Project SIREN: Phase 2a Conceptual Site Model & Groundwater Model

R & D Technical Report P2-208/TR/2

Research Contractors:
AEA Technology Environment and
Shell Global Solutions

Further copies of this report are available from:
Environment Agency R&D Dissemination Centre,
c/o WRc, Frankland Road, Swindon, Wilts SN5 8YF

tel: 01793-511711 fax: 01793-514562 e-mail: publications@wrcplc.co.uk

Project Siren: Phase 2a
Conceptual Site Model & Groundwater Model

R&D Technical Report P2-208/TR/2

R Earle, D Jones, G Lethbridge, P McCarthy and S Thomson

Research Contractors:
AEA Technology Environment and
Shell Global Solutions

Publishing Organisation:
Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD
Tel: 01454 624400 Fax: 01454 624409

ISBN : 1857056027

Dissemination status
Internal: Released to Regions
External: Released to Public Domain

Statement of Use
This report summarises the finding of research carried out by the contractors for this project. The information within this document is for use by Environmental Agency staff and others involved in evaluating the use of natural attenuation for the purposes of remediating contaminated land and groundwaters.

Research Contractor
This document was produced under R&D Project P2-208/TR/2 by :

AEA Technology Environment
National Technology Environment
National Environmental Technology Centre
Culham
Abingdon, Oxfordshire
OX14 3ED
Tel : 01235 463391 **Fax :** 01235 463010

AEA Technology is the trading name of AEA Technology plc
AEA Technology is certified to BS EN ISO9001: (1994)

Environment Agency Project Manager
The Environment Agency's Project Manager for this R&D Project was
Alwyn Hart, National Groundwater and Contaminated Land Centre, Midlands

CONTENTS

LIST OF FIGURES PAGE

LIST OF TABLES PAGE

LIST OF APPENDICES

APPENDIX A

APPENDIX B

APPENDIX C

APPENDIX D

APPENDIX E

EXECUTIVE SUMMARY

SIREN (Site for Innovative Research in Natural Attenuation) is a joint initiative between Shell, the Environment Agency and AEA Technology to promote field-based research in monitored natural attenuation (MNA) and facilitate the development of confidence and acceptance of MNA as a technically defensible risk management option for contaminated sites in the UK.

This report describes the development of a preliminary conceptual site model (CSM) and a groundwater model for the SIREN site which is an operational petrochemical plant.

By far the major contaminants identified in the soil and groundwater are benzene, toluene, ethylbenzene and xylenes (BTEX), followed by styrene, naphthalene and chlorinated aliphatic hydrocarbons (CAH), although the concentrations of the CAH are very low.

There are several BTEX plumes in shallow groundwater some of which have merged. At least two plumes have penetrated a clay layer and at least one of them has entered the Sherwood Sandstone Aquifer which is classed as a major aquifer by the Environment Agency.

The CSM has identified BTEX as the primary contaminants of concern and the sandstone aquifer and nearby surface water bodies, river A and canal A, as receptors potentially under threat from contamination at the site via transport in the groundwater.

The groundwater model predicts that the plumes will stabilise within 16 years of the contamination taking place, none of them will extend greater than 250 metres from the source and that none of them will migrate off site.

This is supported by the fact that an extensive array of monitoring wells on the site boundary are currently uncontaminated. There is direct and indirect evidence that natural attenuation of BTEX and CAH is taking place in the groundwater. Concentrations away from the source areas have declined by 50-99% between 1995/96 and 1999/2000.

Keywords: Biodegradation, contamination, groundwater, modelling, natural_attenuation, soil.

1. INTRODUCTION

SIREN (Site for Innovative Research in Natural Attenuation) is a joint initiative between Shell, the Environment Agency and AEA Technology to promote field-based research in monitored natural attenuation (MNA) in the UK and facilitate the development of confidence and acceptance of MNA as a technically defensible risk management option for contaminated sites. The aim is to provide a well characterised site for research groups to carry out projects potentially on any aspect of MNA that are funded by the Research Councils or other funding bodies. It is envisaged that these projects could range from short-term MSc projects to longer term projects lasting several years. They will either generate new data on the site or analyse existing data which will be made available to any bona fide researchers interested in the site. CLAIRE (Contaminated Land: Applications in Real Environments) has agreed to consider any of these projects for inclusion into its portfolio.

The site was chosen from a wider list of approximately 150 sites, based on agreed criteria including (Towler et al, 2000):

- contamination in a consolidated aquifer (Sherwood Sandstone),
- no off-site receptors were under threat,
- no engineered remediation was underway
- long-term availability (> 5 years)
- good security and services

The site is an operational petrochemicals manufacturing plant. Over its long history (50 years) it has manufactured a variety of chemicals (eg. alcohols, glycols, amines, detergents, polystyrene, polypropylene) from refined petroleum hydrocarbon feedstocks. As a result of the historical processes and activities undertaken on the site both soil and groundwater have been impacted by various chemicals, especially BTEX and CAH. Soil and groundwater surveys undertaken on the site have shown that these chemicals have been detected in the ground, perched water, shallow aquifer and the sandstone aquifer beneath the site.

The purpose of this report is to describe the development of a preliminary conceptual site model (CSM) and a groundwater model for the site. A CSM is a tool to identify plausible source-pathway-receptor scenarios at a site through an understanding of the physical, chemical and biological processes that determine the transport of contaminants from sources through environmental media to receptors. It should be viewed as an evergreen tool which is continually updated as more is learned about the site. The CSM is equally important for highlighting gaps in data and understanding as it is for telling us what we know about a site. It enables hypotheses to be formulated and tested which in turn results in the acquisition of new knowledge which can be used to update the model. The purpose of including the site groundwater model in this report is to enable some of these hypotheses to be tested.

This report is not meant to be a complete summary of all the data that are available on the site, but rather to summarise the key data and our current level of understanding of the site for prospective research groups.

Some general views of the site are shown in the following pages.

2. REGIONAL AND SITE SETTING

2.1 Site Description

The site (180 hectares) is located approximately 1 km south-east of the confluence of a river and a canal (Figure A.1, Appendix A). The river A bounds the northern part of the site boundary and the canal A runs approximately 250m to the west of the site boundary. The site forms part of a larger estate (570 hectares).

Much of the land to the north, east and south is designated as 'green belt', or protected open land. There are several farms in the vicinity

Historically a moss (peat-bog), which is part of the estate to the south of the site, was used for the disposal of domestic waste from a nearby city, which was transported down the canal on barges, distributed over the ground by a light rail system and then ploughed in. This practice resulted in the soils developing elevated (above background) levels of heavy metals (most likely from coal burning waste).

2.2 History of the site and Surrounding Region

Study of Ordnance Survey maps from 1881 to the present day reveals the following development of the site:

1881 -1882

- Canal A not yet created
- Railway to south of site
- Land use of the future site appears to be agricultural, with field boundaries and some wooded areas marked
- Moss marked

1891-1896

- Canal A now present
- Tramway running from Engine shed & Smithy at the Wharf on Canal A to the Moss (deposit of night soil from nearby city / spoil from canal construction)
- Site area still appears to be farm and woodland
- Possible grid of tramways on the eastern side of Moss

1899

- All of Moss now covered with a grid of tramways
- Nursery to the south east of the site
- Sewage tanks in the south west corner & south of the Moss
- Site area still farm and woodland

1904-1910

- Little change from 1899
- Sewage disposal works to the south of the Moss
- Site still appears to be farm and woodland
- Drainage channels on the Moss. If arrows indicate direction of flow, then flow

is towards the south, away from the site, into the Brook A.

1911

- Sewage farm to the south east of the Moss
- Site still farm and woodland

1929-1938

- Large area cleared to the south of the railway that runs south of the Moss. No indication of use.
- Site still farmland, forested area is no longer marked
- Tramways and drains still present on the Moss
- An Iron & Steel works on the west bank of Canal A

1938-1954

- Playing field and housing have appeared in the north east corner of the site
- The words ‘Petrochemical Plant’ appear on the map in the vicinity of the site, but no indication of the extent.
- Tramways and drains still marked on the Moss

1954-1965

- The site is now clearly marked, including tanks and buildings. Covers approximately one third of the current area.
- Overhead power lines skirting around the east of the site, it is therefore possible that the power station adjacent to Canal A was built during this period
- Branch line from railway to the south now leading past the site. This line serves the site and also goes past to the Wharf .
- Gas works to the south west of the site
- Tramways no longer indicated on the Moss, drains still marked
- Reservoir in the north east corner of the then site

1971-1981

- The site has expanded to its current size
- Branch line to site has expanded (more sidings) and the line extends on to the power station (marked as a Mineral Railway). Wharf has disappeared.
- Large petrol storage depot to the west of the site
- Gas works to the south west of the site has expanded considerably
- A quarry has been developed to the north west of the site, on the edge of Canal A (served by the railway that runs through the site)
- Works some distance to the South east of the site
- Rifle range on the eastern edge of the site
- More housing now apparent in the surrounding areas
- Abattoir just to the north of the site, adjacent to the River A

1983-1996

- Air Products site now marked (just to the north west of the site)
- Farm has disappeared from adjacent to the southern boundary fence
- Large lake in the south east corner of the site (bird sanctuary?)

- Main rail line that runs to the south of the site now dismantled to the west of the site branch line. Branch line still exists to site (but does not extend to the Power Station)
- Quarry to the south of the Power Station has doubled in size
- Steel works to the west of Canal A has become an Industrial Park
- The number of buildings on the site has reduced

1999

- Power station to the north west of the site no longer present.
  Business Park marked

2.3 Regional Aquifer behaviour

The groundwater contour map produced in 1995 by Severn Partnerships, Lands Surveyor shows the general flow direction in the sandstone is from the south east heading in a northerly westerly direction. This is a very general map but it does indicate that the river A is the main sink within a large groundwater basin.

2.4 Regional geology

The British Geological Survey Sheet 98, indicates that the site is underlain by Quaternary drift deposits comprising peat, alluvium, glacial clay (boulder clay) and glacial sands and gravels.

Peat deposits underlie the majority of the non-petrochemical area of the site, extending to the north west in the petrochemical part of the site and to the south into the larger sub sites beyond the main site. Within the developed areas of the estate and on the moss the peat has been removed.

Alluvium deposits are located in the area to the north of the operational area of the site, within the meander of the river A. Deposits also extend along the course of the Brook A in the south of the Estate and along the river B.

Underlying the alluvial and peat deposits are layers of glacial clays and glacial sands and gravels. The drift deposits are underlain by rock of the Wilmslow Sandstone and Helsby Sandstone of the Sherwood Sandstone group. The sandstone dips 3^{o} to the south-west. The deepest borehole known records the sandstone down to 85m where the well ends.

Further investigation has been carried out at the site and is described under local geology below.

2.5 Local Geology and hydrogeology

For simplicity it is best to think of there being four layers to the geology; sand and gravels overlying a layer of clay which is overlying another layer of sands and gravels which is all overlying sandstone (Figure 2.1). Borehole logs for some of the deep monitoring wells on the site are included in Appendix E.

Figure 2.1 Site geology

	Thickness range
Sand and Gravels	2.85m-8.50m
Clay	0.36m-30.00m
Sands and Gravels	0.00m-7.60m
Sandstone	>77m

The first layer of sand and gravels consists primarily of sandy material with intermittent layers and lenses of gravel. Overlaying this layer are patches of fill and top soil. Underlying the sand and gravel is a continuous (albeit thin in places) layer of clay, with lenses of sand throughout.

