove any residues of drilling fluid. The bottle and contents were re-weighed to determine the mass of core sample. After this, the bottles were filled completely with de-oxygenated deionised water containing a bromide (Br) tracer (added as KBr), capped and re-weighed to determine the volume of added water for correction of pore water chemical data (see Figure 3.2). All of these samples were stored at 4°C prior to analysis. The intervals over which these samples are integrated is determined by the length of each core run recovered and the amount of core material left after other samples have been removed. For some samples, an entire 3 m core run could be represented, whereas for other sections which were heavily sampled for other investigations, it was possible to sample only a subsection of core runs.

3.3.6.2 Estimation of Matrix Porosity

Rock core samples were analysed for interconnected and total porosity. The interconnected porosity has the potential to interact with the through-flowing groundwater and represents the effective porosity of the Chalk matrix for solute transport. The total porosity of the matrix includes all (non-fracture) pore spaces, regardless of whether they contribute to solute transport. An estimate of the matrix porosity was required to correct chemical analyses of the pore water samples for dilution during the DEE procedure (Spence *et al.*, 2005a) and is an important aquifer property for related investigations in the project.

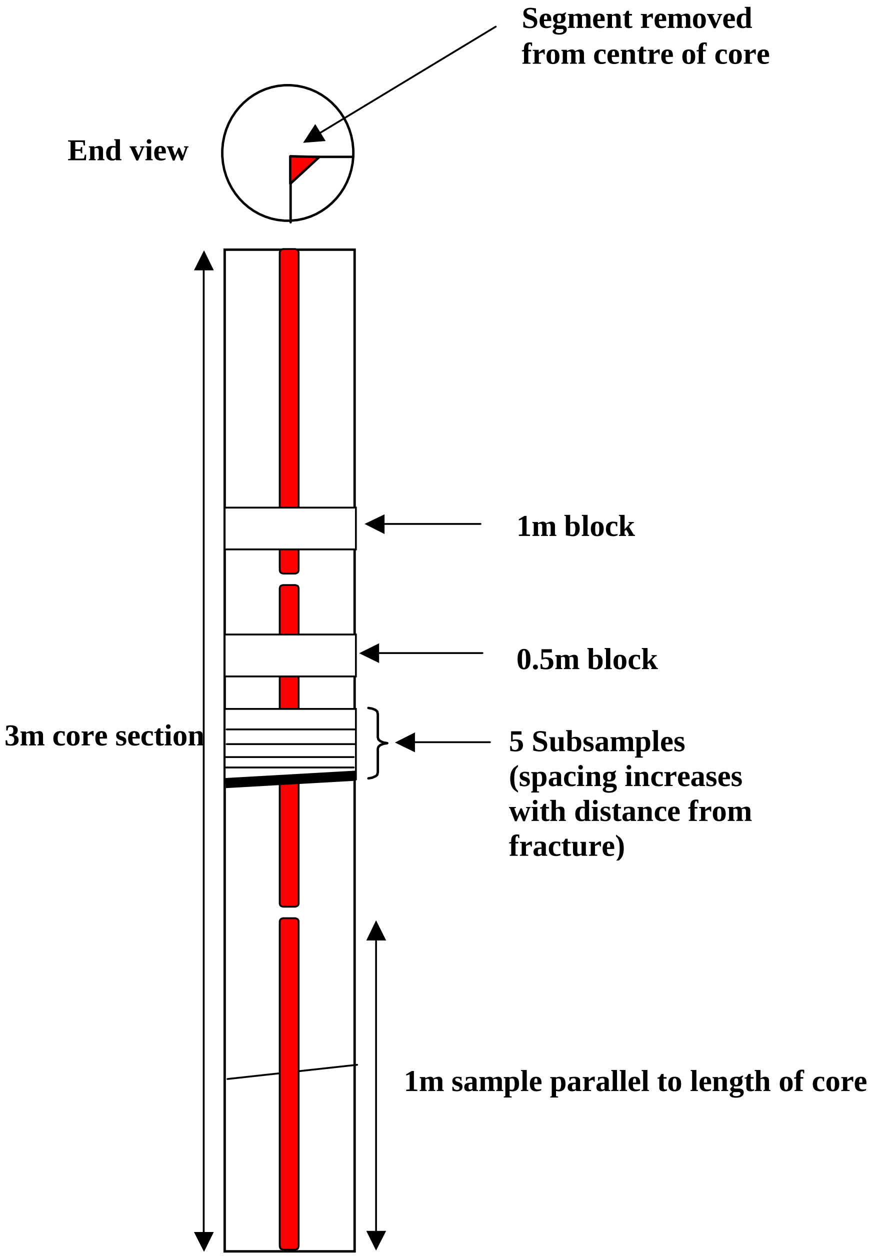

Figure 3.3: Schematic of sub-sampling strategy for a typical 3 m Chalk rock core

Since the density of water is 1 g/cm^3, the total porosity of matrix samples was determined by vacuum drying of rock core samples after DEE analysis, using the following expression:

$$\frac{\text{Wet core mass} - \text{Dry core mass}}{\text{Core volume}} * 100 = \text{Porosity}\,(\%\,\text{by volume}) \qquad \text{(Eq. 2)}$$

This procedure may, however, overestimate the interconnected porosity. During vacuum drying processes, clay mineral shrinkage and hydraulic expansion release water from pores that were previously closed. The interconnected porosity was calculated using the DEE methodology, from the change in the Br tracer concentration of the equilibration water added to the sample bottles (see section 3.3.5.1), according to the following mass balance relationship (Spence *et al.*, 2005a):

When the Br concentration in the interconnected porosity is equal to that in the water surrounding the core blocks:

$$V_{EW} \,.\, Br^{-}_{(I)} = (V_{EW} + V_P) \,.\, Br^{-}_{(F)} \qquad \text{(Eq. 3)}$$

where V_{EW} is the volume of equilibration water added to the bottles (known), V_P is the volume of water in the interconnected porosity which is subject to diffusive exchange with the equilibration water (to be determined), $Br^{-}_{(I)}$ is the initial Br^{-} concentration in the distilled water added to the equilibration bottles and $Br^{-}_{(F)}$ is the final Br^{-} concentration after 2 weeks of equilibration. By re-arrangement of Equation 3, V_P (the interconnected water volume) can be found (Equation 4):

$$V_P = \frac{V_{EW} Br^{-}_{(I)}}{Br^{-}_{(F)}} - V_{EW} \qquad \text{(Eq. 4)}$$

The water surrounding the core blocks was then decanted for further analysis, and the core fragments vacuum dried at 110°C to determine the total porosity using Eq. 2.

3.3.5.3 Sampling for Other Properties

Rock core samples were also required for a range of other investigations within the project. These additional samples and the methods used to collect them included:

- Samples of rock core from uncontaminated and contaminated locations for microbiological analysis. These were collected as 20 cm sections adjacent to fractures at evenly spaced intervals along cores. All samples were sealed in sterilised, Argon (Ar-) flushed, gas-tight containers immediately after collection and stored at 4°C until analysed. These samples were analysed for the range of microbiological determinands outlined in Figure 3.1 using standard methods, to complement the microbiological characterisation of the groundwater samples.
- Samples for laboratory microcosm studies, which were collected as 20 cm sections of intact matrix from uncontaminated and contaminated locations. These samples were required to provide innocula for experiments which assessed the degradation potential of BTEX and MTBE under the range of redox conditions found within the contaminant plume and aquifer. All samples were sealed in sterilised, Ar-flushed, gas-tight containers immediately after collection and stored at 4°C until preparation for the microcosm studies.
- Samples for biofilm analysis, which were collected by visual observation in the field, where these features appeared to be evident. The presence of possible biofilms was identified from (orange) coloured coatings on fracture surfaces. These samples were sealed in sterilised, Ar-flushed, gas-tight containers immediately after collection and stored at 4°C prior to analysis by scanning electron microscopy (SEM).

- Samples for laboratory diffusion tests, which were collected as 20 cm sections of intact, unfractured Chalk matrix. These were stored at 4°C and prepared as 5 mm thick discs of 53 mm diameter. They were fixed in purpose-built glass diffusion cells and equilibrated with a $NaHCO_3$ solution containing sodium azide to prevent calcite dissolution and inhibit biodegradation. An aqueous spike containing Cl, Br, NO_3, SO_4, benzene, MTBE and TAME was added to the donor cell in the diffusion test apparatus and the diffusion coefficients for these species determined using the method of Hill (1984).

- Samples for the analysis of the particulate organic carbon content of the Chalk matrix, which were collected at intervals of 1 m by aggregation of the residue left over from the collection of samples for other properties (e.g. pore water chemistry, microbiology, diffusion tests etc). This provided an integrated analysis of the organic carbon content over a depth profile (analogous to the "strip" sample used for the pore water sampling) in the aquifer, and is used to determine the fraction of organic carbon (f_{oc}) in the Chalk matrix. The integrated Chalk sample was crushed to a fine powder and the organic carbon content determined by chemical digestion and titration using standard methods.

- Samples for mineralogical analysis of the Chalk matrix, which were selected according to visual observation in the field. Attempts were made to collect samples from different depths and specific horizons (e.g. hard grounds) in cores to compare the spatial variation in the mineralogy and fabric of the aquifer matrix across the site. Each sample was prepared using standard methods, for analysis by SEM.

4. RESEARCH DESIGN, SET-UP AND OPERATION

4.1 INTRODUCTION

The research programme included fieldwork and related laboratory studies to support the project goals. The objectives of the fieldwork were to undertake various site investigation activities to further characterise the aquifer properties, install multilevel groundwater sampling wells and collect groundwater samples for the range of analyses described in section 3.3.1. In addition, the fieldwork provided samples of aquifer materials and groundwater for more specific laboratory studies, which assessed contaminant degradation and solute transport in the aquifer. These activities are described below, including the experimental design and procedures used to obtain the requisite data.

4.2 GEOPHYSICAL INVESTIGATION OF AQUIFER PROPERTIES

Geophysical investigation of the aquifer was undertaken on drilled boreholes (MW18, MW24, MW26 and MW28) and cored boreholes (MW17, MW20, MW22 and MW23) to provide information on the lithology and spatial variation in fracture network properties of the aquifer, which may influence contaminant transport and plume development. All boreholes subjected to geophysical investigation were first developed by pumping to ensure that a volume of groundwater equivalent to that lost to the formation during drilling was removed. The purpose of this activity was to:

- Remove settled particulates and suspended solids from the borehole to improve the resolution of the geophysical logging techniques (e.g. optical televiewer log (OPTV))
- Remove drilling fluid (oxygenated groundwater) from the formation to assist the recovery of the borehole towards *in situ* conditions for future groundwater sampling and to develop the formation in advance of the hydraulic tests, by removal of fines entrained in fractures

After development, the boreholes were left to settle overnight and then examined using different downhole geophysical logs, which included caliper log, gamma log, conductivity log and OPTV. These geophysical logs were run to obtain information on the following aquifer properties:

- Caliper log: Open borehole diameter with evaluation of competent and poorly consolidated horizons, to identify zones of increased fracturing or caving (helpful when locating borehole sections suitable for hydraulic testing)
- Gamma log: Identification of low-permeability and/or clay mineral-bearing strata and, by inference, grain size variation in the formation
- Conductivity log: Formation electrical conductivity (inverse of resistivity)
- OPTV: Visual image of fracture type (e.g. horizontal, dipping, sub vertical / vertical), fracture spacing, relative fracture aperture and fracture plane dip, dip direction and strike

These logs were used to assist with the onsite design of the hydraulic tests and installation of multilevel groundwater samplers for individual boreholes. They were also compared for different locations across the site to provide detail on the spatial variation in the specific property measured, correlation with other aquifer properties and contaminant distribution, and refinement of the site conceptual model, which underpinned the investigation and interpretation of contaminant fate in the aquifer.

4.3 INVESTIGATION OF AQUIFER HYDRAULIC PROPERTIES

The evaluation of the aquifer hydraulic properties was undertaken using packered pumping tests and tracer tests. These tests were designed to provide different but complementary information on the hydraulic properties of the aquifer, with respect to the contribution of the fracture network and matrix in solute transport. In addition, the packered pumping tests were evaluated as a site investigation tool, to assist in the design of the monitoring network created through the installation of the multilevel groundwater samplers (see below). These hydraulic tests and the information provided by them are described separately below.

4.3.1 PUMPING TESTS

Packered pumping tests were completed in uncased boreholes after completion of borehole development and geophysical logging (where the latter was undertaken). The tests provide vertical profiles of the aquifer transmissivity (T) or hydraulic conductivity (K) in each borehole, for correlation with similar tests completed on monitoring wells (MW14, MW15 and MW16) during the Phase 2 investigation (section 2.3.2). The data generated by these hydraulic tests is primarily controlled by the fracture network, that is, a vertical profile of groundwater flow through the fractures is obtained under these conditions. This information can be used to deduce a vertical profile of the relative difference in the groundwater flux under a constant pumping rate, as a function of the fracture network properties (e.g. fracture spacing or aperture) if these are known. It can also be used to identify “high-flow” and “low-flow” zones over the monitored depth, which may be important for contaminant migration.

The pumping tests were completed over the full depth of each borehole using either a straddle packer configuration, with test zone interval of 2-4 m, or single packer set-up with variable test zone length of between 2 m and 3 m. In each case, the first straddle packer test was completed at a depth identified from the caliper log where a good seal between the packer and borehole wall could be expected. However, the test zone interval above the first straddle packer test was tested using a single packer, with the base of the test zone positioned at a depth corresponding to the top of the second test zone. The test zone interval in this case corresponded to the height of the water table above the lower packer. This was necessary to take account of the increased borehole diameter near the water table produced by “washout” during drilling, which prevented the use of a straddle packer arrangement for pumping tests. Groundwater samples for hydrochemical and microbiological analysis were collected during each packer test after hydraulic equilibrium had been achieved, based on the drawdown profile, prior to monitoring of the recovery phase. The data from these samples were compared with results obtained from multilevel groundwater samplers, which were subsequently installed in the boreholes. Data loggers and a laptop were used to provide real time monitoring of the hydraulic tests and to establish the timing for groundwater sampling. Slug tests were undertaken for test zones where drawdown of the water table prevented the use of the straddle packer hydraulic tests. In this case, no groundwater samples were collected.

4.3.2 TRACER TESTS

A range of tracer tests were undertaken on different boreholes during the drilling programme in December 2002. These tracer tests were designed as follows:

- Point dilution test on screened monitoring wells (MW7, MW9 and MW13) prior to the drilling works, using NaCl (Plate 4.1)

- Cross-borehole tracer test between MW22 and MW23 after drilling of these boreholes, using NaCl and Photine-CU, with injection into MW22 and pumping from MW23 (upgradient), followed by sampling of both boreholes under the induced gradient.

Plate 4.1: Point dilution tracer test on borehole in site source area

The objective of the tracer tests was to provide information on the vertical distribution of groundwater flux over the monitored section of the aquifer and to deduce the relative rates of fracture flow and diffusion into the matrix, with estimation of the relevant hydrogeological properties. This information is helpful in understanding the location of “high-flow” zones in the aquifer, the contribution of fracture flow and diffusion on solute transport and the hydrogeological controls on contaminant migration and plume development.

In each tracer test the electrical conductivity of the groundwater was logged at 20 cm intervals using a probe lowered down the borehole. Profiles were obtained before tracer injection (background profile), immediately after tracer injection (T_o), and then at increasing time intervals for up to 1 week after injection. Each conductivity profile was referenced to a standard solution to account for instrumental drift over the test period. The conductivity data were then converted into a tracer Cl concentration using the excess conductivity above background and a tracer calibration curve prepared using groundwater samples spiked with NaCl.