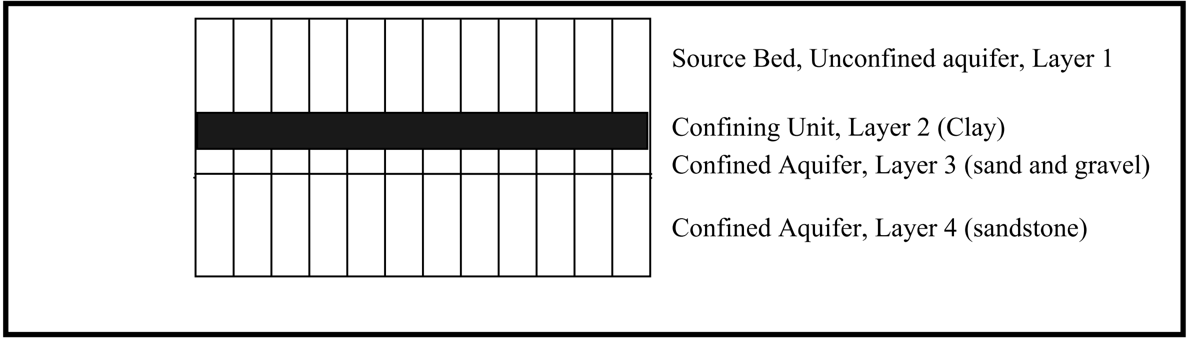
Underlying the clay is a discontinuous layer of gravels and sands. This layer consists of mainly gravel size material containing lenses of sand. Underlying this is a continuous formation (>77m in thickness) of sandstone, which is classified by the Environment Agency as a Major Aquifer. A three-dimensional visualisation of the site geology is shown in Figure A.2 (Appendix A). This waffle diagram was constructed using the site investigation logs as well as 43 geotechnicial logs. It was constructed using the solid model interface within GMS (Groundwater Modelling Software - see section 6.1 for description of GMS). Using this interface similar contacts (i.e. contact between top sand and gravel with the underlaying clay) are linked together to recreate the surface of each layer. The respective site locations of the axes of the waffle diagram are shown in Figure A.3 (Appendix A).

The sandstone appears to have a deep wide trench or channel curving through the site from the eastern boundary and out to the northern boundary towards the river A (Figure A.3, Appendix A). This trench could greatly affect the local groundwater flow system. The highly permeable gravels which overlay the sandstone and underlie the clay could act as a drain thus directing the flow in this direction.

The channel shows up further when a plot is drawn of the depth from the ground surface to the top of the sandstone (Figure A.4, Appendix A). The yellow and orange indicates the deeper parts of the channel. The channel can also be seen in a plot of the thickness of the clay layer (Figure A.5, Appendix A).

In the conceptual site model the 4 layers (Figure 2.2) are represented as:
1) the upper sand and gravel layer (source bed and unconfined aquifer),
2) the confining clay layer
3) the lower sand and gravel layer (confined aquifer)
4) the sandstone (confined aquifer)

Figure 2.2: Model layer perspective



From observed groundwater data the groundwater flow in the sandstone is in a north westerly direction, towards the confluence of river A and canal A. As the water approaches the confluence it fans out and tends to flow either towards the canal or the river (Figure A.6, Appendix A). There is a similar trend in the groundwater flow in the two sand and gravels layers (Figure A.7, Appendix A).

The site has been used as a petrol chemical site for the past 50 years and has used a number of chemicals which could have potentially entered the groundwater system. If these chemicals are released into the subsurface and dissolve into the groundwater they will be transported away from the neighbouring residential areas and towards the river A and the canal A.

Figure 2.3 shows a simplified cross section of the regional conceptual model. Water enters the model from either local recharge (rainfall), or through the geology as groundwater flow from the regional recharge zone. This then flows in a north westerly direction under the site and into canal A or river A.

There have been 26 sets of nested boreholes installed on the site. Their locations and the layers in which the are screened are given in Figure A.8 (Appendix A) and Tables B.1-B.8 (Appendix B). Eighteen of these indicate a downward migration of groundwater from the top sand and gravels to the clay or second layer of sands and gravels. The remaining water elevations are relatively level in each set of nested wells. Overall there is a downwards hydraulic gradient from the upper sand and gravel to the Triassic Sandstone. This could result in diving plumes.

Figure 2.3: Cross-section of Regional Conceptual Model

3. SITE LAND USE

A number of previous reports have summarised the use of various areas of the site by dividing it into three main areas and then further subdividing each of these areas. These divisions are shown on Figure A.9 (Appendix A). This information is discussed in the remainder of this section.

3.1 Site Operations - Past and Present

The site occupies an area of approximately 180 hectares of which just over 100 hectares have been developed for chemical production. Approximately half of the non production area has been used for service accommodation and car parks with the remaining half still undeveloped. No previous use of the land which could lead to contamination has been identified prior to the first chemical plant, a catarole cracking furnace, started in January 1949. The site was acquired by the current owner in 1955. The expansion which followed included additional crackers, gas separation units, ethylene oxide (EO) and derivatives, polystyrene and polyolefins, continued through to the end of the 1970s

Rationalisation during the 1980s left just the polyolefins, polystyrene and EO derivatives plants. Decommissioning and demolition of the redundant plants was progressed during the 1980s. For the sake of this survey, the site has been divided into four areas where soil contamination, if present, is likely to consist of similar types of chemicals. These areas are further subdivided to group similar production units (Figure A.9, Appendix A).

The production units operational in each of the areas are listed below together with the major process chemicals or intermediates which may have contributed to contamination of the soil. Particular note has been made of those compounds, other than hydrocarbons, specified by the EC as substances where discharges to groundwater should be prevented or minimised, where it is considered contamination may have occurred.

A - Non-production areas

A1. This area of approximately 16 hectares has not been developed and is therefore unlikely to contain significant soil contamination. However this does not preclude the possibility of ingress of contaminants via groundwater migration from adjacent areas. In particular, groundwater modelling has shown that contaminants in regions C and D could pass through A1 on their way towards Canal A.

A2. About 27 hectares which has included car parks, laboratories, pilot plant, fire station and a materials compound. A Business Park was set up to utilise a number of redundant office and laboratory buildings in this area and now consists of about 600 people working in a large number of small businesses. The Park is separated from the site by a fence but drainage systems are common. No actual manufacturing processes are operated but some blending of chemicals takes place. It is known that PCBs (polychlorinated biphenyls) are used in the area and small quantities of chemicals such as paints, solvents, printing inks etc. are stored and used by the businesses.

With hard standing throughout the utilised areas there is little likelihood of general soil contamination. Local 'hot spots' could occur however, for example in the garage area where underground fuel storage tanks were located and where spillages have occurred.

A3. Development has been limited in this area which occupies about 34 hectares. A lorry park and tanker wash bay have been in use since 1970 and the east site boiler plant was used from 1965 to 1985 producing high pressure steam for the site. With the exception of the tanker wash bay, which may have given rise to localised soil and groundwater contamination, the potential for significant soil contamination in this area is considered to be low.

B - Alkylene oxides and derivatives production area
A region of approximately 26 hectares in which ethylene oxide is the predominant chemical used although propylene oxide was produced and used in the past. The majority of the derivatives are highly soluble in water and readily leachable into groundwater. They have not formed part of the site investigation chemical analysis suite to date. They are however readily biodegradable.

B1. Within this area are grouped the barrel filling sheds and blending units. No actual production plant is included so volumes are relatively low although transfers and hence the chance of spillage is high. It is also known that leakages have occurred over the years.

- Barrel Filling Shed No. 1 was used from 1950 to 1980 for general chemicals,
- Barrel Filling Shed No. 2 was used from 1951 to 1993 for general chemicals.
- Barrel Filling Shed No. 3 was used from 1958 to 1992 for making aqueous amine, brake fluid and antifreeze blends. Constituents included dyes and the following compounds of sodium :- benzoate, nitrite, tetraborate and mercaptobenzothiazole.
- Barrel Filling Shed No. 4 was used from 1968 to 1980 for detergent blends
- Barrel Filling Shed No. 5 was used from 1968 to 1980 for Caradol blends. Chemicals used included di-methyl cyclohexylamine, tri-chlorofluoromethane, methylene bis phenyl isocyanate and toluene di-isocyanate
- The drum store housed any of the products made within the whole of area B from 1958 to 1993

B2. This is where the first alkylene oxide derivatives production units were built and is therefore the block within this group where the chance of soil and groundwater contamination is most probable.

- Iso-Propyl alcohol was produced from 1950 to 1959 by passing propylene into concentrated sulphuric acid and then diluting with water. Iso-Propyl ether was also produced as a by-product.
- The Chlorohydrin plant was used to manufacture ethylene oxide from 1950 to 1959 and propylene oxide from 1952 to 1973. They were made from the respective olefin (ethylene or propylene) by reaction with hypochlorous acid solution, prepared from chlorine and water. The chlorohydrin produced was saponified by the addition of milk of lime (calcium oxide suspension in water) to form the oxide and calcium chloride. The corresponding dichloride and aldehyde were produced as by-products
- Glycols, both ethylene and propylene, were produced from 1950 to 1985 by the reaction of the respective alkylene oxide with water. Capacity of EG I was 18,000 tonnes per annum.
- Glycol ethers were produced from 1951 to 1980 by reacting ethylene oxide with an alcohol. Methyl, ethyl, iso-propyl and n-butyl alcohols were used as feedstock. Sodium hydroxide was mainly used as catalyst although boron trifluoride was used with the higher alcohols until 1973. GE I had a capacity of 18,000 tonnes per annum and GE II could produce about 50,000 tonnes per annum.

- Alkanolamines were made in this area from 1951 to 1980. Ethanolamines (mono, di and tri) were made by reacting ethylene oxide with ammonia and then separated by distillation. iso-Propanolamines were similarly prepared from propylene oxide.
- Prior to 1959 a building on this plot was used for bottling LPG from the gas separation plant. Organic sulphur compounds were added as odorants.
- Batch production of a whole range of alkylene oxide derivatives has taken place from 1954 to the present day on the PEG plants. PEG I had a capacity of about 20,000 tonnes per annum and PEG II was capable of 55,000 tonnes per annum. Originally the batch size was limited to 12.5 tonnes but has since been increased to 25 tonnes. Products include Polyethylene Glycols (PEGs), Polypropylene Glycols (PPGs), Oxilubes, Oxitexes, Caradols, tri-Ethanolamine (TEA), mixed IPAMs and detergent ethoxylates.

  Initiators included oxitols, octyl cresol, octyl phenol, nonyl phenol and trimethylol propane. Potassium hydroxide is the usual catalyst employed but p-toluene sulphonic acid has been used. Di-methyl cyclohexylamine and di-methyl amino ethanol have been used in blends.
- Initiator and product storage tanks with associated pumps and road car loading facilities are also located in this area.

B3. The most recent expansions are included in this block.

- The detergent ethoxylates plant has run from 1972 to the present day with a capacity of 60,000 te/y. It is a batch process of 35 tonnes in which Dobanol, a linear alcohol, is reacted with ethylene oxide. A whole series of Dobanols are used with various molecular weights within the range C_9 to C_{15}.
- Refrigerated ethylene oxide storage vessels (900 tonnes) and propylene oxide storage tanks (2250 tonnes) are located in this area.
- Extensive product tankage, originally for glycols but now restricted to ethoxylates together with pumps and road tanker loading facilities.
- A pilot plant was operated from 1965 to 1983. Based primarily on alkoxylation using a variety of initiators, a wide range of development chemicals were produced including 1,5 cyclo-octadiene, 1,5,9 cyclo-dodecatriene, pivalolactone, pivaloyl chloride, n-propyl oxitols, Lubad 131, sucrose polyether, sorbitol polyether, n-butyl-glycidyl ether, SME 529 (see area C2 below) and ASD (polyisobutene dimethyl amino propylamine).
- Lime settling ponds were used from 1950 to 1973. In the early '80s they were completely emptied and all material removed from site. It is believed that attempts were made to neutralise these lime pits with acid, prior to emptying. This may account for some of the extremes of pH encountered in some groundwater samples across the site.

B4. This block contained the main ethylene oxide production plants.

- EO1 the first direct ethylene oxidation plant ran from 1959 to 1979 using a silver catalyst. The process also required a large kerosene surge vessel.
- EO2 which also included ethylene glycol production was operational from 1967 to 1985. Capacity was 77,000 tonnes per annum of oxide and 57,000 tonnes per annum of glycol. Again a kerosene reactor cooling system was employed with a capacity of 180 tonnes.
- An air separation plant: operated from 1959 to 1971.