In a second phase of tracer tests, completed in June 2003, a dye tracer test was undertaken over a 6 week period in the site source area. Two different fluorescent dyes (Fluorescein and Amino-G Acid) were introduced into monitoring levels 1 and 2 of MW23, and MW7 was pumped and sampled. This arrangement was adopted as MW7, lies approximately downgradient of the injection point. Samples were filtered (0.45 µm) and analyzed by fluorimetry using a Perkin-Elmer LS-3 fluorescence spectrophotometer located on site. Calibration solutions were prepared using standards diluted in clean groundwater. Originally a two-stage test was envisaged, the alternate stage using a far higher pump rate. However the yield from MW7 was insufficient to permit this.

4.4 ROCK CORE COLLECTION AND LOGGING

Rock cores were collected at the locations of MW14 (uncontaminated and upgradient of the site), MW15 (BTEX/MTBE-contaminated), MW16 (MTBE-contaminated), MW17 (BTEX/MTBE-contaminated), MW18 (MTBE-contaminated), MW20 (uncontaminated), MW26A (MTBE-contaminated) and MW27 (uncontaminated and downgradient of MW26 but not shown on Figure 2.2). All cores were collected and sampled using the procedures described in section 3.3.6. Geophysical and hydraulic tests were completed on the cored boreholes, followed in most cases by the installation of an MLS monitoring well. In most cases, continuous rock core was collected using rotary drilling methods, from a few metres above the water table to depths between 40 m and 58 m below ground level. However, core samples from the unsaturated zone in the site source area were collected using percussion drilling methods (Plate 4.2).

Plate 4.2: Collection of rock core samples from the unsaturated zone in the site source area using percussion drilling methods. Core samples are shown in the foreground.

These samples were collected for analysis of the pore water chemistry below the location of the leaking underground storage tank. The data from this analysis was then combined with similar data from cores collected in the saturated zone, to provide a continuous profile of pore water solute chemistry over ~ 35 m in the contaminated aquifer above and below the water table in the site source area.

All cores were logged after collection, to determine the variation in geology (including presence of hard bands and zones of SO_4-reduction identified from gross discolouration) and the distribution of fractures, as a function of depth. A photographic log was also completed for each core run using a graduated scale. Examples of rock core from the upper and deeper section of the aquifer at the location of MW20 are shown in Plate 4.3. These images show the general variation in the intensity of fracturing with depth in the aquifer. Breaks in the rock core induced by the drilling process and core recovery (which are typified by rough, sharp and angular surfaces), were easily deduced from true fractures (typified by relatively smooth, undulating and often Fe-stained surfaces as shown in image "A" of Plate 4.3 below) in the core logs.

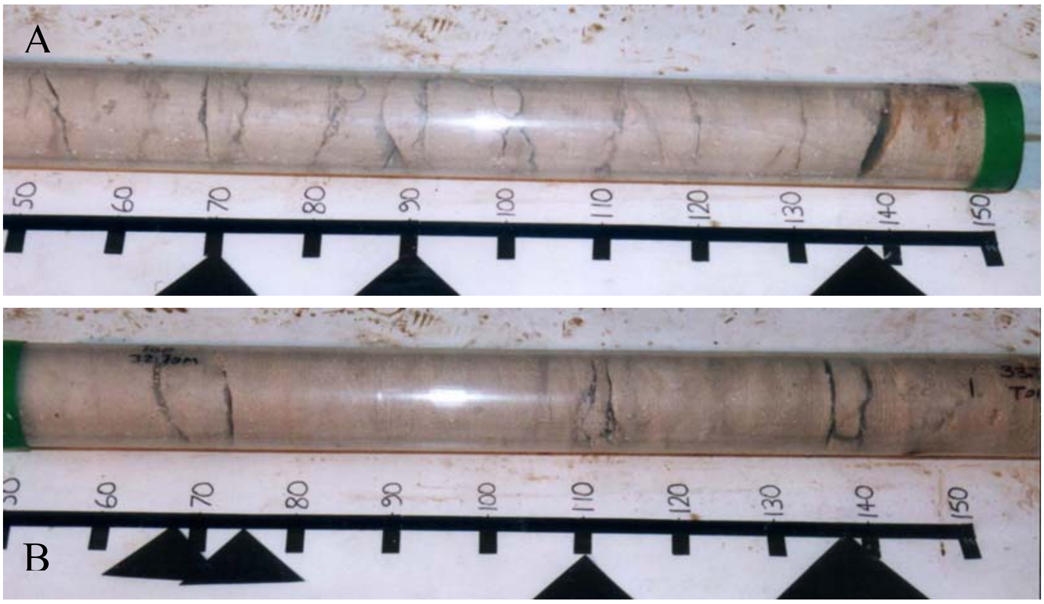

Plate 4.3: Rock core from MW20 showing higher intensity of fracturing near the top of the section (A) and lower intensity of fracturing near the base of the section (B). Black arrows show major fractures against graduated scale.

Plate 4.4 shows the presence of SO_4-reducing zones within a core from MW23, located in the site source area. The zone of SO_4-reduction is finely disseminated throughout the Chalk matrix adjacent to the fractures and in the example shown is evident from the presence of black iron sulphide deposits, which create a grey mottling in the sample.

Plate 4.4: Presence of diffuse iron sulphides throughout the core from MW23, producing a grey mottled effect within the core liner

4.5 INSTALLATION OF MULTILEVEL GROUNDWATER SAMPLERS

Multilevel groundwater samplers (MLS) were installed in boreholes after coring and completion of geophysical and hydraulic tests. The objective of the MLS installations was to develop a monitoring well network for sampling groundwater quality to adequately interpret the spatial and temporal variation in the distribution of contaminants and other dissolved solutes (e.g. electron acceptors and degradation products). In turn, the information provided by this monitoring network was compared with other site data (e.g. measurement of water table fluctuations, matrix pore water chemistry and tracer tests) to deduce the controls on contaminant plume development, quantify degradation and develop the site conceptual model.

The MLS installed in boreholes at the site consisted of 40 mm diameter Continuous Multichannel Tubing (CMT) systems, manufactured from high-density polyethylene (HPDE) and equipped with seven monitoring points (Einarson, and Cherry, 2002). Each system was constructed onsite (Plate 4.5). Monitoring points created in the CMT body are wrapped with a stainless steel mesh to produce an 8 cm screen section for groundwater sampling. When all monitoring points have been completed, the constructed CMT is installed in a 150 mm nominal diameter borehole. A tremie pipe was used to install a sand pack around each monitoring point and to seal monitoring points using bentonite pellets. Each monitoring well was completed with a ground-flush head works. Dedicated 4 mm ID sample tubes were installed in each monitoring point of the MLS boreholes.

Plate 4.5: Construction of CMT multilevel sampler onsite, showing 8 cm screen section around monitoring point.

The depths selected for monitoring levels on each MLS were identified from a review and correlation of the following information:

- Fracture intensity profiles obtained from rock core fracture logs
- Geophysical logs for the borehole, in particular visual identification of fractures on the OPTV log and comparison of these with significant changes in aquifer properties identified from the conductivity log
- Identification of contiguous geological features between boreholes, as identified from a comparison of the conductivity logs
- Profiles of formation hydraulic properties in each borehole, with identification of relative transmissivity based on measured drawdown during the pumping test
- Zones of known contaminant transport based on groundwater quality monitoring of the existing MLS in MW15 and MW16

The key objective of the MLS installations was to provide sufficient resolution of solute distributions in each borehole, whilst sampling as much of the available section as possible. Based on the groundwater quality data from the existing MLS boreholes, the contaminant plume is present to 40 m depth in the aquifer but with higher contaminant concentrations at shallow depths (20-30 m depth). The MLS systems were therefore designed with a higher number of sample ports located at shallow depth in each profile, and thinner sand packs (monitoring horizons) than sample ports located at deeper levels. The emphasis was on identifying known or expected contaminant transport paths and linking these horizons across the monitoring network.

4.6 GROUNDWATER SAMPLING PROGRAMME

Groundwater samples were collected on different occasions throughout the project to provide an improved understanding of the distribution of contaminants, redox processes and microbial ecology in the aquifer, as an input to the site conceptual model. These results were compared with profiles of pore water chemistry obtained from sampling of the rock cores, to deduce the relationships and interactions between solutes present in the fracture water and matrix water.

Comprehensive surveys of groundwater quality were completed on all single screen and MLS monitoring wells installed at the site, at approximately annual intervals in the summer between 2001 and 2004 (three surveys). Due to the staged installation of the monitoring well network, the time-series data over this period is incomplete for some monitoring wells. On each of the annual surveys, groundwater samples were collected using the procedures described in section 3.3 and for the range of determinands summarised in Figure 3.1. In addition, groundwater samples were collected from different aquifer horizons during hydraulic testing of drilled boreholes and analysed for a restricted range of determinands (standard microbiological assays, dissolved contaminants, anions, cations and metals).

Plate 4.6 illustrates the apparatus used to collect groundwater samples during the annual surveys. It shows the sample processing rig connected to the dedicated sample tube from the MLS. This set-up allows groundwater samples to be collected without exposure to the atmosphere for the range of determinands shown in Figure 3.1.

Plate 4.6: Apparatus used to collect groundwater samples, showing dedicated sampling tube from MLS monitoring well connected to the sample processing rig.

Real-time measurements of groundwater pH, temperature, dissolved oxygen concentration, electrical conductivity and redox potential (Eh) were made onsite using a perspex flowcell connected to the sample stream passing through the sampling rig (Plate 4.7). Samples for dissolved sulphide analysis were collected in the white barrels connected to the sampling rig via a separate bypass circuit. All groundwater samples were collected after appropriate purging of the sampling tubes.

Plate 4.7: Flowcell used to obtain onsite measurements of groundwater dissolved oxygen concentration, temperature, redox (Eh), pH and electrical conductivity.

4.7 DESIGN OF LABORATORY MICROCOSM EXPERIMENTS

Laboratory microcosm studies were developed to assess the degradation of BTEX and MTBE under a range of conditions in the aquifer. The conditions used in the microcosm experiments were identified primarily from the site conceptual model, groundwater quality data from the monitoring network and pore water chemistry from sampling of rock cores. Attention was given to understanding the effect of different redox conditions and contaminant concentration on the potential for hydrocarbon degradation as contaminants passed through the plume. Groundwater and core samples from the site investigation were used as inocula in these experiments, which included sacrificial and serial analysis of microcosms to assess temporal variation in contaminant degradation. This design enabled a wider range of environmental parameters to be included in the experiments, with mass balances and stable isotope analysis of specific degradation pathways.

Initial experiments evaluated BTEX degradation under aerobic, NO_3-reducing and SO_4-reducing conditions, with these oxidants present in isolation or as a mixed $O_2/NO_3/SO_4$ system. Subsequent experiments assessing MTBE degradation were designed as aerobic and NO_3-reducing systems. They included a comparison of degradation under “natural” conditions and in the presence of non-indigenous MTBE-degrading microorganisms, to understand the MTBE-degrading potential of the indigenous microbial community in the aquifer (Table 4.1). The non-indigenous MTBE-degraders used in these experiments were the PM-1 strain (Bruns *et al.*, 2001), which degrades MTBE as a sole source of carbon and energy.

Table 4.1: Design of laboratory microcosms assessing MTBE degradation

Experimental system	Materials (substrate/inocula)	Aim of experiment
Natural potential	MTBE[1], active groundwater[2], active core[3].	Assess potential for MTBE degradation in the plume at MTBE concentrations close to source area values
Natural potential, positive control	MTBE[1], active groundwater[2], active core[3], control strain PM-1.	Assess if conditions in the aquifer are conducive to MTBE biodegradation (using addition of known MTBE-degraders)
Positive control	MTBE[1], sterile groundwater[2], sterile core[3], control strain PM-1	Determine the relative contribution of the control strain PM-1 to degradation in the mixed system
Blank	MTBE[1], sterile groundwater[2], sterile core[3], sodium azide at 0.2 g/L.	Sterile system assessing abiotic losses of MTBE
Uncontaminated	MTBE[1], active groundwater[4], active core[5].	Assess potential for MTBE degradation in the uncontaminated aquifer at MTBE concentrations close to source area values
Uncontaminated NO_3-amended	MTBE[6], active groundwater[4], active core[5].	Assess natural potential for MTBE degradation in the uncontaminated aquifer under anaerobic NO_3-reducing conditions at MTBE concentrations close to source area values

Notes
1. Nominal MTBE concentration of 6 mg/L
2. Contaminated groundwater from MW9 containing <200 μg/L of MTBE but no BTEX
3. Core from MTBE-contaminated (BTEX-free) section of MW17
4. Uncontaminated groundwater from MW11
5. Uncontaminated core from MW20
6. Nominal MTBE concentration of 10 mg/L

No assessment of the potential for TAME biodegradation was made in the microcosm studies during this research, since the primary focus was the assessment of the MTBE biodegradation potential. The experiments were operated for a period of nearly two years, with sampling at intervals for the analysis of MTBE, TBA, dissolved electron acceptors and inorganic reaction products of degradation processes. Some microcosms were also sampled for microbiological analysis of MTBE-degrading microorganisms.

4.8 DESIGN OF LABORATORY DIFFUSION CELL TESTS

Laboratory diffusion experiments were undertaken to estimate diffusion coefficients of selected chemical species through samples of Chalk core taken from different depths in MW20. The diffusion coefficients were determined for analytical and numerical modelling of solute transport in the aquifer. The diffusion tests were completed for Cl, NO_2, SO_4, benzene, MTBE, TAME and fluorescein, as representative organic, inorganic, reactive and conservative species. Bespoke glass diffusion cells were constructed for the diffusion tests, which were run at 10°C to simulate aquifer conditions (Plate 4.8).

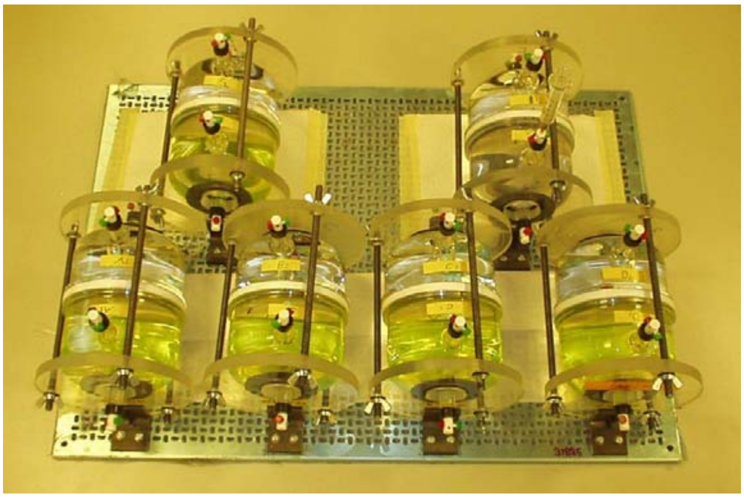

Plate 4.8: Glass cells used in diffusion tests

Deionised water containing 200 mg/L HCO_3 and 2000 mg/L sodium azide was used to prevent calcite dissolution and biological activity in the cells. The donor cells were spiked with 100 mg/L of the anions, 3 mg/L of the organic compounds and 1 mg/L of fluorescein. The donor and receptor cells were sampled at regular intervals to determine the diffusion coefficients for each species as a function of depth in the aquifer, using the method of Hill (1984).