By the nature of the plants and the fact that the feedstock and the products are predominantly gaseous, there is a lower chance of contamination having occurred in this block.

C - Hydrocarbon Crackers and Derivatives Areas
This area of about 45 hectares encompasses the original site of the chemical plant.

C1. The following units operated in this block :-

- A resin plant operated from 1950 to 1956 using indene (benzocyclopentadiene) and from 1951 to 1970 using o-xylene and styrene as feedstock.
- A propylene glycol plant operated from 1961 to 1973 making and separating mono, di, tri and tetra propylene glycols. Propylene oxide was the feedstock,
- A plant producing paint bases was operated. Major process chemicals included toluene, styrene and/or butadiene rubbers and acrylonitrile.
- DCPD (di-cyclopentadiene) was produced from 1957 to 1970.
- The LADU (Light Aromatics Distillation Unit) was in use from 1949 until 1970 producing benzene, toluene, ethyl benzene, m- and p-xylenes, o-xylene and styrene and heavier aromatic hydrocarbon fractions. Methyl alcohol was used to azeotrope non-aromatics from the crude benzene and toluene fractions. The aromatics were then treated with concentrated sulphuric acid and rectified to produce pure chemicals.
- Naphthalene was produced by crystallisation from 1949 to 1970. There was some distillation activity involving naphthalene prior to 1959.
- Pitch was produced from 1949 to 1965.

The probability of soil contamination in this area is high due not only to the type of compounds processed, but also the period during which the plants operated. Environmental awareness was not so high and housekeeping was not practised to present day standards. Contamination could be by any of the products or process chemicals mentioned above, with the predominant ones being aromatic hydrocarbons .

C2. This area has been utilised for polystyrene production since 1958 until the present day by the following units :-

- A polystyrene plant was operated from 1950 to 1958.
- Suspension polymerisation unit with Carinex bead extrusion, mixing and dyeing was operational from 1958 to 1976 with board being manufactured until 1964. Risella oil and pigments were also stored in this area.
- Toughened polystyrene (high impact) line 1 was commissioned in 1961 with additional lines being added in '63, '71 and '72. Lines 1 & 2 were shut down in 1980, but since 1985 the other lines have been operated and a fifth one added. Maximum capacity achieved has been about 50,000 tonnes per annum. Small amounts of ethyl benzene are now used in the process.
- Expandable polystyrene (Styrocell) line 1 was started in 1960 and line 2 in 1964. Both were shut down following the commissioning of line 3 in 1972 with a capacity of 50,000 tonnes per annum. This unit is still operational. Zinc and magnesium stearates are used as coating agents, pentane is added as blowing agent, and hexabromocyclododecane is added as a flame retardant to some grades.
- A polyolefins pilot plant (1000 tonnes per annum) operated in this area from 1959 to 1963,

- Storage and packaging facilities for product have been available since 1958 as well as tankage for styrene monomer (6,000 tonnes), toluene (10 tonnes) and pentane (360 tonnes),

Other processes were operational for short periods of time.

- SME 529 (2-hydroxy, 5-nonyl acetophenone oxime), a metal extractant, was produced in this area from 1974 to 1976. Perchloroethylene and p-nonyl phenol were the feedstocks with 2-hydroxy, 5-nonyl acetophenone being produced as an intermediate prior to oximation. Process chemicals included toluene, aceticanhydride, sulphuric acid, sodium hydroxide, hydroxylamine and MSB 210, a high boiling aliphatic solvent. Aluminium chloride was used as catalyst.
- The reactors were used for batch aromatics distillation to recover the volatile fraction.
- Teepol 610S was prepared by sulphation of C_8 to C_{18} alpha olefins ex cracked urea wax oils with concentrated sulphuric acid.
- Shellswim 11T was made for a short period in the late '70s. "Behenyl" alcohol, a mixture of even carbon number alcohols from C_{16} to C_{22} was reacted with acrylic acid in toluene using p-toluene sulphuric acid catalyst. The behenyl acrylate was then copolymerised with 4-vinyl pyridine in toluene solution.
- A polystyrene pilot: plant was used. in 1987 / 88 for making polyphenylene oxide by the oxidative polymerisation of 2,6 xylenol in toluene. Air was passed through the solution, the catalysts used being di-n-butylamine, cuprous chloride and sodium bromide. At the end of the reaction the copper was removed by complexing with ethylene diamine tetra-acetic acid. Methanol was used to precipitate the poly (2,6 dimethyl -1,4 phenylene oxide) for recovery by filtration.

Soil contamination by styrene and toluene is highly probable because of these activities. There was also a bulk loading facility where spillages could have occurred.

C3. This block contained the central utilities services but was predominantly occupied by cracking units and gas separation plants.

- Central utilities providing steam, cooling water and compressed air operated from this area between 1948 and 1973. Units included de-aerators, demineralisation beds and boilers.
- Ethylene 1 - Catarole cracking unit was operational from 1949 to 1972 with a capacity of 75,000 te/y naphtha.
- Ethylene 1 - Gas separation unit ran from 1949 to 1969 with a capacity of about 20,000 te/y of ethylene.
- Ethylene 2 with a capacity of 80,000 te/y ethylene was commissioned in1960 and ran until 1980. It comprised steam crackers with gas separation. Sodium hydroxide was used to remove hydrogen sulphide from the gases, the sulphide liquor being taken off site for disposal. "Thermex", a mixture of diphenyl and diphenyl ether was used as a heat exchange medium.
- A benzene recovery unit, using the freeze process, ran from 1964 to 1969. This was a two phase process using calcium chloride solution as the aqueous phase,
- An ultra severe cracking unit was operational between 1966 and 1972
- Extensive tankage for naphtha feedstocks, liquified petroleum gases, benzene, toluene and

crude aromatic intermediates as well as light and heavy fuel oils have all been situated within this area at various times from 1948 to the present day. Inventories of liquid storage ranged up to 7,000 tonnes with a total capacity in this area of about 35,000 tonnes.

There is a strong possibility that soil and groundwater contamination occurred within this area. Contaminants will be mainly petroleum hydrocarbons, predominantly aromatic in nature, ranging from benzene to heavier polyaromatic hydrocarbons.

C4. This area contained the following production units.

- An ethyl benzene production unit operated from 1960 to 1979 using benzene and ethylene feedstocks with aluminium chloride catalyst. The capacity of this unit was 80,000 tonnes per annum.
- A styrene monomer plant was operated from 1960 to 1979 with a capacity of 80,000 tonnes per annum. The process used was the dehydrogenation of ethyl benzene over iron oxide catalyst. Sulphur was used as a polymerisation inhibitor during production but this was removed and tertiary butyl catechol added to the finished product.
- Tankage for feedstocks and products with associated pumps and pipework were located in a plot adjacent to the plants. Total styrene capacity was in excess of 6,000 tonnes. LPGs were stored under pressure with some being semi-refrigerated. Inventories ranged from 50 to 4,500 tonnes with a total capacity of about 12,000 tonnes.

The probability of localised contamination of the soil by benzene, ethyl benzene and styrene monomer must be considered as high.

C5. This area is similar to C3, being occupied by crackers and gas separation plant.

- Ethylene 3 was in production from 1967 to 1985 with an associated gas oil hydrotreater and 1,3-butadiene plant using acetonitrile extraction. Capacity was about 135,000 tonnes per annum of ethylene,
- A gas oil cracker was also used between 1979 and 1985

As these were more modern plants than those in area C3, although the throughput was much greater, the possibility of soil contamination should have been less although spillages are known to have occurred.

D - Polyolefins production area

This plot of approximately 33 hectares has been developed in the most recent past and as the feedstocks are all gaseous and products solid, the probability of soil contamination is considered relatively low and will be restricted to the process chemicals used. This does preclude migration of contaminants from other areas via groundwater movement.

D1. Low density polyethylene has been produced since 1962 to the present day using the high pressure process. Capacity has ranged from about 15,000 tonnes per annum to the present level of 165,000 tonnes per annum polymer. Releases of product and oligomers via the vents do occur but this is not considered to be harmful to soil or groundwater.

Xylene was used as a process chemical in the early days but those now used in appreciable quantities are n-butyl acrylate, propionaldehyde and lubricating oils. Storage capacities are for 135 tonnes of n-butyl acrylate and 20 tonnes of propionaldehyde. The bleed gas purification unit contains about: 1.5 tonnes of chlorofluorocarbon refrigerant R22 and can store 5 tonnes of bleed gas.

D2. Polypropylene and polyolefins (polypropylene/polyethylene co-polymers) have been produced in this area from 1962 to the present day. Capacity has increased from 15,000 te/y to the present 185,000 te/y polymer.

- PP2 uses aviation alkylate (iso-octane) and sec-butyl alcohol as the major process chemicals with about 2,000 tonnes of aviation alkylate normally present on the plot. Soil contamination is likely around storage tanks and the PP2 plant area. The catalyst used is $TiCl_3$, prepared by the reduction of $TiCl_4$ with triethyl aluminium chloride and di-ethyl aluminium chloride co-catalyst. Closure is imminent.
- PPLS (LIPP/SHAC) a liquid propylene polymerisation unit using a high activity catalyst was commissioned in 1983. The catalyst is again based on titanium chloride and ethyl aluminium. A total of about 30 tonnes of the aluminium alkyls are held on the unit.

The site, from its inception, was designed and built as an integrated chemical plant. The industry standard methods of avoiding soil and groundwater contamination have been practised to the levels of the day. Feedstock and product tanks are above ground and adequately bunded. The majority of the pipework carrying chemicals within the site is above ground. Pipelines enter the site underground and although only used for gases now, have carried naptha, gasoline, gas oil, and fuel oil in the past. Maintenance, shutdowns, decommissioning and demolition have all been conducted so as to avoid spillages. Unloading, loading, transfer points and drum storage areas are over hard standing.

However, spillages are known to have occurred and leakages have been discovered. Historical records of spillages are not very detailed, a more comprehensive system of environmental incident reporting being initiated in 1990. It is believed that some xylo-styrene resin was buried in plot C1 in the early years. Open areas adjacent to plants have been used for high pressure water jetting of pipework etc. and degreasing with 1,1,1-trichloroethane was practised.

3.2 Timeline of Operations

The above information has been summarised in Table 3.1.

Table 3.1: A Site History (coloured section)

Table 3.1 (A Site history) (black & white section)

4. IDENTIFICATION AND CHARACTERISATION OF CONTAMINANT SOURCES, PATHWAYS AND RECEPTORS

Source characterisation is made up of five components: the location, the extent, the amount, the identity and the behaviour of the contaminant. For the purposes of this study the sources of contamination have been divided into confirmed and potential sources. The confirmed sources are those areas of the site where an investigation has revealed contamination in the soil (Table 4.1) and groundwater, or where spills and leaks are known to have taken place from records, visual observation and anecdotal evidence (Tables 4.2 & 4.3). The potential sources are those areas for which there has been no intrusive investigation and chemical analysis to confirm contamination, but where an investigation of the site history has shown there were activities which could have led to contamination, such as production, loading/unloading, transfer, storage and land fill. Tables 4.4 to 4.9 list the information on potential source areas for the site

To make it easier to visualise the source areas the site has been divided up into 4 areas where soil contamination if present, is likely to consist of similar types of chemicals. These areas are further subdivided to group similar production units. Figure A.9 (Appendix A) shows the areas A to D with subdivisions. .

4.1 Confirmed sources

Since there are no quantitative historical site records of spills, the total amount of contamination in a particular source area has been investigated from the intrusive site investigation data (laboratory analysis and field screening using a Light Induced Fluorescence probe on a cone penetrometer) collected since 1988. By their very nature, these estimates are only rough approximations since the sparse data set on which they are based means assumptions had to be made on the depth and the area of contamination, based among other things on our knowledge of the site activities and estimations of the area of hard standing. These assumptions have been documented and can be changed later as more information comes to light.

The site investigations show that there are at least nine confirmed sources of contamination. Seven of these sources have been divided into major and minor sources by estimating the potential amount of contamination within each area. (Table 4.1). The approximate locations of the sources are indicated schematically in Figure A.10 (Appendix A) as they have not been rigorously delineated.