These data were compared with other rock properties to understand the geological and stratigraphical influences on solute transport at the site. The diffusion tests showed that the effective diffusion coefficients for the species examined decreased with depth (from 23-40 mbfl) by nearly a factor of two. This was correlated with changes in the estimated matrix porosity (which decreased from 55% to 30% over the same depth interval), vertical variation in the aquifer hydraulic conductivity (general decrease with depth) and the presence of a Chalk hard band, which separated the aquifer into a “high” flow zone (between 20-30 mbfl) and a “low” flow zone (between 30-40 mbfl) over this section. It was also noted that the estimated effective diffusion coefficients for the organic contaminants considered (benzene, MTBE and TAME) were consistently less than those estimated for Cl, NO_3 and Br, by more than a factor of two. These results imply that diffusion of these solutes between the fractures and matrix will be faster in the upper section of the aquifer, between 20-30 mbfl, than in the lower section of the aquifer, between 30-40 mbfl, and that diffusion of the organic contaminants will be slower at all depths compared with the inorganic chemical species examined. The primary control on this behaviour appears to be the higher matrix porosity at shallow depth in the aquifer, which may equate to a higher interconnected porosity and lower tortuosity (path length) for solute diffusion. Overall, contaminant transport and diffusion rates in the aquifer are therefore higher above the hard band than below it. The diffusion studies suggest that reliable estimates of the effective diffusion coefficients for these (and probably other relevant species) should be based on the analysis of field samples collected from the site under investigation, since these are likely to vary with the rock properties.

5. RESULTS AND DISCUSSION

5.1 INTRODUCTION

The results and discussion arising from this work are presented in sections which address each of the research objectives listed in section 1.3. There is an additional section summarising the research outputs and dissemination activities of the project. The main results of each section are summarised as bullet statements before the detailed analysis, upon which these are based, is presented and discussed.

5.2 THE IMPORTANCE OF AEROBIC MTBE DEGRADATION IN THE AQUIFER

The evidence for aerobic degradation of MTBE and its contribution to the natural attenuation of MTBE in the aquifer includes the results from the field and laboratory studies, with emphasis in deducing the MTBE degradation potential under aerobic and anaerobic conditions within the plume and aquifer. The methods used include laboratory microcosm experiments, microbial assays of MTBE degradation potential in groundwater using labelled ^{14}C-MTBE, stable isotope analysis of MTBE in samples from the plume and microcosm experiments and ratios of dissolved TBA/MTBE in the aquifer. The main results of this analysis, with respect to the research objective listed in 1.3, are summarised as follows:

- MTBE, TAME and TBA form overlapping plumes in the aquifer, and although TBA is a metabolite of aerobic MTBE degradation, it is released from the source area at this site as an impurity in MTBE and may not be evidence of *in situ* aerobic MTBE degradation
- Temporal variation in the release of TBA and MTBE from the source area and changes in the groundwater chemistry produced by aerobic degradation of BTEX may make it difficult to deduce MTBE degradation at field scale using conventional measurements of groundwater quality
- The aquifer contains microorganisms with the potential to degrade MTBE under aerobic and anaerobic conditions
- A range of MTBE-degrading microorganisms have been identified in the aquifer at this site and their ecological characteristics assessed, which may be useful in evaluating MTBE degradation potential at other sites on the aquifer
- Laboratory experiments using aquifer material and groundwater from the site showed that aerobic degradation of MTBE can occur at MTBE concentrations up to those (6 mg/L) found in the source area, with the production of TBA, and with a first-order degradation rate of 0.0025-0.0075/day
- Aerobic MTBE degradation in the aquifer appears to be limited by slow growth on MTBE and the availability of dissolved oxygen in groundwater, with no significant degradation under the anaerobic conditions assessed in the experiments
- Stable isotope analysis of MTBE was used to confirm degradation of MTBE by an aerobic pathway in the laboratory microcosm experiments and to suggest the absence of significant MTBE degradation in the plume at the field scale
- The aerobic degradation of MTBE in the plume may be restricted or inhibited by the preferential aerobic degradation of BTEX or other hydrocarbons and may only occur at the periphery (fringe) of the contaminant plume where more dissolved oxygen is available
- A key result is that the aquifer contains microorganisms which can biodegrade MTBE after relatively short exposure to MTBE and that this potential should be considered in risk assessments undertaken for petroleum fuel releases at other sites on the aquifer

There is a TBA plume in the aquifer, co-mingled with the MTBE and TAME plumes. TBA is a metabolite of aerobic MTBE degradation and is often used as evidence of *in situ* aerobic MTBE degradation. A relative increase in TBA concentration at the expense of MTBE along the plume flow path may indicate MTBE degradation, if MTBE is metabolized to TBA and the latter accumulates in groundwater. However, TBA/MTBE ratios in groundwater cannot be used to deduce aerobic MTBE degradation in the aquifer along the plume flow path at this site due to temporal variations in the proportions of TBA and MTBE released from the source area. This means that the distribution of TBA in groundwater at the site cannot be used to interpret aerobic MTBE degradation at field scale. This problem may apply at other sites contaminated with unleaded petroleum fuel containing MTBE.

The distribution of the ether oxygenates, BTEX and redox-sensitive indicators in groundwater is discussed in more detail in section 5.3.1. The MTBE and TAME plumes have migrated further downgradient and to deeper depths in the aquifer than the BTEX plume. However, the dissolved oxygen concentration in the ether oxygenate plumes is very low or zero. This occurs due to preferential degradation of the BTEX compounds, upgradient of the ether oxygenate plumes, and makes identification of aerobic MTBE degradation at field scale very difficult using conventional groundwater quality data (including the distribution of TBA).

The study has shown that the aquifer contains microorganisms which have the potential to degrade MTBE aerobically and anaerobically. The diversity and activity of these microorganisms is not depressed by the current level of contamination, contrary to observations made in other contaminated aquifers (Pickup *et al.*, 2001). This MTBE degradation potential exists in the contaminant plume and uncontaminated aquifer at comparable levels. A range of aerobic and anaerobic MTBE-degrading bacteria have been isolated from groundwater and core samples, assessed for their ability to degrade ^{14}C-MTBE and characterised to a species level, which may provide a database for evidence of MTBE-degrading microorganisms at other sites. The assessment for anaerobic MTBE biodegradation potential was made using degradation of ^{14}C-MTBE and bacteria grown on a mineral media which contained NO_3 and/or SO_4. However, the specific redox conditions (e.g. NO_3-reduction or SO_4-reduction) under which the anaerobic MTBE degradation occurred in the ^{14}C-MTBE assays was not evaluated. A key finding is that the majority (80%) of the MTBE-degrading bacteria identified possessed dual capability for aerobic and anaerobic MTBE-degradation, and many were tentatively identified as pseudomonads. Similar microbial populations and MTBE-degrading activity were found in successive years, indicating the presence of a stable MTBE-degrading community in the aquifer.

The laboratory microcosm studies demonstrated that MTBE concentrations of up to 6 mg/L (ca. plume source area) can be degraded aerobically by native microorganisms from the plume and uncontaminated aquifer, with a lag of <50 days. Aerobic degradation was confirmed from the production of TBA in these systems. However, first order MTBE degradation rates for the plume systems (0.0025/day) were lower than those for the uncontaminated systems (0.0074/day). The experiments using a known MTBE-degrading non-indigenous culture (PM-1), added to the native systems, established that degradation rates for the native MTBE-degrading population are linked to slow growth on MTBE. No significant degradation of MTBE occurred under anaerobic conditions in NO_3-amended and SO_4-amended microcosms containing uncontaminated innocula, even though the microbiological analysis showed that the aquifer microorganisms have the capability for anaerobic MTBE degradation. However, in mixed O_2, NO_3 and SO_4 systems, degradation of MTBE or its metabolites continued after O_2 depletion, suggesting the presence of a community of facultatively anaerobic bacteria which may biodegrade MTBE under aerobic and anaerobic conditions. Evidence from the field studies suggests that MTBE degradation in the (anaerobic) plume is slow.

MTBE degradation in the laboratory microcosm experiments and at field scale was evaluated using stable isotope analysis. The observed change in the carbon isotope composition of MTBE during aerobic degradation, termed the isotope enrichment factor, is consistent with that identified in other studies and can be used to quantify MTBE degradation at field scale. The stable isotope studies suggest that there has been no significant MTBE degradation in the plume, but the sensitivity of this technique in deducing the extent of MTBE degradation will be low if the isotope enrichment factors are small in this setting. The low rates of MTBE degradation in the field may be due to preferential removal of dissolved O_2 by degradation of BTEX or other uncharacterised dissolved hydrocarbons in the plume, or suppression of MTBE degradation by other factors in the plume.

Aerobic degradation is unlikely to be important for MTBE attenuation *within the plume*, particularly in the presence of more biodegradable (e.g. BTEX) hydrocarbons, but could be significant at the periphery of the BTEX/ether oxygenate and ether oxygenate plumes, where O_2 is more available. An important conclusion from these studies is that a community of native MTBE-degrading microorganisms is widespread throughout the uncontaminated aquifer and can degrade MTBE by aerobic and anaerobic pathways after relatively short exposure to MTBE contamination. The identification of an anaerobic MTBE-degradation potential in the aquifer is significant, as this is not widely established in the literature. These results imply that MTBE-degradation potential may exist at other petroleum fuel-contaminated sites on the Chalk aquifer and should be considered in risk assessments.

5.3 FACTORS CONTROLLING DEGRADATION IN THE AQUIFER AND ESTIMATES OF PARAMETER VALUES FOR PROCESSES

The factors identified as being important in controlling contaminant degradation in the aquifer include properties related to the contaminant mixture, the indigenous microbial community and the aquifer setting. An assessment was made of the interrelationships between these factors, with respect to qualitatively predicting the potential for contaminant attenuation in this aquifer. The analysis includes results from the laboratory, field and modelling studies, but focuses on the fate of the BTEX compounds. This is because there is strong and diverse evidence of degradation processes for BTEX, and factors controlling MTBE fate are considered in the previous section. However, reference is made to the interrelationships between MTBE and BTEX, where this is appropriate in the analysis. This assessment is conveniently made by firstly considering the evidence based on the spatial distribution of contaminants and redox-sensitive species in groundwater, and then the relationships between contaminant degradation processes and estimated parameter values for these processes, as below. For illustration, the range of degradation processes considered for BTEX hydrocarbons in this analysis is shown in Table 5.1, using toluene as an example.

Table 5.1: Degradation processes for toluene in groundwater

Degradation Process	**Reactions for toluene (C_7H_8)***
Aerobic respiration	$C_7H_8 + 9\mathbf{O_2} \Rightarrow 7CO_2 + 4H_2O$
Denitrification	$5C_7H_8 + 36\mathbf{NO_3}^- + H^+ \Rightarrow 35HCO_3^- + 3H_2O + 18N_2$
Manganese (IV)-reduction	$C_7H_8 + 18\mathbf{MnO_2} + 29H^+ \Rightarrow 7HCO_3^- + 18Mn^{2+} + 15H_2O$
Iron (III)-reduction	$C_7H_8 + 36\mathbf{FeOOH} + 65H^+ \Rightarrow 7HCO_3^- + 36Fe^{2+} + 51H_2O$
Sulphate reduction	$2C_7H_8 + 9\mathbf{SO_4}^{2-} + 6H_2O \Rightarrow 14HCO_3^- + 5H_2S + 4HS^-$
Methanogenesis	$2C_7H_8 + 10H_2O \Rightarrow 5CO_2 + 9CH_4$

*Note: Electron acceptors (oxidants) used in the reaction are shown in bold. MnO_2 and FeOOH are solid phase oxidants.

5.3.1 SPATIAL DISTRIBUTION OF CONTAMINANTS AND REDOX-SENSITIVE SPECIES IN GROUNDWATER

The main results of this analysis, with respect to the research objective, are summarised as follows:

- The MTBE, TAME and TBA plumes extend at least 220 m downgradient of the site and to a depth of >15 m below the water table, whereas the BTEX plume extends < 125 m downgradient of the site and <10 m below the water table
- The more extensive migration and relative concentrations of dissolved MTBE, TAME and TBA compared with BTEX in the aquifer primarily reflects the relative proportions of the ether oxygenate compounds in the fuel mixture, their higher relative solubility and the greater potential for attenuation of BTEX by sorption and degradation
- Biodegradation of BTEX occurs in the aquifer using dissolved oxidants (O_2, NO_3 and SO_4) in the groundwater and solid phase oxidants (Mn oxides and Fe oxides) on the aquifer matrix, creating a series of redox zones, which can be defined by the distribution of redox-sensitive chemical species and reaction products representing the different processes
- Degradation of contaminants by methanogenesis is occurring but is not significant compared with other degradation processes and the groundwater chemistry data, in combination with related laboratory microcosm experiments, provide convincing evidence that the BTEX components are biodegraded under aerobic and anaerobic conditions in the aquifer
- Time-series groundwater quality data indicate that the BTEX plume has probably reached a steady-state condition, where attenuation by biodegradation balances the flux of dissolved BTEX contaminants from the source

The distribution of selected contaminants and redox-sensitive species in groundwater is shown in Figure 5.1, along a 260 m section from MW23 to MW18 (Figure 2.1). These plots include data from all multilevel sampler monitoring wells (denoted MLS) and single screen wells sampled in July 2003. The MTBE plume defined by the 10 µg/L contour has migrated approximately halfway between MLS16 and MLS18. TBA has a similar distribution to MTBE; the lateral extent of the TBA plume is probably similar to that of the MTBE plume, but beyond MW16 the TBA concentration is below detection limits (~1 µg/L). TAME shows a very similar distribution to MTBE but at half the concentration. This distribution reflects the initial ether oxygenate composition of the fuel, which contained 2.88 vol % MTBE and 1.65 vol % TAME. The BTEX compounds have migrated downstream much less than the ether oxygenate compounds and the benzene plume has migrated the most within the BTEX suite.

This distribution reflects greater attenuation of the BTEX contaminants by biodegradation and sorption to the aquifer matrix, compared with MTBE, TAME and TBA. Note also the difference in the vertical extent of the plumes and preferential attenuation of components (e.g. toluene and o-xylene) within the BTEX mixture, where most of the contaminant mass is restricted to shallow depth near the water table. The BTEX plumes lie above the nodular hard band horizon (Figure 5.1), which coincides with a large decrease in aquifer hydraulic conductivity (Figure 5.6).

The distribution of dissolved electron acceptors (O_2, NO_3^-, SO_4^{2-}) and products (TDIC, HS^-, Mn^{2+}, Fe^{2+}) of contaminant biodegradation in groundwater defines a series of biogeochemical redox zones produced by different contaminant degradation processes. Upgradient of the site at MW14 dissolved O_2 is present at 8 mg/L, with NO_3 and SO_4 concentrations from 29-105 mg/L and 9-146 mg/L, respectively. Highly reducing conditions exist close to the plume source, where O_2, NO_3 and SO_4 in the groundwater have been consumed by degradation and the product of bacterial sulphate reduction, HS^-, is present in relatively high concentration (Figure 5.1: MW7, MLS15). This zone also corresponds to elevated concentrations of Fe^{2+} and Mn^{2+}, which reflect the use of mineral oxidants (Mn-oxides and Fe-oxides) on the aquifer solids in contaminant degradation. Methane was either not detected or present at low concentration (<0.3 mg/L) in groundwater near the source area, indicating that contaminant degradation by methanogenesis is also occurring but is less important than other degradation processes. The development of these redox zones is a function of spatial and temporal variations in contaminant flux from the plume source and the supply of electron acceptors for degradation in the aquifer. Time-series groundwater quality data shows that episodes on increased contaminant flux from the source area coincide with the temporary downgradient expansion of the NO_3-reducing and SO_4-reducing zones, as these dissolved electron acceptors (NO_3 and SO_4) are consumed by degradation of BTEX. However, it appears that the availability of dissolved electron acceptors (O_2, NO_3 and SO_4) in the aquifer is adequate to restrict the migration of the BTEX plume at the site.

The 0.2 mg/L dissolved O_2 contour defines the effective volume of the degrading plume. The presence of dissolved O_2 in groundwater downgradient of MLS16 indicates that most of the biodegradable contaminants in the plume have been removed by biodegradation upgradient of this location, otherwise the dissolved O_2 would be below detection. Nitrate is absent from the zone of BTEX contamination (cf Figure 5.1) and a region of NO_3 depletion extends downstream of the BTEX plume, continuing beyond MLS18. Sulphate is strongly depleted and locally absent within the BTEX plume. The distribution of dissolved sulphide (HS^-), formed by bacterial SO_4 reduction, coincides well with the zone of SO_4 depletion. A zone of high SO_4 concentration around MLS16 may be associated with the re-oxidation of reduced sulphur species (e.g. HS^-). The background SO_4 concentration is high close to the water table and low at depth (<50 mAOD) due to dissolved SO_4 input from the unsaturated zone. The origin of this SO_4 input was not resolved but it provides additional SO_4 (oxidising capacity) for degradation in the BTEX plume.

Further downstream, concentrations of dissolved electron acceptors are re-established at MLS16 and MW9, and dissolved Fe, Mn and HS^- are absent in groundwater. Concentrations of dissolved electron acceptors are close to background values at MLS18, the most downgradient borehole used in this analysis. The groundwater TDIC concentration (measured as alkalinity) is elevated above background levels in the plume, which is consistent with the origin of this as an inorganic product (CO_2) of BTEX biodegradation.

The groundwater quality data provide convincing evidence for the biodegradation of BTEX compounds under aerobic and anaerobic conditions in the aquifer. This is supported by the results of laboratory microcosm experiments using groundwater and aquifer materials from the site, which demonstrate that the BTEX compounds can be degraded using dissolved O_2, NO_3 and SO_4 and solid phase Mn-oxides and Fe-oxides in the aquifer. Time-series groundwater quality data indicate that the BTEX plume has not migrated beyond the location of MLS16 during the last 5 years and has probably reached a steady-state condition, where the flux of dissolved BTEX contaminants from the source is balanced by the rate of attenuation via biodegradation.

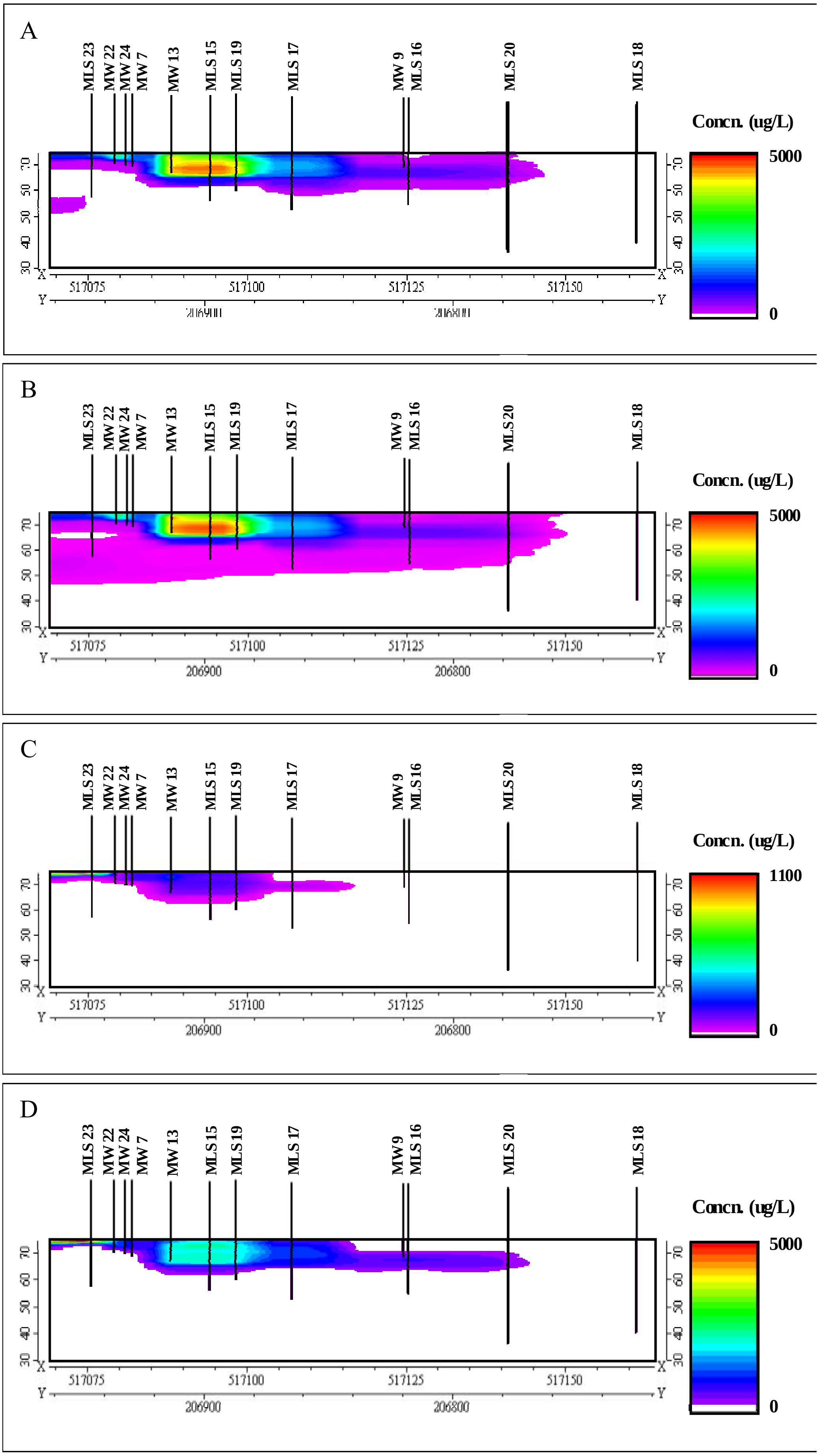

Figure 5.1: Solute profiles in groundwater along the plume flow path: A: MTBE (outer contour = 100 µg/L); B: MTBE (contour = 10 µg/L); C: TBA (contour = 10 µg/L); D: TAME (contour = 100 µg/L)

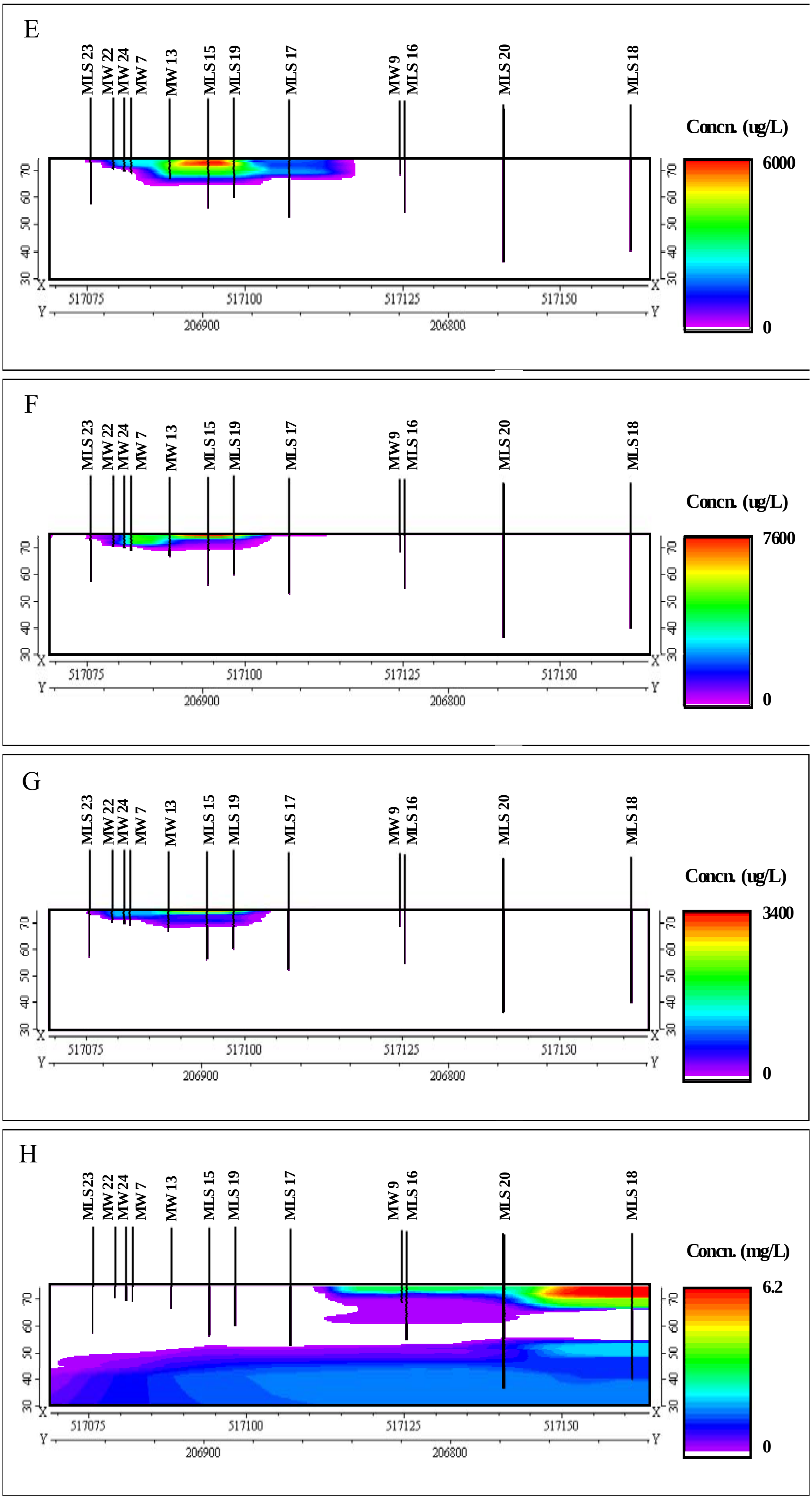

Figure 5.1: continued. Solute profiles in groundwater along the plume flow path: E: Benzene (outer contour = 100 µg/L); F: Toluene (contour = 100 µg/L); G: o-Xylene (contour = 100 µg/L); H: O_2 (contour = 0.2 mg/L)

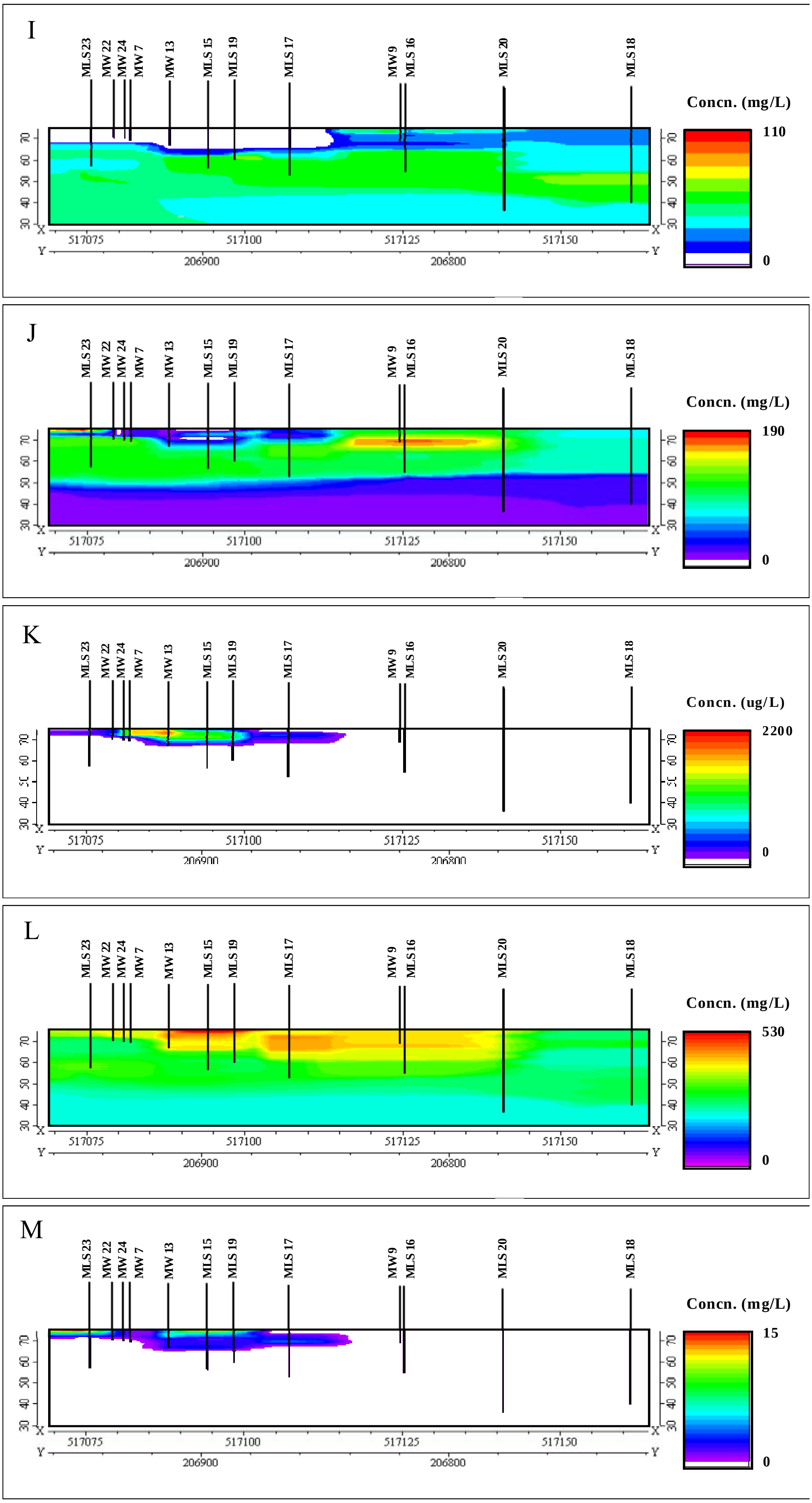

Figure 5.1: continued. Solute profiles in groundwater along the plume flow path: I: NO_3; J: SO_4; K: Sulphide (outer contour = 100 µg/L); L: Alkalinity; M: Fe^{2+} (outer contour = 0.5 mg/L $CaCO_3$)

5.3.2 RELATIONSHIPS BETWEEN CONTAMINANT DEGRADATION PROCESSES AND ESTIMATED PARAMETER VALUES

The distribution of redox zones in the plume is clearly linked to the degradation BTEX contaminants. A zone of depleted O_2, NO_3 and SO_4 extends downstream of the BTEX plume, although concentrations of these dissolved electron acceptors are progressively re-established towards background levels with increasing distance from the source area. The interpretation of aerobic MTBE degradation at field scale using the groundwater chemistry data is complicated by the zone of dissolved O_2 depletion in the aquifer. This is because the zone of dissolved O_2 depletion or “O_2 shadow” could result from the degradation of BTEX near the source area, with subsequent transportation of this degradation “history” downstream (within the MTBE plume), or aerobic MTBE degradation downstream of the BTEX plume. Neither cause can be deduced with the dissolved O_2 data. This transported history of degradation is a common feature in contaminant plumes and is used to confirm that the monitoring wells sample groundwater on the plume flow path (Wiedemeier *et al.*, 1999).