The 3 largest sources are :

- the former light aromatics distillation plant in C1,
- the former tank farm near the Styrocell warehouse in the South, it is probable these tanks contained styrene and toluene (C2) ,
- and in the former Styrene monomer tank farm in the South East of the site (C4).

The sizes of these sources have been estimated at between 37,000 and 41,000 kg of total petroleum hydrocarbon (TPH) in C2, between 55,000 and 174,000 kg of Styrene in C4 and between 1,400 and 23,200 kg of Styrene in C1 (Table 4.1). The other apparent smaller sources cannot be discounted as large sources since they may represent parts of much bigger areas of contamination which it has not been possible to confirm with the currently available data..

The presence of free product during sampling in areas C4 and C2 was observed supporting the assumptions that these are source areas. (Table 4.2)

Table 4.1 Confirmed sources of contamination on the site based on soil sampling and analysis

Location	Area	Plant	Contamination	Low Estimate (kg)	High Estimate (kg)	Date of investigation
Area 20	C5	Ethylene production	BTEX Styrene Naphthalene	1480 480 440	3390 1110 1000	1998
Tankage 40s	C2	Storage of styrene	Hydrocarbon	37000	41000	1989
TP1 - TP6	C4	Ethylbenzene / Styrene monomer production site	Styrene Ethylbenzene	54700 4000	174000 12700	1989
W17	B2	Alkylene oxides derivatives, glycols	BTEX Styrene Naphthalene	9 2 1	3900 870 500	1996
CPT 35	B1	Barrel filling sheds and blending units	BTEX Butyl,propyl, methyl-benzenes Napthalene	325 40 220	520 63 352	1996
CPT 24	C3	Ethylene production plant	BTEX Naphthalene	3800 3000	6000 4800	1996
DW4	C1	LAD(Light aromatics distillation) plant, near heavy aromatics	BTEX Styrene Naphthalene	390 1360 133	6600 23200 2300	1996

Table 4.2 Areas on the site where free product was observed during excavation and/or sampling

Area	Activity	Free product	Date of observation
C4 Trial pits	Ethylbenzene/Styrene monomer site	Some product thought to be benzene	1988
D1	LDPE	Free hydrocarbons on surface of water samples	1991
D2	Carilon, Polyproylene	Free hydrocarbons on surface of water samples	1991
C2	South of Styrocell plant	Free hydrocarbons on surface of water samples	1991

In addition areas of D1 and D2 are sources of contamination because free product was observed during the sampling of groundwater in 1991. No measurements of free product thickness were reported. There are no analytical data to estimate the size of these sources.

Figures A.11-A15 (Appendix A) show Benzene, Ethylbenzene, naphthalene, styrene and total petroleum hydrocarbon (TPH) contamination measured in the soil from the fill and the upper sand and gravel during site investigations since 1988. The contamination is spread mainly over the central areas of the site B1, C1, C2 and South Western Areas C4 and C5.

Styrene is a major contaminant in the soil, although high levels of styrene were measured in only three wells on the site in the last round of sampling between 1999 and 2000 (311 -12 mg/l, DW4 S - 48 mg/l, DW4I - 1.2 mg/l) in contrast to other contaminants such as BTEX. The analysis of waters containing very high levels of benzene i.e. tens of thousands of mg/l needed high dilutions thus increasing the detection limit of other contaminants such as styrene to <0.5 or < 1mg/l. Thus styrene may be more widely spread in the groundwater than is currently reported. However much of the styrene is likely to have been immobilised in the soil due to polymerisation and may not have entered the groundwater in such high concentrations.

Figures A.16 to A.19 (Appendix A) show the presence of the major contaminants, BTEX in the ground water measured during March 2000. The elevated levels are present in the same areas as the soil contamination in B1, C1, C2 and South Western Areas C4 and C5.

Odours have been observed during the sampling of areas C4 and C5 (Table 4.3) supporting the analytical data that shows these areas are sources.

Table 4.3 Areas on the site where odours were noticed during excavation and/or sampling

Area	Activity	Odour	Date of observation
C4 Trial pit B2,B3, B5,B10, B14	styrene monomer production site	Aromatic smell - thought to be benzene, ethyl benzene,	1988
Area 20 C5	Ethylene production	Solvent smell from soil	1998

Table 4.4 Areas on the site where spillage or leaks are known to have occurred

Area	Activity	Type of release	Evidence	Date
A2	Garage area - under ground storage tanks	Spillage	Anecdotal	unknown
B1	Barrel filling sheds	Leaks	Anecdotal	1950 - 1992
D1	LDPE	Spillage of oil onto concrete	Observation	1999
D1	Area just North of LDPE	Spillage of diesel on to concrete	Observation	1999
D2	Carilon	Spillage of oil onto concrete	Observation	
B3	Detergent ethoxylate plant	Spillage of detergent onto concrete	Observation	1999
D2	Polyproylene	Spillage	Anecdotal	before 1999
C5	Crackers & gas separation plant	Spillage	Anecdotal	1967 - 1985

4.2 Potential sources

These are areas of the site where there are no analytical data or anecdotal evidence to identify a source but activities have taken place that might have caused contamination of the soil. Areas of the site with high potential to include a source are those where there has been production over periods of several years, storage of products and feed stocks. These are summarised in Table 4.7.

The activities that could have led to contamination of the site are summarised in Tables 4.5 to 4.9. Events that can result in contamination took place in the above mentioned areas:

Spillage and leaks have occurred in areas C5 and B1 (Table 4.4). Areas B1, C2, and C4 have been used for storage (Table 4.5) . Transfers of chemicals have taken place in B1 (Table 4.6).:

Table 4.5 Storage areas at Site

Table 4.6 Areas of Site where loading/unloading has taken place

Table 4.7 Location of waste transfer sites (side sumps in oily drainage system) on the site

Table 4.8 Vehicle washing areas on the site

Table 4.9 Summary of contamination source potential of site activities

A lime settling pond (now empty) was present in B3, and could have been a source of contamination with alkali.

Table 4.5 Storage areas at Site

Area	Storage	Amount (tonnes) (if known)
A2	Small quantities of chemicals such as paints, solvents and printing inks, Underground fuel storage tanks	
B1	Drum store	
B2	Initiator and product storage tanks,	
B3	Polypylene oxide storage tanks, Refrigerated ethylene oxide storage vessels Drum store containing products made in area B, Extensive product tankage	2250 900
C2	Storage and packing facilities, Risella oil and pigments storage, Tankage for styrene monomer, toluene and pentane	 6 10 360
C3	Extensive tankage for naptha feedstocks, liquified petroleum gases, toluene and crude aromatic intermediates as well as light and heavy fuel oils	Total capacity 35 000
C4	Tankage for feedstocks and products, Storage of LPGs (semi-refrigerated)	Total capacity 12 000
D2	Storage tanks, Feedstock and product tanks (above ground)	> 2000

Table 4.6 Areas of Site where loading/unloading has taken place

Area	Loading
B1	Barrel filling sheds
B2	Road car loading facilities
B3	Road tanker loading facilities
C2	Bulk loading facility

Table 4.7 Location of waste transfer sites (side sumps in oily drainage system) on the site

Area	Transfer site	Chemicals
B2 Oxide derivatives	Tank 110T	Waste polyols & detergents
NA	West Central interceptor	Waste aromatic oils
D2 Polypropylene plant	V7O4A & V704B	Waste oil
NA	West site oil catcher	Waste oil
A2 business park	Grosvenor Power Services	PCB

Table 4.8 Vehicle washing areas on the site

D2 Carilon
A2 South east of air products site
A2 Key leasing - north of site

Table 4.9 Summary of contamination source potential of site activities

Area	Activity	Source Potential
A1	No known plant, storage, facilities, contractors compounds	Low
A2	No known plant, storage, facilities, contractors compounds	low
A2	Interceptor , modern plant with concrete standing	Low to medium
A3	No known plant, storage, facilities, contractors compounds	Low
A3	East site boiler plant, contractors compound	No chemicals produced - low However, site investigation reveals elevated contamination in soil and water
B1	Barrel filling sheds and blending units	High
B2	Alkylene oxide derivatives production, chlorohydrin plant, glycols and glycol ethers	High
B3	Detergent ethoxylates, ethylene oxide storage , product tankage pilot plant, lime ponds	High
B3	East site lab	Low
B3	Contractors compound -	Low - medium
B4	Ethylene oxide production plants, workshops	Medium
C1	Resin, propylene glycol, styrene co-polymers,	High

	di-cyclopentadiene, LADU and naphthalene production	
C2	Polystyrene production, Tankage 40s & 20s	High
C3	Cracking units and gas separation plants, tankage naptha, tankage LPG	High
C3	Pump house	Low
C4	Ethylene benzene, styrene monomer plants, feedstock and product tankage	High
C5	Ethylene cracker and gas separation plant.	High
D1	Low density polyethylene production	Low - medium
D2	Polypropylene and polyolefins production	Low - medium

4.3 Groundwater plumes

BTEX

By far the major contaminants identified in the groundwater are BTEX components (Figures A16 - A19, Appendix A), followed by styrene, naphthalene and chlorinated aliphatic hydrocarbons (CAH), although the concentrations of the CAH are now very low (< 500 μg/l).

Based on the March 2000 round of sampling there are at least two plumes of BTEX, a large one emanating from the former styrene plant in the south-east corner of the site and a smaller one emanating from the tank farm (tankage 20s) in the south-west corner of the site (Figure A.10, Appendix A). The information on sources (Figure A.10, Appendix A) suggests that the larger plume is probably made up of several smaller plumes which may or may not have co-mingled. The data on dissolved methane in the groundwater (Figures B.5a-d, Appendix B) suggests that there at least two plumes making up the larger one in the upper sand and gravel.

Both plumes have penetrated the clay layer (Figures A17 - A19, Appendix A). To the best of our knowledge, this layer is continuous across the whole site, although it does get very thin in places (< 0.5 m), so it is possible the contamination has migrated through cracks in the thinner regions of the clay. Alternatively, preferential pathways may have been created through the clay during piling down to the sandstone (the site is peppered with piles) or through poor monitoring well completion.

All BTEX components are found in relatively high amounts in the groundwater in the upper sand and gravel but in the lower sand and gravel and sandstone aquifer the contamination is primarily benzene. This observation is not unusual at petroleum hydrocarbon contamination sites and is consistent with TEX biodegrading faster under anaerobic conditions than benzene. The groundwater is essentially anaerobic within the BTEX plumes.

Monitoring wells located in all four layers (upper sand and gravel, clay, lower sand and gravel and the sandstone) on all four boundaries of the site, but especially on the northern boundary (as this is the direction the groundwater is moving) are all clean (BTEX < 1ppb), indicating that none of the plumes have migrated to the boreholes on the site boundary. It should , however, be noted that the space between these monitoring wells is 150-250 metres, so a thin plume could migrate between them undetected. This is considered unlikely given the width of the co-mingled plumes in the centre of the site.

Other contaminants

Other contaminants found in the groundwater in March 2000 include: tri-methyl benzenes in the ppb range (Figures A.20 - A.23, Appendix A), naphthalene (Figures A.24 - A.27, Appendix A), styrene (Figures A.28 - A.31, Appendix A) and CAH (Figures A32 - A35), but there is no evidence to suggest that these chemicals are present in the Sandstone aquifer in significant concentrations.

4.4 Identification of plausible exposure scenarios

Potential receptors at or in the vicinity of the site are river a, canal a, the sandstone aquifer, the minor aquifers beyond the site boundary and on-site workers (the site will continue to operate as a chemical manufacturing plant for the foreseeable future). potential exposure routes for on-site workers are either via inhalation of vapours emanating from the soil or groundwater or direct contact during site excavation. at petrochemical facilities operator exposure to vapours emanating from above ground plant, far outweigh those from exposure to vapours emanating from the sub-surface. exposure of workers by direct contact during site excavation can be managed by use of personal protective equipment. therefore, the receptors most at risk from contamination at the site are river a, canal a and the sandstone aquifer via migration of contaminants in the groundwater. consequently, work has focused on the groundwater pathway and the sandstone aquifer and surface water receptors.