The main results of this analysis, with respect to the research objective, are summarised as follows:

- The aquifer contains a widespread community of hydrocarbon-degrading microorganisms and BTEX degradation is controlled by the availability of dissolved and mineral-based oxidants supporting degradation, in addition to the composition of the hydrocarbon mixture and the plume source
- A mass balance assessing the aquifer attenuation capacity and incorporating probabilistic analysis with Monte Carlo methods, indicates that 97% of the BTEX degradation is related to the consumption of dissolved NO_3 and SO_4, with the balance contributed by consumption of O_2, Mn-oxide, Fe-oxide and methanogenesis
- The dominance of NO_3 and SO_4 for BTEX degradation is due to the relatively high concentration of these electron acceptors in the groundwater, low dissolved O_2 concentration and scarcity of Mn-oxide and Fe-oxide in the aquifer, with most of the NO_3 and SO_4 being provided by advection of uncontaminated groundwater into the plume and diffusion from the uncontaminated aquifer matrix
- Using the plume-scale mass balance, it was possible to statistically determine the likely plume source term composition and to estimate that 65% of the original petroleum fuel released may still remain within the unsaturated zone as a long-term source of hydrocarbon contamination to groundwater
- The contaminant properties have an important influence on the potential for biodegradation in the aquifer, and whereas more biodegradable hydrocarbons such as ethylbenzene and toluene are degraded under most redox conditions, degradation of benzene and the ether oxygenate compounds may only occur in the presence of dissolved O_2 and NO_3
- Competition for available dissolved O_2, NO_3 and SO_4 during degradation of different hydrocarbons within the plume may prevent degradation of benzene and the ether oxygenates until these contaminants have migrated further downgradient into zones where dissolved O_2 and NO_3 are available
- The laboratory and field stable isotope studies confirm these general relationships and have been used to estimate isotope fractionation factors for benzene degradation and the extent of SO_4-reduction, which may be used to quantify attenuation at the field scale
- The stable isotope studies of groundwater samples from the aquifer and between the matrix pore water and fracture water chemistry indicate that there is rapid diffusion of dissolved electron acceptors from the matrix to support hydrocarbon degradation, which is an important process controlling the attenuation of dissolved contaminants in the aquifer

- First-order degradation rates of 0.14/day and 0.0108/day have been estimated for ethylbenzene and toluene degradation, respectively, from the microcosm studies and these parameters may be used to interpret hydrocarbon degradation at other sites on the Chalk aquifer
- Residual and free product trapped within the unsaturated and saturated zone at the site will provide a long-term source of dissolved contaminants to groundwater, characterised by the episodic release of different fractions into the plume due to water table fluctuations which will create significant temporal variability in the dissolved contaminant concentrations measured in downgradient monitoring wells
- Time-series groundwater quality data shows that the plume source term has evolved over the last four years and is now characterised by much lower dissolved contaminant concentrations, with a higher relative proportion of BTEX, a behaviour which can be predicted from the solubility and original composition of constituent fractions in the unleaded petroleum fuel, and which indicates that BTEX will represent the long-term source composition for the plume

The research has demonstrated that hydrocarbon degradation in the aquifer is controlled by oxidant availability, the contaminant mixture and plume source composition. A diverse population of heterotrophic bacteria, capable of degrading BTEX and MTBE is present in the aquifer and the dissolved hydrocarbons found in the plume do not significantly affect the distribution, diversity and activity of the indigenous hydrocarbon-degrading microorganisms. Analysis of the matrix pore water and fracture water chemistry shows that hydrocarbon degradation within the aquifer occurs via aerobic respiration, denitrification, Mn(IV)/Fe(III)-reduction, SO_4-reduction and methanogenesis using dissolved O_2, NO_3, SO_4 in groundwater and Mn-oxides and Fe-oxides on the aquifer sediment.

A mass balance model was developed within the study, incorporating measurements of aquifer hydrogeological and geochemical properties, groundwater chemistry from monitoring wells and pore water chemistry from the unsaturated zone and saturated zone rock cores. The model was used to complete a plume-scale carbon and electron balance to quantify the aquifer attenuation capacity, taking account of uncertainty in model inputs with Monte Carlo methods. This probabilistic analysis indicated that denitrification and SO_4-reduction account for respectively 39% and 58% of carbon turnover in the plume, with aerobic respiration, mineral oxide reduction and methanogenesis contributing 2.2%, 0.8% and <0.1%, respectively. The dominance of denitrification and SO_4-reduction is due to the relatively high concentrations of NO_3 and SO_4 in groundwater. Aerobic respiration is limited by the relatively low O_2 concentration in the aquifer. The contribution of mineral oxide-reduction to hydrocarbon degradation in the plume is negligible because these (Mn and Fe) oxidants are relatively sparse in the aquifer matrix, and are confined to isolated coatings on fracture surfaces. Methanogenic degradation of contaminants appears to be suppressed by the dominance of SO_4-reduction, which can occur in contaminant plumes where SO_4 concentrations are high (Chapelle, 1993). The mass balance also indicated that advection and matrix diffusion are the dominant processes contributing dissolved electron acceptors for degradation in the saturated zone over the three year timescale of the analysis. It was possible to statistically determine the likely plume source term composition with the model, in order to predict the long-term dissolved contaminant flux into the aquifer. The model predicted that at least 65% of the estimated original hydrocarbon mass spilled is present in the unsaturated zone as a long-term source for the plume.

Contaminant properties were found to influence the potential for degradation under different redox conditions. The laboratory and field studies show that toluene and ethylbenzene are relatively biodegradable under a variety of redox conditions, but that benzene and MTBE degradation will only occur under aerobic or denitrifying conditions (Spence *et al.* 2005b). Competition for O_2, NO_3 and SO_4 from more biodegradable compounds (e.g. ethylbenzene and toluene) in the hydrocarbon plume appears to restrict benzene and MTBE degradation until these compounds have migrated downstream into zones where O_2 and NO_3 are available and other hydrocarbons are absent. This is illustrated in Figure 5.2, which shows the carbon isotope composition of benzene and MTBE at different locations in the plume.

Heavier (less negative) carbon isotope compositions confirm that benzene degradation occurs near the aerobic plume fringe (38 m depth) in the source area (A) and further downstream under less reducing conditions (B), whereas MTBE is not significantly degraded.

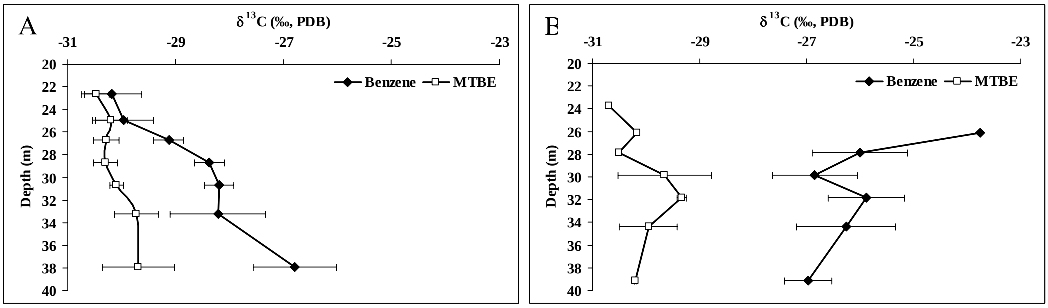

Figure 5.2: δ^{13}C Composition for benzene and MTBE from A: MLS15 (30 m from source); and B: MLS16 (115 m from source).

The stable isotope studies show that degradation by denitrification and SO_4-reduction in the aquifer has limited BTEX migration to < 100 m of the site over the last 3 years. *In situ* isotope enrichment factors have been derived to predict benzene degradation and the extent of SO_4-reduction at field scale (Spence *et al.,* 2005b). A further analysis of the role of denitrification and SO_4-reduction in contaminant degradation is provided in Figure 5.3, which shows a plot of the carbon isotope composition of TDIC (δ^{13}C of TDIC) vs. the sulphur isotope composition of SO_4 (δ^{34}S of SO_4) in groundwater for all monitoring wells. The data show a cluster (A on Figure 5.3) with low (isotopically light) δ^{34}S (< 5 ‰) and $\delta^{13}C_{TDIC}$ between around –12 and –16 ‰; these are all locations that are remote from the plume core. Samples from the plume core and from MLS levels with high contaminant loads have elevated (isotopically heavy) δ^{34}S (>20 ‰) and $\delta^{13}C_{TDIC}$ of –20 to –25 ‰ (B on Figure 5.3). There is also an array of data between group B and a grouping of data from MLS16, labelled C on Figure 5.3. Samples in group B have undergone extensive SO_4-reduction, producing the increased δ^{34}S and added ^{13}C depleted carbon to the TDIC pool. MLS16 is downstream of the most heavily contaminated part of the plume but still contains residual MTBE and benzene in the samples in group C.

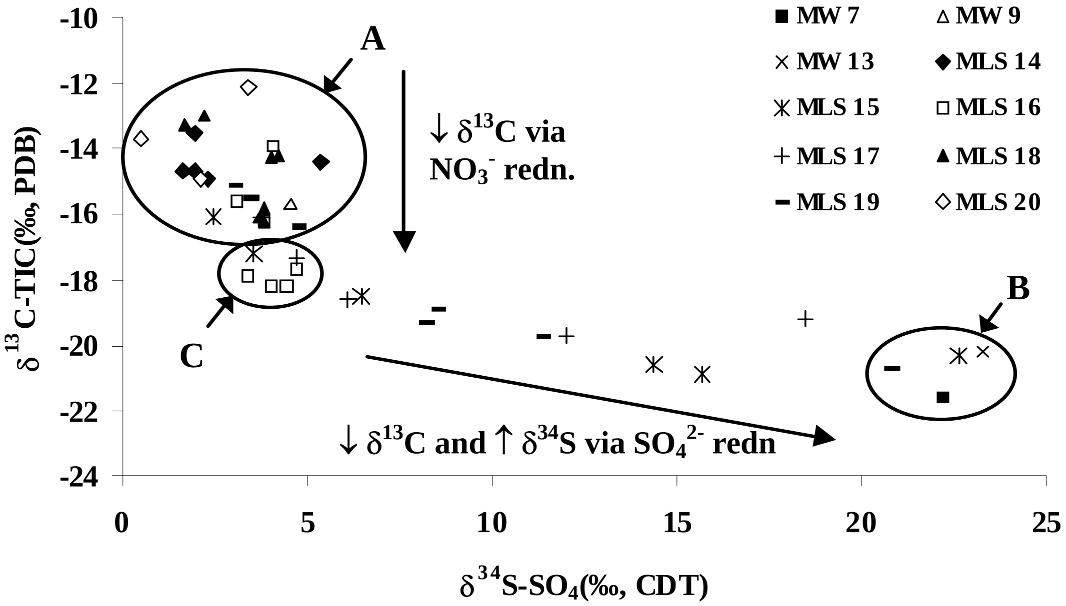

Figure 5.3: Plot of δ^{13}C-TDIC versus δ^{34}S-SO_4 for groundwater samples. Group A is uncontaminated and Group B is close to the contaminant spill. Elevated δ^{34}S is a sensitive indicator of SO_4-reduction, while depletion in δ^{13}C indicates the addition of inorganic carbon via contaminant mineralization reactions. The figure delineates zones where SO_4-reduction is dominant and zones where other biodegradation processes (principally denitrification) provide the major contribution to TDIC in the plume (e.g. Group C).

The samples in the array between groups B and C are from locations downgradient of the BTEX plume core. These form a linear trend, which indicates a mixing relationship between these groups away from the BTEX plume core, with progressively more “background” SO_4 from outside the plume mixing with residual, ^{34}S-enriched, SO_4 that has undergone partial SO_4-reduction during BTEX degradation. Although the group C data have almost no remaining shift in δ^{34}S, they are still shifted to significantly lower δ^{13}C values than the more remote “aquifer background” samples in group A. This apparently smaller degree of mixing with background TDIC (compared with SO_4) is attributed to the continued production of isotopically light carbon in TDIC from denitrification in the outer part of the plume. In this zone, the dissolved NO_3 and SO_4 concentrations increase, but there is only evidence for active denitrification at MLS16, based on the NO_3 isotope data. The return of SO_4 isotopic compositions to background values in the downgradient part of the plume indicates that there must be significant and rapid interaction between the fracture water and dissolved electron acceptors in the aquifer matrix, which supports continued hydrocarbon degradation in the plume.

The redox conditions associated with contaminant degradation in the plume and sequence of hydrocarbon utilisation, deduced from the groundwater hydrochemistry and isotope studies is summarised in Figure 5.4. In an inner anaerobic zone, close to the contaminant spill, biodegradation is dominated by bacterial SO_4-reduction and NO_3 is completely removed. In this zone many fuel hydrocarbons are mineralized, but benzene and MTBE are not significantly degraded (Figure 5.4). Downgradient, in an outer anaerobic zone, denitrification is the dominant degradation process and here benzene is degraded but MTBE is not. In this outer anaerobic zone, the SO_4 concentration in the fracture water is rapidly re-established (i.e. re-supplied) by efficient equilibration (through diffusion) with the aquifer matrix pore water. Diffusion also re-supplies dissolved NO_3 to the fracture water, but the fracture water NO_3 concentrations remain low as NO_3 is very quickly consumed by denitrification in the hydrocarbon plume. In both anaerobic regions, degradation by Mn(IV) and Fe(III)-reduction is limited by the lack of available Mn and Fe oxides in the aquifer matrix.

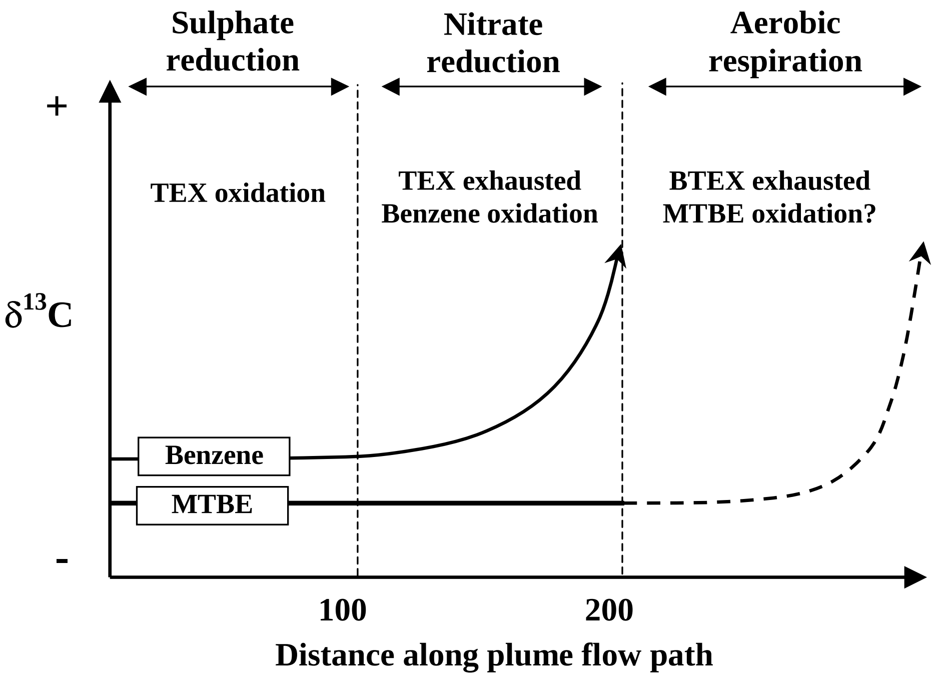

Figure 5.4: Diagram summarising changes in carbon isotope composition associated with BTEX utilisation for different redox environments along the plume flow path. Dashed line shows hypothetical enrichment for expected MTBE degradation pathway.