5. GROUNDWATER GEOCHEMISTRY AND EVIDENCE FOR NATURAL ATTENUATION

5.1 Field measurements

Temperature, pH, dissolved oxygen, conductivity and oxidation-reduction potential were measured on site using a flow through cell (Well Wizard). In addition, dissolved oxygen and Fe(II) were measured in selected wells using colorimetric test kits (Hach) for comparative purposes. This is particularly important for Fe(II), given the rapid changes that can take place in iron speciation between sampling and laboratory analysis if the time delay is too long.

Groundwater temperature ranged from 8.0°C to 12.7°C, with the average being 10°C (Table B.1, Appendix B).

Across the majority of the site the pH of the groundwater is in the range pH 6-8 (Table B.1, Figure B.1a-d, Appendix B), but there are discrete regions where the groundwater is quite acidic (pH 3.9-5.7) and highly alkaline (pH 9.4-14). One (but by no means the only) source of this alkalinity is likely to be the lime ponds in area B3. The acidic pHs could be due to the presence of peat, as the boreholes from which these samples came are located in the south-west corner of the site close to the site boundary where there are natural peat deposits.

Conductivity of the groundwater in the upper sand and gravel in general ranged from 187µS/cm to 887 µS/cm, with two higher values of 1880 µS/cm and 4365 µS/cm, corresponding to wells whose pH was 11.9 and 14 respectively (Table B.1, Appendix B) . Conductivity in the clay ranged from 238 µS/cm to 348 µS/cm with one exceptional value of 1140 µS/cm which was not associated with an extreme pH. Conductivity in the lower sand and gravel generally ranged from 400 µS/cm to 658 µS/cm, with four much higher values which corresponded to samples with high pH: 5728 µS/cm at W12D (pH 14), 2311 µS/cm at W13D (pH 13.5), 1175 µS/cm at W5D (pH 14)and 5190 µS/cm at W9D (pH 13.5).

Dissolved oxygen (DO) in the groundwater in the upper sand and gravel is generally < 2 mg/l across the centre of the site (Table B.1 and Figure B.2a-d, appendix B) with higher concentrations on the periphery (up to 10.7 mg/l in W4S). DO in the clay layer is < 1.7 mg/l apart from at W19I on the northern boundary where the concentration was 3.1 mg/l. DO in the groundwater in the lower sand and gravel is < 1.5 mg/l, apart from three locations, W12D (3.5 mg/l) and W9D (5.5 mg/l) on the northern boundary and W5D (3.2 mg/l) on the southern boundary. DO in the sandstone aquifer is < 1.1 mg/l, even on the upstream boundary of the site. So although there may be some aerated water coming onto the site to support some aerobic biodegradation of contaminants in the upper groundwater, there appears to be little dissolved oxygen coming onto the site to support aerobic biodegradation of contaminants in the sandstone aquifer.

Oxidation reduction potential (ORP) in the groundwater in the upper sand and gravel ranges from +118 mv to –188 mV, with the higher positive values being in the more oxygenated periphery of the site (Table B.1, Appendix B). ORP in the clay layer ranged from -27 mV to –74 mV. ORP in the groundwater in the lower sand and gravel ranged from -13 mV to -203 mV. ORP in the sandstone aquifer ranged from +6 mV to -230 mV. In general the ORP measurements confirm the observations resulting from measurements of dissolved oxygen and other electron acceptors (see section 5.4).

5.2 Major ions

Chloride ion levels in the groundwater were similar in all four layers and in general ranged from 6 - 150 mg/l, with the majority being < 100 mg/l (Table B.2, Appendix B). There were however, three exceptionally high values in wells W18D (370 mg/l) in the upper sand and gravel, 308I (204 mg/l) in the clay and W13D (220 mg/l) in the lower sand and gravel. The groundwater pH in these three wells was 14, 9.9 and 13.5 respectively.
There was no correlation between the concentrations of chloride and chlorinated hydrocarbons in the groundwater. Indeed, the concentrations of chloride in the groundwater across the site are such that any chloride release from chlorinated hydrocarbon biodegradation would most likely be masked by the high background. No off-site measurements of chloride in groundwater upstream of the site have been made, but monitoring wells on the southern boundary of the site (eg. W16S, 305, W5S, W5I) may well be representative of water quality entering the site. They contained 10-33 mg/l chloride.

The concentrations of calcium ions in the groundwater were similar in all four layers and in general ranged from 12 - 140 mg/l with the majority being <100 mg/l (Table B.2, Appendix B). There were however, four exceptionally high values in wells W18D (494 mg/l) in the upper sand and gravel, W14D (270 mg/l) in the clay, W12D (614 mg/l) and W13D (657 mg/l) in the lower sand and gravel. The groundwater pH in these four wells was 14, 9.9, 14 and 13.5 respectively.

The concentrations of magnesium ions in the groundwater were similar in all four layers and ranged from 0.1 - 32 mg/l, with the majority being less than 10 mg/l (Table B.2, Appendix B).

The concentrations of sodium ions in the groundwater were similar in all four layers and in general ranged from 5 - 124 mg/l with the majority being < 50 mg/l (Table B.2, Appendix B). There were however, four exceptionally high values in wells 308S (609 mg/l) and W18I (208 mg/l) in the upper sand and gravel, 308I (644 mg/l) in the clay and W5D (204 mg/l) in the lower sand and gravel. The groundwater pH in these four wells was 11.9, 9.4, 9.9 and 14 respectively.

The concentrations of potassium ions in the groundwater were similar in all four layers and in general ranged from 1 - 23 mg/l, with the majority being < 10 mg/l (Table B.2, Appendix B). There were however three exceptionally high values in wells 309S (40 mg/l) in the upper sand and gravel, and W13D (33 mg/l) and W5D (118 mg/l) in the lower sand and gravel. The groundwater pH in these three wells was 7.9, 13.5 and 14 respectively.

The concentration of aluminium ions in the groundwater were similar in all four layers and in general was < 1 mg/l, with the majority being < 0.01 mg/l (Table B.2, Appendix B). There were however two exceptionally high values in wells 308S (2.12 mg/l) in the upper sand and gravel and 308I (3.15 mg/l) in the clay. The groundwater pH in these two wells was 11.9 and 9.9 respectively.

5.3 Organic carbon and solids content

Total organic carbon (TOC) in groundwater ranged from 3 - 47 mg/l (with one exceptionally high value of 140 mg/l in well 308S) in the upper sand and gravel, 3-29 mg/l (with one exceptionally high value of 180 mg/l in well 308I) in the clay layer, 4-26 mg/l in the lower sand and gravel and from 4-18 mg/l in the sandstone (Table B.3, Appendix B).

In general total dissolved organic carbon (TDOC) values were very similar to TOC values. TDOC in groundwater ranged from 3 - 40 mg/l (with one exceptionally high value of 110 mg/l in well 308S) in the upper sand and gravel, 3-25 mg/l (with one exceptionally high value of 150 mg/l in well 308I) in the clay layer, 4-26 mg/l in the lower sand and gravel and from 4-18 mg/l in the sandstone (Table B.3, Appendix B). Wells 308S and 308I are located in the centre of the site and contain 18 mg/l and 21 mg/l BTEX respectively. There is clearly some additional dissolved phase relatively non volatile organic contamination at location 308 other than BTEX.

Total dissolved solids (TDS) in groundwater ranged from 187 - 646 mg/l (with two exceptionally high values of 1700 and 1740 mg/l at 308S and W18D respectively) in the upper sand and gravel, 192 - 830 mg/l (with one exceptionally high value of 3140 mg/l at 308I) in the clay, 193 - 778 mg/l (with two exceptionally high values of 1440 and 1760 mg/l at W12D and W13D respectively) in the lower sand and gravel and from 340 - 614 mg/l (with one exceptionally high value of 10500 mg/l at well 302 (Table B.3, Appendix B). All the groundwater samples with exceptionally high TDS have pHs > 10 with one exception, well 302 which has a pH of 8.5.

Total suspended solids (TSS) was measured as it is a useful indicator of the “cleanliness” of a groundwater samples and can be helpful in understanding outlying data points. It ranged from 0.048 - 312 g/l, with the majority < 10 g/l (Table B3, Appendix B)

5.4 Electron acceptors and products

Nitrate concentrations in the groundwater of all four layers are in general very low (< 1 mg/l NO3-N), throughout the site (Table B.4, Appendix B). Only 13 (10 in layer 1 and three in layer 3) of the 76 wells had NO3-N concentrations > 1 mg/l (ranging from 1.2 mg/l to 12 mg/l) and these tend to be scattered around the site. Nitrate is unlikely to be a significant electron acceptor for anaerobic biodegradation of organic contaminants as concentrations coming onto the site are very low.

Fe (II) concentrations in the groundwater of all four layers are typically < 1.5 mg/l across the site with the majority being < 0.5 mg/l (Table B.4, Appendix B). The only exception is the perimeter monitoring well in the upper sand and gravel (W5S) on the southern boundary of the site where the concentration is 5.7 mg/l. It therefore appears that Fe(III) is not acting as a significant electron acceptor for anaerobic biodegradation of organic contaminants, although the potential may well be there in parts of the site as eight of the wells had total dissolved phase iron concentrations ranging from 6.1 mg/l to 62.3 mg/l. The high values are not artefacts of acidification of “dirty” groundwater samples, solublising iron, because the samples were filtered on-site before acidification and there is no correlation between groundwater samples with high total dissolved phase total iron and high suspended solids content.

It has been suggested that the Fe(II) concentrations are surprisingly low. It is possible that some oxidation took place between sampling and analysis, although measures were taken to minimise this. Comparison of the Fe(II) laboratory data with that derived using the Hach field test kit shows that the latter consistently gave higher values than the former by at least an order of magnitude (Table B.5, Appendix B). This suggests that Fe(III) reduction driven contaminant degradation is a possibility in parts of the site.

It is clear that the methodology for iron speciation in groundwater requires further evaluation. This will form one of the first SIREN projects and will be carried out by the University of Leeds. The project will evaluate a method that has been developed for speciating inorganic and organic forms of iron.

The data for Mn(II) are very similar to that for Fe(II). Mn (II) concentrations in the groundwater of all four layers are typically < 1.5 mg/l across the site with the majority being < 1 mg/l (T able B.4, Appendix B). The only exception is the perimeter monitoring well in the upper sand and gravel (W12I) close to the northern boundary of the site where the concentration is 6 mg/l. It therefore appears that Mn(IV) is not acting as a significant electron acceptor for anaerobic biodegradation of organic contaminants. Total dissolved phase manganese was little different from Mn(II).

There is good evidence for sulphate reduction driven anaerobic BTEX biodegradation in the sandstone (Table B.4 and Figures B.3a-d, Appendix B). Upstream sulphate concentrations in wells W6D and W7D on the southern boundary of the site which are free of BTEX (< 1 μg/l) are 178 mg/l and 186 mg/l sulphate-sulphur (SO4-S) respectively, whereas in well 309D where there are 2360 μg/l BTEX, the SO4-S concentration falls to 3 mg/l.

The situation is less clear in the lower sand and gravel. The upstream concentration of SO4-S in well W5D is 189 mg/l. Concentrations across the site are generally much lower (1-72 mg/l with the majority being < 15 mg/l). Low sulphate does not correlate with high BTEX.

There is no clear inverse correlation between sulphate and BTEX in the groundwater of the upper sand and gravel.

There is good evidence for methanogenic driven BTEX biodegradation in the groundwater of all four layers. High dissolved methane levels correlate well with high BTEX (Figure 5.1 and Table B.4, Appendix B). Dissolved methane ranges from 3 - 29 mg/l in the presence of high BTEX, whereas it is generally < 1 mg/l in the absence of BTEX and < 0.1 mg/l in 50% of the wells (Figure B.4a-d, Appendix B).