These general observations are supported by the microcosm studies used to simulate degradation under the plume conditions. First-order degradation rate constants of 0.14/day and 0.0108/day have been estimated for ethylbenzene and toluene degradation, respectively. These parameters are comparable to estimates in the literature (Wiedemeier *et al.*, 1999) and may be used to interpret hydrocarbon degradation at other sites on the Chalk aquifer.

The unsaturated zone down to the water table contains a high mass of residual BTEX and ether oxygenates, which continues to sustain the plume in the long-term. Peak concentrations of these contaminants occur at 10 m depth, although the entire section down to the water table is contaminated. Fluctuations in the water table will result in periodic flushing of contaminants from this zone into groundwater to sustain the plume in the longer term. However, time-series data from source area monitoring wells sampled over the last four years shows that dissolved hydrocarbon concentrations in groundwater have decreased significantly from peak values in 2000-01. This indicates that the source term composition has changed over this period and the contaminant flux into the plume is now dominated more by BTEX than ether oxygenates. This behaviour is consistent with the relative solubility of BTEX and the ether oxygenate fractions and can be robustly estimated from the petroleum fuel composition using Raoult's Law. The analysis shows that BTEX will be the main source term composition for the plume in the long-term. However, the study has shown that the aquifer has sufficient degradation capacity to meet this BTEX loading.

5.4 IDENTIFICATION OF WHETHER DEGRADATION OCCURS IN THE FRACTURES OR MATRIX

The identification of whether degradation occurs in the fractures or Chalk matrix is important because it is often thought that bacteria are prevented from colonising the matrix due to physical restriction of cells by the small diameter of pore throats. It is therefore assumed that degradation can only occur within biofilms attached to fracture surfaces. This distinction has important implications with respect to the potential for degradation in the aquifer and whether the internal structure of the aquifer matrix is considered to be a location for biodegradation or a storage reservoir for solutes. The main results of this analysis, with respect to the research objective (above), are summarised as follows :

- The microbial ecology of groundwater in the fractures and the aquifer matrix in the uncontaminated and contaminated aquifer is generally comparable, with respect to the structure and diversity of microbial populations, suggesting that microorganisms able to degrade the hydrocarbon and ether oxygenate contaminants exist *within* the Chalk matrix
- Biofilms were identified on fracture surfaces but could not be successfully investigated and the microbial activity of the matrix appears to reflect colonisation of microfractures within larger matrix blocks, which provides an increased surface area for biofilm development
- Pore throat diameters measured in samples of the aquifer matrix vary from < 1 µm to >1 µm, with higher values and bimodal distributions found in samples from shallow depth in the aquifer
- The distribution of measured pore throat diameters in the aquifer matrix suggests that bacteria with typical cell diameters of 1 µm will not be able to colonise the matrix at deeper levels in the aquifer, but that colonisation of the matrix could be possible at shallow depth
- The potential control on microorganism distribution and colonisation in the aquifer by size exclusion of bacterial cells from the matrix implies that biodegradation may only occur in the fracture water or on fracture surfaces at depth in the aquifer, but could occur in the aquifer matrix and fracture surfaces at shallow depth
- Until these observations are qualified by further research, it is recommended that biodegradation is assumed to occur on the fracture surfaces only for the purposes of risk assessment

The distribution of microbial populations between the fractures and matrix was found to be a function of the fracture network and matrix properties. The microbial ecology of the uncontaminated and contaminated aquifer matrix is comparable and the microbial community structure and diversity of aquifer matrix and fracture water samples is similar, with measurements generally within an order of magnitude. This suggests that microorganisms with the potential to degrade the hydrocarbon and ether oxygenate compounds exist *within* the Chalk matrix. Biofilms were identified on isolated fracture surfaces, but interpretation using SEM imaging was unsuccessful due to biofilm instability during preparation for SEM analysis. Much of the microbial activity associated with the matrix appears to reflect colonisation of a dense network of fine micro-fractures that dissect larger matrix blocks, particularly at shallow depth (20-30 m). This micro-fracturing provides a substantially increased surface area for biofilm development.

The matrix pore throat distribution was also found to be a key control on the potential for bacterial colonisation of the matrix. The vertical distribution of matrix pore throat diameters down to 50 m depth was determined using Hg-intrusion porosimetry. Figure 5.5 shows that the matrix pore throat diameter varies from a bimodal population at shallow depth, to a unimodal population at deeper levels in the aquifer. The diameter at depth is close to or less than the generally accepted diameter of bacterial cells (1 µm). In this case, bacteria may be physically impeded by the pore throat diameter from entering and colonising the aquifer matrix. However, this does not preclude the presence of bacteria within the Chalk matrix, which have a cell diameter less than 1 µm. If physical exclusion of bacteria from the aquifer matrix exists, based on the cell size, this implies that biodegradation cannot occur in the matrix and must instead occur in biofilms on the fracture surfaces or in the (micro) fracture water under these conditions. Colonisation of the matrix by bacteria could be possible at shallow depth in the aquifer, where the matrix pore throat diameter is >1 µm. For conservative estimation of hydrocarbon attenuation in the aquifer, degradation can be assumed to occur in the fractures only.

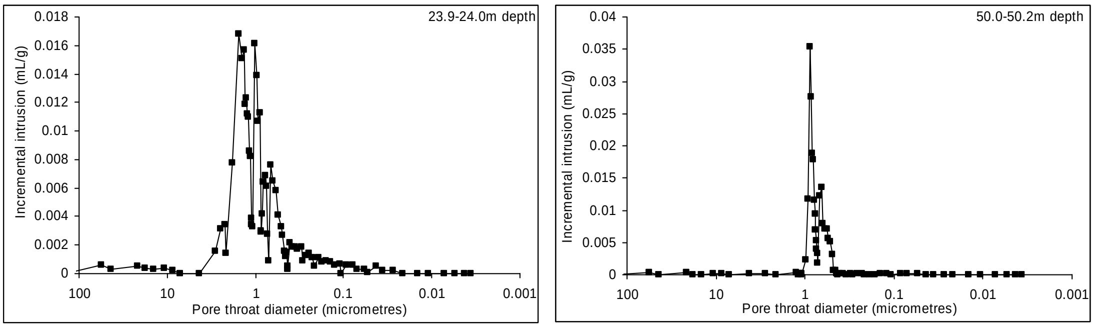

Figure 5.5: Matrix pore throat diameter at different depths

5.5 UNDERSTANDING HOW DUAL-POROSITY AFFECTS THE POTENTIAL FOR BIODEGRADATION

Dual porosity transport in the Chalk aquifer arises from the hydraulic properties of, and interaction between, the fracture network and porous matrix. In turn, this interaction exerts an important control on solute exchange between these two physical domains in the aquifer and ultimately the nature, magnitude and relative importance of different processes in contaminant attenuation. These issues are considered here in the context of results from the site and also transferable concepts, which may be more generally applied in other similar hydrogeological settings.

The main results of this analysis, with respect to the research objective, are summarised as follows:

- There is significant spatial variability in the distribution of aquifer hydraulic conductivity (K) at the site, with values changing by a factor of 10 for comparable depths along the plume flow path, but by a factor of 100 with depth over the 30 m thick plume section, where the presence of a hard band enables the hydrogeology to be conceptualised in terms of a “high” flow zone, from the water table to 33 m depth, and a “low” flow zone below this depth
- The fracture network dominates groundwater flow at the site and the statistical analysis of fracture logs shows that the distribution of fracture spacing is skewed towards closely spaced fractures, with a mean separation of 0.22 m and that the fracture spacing is statistically similar at locations across the site, but different with depth across the section of contaminated aquifer
- Considering the fracture network analysis, the variation in fracture aperture with depth appears to exert an important influence on contaminant distribution and migration, such that the increased contaminant flux observed in the “high” flow zone of the aquifer (water table to 33 m depth) results from the presence of wider fractures (increased fracture aperture) rather than a greater number of fractures overall, whereas the restricted vertical migration of dissolved contaminants below 33 m depth is attributed to the continuous/semi-continuous hand band and absence of a significant vertical hydraulic gradient in the aquifer
- Diffusion is an important process affecting contaminant migration and degradation in the aquifer, and a comparison of the matrix pore water chemistry (obtained from rock core samples) with fracture water chemistry (obtained from MLS installations), suggests that MLS monitoring wells can provide a reliable indication of the vertical distribution of solutes (contaminants and electron acceptors) in the fracture network as well as that resulting from diffusion into the aquifer matrix and vice versa

- The effect of dual porosity on degradation and plume development is a function of the relative timescales of fracture vs diffusive transport, as controlled by the matrix properties (diffusion coefficients) and fracture properties (spacing and porosity)
- Modelling studies using representative values of aquifer properties obtained from the research and different scenarios for groundwater flow, matrix block size and fracture porosity demonstrated that complete fracture-matrix equilibration of solutes by diffusion is achieved within one day, implying that contaminants migrating into the uncontaminated aquifer will be attenuated very quickly by diffusion
- This modelling also showed that contaminant pulses could be completely attenuated by diffusion within 1 m of downgradient migration into the uncontaminated aquifer for typical conditions (groundwater velocity and aquifer properties), but that this distance would increase to only 10 m for the maximum fracture porosity and groundwater velocity found at the site
- Attenuation by diffusion was found to decrease as flow velocity, fracture porosity and matrix block size increase
- Dual porosity transport has a significant effect on contaminant attenuation and degradation potential in the aquifer, in that the diffusion of dissolved electron acceptors from the matrix into the fractures is fast and does not limit degradation, plume expansion is linked to the utilisation of a finite reservoir of dissolved oxidants in the matrix which are supplied by diffusion into fractures, and back-diffusion of contaminants out of the matrix creates a secondary contaminant source for transport in the fractures after the primary contaminant source has decreased or been exhausted

Profiles of aquifer hydraulic conductivity (K, m/day), determined from straddle packer pumping tests, are shown in Figure 5.6. These show spatial variability in the aquifer hydraulic conductivity across the site, which is determined primarily by the fracture network properties. The data are presented as a function of depth in metres below forecourt level (mbfl) and distance along the plume flow path, with MW14 located upstream of the source area (represented by MW23). It is clear that there is a large variation in K along the flow path, with values for the same depth varying by a factor of 10. However, there is a greater variation in K with depth, where values differ by a factor of nearly 100. At most locations, there is a step change in the K profile at 33-35 m depth. Values of hydraulic conductivity decreases significantly below this depth, which coincides with the hard band identified in cored boreholes.

The variation in K with depth across the site can be used to distinguish between a “high” flow zone, from the water table to 33 m depth, and a “low” flow zone below 35 m depth in the aquifer. This is a relative difference, but it is significant in that it is correlated with the depth of a hard band in the aquifer and a possible change in lithology. However, measurements of groundwater head in straddle packer tests and multilevel samplers show little evidence of a vertical hydraulic gradient across the hard band. This suggests that it may be laterally discontinuous across the site or that there is vertical leakage across it. Leakage may occur as a result of penetration by vertical fractures, which were occasionally sampled in cores at depths below or close to the hard band. Groundwater flow rates below the hard ground are relatively constant.

Statistical analysis of fracture logs obtained from the rock cores shows that the fracture spacing is heavily skewed towards closely spaced fractures, with 70% of the fractures having a spacing less than 0.3 m. Fractures with spacing above 0.5 m are of negligible importance in the fracture network. The mean fracture spacing (n = 506) for all cores is 0.22 m. This distance reflects the mean spacing of *macro* fractures, which are visible during core logging. It does not represent the spacing of *micro* fractures, which may exist in greater intensity within the “matrix blocks” separated by the macro fractures.

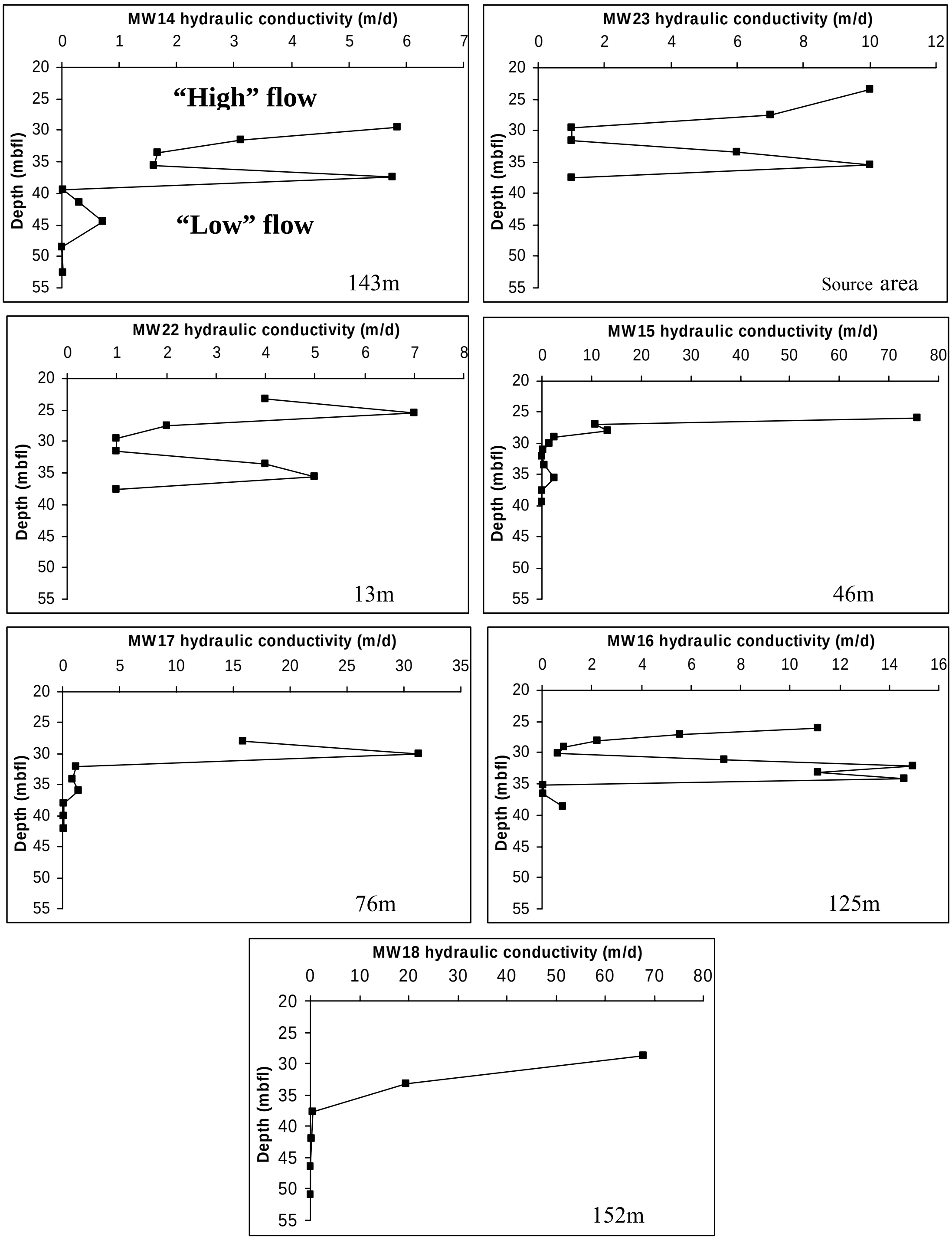

Figure 5.6: Profiles of aquifer hydraulic conductivity, with location of borehole relative to plume source area

The mean "whole core" fracture spacing is similar (ca. 0.2 m) for each borehole. However, the fracture spacing is very similar above and below the inferred hard band (33 m depth) in MW15 and MW20, but different for MW16, 17, 22 and 23. In the latter boreholes the mean fracture spacing down to 33 m depth is 0.24 m or greater, but 0.15 m or less for depths below 33 m. A Single Factor ANOVA test of the fracture network distribution indicates that the fracture spacing above and below 33 m depth in MW16, 17, 22 and 23 is statistically different ($P = 0.05$) but not for these intervals in MW15 and MW20. This vertical differentiation, based on the depth of the hard band, corresponds approximately to the base of the BTEX plume in most monitoring wells. An assumption is made that any variation in fracture distribution with depth also applies to MW20, MW22 and MW23, even though no hard band was found during the coring of these boreholes.

This analysis implies that there is a consistent fracture network distribution, in terms of fracture spacing at different locations across the site, but a statistically significant difference in fracture spacing across the depth of aquifer contaminated by the plume. The restricted vertical migration of contaminants, particularly BTEX, to depths greater than 33 m is correlated with the presence of a hard band (lateral extent unknown), and a decreased fracture spacing. However, the contribution of this variation in fracture spacing to contaminant migration remains unknown, and may be subordinate in importance to vertical variations in fracture aperture or the presence of hard bands. This suggests that any variation in contaminant distribution and plume migration with depth in the aquifer do not result from variations in the fracture spacing. It is more likely that variation in fracture aperture with depth, rather than fracture spacing, control the spatial distribution of contaminants in the aquifer. The profiles of hydraulic conductivity suggest that fracture aperture is significantly greater above the hard ground than below it. Beneath the hard ground the aquifer hydraulic conductivity is 100 times lower, restricting the vertical extent of plume migration.

This study has shown that diffusion between the fractures and porous matrix is an important process for contaminant attenuation and degradation in the Chalk aquifer. It influences contaminant flux through the system and the availability of dissolved oxidants for degradation. Figure 5.7 compares matrix pore water (obtained from rock core) and fracture water (obtained from MLS) composition in the uncontaminated aquifer (MW20) and plume (MW17).

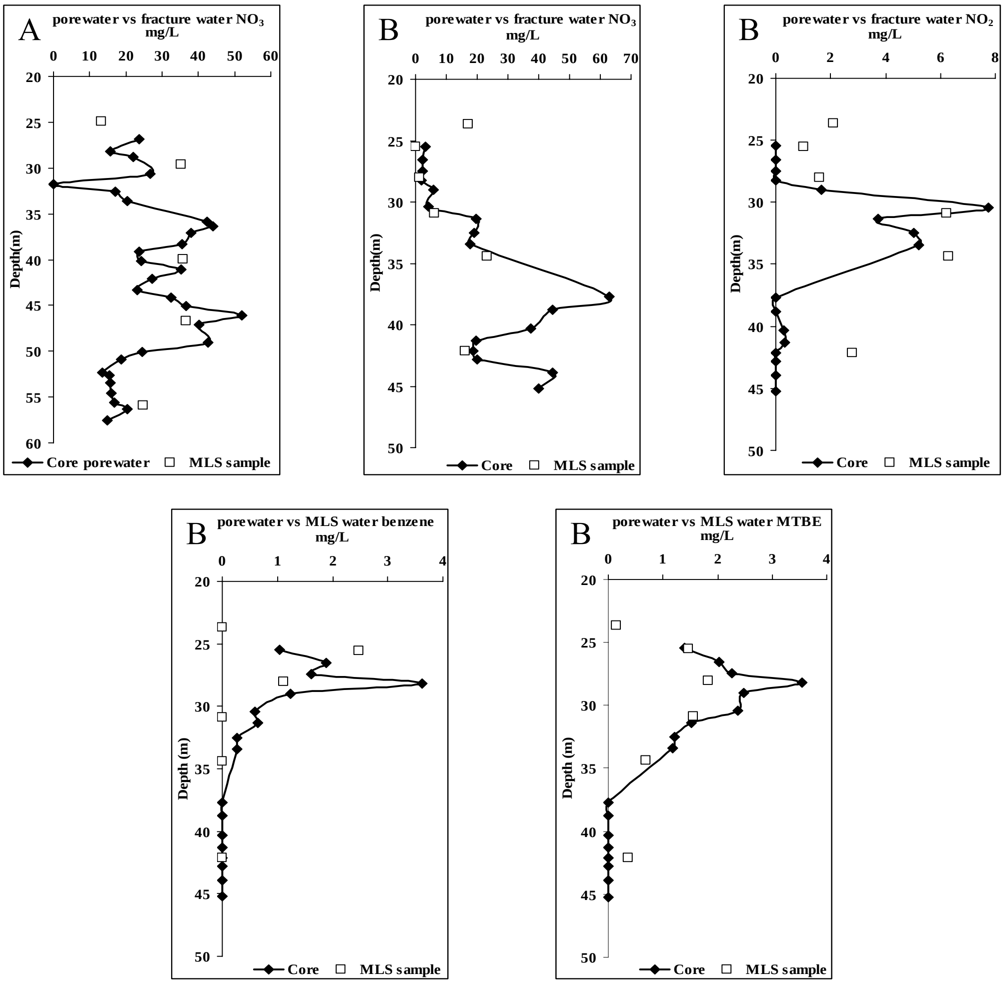

Figure 5.7: Matrix pore water and fracture water composition for uncontaminated (A) and plume (B) locations

The good agreement between pore water and fracture water chemistry shows that the latter is buffered by the matrix water chemistry and that the MLS installations can be used to robustly identify the matrix water chemistry. Differences between the fracture water and matrix water chemistry imply chemical disequilibrium at the time of sampling and diffusion in the direction of the concentration gradient. This is evident in a highly fractured zone between 25-30 m depth, where the aquifer hydraulic conductivity is orders of magnitude higher than the aquifer below 30 m depth. Relative to the uncontaminated aquifer (A), NO_3 in the matrix in the plume is depleted by diffusion into the fractures, where it has been consumed by BTEX degradation. Contaminants have also diffused into the matrix within the plume (B). The effect of dual porosity on degradation and plume development is a function of the relative timescales of fracture vs diffusive transport, as controlled by the matrix properties (diffusion coefficients) and fracture properties (spacing and porosity). These interrelationships were evaluated for representative scenarios (matrix block size and fracture porosity) using an analytical model for solute diffusion into a sphere (Crank, 1975). The inputs for this modelling were mean fracture spacing (0.22 m, n = 506), determined from core logging, experimentally-determined solute diffusion coefficients obtained for core samples and fracture porosity (2-10%) estimated from field tracer tests and the literature. Flow rates estimated from point dilution tests at times of high and low water level, were used in this analysis to estimate the attenuation of contaminant pulses moving into the uncontaminated aquifer. Figure 5.8 shows that the timescale for solute diffusion into matrix blocks with radii found in the aquifer is fast, with >90% fracture-matrix water equilibrium after only 24 hours for a matrix block of 10 cm radius (~ 0.22 m fracture spacing). This is due to the large surface area/fracture volume ratio and short diffusion path lengths.

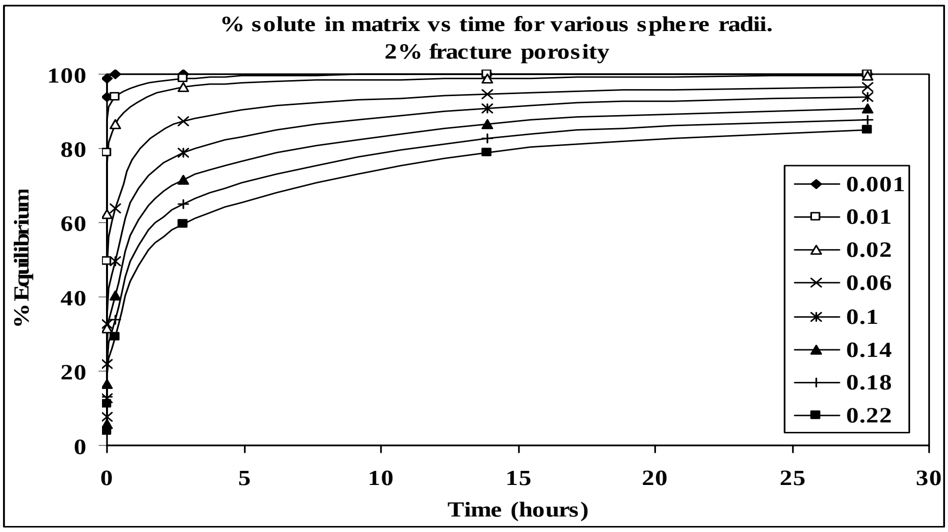

Figure 5.8: Timescale for diffusive equilibration in matrix blocks with different radii (legend), for 2% fracture porosity

If no degradation occurs in the matrix the maximum matrix block radius estimated with this model, for complete diffusion of NO_3 out of the matrix over the age of the plume, is ~ 0.15 m (consistent with field results, Figure 5.7). Using this model, the attenuation of a contaminant pulse into the uncontaminated aquifer was evaluated for different matrix block sizes as a function of fracture porosity and groundwater velocity. Figure 5.9 shows that for typical conditions (~ 0.1 m block radius and 2% fracture porosity), there is 50% attenuation of a contaminant pulse (concentration expressed as C/Co) within 0.2 m, by diffusion into the matrix, and almost complete attenuation within 1 m of downstream migration. For a maximum fracture porosity of 10% and groundwater flow velocity of 100 m/day, the modelling showed that there would be 90% attenuation of a contaminant pulse by diffusion within 10 m migration into the uncontaminated aquifer. At depths greater than 31 m the fracture flow velocity is lower, at 2-23 m/day, giving a contaminant pulse migration distance of ~ 2 m, which is insignificant relative to the length of the observed plume (~ 300 m). Attenuation by diffusion was found to decrease as flow velocity, fracture porosity and matrix block size increase. The breakthrough and recovery of tracer during cross-borehole tracer tests at the site is consistent with the fracture water-matrix water solute exchange predicted in these modelling scenarios.

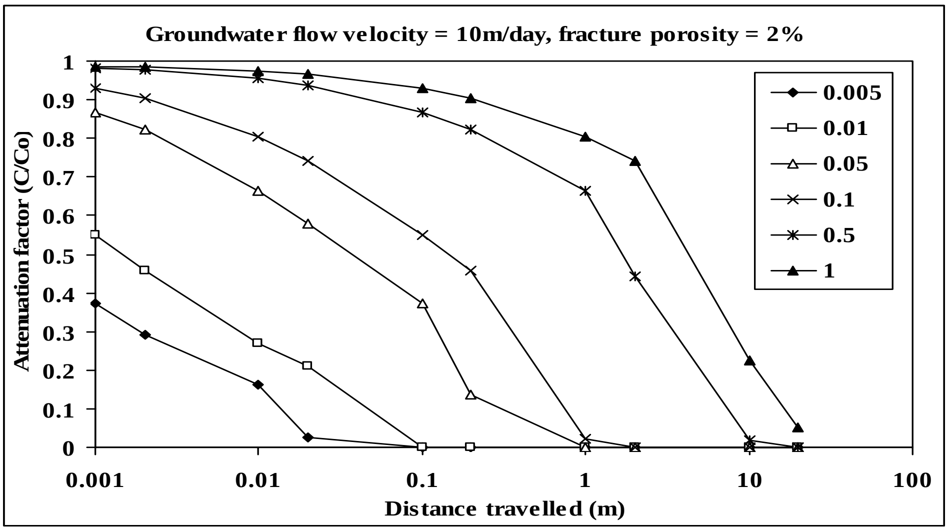

Figure 5.9: Predicted attenuation (C/Co) of contaminant pulse for different matrix block radii, for 2% fracture porosity

Using this analysis the mean matrix block radius has been estimated as ~ 0.14 m within the plume (similar to measurements from cores), which implies quasi-equilibrium with the fracture water after ~ 4 years. This is similar to the age of the plume. It implies that on the timescale of plume migration the transfer of dissolved electron acceptors from the matrix to the fractures is not limited by diffusion.

This analysis shows that dual porosity transport has a significant effect on the attenuation and degradation potential for contaminants in the Chalk aquifer. There is a significant reservoir of dissolved oxidants in the matrix available for degradation. On the timescale of the plume migration diffusion of electron acceptors from the matrix to the fractures is fast and does not limit degradation. This means that contaminant degradation and plume migration are not critically dependent on the presence of bacteria in the matrix. Plume expansion is linked to the progressive utilisation of a finite reservoir of dissolved oxidants in the matrix, which are supplied by diffusion into fractures. Back-diffusion of contaminants out of the matrix creates a secondary contaminant source for transport in the fractures. Contaminant breakthrough in monitoring wells occurs when fracture transport exceeds rates of attenuation by matrix diffusion.

5.6 DEMONSTRATION OF THE VALIDITY OF THE CONCEPTUAL MODEL AND PARAMETER VALUES

A complex process-based model describing the NA of petroleum fuel hydrocarbons and MTBE in the Chalk aquifer has been developed from the field and laboratory studies within the project. This process model describes the distribution of contaminants, degradation processes and microbial activity in relation to the geological and hydrogeological characteristics of the site and Chalk aquifer. Together, these components represent a unified conceptual model, which qualitatively predicts the NA of petroleum hydrocarbons in the aquifer, and identifies the key factors controlling contaminant fate and transport.

Numerical modelling with a dual-porosity transport code developed in parallel with this project was used to independently evaluate the process-based model describing contaminant fate in the aquifer. This activity supported the analytical modelling described previously, with the aim of validating the conceptual model for the site, by testing possible scenarios using the experimental data to identify the key parameters, aquifer properties and processes controlling attenuation in the aquifer. A key aspect of this validation exercise was to assess whether the conceptual model and the input parameters describing its function and interrelationships between components are realistic in predicting attenuation in the aquifer, by comparison with the existing conditions at the site. This allows the transferable concepts which may apply at other sites on the aquifer to be identified. Transport simulations were therefore undertaken using various conceptualisations of the aquifer hydrogeology and plume source term, with sensitivity analyses to test the performance of the model to variations in inputs considered to be the most important for plume development.

The main results of this modelling analysis, with respect to the research objective are summarised as follows:

- The numerical dual-porosity modelling demonstrated that the temporal variation in dissolved contaminant flux observed in monitoring wells at the site results from the combined effect of water table fluctuation and source term changes
- Peak concentrations of contaminants, observed simultaneously at different locations across the site, appear to reflect rapid transport through the fracture system at periods of high water table elevation, and this process is primarily controlled by temporal variation in the aquifer hydraulic gradient and its related effect on groundwater velocity
- The current distribution of the BTEX and MTBE plumes at the site was reproduced using the laboratory derived degradation parameters, suggesting that well-constrained experimental studies conducted under representative *in situ* conditions, can provide realistic transport parameters for predictions of natural attenuation in the aquifer
- Diffusion of dissolved electron acceptors from the matrix into the fracture system was shown to have contributed significantly to degradation of BTEX in the plume and to be an important process supporting organic contaminant attenuation in the aquifer
- The diffusion of contaminants between the fracture system and matrix is important in reducing the rate of contaminant migration, moderating the effect on groundwater quality of transient contaminant inputs from the source area and the creation of secondary contaminant sources through the process of back-diffusion into fractures of contaminants stored in the matrix
- Dual porosity transport (influenced by water table fluctuation, fracture flow and fracture-matrix diffusion) may exert a greater control on dissolved MTBE concentrations in the aquifer than the MTBE degradation rate (if the latter is small), suggesting that it may be difficult to deduce changes in MTBE plume development and degradation at field scale from typical groundwater quality surveys used for the assessment of NA in groundwater
- The conceptual model developed from an understanding of the processes controlling the NA of these contaminants in the aquifer can subsequently be simplified into a *performance* model for the prediction of contaminant attenuation at similar sites elsewhere, using basic analytical models and a subset of key input parameters identified from this study

Transient contaminant fluxes, simultaneously observed at different locations in the plume, could be simulated in the dual porosity transport model as the combined effects of water table fluctuation and source term changes. This behaviour reflects the rapid migration of contaminants through the fracture system at periods of high water table elevation and is controlled primarily by the aquifer hydraulic gradient, which increases fracture flow velocity. It implies that contaminant migration in the fracture system is very sensitive to water table fluctuation and that this response occurs very quickly at different locations across the site.