There is no correlation between dissolved carbon dioxide (1-168 mg/l) and BTEX in the groundwater (Table B.4, Appendix B).

There is no correlation between alkalinity and BTEX (Table B.4, Appendix B). Alkalinity ranged from 50 - 1510 mg/l with the majority of the values falling in the range 100 - 500 mg/l.

5.5 Breakdown products of BTEX and CAH biodegradation

Anaerobic breakdown products of BTEX biodegradation (eg. phenols and cresols) were below the limit of detection in the vast majority of the wells (Table B.6, Appendix B). Only five out of the 18 wells which contained > 10 µg/l BTEX, contained detectable levels of phenol (DW3S, W17I, W18I, DW3D and 309D) in the range 100-300 µg/l, which is just above the limit of detection of 100 µg/l. The first three are in the upper sand and gravel and the last two are in the lower sand and gravel and sandstone respectively. These five wells did, however, contain some of the highest levels of BTEX in their respective layers. Cresol was detected in only one well (DW3S in the upper sand and gravel) at 200 µg/l (detection limit 100 µg/l). It is clear that the detection limit for anaerobic products of BTEX biodegradation is currently unsatisfactory and needs reducing by at least one order of magnitude if further studies are to be done in this area.

Breakdown products of CAH (vinyl chloride, ethene and ethane) were detected in several wells (Table B.6, Appendix B).

Vinyl chloride was detected DW2I and W10I in the upper sand and gravel at 21 µg/l and 44 µg/l respectively. These two wells also contained ethane at 101 µg/l and 11 µg/l and CAH at 239 µg/l and 106 µg/l respectively.

Ethane was detected in nine additional wells (eight in the upper sand and gravel and one in the clay) at concentrations ranging from 11-31 µg/l.

Ethene was only detected in two wells both in the upper sand and gravel, 311 (12 µg/l) and W8I (10 µg/l). The former contained 110 µg/l CAH and 30 µg/l ethane, but vinyl chloride was not detectable.

These observations confirm that biodegradation of CAH is taking place at the site naturally. Indeed, reductions in CAH concentration over the last 5 years have been so great that the current concentrations (3 - 519 µg/l) are really too low to develop a project on in situ MNA of CAH at the site, although the possibility of higher concentrations in parts of the site where there are no monitoring wells cannot be ruled out.

Ten of the 13 wells showing good evidence for this have groundwater pH in the range 6.9 - 7.8. although three wells containing ethane have groundwater with pHs of 9.9, 11.9 and 13.5.

Breakdown products of other confirmed contaminants such as styrene and naphthalene and potential contaminants such as polyolefins were not analysed.

Figure 5.1: Correlation between methane and BTEX in groundwater

5.6 Historical trends in BTEX and CAH

Of the 76 monitoring wells, 37 have contained BTEX at some time over the period 1995-2000 (Table B.7, Appendix B). In 25 of these 37 wells, BTEX concentrations have declined over time, to non detect in 17 of the less highly contaminated wells with initial concentrations < 20,000 µg/l and by 50-95% in the more heavily contaminated wells. Two wells, DW4I and W18D in the upper sand and gravel, have shown increasing concentrations from 1996 to 1999 which have continued increasing in 2000. Another two wells 308I in the clay and 309D in the sandstone have shown increasing concentrations during the three monitoring events which took place in between December 1999 and March 2000. Eight wells are showing no discernible trend in BTEX concentrations over time.

Of the 25 wells where BTEX concentrations have declined or are declining three have groundwater pHs which would not be generally considered favourable for biodegradation namely 308S (pH 11.9), W18I (pH 9.4) and DWID (pH 10.2). The site does therefore offer the potential to study MNA of BTEX in highly alkaline groundwater.

While the reductions in BTEX concentrations on their own do not necessarily conclusively prove that biodegradation is taking place naturally at the site, when coupled with the electron acceptor/product data discussed above and the results of laboratory microcosm studies (carried out by Shell Global Solutions - data to be included in a future report) on BTEX contaminated groundwater from the site, this combined information supports the theory.

Of the 76 monitoring wells, 15 have contained CAH at some time over the period 1995-2000 (Table B.8, Appendix B). In 6 of these 15 wells, CAH concentrations have declined over time, to non detect in 3 of the less highly contaminated wells with initial concentrations < 18 µg/l and by 50-70% in the more heavily contaminated wells. Two wells, W11S and W11I in the upper sand and gravel, have shown increasing concentrations from 1996 to 2000 (4 µg/l to 112 µg/l and 133 µg/l to 519 µg/l respectively. Seven wells are showing no discernible trend in CAH concentrations over time.

Note that the high concentrations of 1,2-dichloroethane (1,2-DCA) in the groundwater from the 1996 round of sampling reported in the SIREN Phase 1 report (Towler et al, 2000) are artefacts of the laboratory analysis, due to interference from high concentrations of benzene.

WHILE THE REDUCTIONS IN CAH CONCENTRATIONS ON THEIR OWN DO NOT NECESSARILY CONCLUSIVELY PROVE THAT BIODEGRADATION IS TAKING PLACE NATURALLY AT THE SITE, THE PRESENCE OF INTERMEDIATES IN THE BREAKDOWN OF CAH (VINYL CHLORIDE, ETHENE AND ETHANE) STRONGLY INDICATE THAT IT IS TAKING PLACE.

6. GROUNDWATER MODEL CONSTRUCTION

The purpose of the groundwater model is to:

- aid understanding of the groundwater flow system
- determine groundwater flow paths
- evaluate contaminant plume migration and predict future behaviour

6.1 Software

The software used for this project was the Groundwater Modelling System (GMS) developed by the Engineering Computer Graphics Laboratory of Brigham Young University in Partnership with the U.S Army Engineer Waterways Experiment Station. The GMS system comprises of a graphical user interface and the analysis codes for MODFLOW, MODPATH and RT3D.

MODFLOW is a modular three dimensional finite-difference groundwater model. Due to source code being freely available it has become the industrial standard for groundwater modelling.

MODPATH is a particle tracking post processing program that was developed to compute three-dimensional flow paths using outputs from steady-state or transient groundwater flow simulations by MODFLOW.

RT3D (Reactive Transport in 3-Dimensional) is computer code that solves the coupled partial differential equations that describe reactive-flow and transport of multiple mobile and/or immobile species in MODFLOW.

More information on GMS and the associated models is available on the Environmental Modelling Systems Incorporated webpage on www.ems-i.com.

6.2 Boundary Conditions

In order to construct a groundwater model, catchment area and boundaries have to be defined. An aquifer boundary is usually defined by groundwater divides, water bodies (rivers lakes or coast line), hill or ridge line. It is reasonable to assume that the underlying groundwater contours reflect the surface relief, albeit somewhat mutedly.

The site area is bounded on three sides by rivers. The River A on the north, then River A joins the Canal A which flows on the western boundary and the River B flows along the southern boundary. These were used for three of the boundaries.

For the eastern boundary, the Canal B was selected. This may not be a groundwater divide, but as it is a reasonable distance (~4km) from the site it should not affect the local model. (Figure C.1, Appendix C).

By using rivers as the boundaries this effectively simulates the flow of water into and out of the model. The flow is a factor of the difference between the stage of the river and the head in the adjoining cells. When the head in the adjoining cell is greater than the river stage, water flows into the river and when the river stage is higher than the head in the adjoining cell water flows into the cell. The amount of water that flows between the river cells and adjoining cells is limited by the conductance term. The conductance term is discussed in more detail in section 6.5.

6.3 Model Discretisation

In MODFLOW each layer is divided up into cells of which the water balance is solved for each cell. A cell is usually the depth of a layer in the model but the width can be of any dimension as long as it is not more than twice the width of the neighbouring cells. Here the cells widths in the x and y directions are 100m by 100m.

6.4 Aquifer Properties

Rising head tests were carried out on the different stratagraphic units to determine their hydraulic conductivity. The results are shown in Tables 6.1 a-d . Rising head tests give highly variable results from one well to another and can be greatly influenced by well construction. Here the field test results have been compared with standard published data from the BGS/EA Major Aquifer Properties Manual (Allen et al, 1997) and Freeze and Cherry (1979) to check that the field values are within a realistic range.

Table 6.1a: Rising head test for Layer 1, upper sand and gravel

Borehole	Strata	Mid depth of screen (m)	Rising head test (y/n)	Hydraulic conductivity (m/s)
307(S)	Sand	3.5	y	6.00E-05
308(S)	Sand	5	y	4.00E-05
309(S)	Sand	4.5	y	2.10E-05
310	Sand	2.5	y	3.50E-05
311	Sand	3	y	1.40E-06
DW2(I)	Sand	4	y	1.52E-05
DW4(I)	Sand	5	y	9.93E-05
W1(I)	Sand	2.5	y	1.60E-04
W2(D)	Sand	4	y	1.84E-05
W4(I)	Sand	6	y	9.93E-05
W5(S)	Sand	2	y	6.10E-05
W6(S)	Sand	2	y	3.56E-05
W7(I)	Sand	2	y	2.85E-04
W10(I)	Sand	2	y	1.19E-04
W11(I)	Sand	2.5	y	3.56E-05
DW1(S)	Sand	4	y	1.38E-04

Table 6.1b: Rising head test for Layer 2, clay layer

Borehole	Strata	Mid depth of screen (m)	Rising head test (y/n)	Hydraulic conductivity (m/s)
308(I)	Clay (lamin)	19	y	3.60E-08

Table 6.1c: Rising head test for Layer 3, lower sand and gravel

Borehole	Strata	Mid depth of screen (m)	Rising head test (y/n)	Hydraulic conductivity (m/s)
304	Gravel	32	y	5.30E-07
309(I)	Gravel	26.5	y	1.20E-06
DW3(D)	Gravel	6.5	y	1.02E-04

Table 6.1d: Rising head test for Layer 4, sandstone

Borehole	Strata	Mid depth of screen (m)	Rising head test (y/n)	Hydraulic conductivity (m/s)
301	S/Stone	18.5	y	2.60E-07
302	S/Stone	21	y	1.10E-05
303	S/Stone	43	y	5.30E-08
305	S/Stone	15	y	1.70E-07
307(D)	S/Stone	14	y	9.10E-08
309(D)	S/Stone	30.5	y	2.10E-05

Hydraulic Conductivity (horizontal)

Layer 1

Layer 1 is the top sands and gravels. This layer has been described as a coarse sand in some boreholes and as sands and gravels in others. Therefore the results of the rising head test have been compared to a course sand from published data. As they compare favourably the mode of the data set was used as the starting hydraulic conductivity in the aquifer. The hydraulic conductivity for the top sands and gravels used in the model was 5E-5 m/s (4.3 m/d).

Layer 2

Between the two layers of sand and gravels is a confining layer of clay. There are small lenses of sands and gravels within the clay, but for the purpose of the model it has been assumed that the clay is continuous in both the horizontal and vertical direction. There has only been one rising head test carried out on the clay layer, which is higher than the range in the published data. This is most likely due to the influence of the sand and gravel lenses within the clay. So for the purpose of the model the test value will be used. The starting hydraulic conductivity for the clay used in the model was 3.6E-8 m/s (0.003 m/d).

Layer 3

Layer 3 is the second layer of sand and gravels. Once again the results have been compared to a coarse sand in the published data. As they compare favourably the mode will be used. This is a small highly variable data set, but as this is the only data available and it is within a realistic range this is the best option. The starting hydraulic conductivity for the second layer of sand and gravels used in the model was 1.2E-6 m/s (0.10 m/d).

Layer 4

Layer 4 is the sandstone underlying the whole site, this has been classed by the Environment Agency as a major aquifer. Once again the data are field test data are highly variable (ranging from 0.0046 to 1.8 m/d) and two of the test results lie outside the range of the published data (8.64×10^{-5} to 8.64 m/d) . However the mode of the test data set lies within the published range (MAP Manual - Allen et al, 1997 and Freeze and Cherry, 1979) and was therefore used. The starting hydraulic conductivity for the sandstone used in the model was 2.15E-7m/s (0.018 m/d).

Since the mode of the field test results falls at the low end of the published values (MAP Manual - Allen et al, 1997 and Freeze and Cherry, 1979) the former are believable and hence were used in the absence of better data. A possible explanation for the difference between the field test results and data in the MAP Manual (Allen et al, 1997) could be that the monitoring wells tested are installed in the upper sandstone and represent point measurements which likely represent bulk sandstone. The MAP Manual (Allen et al, 1997) values may be the result of aquifer testing of abstraction wells screening a greater thickness of sandstone which is likely to be influenced by secondary porosity (layers, fractures) resulting in higher K values. It is intended to perform aquifer testing in phase 2b to obtain better k values for the site. The modelling performed for phase 2a incorporates the uncertainty of the K values within the calibration and sensitivity analysis.

Hydraulic Conductivity (vertical)

For starting vertical hydraulic conductivity 1/5 of the horizontal conductivity was used.

Porosity

No field porosity data is available so the following generic values were used (Freeze and Cherry 1979):

Top sand and gravel:	0.35
Clay:	0.50
Second sand and gravel:	0.30

Sandstone	0.20

6.5 Water Budget

Recharge

Recharge is difficult to predict accurately, as it depends on the following three highly variable attributes

- climatological data, i.e. sunshine hours, rainfall, windspeed, humidity,
- site morphology, i.e. rolling, flat, aspect, vegetation type,
- soil characteristics, i.e. porosity, soil type,

There is a range of methods to determine recharge which are outlined in the API's "Estimate of Infiltration and Recharge for Environmental Site Assessment" manual. Due to limited field data the best option for the site is to use average recharge figures (in percentage rainfall) from predetermined tables. Taking information from the tables in the API manual recharge for the site should be in the order of 10-15 percent of rainfall. With average yearly rainfall being 840mm/yr this leaves a recharge of between 84 and 126 mm/year. The lower value of 84 mm/yr (0.000230 m/d) was used over the built-up areas and the higher value of 126mm/yr (0.000345 m/d) was used over the agricultural land. There are two main reasons for this: firstly for the built-up areas the increase in solid surfaces (i.e. roads and roofs) decreases the amount of runoff reaching layer 1 of the model and secondly the agricultural land surrounding the site contains many drains, due to the shallow groundwater, which increases runoff.

Groundwater Abstractions

Enquiries with the Environment Agency located two abstraction wells within the area of the model. These are J Priesner (grid reference SJ 3728 3892) which is licensed to abstract 10Ml/yr and H Booth and Son (grid reference SJ 3723 3906) which is licensed to abstract 15Ml/yr. Attempts to obtain information on unlicensed abstractions from the Local Authority have so far proved unsuccessful.

Rivers and Canals

Groundwater either flows into or out of a river or canal and they, especially rivers, are usually the main controlling influence on a groundwater system. The following rivers and canals are within the site model area or are located on a boundary:

- Canal A,
- River A,
- Canal B,
- River B,
- Brook A,
- Unnamed tributary of Brook A

MODFLOW requires the following parameters,

: stage, this is the elevation of the water surface in the river or channel.

: bed elevation, is the elevation of the River bed,

: streambed conductance, which is a factor of the width (W) of the River bed, the thickness (M) of the River bed and length (L) of the stream reach in the cell and the hydraulic conductivity (K) of the steam bed.

Conductance is the controlling factor for the amount of water that flows into or out of a river cell and is significantly dependent on the hydraulic conductivity term, (Figure 6.1).

Conductance is defined as::

$$\boxed{\text{Conductance} = \frac{KxLxW}{M}}$$

this equation should be used when the cell head is greater than or equal to the bed elevation, where the cell head is below the bed elevation the following equation should be used;

$$\boxed{\text{Conductance} = \frac{KxLxW}{(\text{Head}_{\text{river}}\text{-River Bot elevation})}}$$

For River A, Canal A River B and the Brook A the first conductance equation, where the cell head should be above the bed elevation was used, but for the Canal B the second equation was used. The following conductance's were calculated for the total length of each of the rivers and canals in the model, (in brackets is the conductance term per meter).

Table 6.2 summarises the values used for each river and their conductance, it also includes the Brook A and its tributary as for the boundaries the conductance value is also required.

Table 6.2: Parameters and conductance terms used for each river

Parameter	River A	Canal A	River B	Canal B	Brook A + Tributary
K of bed material	2E-6 m/s	2E-9 m/s	2E-6 m/s	2E-10 m/s	2E-6 m/s
Length (L)	12,483m	3,829m	6,028m	9,578m	8,905m
Thickness (M)	0.5m	1m	0.5m	-	0.5m
Width (W)	25m	75m	5m	5m	2m
Head $_{\text{river}}$	-	-	-	28m	-
River A bottom Elevation	-	-	-	26m	-
Conductance	**107853 m^2/d (8.64m^2 $/d/m^{-1}$)**	**117 m^2/d (3.05E-2 m^2 $/d/m^{-1}$)**	**10,416 m^2/d (1.7m^2 $/d/m^{-1}$)**	**0.41m^2/d (4.3E-5 m^2 $/d/m^{-1}$)**	**6,155 m^2/d (0.69m^2 $/d/m^{-1}$)**

6.6 Model Calibration

Calibration of a model is an essential step in the modelling process and is necessary to do before predictive modelling can proceed. Calibration is the process of adjusting model inputs within reasonable ranges until output agrees well with known data from the field.

Calibration Parameters

Table 6.3 contains the parameters which where altered during the calibration process. For this model the “trial and error” approach was used. i.e. a parameter was changed, the model was rerun and the modelled heads were statistically compared with the observed heads, this was carried out until acceptable results were achieved. In this case an acceptable result was considered to be less than 0.5m difference in heads (modelled vs observed) and less than 1% discrepancy between inputs into the model and outputs from the model.

Figure 6.1: Schematic explaining the conductance of river/canal sediments

Table 6.3 Parameters and their ranges which were altered in calibration

Hydraulic Conductivity (horizontal)	**Ranges**
■ Top sand and gravel ■ Clay ■ Gravel and sand ■ Sandstone	10^{-1} to 10^{3} m/d 10^{-7} to 10^{-3} m/d 10^{-1} to 10^{3} m/d 10^{-5} to 1 m/d
Recharge	0% to 15% of rainfall
Conductance, (varied the hydraulic conductivity of the bed material value in the conductance equations)	
	Ranges of Conductance
■ River A	8.64 to 0.864 $m^2/d/m^{-1}$
■ Canal A	3.05E-1 to 3.05E-3 $m^2/d/m^{-1}$
■ River B	17.0 to 0.17 $m^2/d/m^{-1}$
■ Brook. A	6.9 to 0.069 $m^2/d/m^{-1}$
■ Canal B	4.3E-4 to 4.3E-6 $m^2/d/m^{-1}$

Figure 6.2 shows the statistical output of the final comparison. Each of the parameters had predetermined ranges and it was decided that during the calibration process that it was unacceptable to go outside these ranges.

Figure 6.2: Error summary of final calibration of groundwater model

After the calibration process the parameters in Table 6.4 were selected for predictive modelling .

Table 6.4 Parameters and their values used in the modelling

Hydraulic Conductivity (horizontal)	**Value**
Top Sand and Gravel	21.6 m/d
Clay	0.03 m/d
Second Sand and Gravel	0.10 m/d
Sandstone	0.002 m/d
Hydraulic Conductivity (vertical)	**Value**
Top Sand and Gravel	0.43 m/d
Clay	0.006 m/d
Second Sand and Gravel	0.021 m/d
Sandstone	0.0004 m/d
Recharge	**Value**
Areal Recharge	0.0002 m/d *
Conductance	**Value**
River A	8.6 $(m^2/d)/m$
Canal A	0.30 $(m^2/d)/m$
River B	0.17 $(m^2/d)/m$
Brook A	0.069 $(m^2/d)/m$
Canal B	0.00004 $(m^2/d)/m$

* in the calibration process the two zones of recharge were removed and it was decided to have uniform recharge over the whole of the regional model.

6.7 Summary of Water Balance

A water balance of a model simply states that the inputs into a model should equal the outputs. For this model the inputs are: recharge and inputs from the rivers and the outputs are: groundwater abstractions and losses to the rivers.

RECHARGE - GROUNDWATER ABSTRACTIONS = RIVERS (+or-)

Inputs

Total Recharge = Area x Recharge

= 38425899 m^2 x 0.0002 m/d

= 7516 m^3/d

Outputs

Well Abstractions = 68 m^3/d

Therefore the predicted loss of water to rivers = 7516 - 68 = 7448 m^3/d

From the constructed groundwater model the sum of water into or out of all the rivers is the total amount out of the model from river leakage minus the amount of flow into the model from river leakage, which is 7819 m^3/d (Table 6.5).

Table 6.5 Water balance from calibrated groundwater model

IN	**m^3/day**
STORAGE =	0
CONSTANT HEAD =	0
WELLS =	0
RECHARGE =	7920.7
RIVER LEAKAGE =	736.04
TOTAL IN =	8660.7
OUT	
STORAGE =	0
CONSTANT HEAD =	0
WELLS =	68.000
RECHARGE =	0
RIVER LEAKAGE =	8555.1
TOTAL OUT =	8623.1
IN - OUT =	37.593
PERCENT DISCREPANCY =	0.44

6.8 Sensitivity Analysis

A sensitivity analysis was performed on the model to evaluate the impact of the uncertainty of particular key model parameters. The two most sensitive parameters, hydraulic conductivity and recharge, were varied over a broad range considered to encompass, if not exceed their uncertainty.

A total of 10 additional runs were performed, including particle tracking for each case. The cases were:

Hydraulic conductivity increased by a factor of 10 for each layer

Hydraulic conductivity decreased by a factor of 10 for each layer

Recharge doubled

Recharge reduced by 50%

Table 6.6 and Figures 6.3 a-e summarise the sensitivity test and Figures C2.a to C.2j (Appendix C) contain the output from the particle tracking for each of the runs carried out for the sensitivity tests. The sensitivity test shows that the model is most sensitive to the hydraulic conductivity in the clay layer (layer 2) and the recharge.

Table 6.6 : Table summarising the results of the sensitivity testing of the groundwater model

Value Changes	**Change**	**Heads**	**Mean error**	**Discrepancy**	**Min travel time**	**Max Travel Time**
Solution			0.11	0.44	1.72×10^3	1.69×10^4
K in Top Sand and Gravel (layer 1)	Increase by a factor of 10	decrease	-0.29	-42.95	2.8×10^2	1.25×10^3
K in Clay (layer 2)	Increase by a factor of 10	increase	9.46	-161.25	4.35×10^2	1.03×10^3
K in Second Sand and Gravel (layer 3)	Increase by a factor of 10	no change	0.11	2.19	1.72×10^3	8.88×10^3
K in Sandstone (layer 4)	Increase by a factor of 10	decrease	-0.10	-2.76	1.9×10^3	6.95×10^6
K in Top Sand and Gravel (layer 1)	Decrease by a factor of 10	increase	5.13	4.10	6.71×10^3	8.54×10^5
K in Clay (layer 2)	Decrease by a factor of 10	increase	0.37	-7.30	1.55×10^3	1.04×10^4
K in Second Sand and Gravel (layer 3)	Decrease by a factor of 10	increase	0.12	-6.84	1.69×10^3	9.14×10^6
K in Sandstone (layer 4)	Decrease by a factor of 10	increase	0.25	-3.58	1.69×10^3	8.13×10^3
Recharge	Doubled	increase	1.79	18.79	1.13×10^3	1.67×10^5
Recharge	Halved	decrease	-0.97	-44.60	3.3×10^3	9.5×10^3

Figure 6.3a: Graph showing changes mean error with changes in hydraulic conductivity in layer 1

Figure 6.3b: Graph showing changes mean error with changes in hydraulic conductivity in layer 2.