The numerical modelling established limits on degradation rates for MTBE and BTEX in the plume, which are consistent with the experimental results from the laboratory microcosm study. The sensitivity analyses showed that MTBE concentration in groundwater is affected more by variation in the aquifer properties and hydrogeology, than degradation rate. It was found that variations in MTBE concentration arising from dual-porosity transport in the aquifer (e.g. water table fluctuation, fracture flow and matrix diffusion) may be much greater than the variation caused by degradation. This implies that dual-porosity transport will have a significant influence on MTBE plume development. The variation in contaminant concentration arising from dual porosity transport may therefore obscure the effect of degradation, that is, changes in MTBE plume development from degradation may not be easily deduced at field scale from groundwater quality surveys. Moreover, in combination with the results of the plume chemistry analysis (section 5.2), it suggests that it may be very difficult to deduce the occurrence of MTBE degradation at field scale from trends in the profile of contaminant concentration along the plume flow path and the distribution of typical groundwater quality parameters measured in NA assessments for groundwater.

Diffusion was demonstrated by the numerical modelling to be an important process for the development of contaminant plumes in the aquifer, through the combined effect of this process on the rate of contaminant migration and capacity for degradation. The simulations showed that diffusion of dissolved electron acceptors from the matrix into the fracture system has contributed significantly to BTEX degradation in the groundwater. In addition, the modelling showed that diffusion is important in moderating the effects (e.g. reducing peak concentrations) of transient contaminant inputs from the source area and is responsible for the creation of secondary contaminant sources through the process of back-diffusion into fractures of contaminants stored in the matrix. These processes are likely to be important in controlling the NA of petroleum hydrocarbons and MTBE at similar sites elsewhere on the Chalk aquifer.

The validation exercise described above has demonstrated that the BTEX and MTBE plume development can be adequately simulated using site-specific data and parameter values for aquifer properties and processes. This provides important confirmation that the current conceptual model is satisfactory for interpreting the NA of these contaminants in the aquifer. From this analysis the complex process-based model describing petroleum hydrocarbon and MTBE attenuation at the site can be transformed into a simplified *performance* model for the assessment of NA and plume migration at other similar sites. This simplification is represented by a subset of inputs and parameters in the conceptual model, which allow the robust prediction of contaminant transport using more basic analytical models. The input terms identified in this study, which can be used in such models, include (1) source concentration (as a lumped group of compounds if desired) and transient behaviour, (2) aquifer hydraulic conductivity and gradient, (3) groundwater velocity (as alternative to (2)), (4) fracture-matrix mass transfer coefficient, (5) fracture spacing, (6) contaminant degradation rate.

6. CONCLUSIONS

The key advances arising from this research have been in process understanding and parameterisation, improved site investigation methodologies and performance assessment approaches for interpreting NA of petroleum hydrocarbons in the Chalk and other dual porosity aquifers. These science and technology advances are summarised below:

- Development of a detailed, process model describing the NA of petroleum hydrocarbons and MTBE in the UK Chalk aquifer, providing data on:
    - Relationships between physico-chemical properties and reactions which determine transport and attenuation capacity, with parameter values, including degradation rates for BTEX and MTBE under different redox and environmental conditions
    - Effect of environmental factors and contaminant interactions on degradation potential and rates
    - Contribution of dual-porosity transport and biodegradation in attenuation
- Development of new improved analytical method for the simultaneous determination of ether oxygenate compounds, their metabolites and BTEX in petroleum fuel-contaminated groundwater, with superior performance to existing methods (Dewsbury *et al.*, 2003)
- Development of novel method for the onsite sampling of porewater chemistry in contaminated consolidated aquifers (Spence *et al.*, 2005a)
- Development of process-based mass balance model as a decision-making tool for the performance assessment of NA in dual-porosity aquifers using typical site data and accounting for uncertainty in predictions with Monte Carlo analysis
- Validation of conceptual model and parameters describing NA of petroleum hydrocarbons in the Chalk aquifer, allied to development of advanced numerical code, with identification of dual-porosity effects and performance prediction for NA
- Demonstration that the aquifer microorganisms have the potential to degrade MTBE under the conditions in the aquifer

An important finding is that natural attenuation of BTEX and MTBE in the Chalk aquifer can be significant, although by different mechanisms. For BTEX, attenuation by biological processes such as degradation is more important than physical processes and the aquifer has a large reservoir of dissolved oxidants to support degradation processes for BTEX. For MTBE, attenuation by physical processes such as diffusion is as important (or more so) than degradation, based on the evidence from this study, although this conclusion may **not** apply in all cases at other MTBE-contaminated sites. The evidence from this study is that natural attenuation can provide an important role in the management strategy for sites on the Chalk aquifer which are contaminated with petroleum hydrocarbons and MTBE. It should be considered within risk assessments for such sites, taking account of the various processes and controls on contaminant behaviour in the aquifer, which have been identified and quantified in this study.

Furthermore, the research has shown that a more detailed site investigation methodology, considering a wider range of techniques and measurements of aquifer properties, groundwater chemistry and other parameters, is required to provide the information necessary to consider natural attenuation within a management strategy for such sites. This objective can only be achieved by the development of more sophisticated groundwater monitoring networks than is currently practised, with the installation of multilevel samplers at sites, to provide the necessary increased spatial and temporal resolution of the plume geometry and distribution of dissolved contaminants and degradation processes in the aquifer.

7. DISSEMINATION AND PROJECT OUTPUTS

7.1 DISSEMINATION OF RESEARCH RESULTS AND PROJECT OUTPUTS

The results of the research over the last four years have been developed into a wide variety of project outputs. These have been disseminated to the end-user community in different formats and at a variety of levels. In addition, the research has stimulated new studies and collaboration with other institutes. These outputs and additional activities include:

- Peer-reviewed journal publications
- Conference papers and other articles
- CL:AIRE bulletins
- Presentations at conferences and technical workshops
- Short-courses in professional development
- Undergraduate and MSc teaching
- PhD dissertations

Further details of these outputs are provided below.

7.2 JOURNAL PUBLICATIONS

Spence, M.J., Bottrell, S.H., Thornton, S.F., Richnow, H. and Spence, K.H. 2005. Hydrochemical and isotopic effects associated with fuel biodegradation pathways in a Chalk aquifer. *Journal of Contaminant Hydrology*, 79, 67-88.

Spence, M.J., Thornton, S.F., Bottrell, S.H. and Spence, K.H. 2005. Determination of interstitial water chemistry and porosity in consolidated aquifer materials by diffusion equilibrium-exchange as an alternative to centrifugation. *Environmental Science and Technology*, 39, 1158-1166.

Dewsbury, P., Thornton, S.F. & Lerner, D.N. 2003. An improved analysis of MTBE, TAME and TBA in petroleum fuel-contaminated ground water by SPME using deuterated internal standards with GC-MS. *Environmental Science & Technology,* 37, 1392-1397.

7.3 CONFERENCE PAPERS

Wealthall, G.P., Thornton, S.F. & Lerner, D.N. 2001. Natural attenuation of MTBE in a dual porosity aquifer. Proc. 6th International Symposium on *In situ and on-site bioremediation.* San Diego, 4-7 June. Battelle Press, 59-66.

Wealthall, G.P., Thornton, S.F. & Lerner, D.N. 2002. Assessing the transport and fate of MTBE-amended petroleum hydrocarbons in the UK Chalk aquifer. In *GQ2001: Natural and Enhanced Restoration of Groundwater Pollution*, Sheffield, U.K., 16-21 June 2001. (eds, Thornton, S.F & Oswald, S.O.), IAHS Publ. No. 275, 205-212.

Thornton, S.F., Wealthall, G.P. & Lerner, D.N. 2002. Investigating the transport and fate of petroleum hydrocarbons in the Chalk aquifer: A case study assessing natural attenuation. Proceedings of the CL:AIRE Annual Project Conference, Imperial College, London, 11 April, pp.7. ISBN 0-9541673-1-7.

Spence, M.J., Thornton, S.F., Bottrell, S.H., Spence, K.H. & Richnow, H. 2003. Natural attenuation of BTEX/MTBE in a dual porosity Chalk aquifer Proc 7th International

Symposium on *In situ and on-site bioremediation.* San Diego, USA, 13-17 May, 2003. Battelle Press. Paper H-10.

Beck, P., Thornton, S.F., Wealthall, G.P. and Spence, M.J. 2004. Management of MTBE and perchlorate contaminated groundwater. *National Ground Water Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy*. Costa Mesa California, USA, 2-4 June 2004, 5-19.

Beck, P., Thornton, S.F. & Wealthall, G. P. 2004. The use of multilevel sampling systems to provide depth discrete data for characterization of groundwater flow and groundwater quality. *Groundwater Quality 2004*. Proc. 4th International IAH Conference, University of Waterloo, Waterloo, Canada. July 19-22, 2004.

7.4 CL:AIRE BULLETINS

These include material specifically related to or including concepts and information from this study:

CL:AIRE 2002. Introduction to an integrated approach to the investigation of fractured rock aquifers contaminated with non-aqueous phase liquids. Technical Bulletin TB1

CL:AIRE 2002. Multilevel sampling systems. Technical Bulletin TB2

CL:AIRE 2002. Site characterisation in support of MNA of fuel hydrocarbons and MTBE in a Chalk aquifer in southern England. Case Study Bulletin CSB1

CL:AIRE 2005. Management of a petroleum plume by monitored natural attenuation. Site Bulletin SB1.

7.5 PRESENTATIONS

Natural attenuation of MTBE in a dual porosity aquifer. Presented at 6th International Symposium on *In situ and on-site bioremediation.* San Diego, USA, 4-7 June, 2001.

Assessing the transport and fate of MTBE-amended petroleum hydrocarbons in the UK Chalk aquifer. Presented at *GQ2001: Natural and Enhanced Restoration of Groundwater Pollution*, Sheffield, U.K., 16-21 June, 2001.

Natural attenuation of fuel hydrocarbons and MTBE in a fractured Chalk aquifer: A case study. Presented at joint NNAGS/NICOLE workshop on MNA, Rotterdam, 15 November, 2001. **Invited talk**.

Investigating the transport and fate of petroleum hydrocarbons in the Chalk aquifer: A case study assessing natural attenuation. Presented at *CL:AIRE Annual Project Conference*, Imperial College, London, 11 April, 2002.

Approaches to investigating the transport and fate of MTBE-amended petroleum hydrocarbons in fractured aquifers. Presented at *Contaminated Land Meets Groundwater*, University of Birmingham, 10 July, 2002. **Invited talk**.

MTBE/BTEX degradation in the UK Upper Chalk aquifer. Presented at *International Symposium on Subsurface Microbiology*, Copenhagen, Denmark, 9 Sept, 2002.

An investigation of MTBE/BTEX degradation in a dual-porosity Chalk aquifer. Presented at *Geological Society of America Conference*, Denver, USA, 28 October, 2002.

Partitioning of petroleum hydrocarbons and electron acceptors between matrix and fracture waters in the Chalk aquifer: It's role in natural attenuation. Presented at *CL:AIRE Annual Project Conference*, Imperial College, London, 31 March, 2003.

The role of matrix diffusion in BTEX and oxygenate attenuation in the Chalk aquifer. Presented at *What's new in Contaminated Land Meets Groundwater. Annual Conference and Darcy Lecture*, University of Birmingham, May, 2003.

Natural attenuation of BTEX/MTBE in a dual porosity Chalk aquifer Presented at 7th International Symposium on In situ and on-site bioremediation. San Diego, USA, 2-5 June, 2003.

St Albans Site: Site investigation and refinement of the site conceptual model. Presented at the *CL:AIRE conference on Monitored Natural Attenuation: A Method to Measure, Monitor and Minimise Risk Associated with the Management of Contaminated Land in the UK*, University of Sheffield, 14 October, 2003.

Evaluation of monitored natural attenuation for petroleum hydrocarbons and MTBE in the Chalk aquifer. Presented at the *CL:AIRE conference on Monitored Natural Attenuation: A Method to Measure, Monitor and Minimise Risk Associated with the Management of Contaminated Land in the UK*, University of Sheffield, 14 October, 2003.

Using tracer tests to constrain groundwater flow structure in the Chalk aquifer. Presented at the *CL:AIRE conference on Monitored Natural Attenuation: A Method to Measure, Monitor and Minimise Risk Associated with the Management of Contaminated Land in the UK*, University of Sheffield, 14 October, 2003.

The role of the Chalk matrix in processes leading to natural attenuation. Presented at the *CL:AIRE conference on Monitored Natural Attenuation: A Method to Measure, Monitor and Minimise Risk Associated with the Management of Contaminated Land in the UK*, University of Sheffield, 14 October, 2003.

St Albans Site: Microbial ecology. Presented at the *CL:AIRE conference on Monitored Natural Attenuation: A Method to Measure, Monitor and Minimise Risk Associated with the Management of Contaminated Land in the UK*, University of Sheffield, 14 October, 2003.

7.6 COURSES IN PROFESSIONAL DEVELOPMENT

Material and outputs from this research have been incorporated into the following professional development short courses at the University of Sheffield:

- Natural Attenuation of Pollutants (2003-date)
- Investigation and Remediation of NAPLs (2003-date)

7.7 UNDERGRADUATE TEACHING AND POSTGRADUATE TRAINING

Material and outputs from this research have been incorporated into the following graduate and postgraduate training programmes:

University of Sheffield

- Groundwater Remediation using Natural Attenuation

MEng in Civil and Structural Engineering (2003-date)

- Natural Attenuation of Pollutants

MSc in Environmental Management of Urban Land and Water (2003-date)

MSc in Contaminant Hydrogeology (2004-date)

- Field Investigation Methods

MSc in Environmental Management of Urban Land and Water (2003-date)

MSc in Contaminant Hydrogeology (2004-date)

- Remediation of NAPL Pollutants

MSc in Environmental Management of Urban Land and Water (2003-date)

MSc in Contaminant Hydrogeology (2004-date)

- Urban and Industrial Hydrogeology

MSc in Environmental Management of Urban Land and Water (2003-date)

MSc in Contaminant Hydrogeology (2004-date)

University of Leeds

- The Geochemistry of Groundwater Pollutants and their Remediation

MSc in Hydrogeology (2004-date)

MSc in Environmental Geochemistry (2004-date)

7.8 DOCTORAL DISSERTATIONS

The research undertaken in this project has supported, and in turn been enhanced by, the following PhD studies:

Spence, K. S. 2005. The biodegradation of MTBE and fuel hydrocarbons in the Chalk aquifer, School of Earth and the Environment, University of Leeds

Cheng, L. 2006. Dual porosity reactive transport modelling, Dept of Civil and Structural Engineering, University of Sheffield

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