Figure 6.3c: Graph showing changes mean error with changes in hydraulic conductivity in layer 3

Figure 6.3d: Graph showing changes mean error with changes in hydraulic conductivity in layer 4

Figure 6.3e: Graph showing changes in mean error with changes in hydraulic conductivity in recharge

Sensitivity of model predictions

Groundwater flowpaths

Head values are fairly insensitive to changes in K and the heads are mostly influenced by boundary conditions and recharge. By matching the measured heads and using regional boundaries, flow directions within the model should be very reliable. Thus particle tracking should give a very reliable indication of the migration pathways from sources to potential receptors.

Groundwater velocity

The migration rates of modelled plumes will be influenced by groundwater velocity. The particle tracking sensitivity analysis shows that the migration rates of water particles along the flowpaths to vary from:

Layer 1: 6 to 14.5 years
Layer 2: 4932 to 8219 years
Layer 3: 1233 to 7397 years
Layer 4: 38,356 to 79,452 years

Thus the timeframe for conservative contaminants to migrate across the site could vary considerably from 6 to 79,452 years and the fastest value should be used for evaluating potential impacts to receptors from these contaminants. To improve these estimates, aquifer testing and/or tracers could be used to reduce the uncertainty of these parameters.

Plume migration

For non-conservative contaminants other factors besides groundwater velocity are important for predicting plume migration. These factors include loss mechanisms (i.e. biodegradation) and retardation. For contaminants with high biodegradation rates (e.g. benzene) the results of plume simulations are mostly controlled by the biodegradation rate which dominates over the aquifer hydraulics. Thus, by using a conservative decay rate (0.01 per day) and constant source terms, the benzene plume simulations should provide a conservative and realistic estimate of the maximum benzene plume migration length and associated time frame to reach stability.

To confirm that decay rate was the controlling factor for plume migration, a simulation was carried out with the hydraulic conductivity in the top layer ten times that used in the calibrated model. The resulting plume was the same length as that in the calibrated model Figure D8, Appendix D).

For contaminants with low biodegradation rates (e.g. chlorinated VOCs), the plume migration is controlled by a combination of retardation and aquifer hydraulics which vary depending on the properties of each layer. The plume migration rates for these contaminants should be slower than the fastest particle tracking time-frames above. There is also great uncertainty in predicting the maximum plume lengths. To produce realistic simulations for these types of contaminants further study is required to collect site specific data on transport properties for each layer.

6.9 Particle Tracking

Particle tracking is used to trace out flow paths, or pathlines, by tracking the movement of infinitely small imaginary particles placed in the flow field. The software used for this was MODPATH.

Porosity of each of the layers was the only extra parameter required, the following values were used:

Layer	Porosity
Top Sand and Gravel	0.35
Clay	0.5
Second Sand and Gravel	0.3
Sandstone	0.2

Due to the lack of on site data, conservative porosity values were used taken from Anderson and Woessner (1992).

Three particle tracking runs where undertaken:

Run 1. Particles were placed across the site to try and identify the groundwater divide that exists on site.

Run 2. Particles were placed at the two locations where the highest levels of BTEX in groundwater were recorded, in the first layer, source 1 and source 2 on Figure C.3 (Appendix C).

Run 3. Particles where placed in the same locations as in RUN 2 but this time in the fourth (sandstone) layer.

6.10 Plume Modelling

As discussed in the conceptual model there is an area of elevated BTEX in the central portion of the plant. From the variations in concentrations and locations it appears that these elevated levels are from multiple sources.

As 99.5% of the BTEX is composed of benzene and since benzene is the greatest risk driver of the BTEX compounds it was decided to simulated benzene plumes. The benzene contamination was simulated by running MT3D using continuous sources at the two points of highest recorded levels of BTEX. MT3D was run for a period of 50 years which is the time the plant has been in operation. Two simulations were carried out each with a different decay rate for benzene, λ=0.01 %/day and λ=0.1%/day for benzene (entered into MT3D as 0.0001 /day and 0.001/day respectively). These decay constants, recommended for use in Fate 5 and BIOSCREEN are very conservative when compared to the rates published by Salinitro, 1993, which range between 0.4 to 6.7 %/day. The other information required for MT3D is shown in Table 6.7.

Table 6.7 Input parameters for MT3D

Package	Input Parameter
Advection package	Concentration weighing factor: 0.5
Dispersion package (for each layer)	Longitudinal dispersivity: 10m Ratio transversal dispersivity/longitudinal dispersivity: 0.3 Ratio vertical dispersivity/longitudinal dispersivity: 0.05 Effective Molecular diffusion: 0
Sorption package	Bulk density (layer 1): 1.4E+9 mg/m^3 (Freeze and Cheery 1979) Bulk density (layer 2): 1.0E+9 mg/m^3 (Freeze and Cheery 1979) Bulk density (layer 3): 1.4E+9 mg/m^3 (Freeze and Cheery 1979) Bulk density (layer 4): 1.6E+9 mg/m^3 (Freeze and Cheery 1979) Kd(layer 1): 2e-10 (Lethbridge et al, 1993). Kd(layer 2): 7.8e-10 (Lethbridge et al, 1993). Kd(layer 3): 2e-10 (Lethbridge et al, 1993). Kd(layer 4): 2e-10 (Lethbridge et al, 1993). Rate of decay constant (dissolved, for all layers): 0.0001 to 0.001 Rate of decay constant (sorbed, for all layers): 0.0001 to 0.001

Using the groundwater model two injection wells were added at the two points in the top layer (source 1 and source 2 on Figure C.3, Appendix C) with the highest BTEX levels. Water was injected through these wells at a rate of 2m^3/day, the concentrations of benzene were 91 mg/1 at Point 1 and 297 mg/l at Point 2. Using this method, the wells simulate a continuous source of benzene as would be the case if there was a NAPL present. Note this is a very conservative approach as some depletion of source over time would be expected.

7. SIMULATION RESULTS

7.1 Groundwater Model

The groundwater model supports the view that the groundwater flow is towards River A and Canal B. There is also a “mini” groundwater divide, at about the area of the site, where the groundwater in all four layers either flows towards River A or Canal B. (Figures D.1 - D.3, Appendix D).

There is a slight discrepancy in the groundwater contours in Figure D.2 (Appendix D) and the 1:10,000 topographic map. The model boundaries were located a sufficient distance away from the site so that boundary effects would not influence groundwater heads within the area of interest. Thus, outside the site boundaries minor distortions are not important and the overall flow within the aquifer makes good sense for the area modelled. Within the site area, the modelled heads are in close agreement with surveyed, measured values. Care must be taken when comparing topographic maps with groundwater contours as the former can have errors which are within the contour interval (i.e. +/- 10 m).

The groundwater contours in the sandstone show similar trends to the contours in the top sand and gravels (Figure D.3, Appendix D), except, there is some variation due to the extraction wells. The modelled heads are in good agreement with measured. The mean error is 0.5 m. There is a slight vertical gradient at the site, so the average mean error for all the layers is indicative of the agreement within the sandstone layer. The calibration of heads was not continued to achieve a closer match (i.e. < 0.5 m), because the calibration at this point becomes an arbitrary exercise of tweaking parameters by making changes which are much smaller than their range of uncertainty. In addition, at this point, the match criteria become similar to measurement errors.

7.2 Particle Tracking

Run 1: Placing particles in a line across the site clearly shows the apparent groundwater divide which is present under the site. (Figure D.4, Appendix D). Therefore potential plumes at different areas of the site could migrate in different directions. Note the red line indicates the “mini” groundwater divide.

Run 2-Run 5: Placing particles in all four layers at the locations of the two highest BTEX source concentrations give significantly different travel times (Figures D.5 a-d, Appendix D). One set of particles travels towards Canal A while the other travels towards River A. The travel times are summarised below:

Layer	**River A**	**Canal B**
one	6 years	14.5 years
two	4,931 years	8,219 years
three	1,233 years	7,397 years
four	38,356 years	79,452 years

The cross sections in Figure 7.1 a-d show that the particles stay in the top layer until they get into the cell adjacent the canal where they drop down through the clay to the canal.

Figure 7.1a: Cross-section of particle tracking in Layer 1

Figure 7.1b: Cross-section of particle tracking in Layer 2

Figure 7.1c: Cross-section of particle tracking in Layer 3

Figure 7.1d: Cross-section of particle tracking in Layer 4

7.3 Plume Modelling

Plume modelling was carried out over a fifty year period for the two different decay rates (λ=0.01 %/d and λ=0.1%/d) and from two sources. The visual outputs from these are shown on Figures D6a-d and D7a-d. Table 7.1 summarises the outputs:

Table 7.1 Outputs from plume modelling.

	Source 1		**Source 2**	
Decay rate (percent/day)	**0.1**	**0.01**	**0.1**	**0.01**
Max' plume length	120	180	170	250
Years to stabilisation	10	10	10	16

The biodegradation rate of 0.01 per day is at the low end of published values (0.1-0.01 per day) and was chosen intentionally to be conservative. The plume lengths are realistic based on migration from the known sources chosen which have high concentrations of benzene in groundwater. The width of the contaminated area could be modelled by in-puting more sources which are suspected but not yet measured. The down-gradient limits of the plume are well defined with monitoring wells.

In none of the simulations does the benzene reach the lower sand and gravel or sandstone below the clay. Raising concerns that a pathway might have been created through the clay enabling contaminates to reach the sandstone. These pathways might have been created by the installation of geotechnical boreholes, building foundation, which go down to the sandstone or boreholes installed in the site investigations.

The site data shows a wider spread of contamination in the groundwater than indicated from the simulated plumes. It was a first thought that this contamination might have originated from one or two large sources, but as can be seen the simulation plumes cover a lot smaller area. It probably can safely be assumed that the contamination in the groundwater comes from a series of smaller source scattered over the site.

8 CONCLUSIONS FROM THE CSM AND GROUNDWATER MODEL

8.1 Conceptual site model

By far the major contaminants identified in the soil and groundwater are BTEX (benzene, toluene, ethylbenzene and xylenes) components, followed by styrene, naphthalene and chlorinated aliphatic hydrocarbons (CAH), although the concentrations of the CAH are very low.

There are several BTEX plumes in the shallow groundwater some of which have merged. At least two plumes have penetrated a clay layer and at least one of them has entered the Sherwood Sandstone Aquifer which is classified as a major aquifer by the Environment Agency.

The conceptual site model has identified BTEX as the primary contaminants of concern and the sandstone aquifer and nearby surface water bodies, River A and the Canal A, as receptors potentially under threat from contamination at the site via transport in the groundwater.

There is direct and indirect evidence that natural attenuation of BTEX and CAH is taking place in the groundwater. Concentrations away from the source areas have declined by 50-99% between 1995/96 and 1999/2000 and biodegradation products of CAH (vinyl chloride, ethene and ethane) have been detected.

8.2 Site groundwater model

The model concurs with the view that the groundwater is flowing towards Canal A or River A and that there is a groundwater divide under the site.

The model predicts that:
- the BTEX plumes stabilise within 16 years of the contamination taking place.
- none of the BTEX plumes will migrate off-site. This is supported by observations in the perimeter monitoring wells.
- maximum plume length is expected to be 250 m in the worst case scenario.

The simulated plumes do not show benzene contamination reaching the sandstone, whereas the observed data show benzene contamination in the sandstone. This indicates that a man-made pathway has most likely been created through the clay, resulting from building foundation piles, geotechnical boreholes or site investigation boreholes.

Cross sections of the particle tracking show that the particles do not migrate down through the clay layer until they are adjacent to River A or Canal A. However there is a slight head difference between the perched water and the water in the lower layers (clay, sand and gravel and sandstone) indicating a very slight downward migration in groundwater.

9. REFERENCES

Allen, D.J., Brewerton, L.J., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S.J. and Williams, A.T. (1997). The physical properties of major aquifers in England and Wales. BGS Technical Report WD/97/34 (equivalent to Environment Agency R&D publication 8).

American Petroleum Institute (1996). Estimate of Infiltration and Recharge for Environmental Site Assessment. API Publication No 4643. Prepared by D.B. Stephens & Associates Inc, Albuquerque, New Mexico.

Anderson, M.P. and Woessner, W.W. (1992). Applied Groundwater Modelling: Simulation of Flow and Advective Transport. Academic Press.

Freeze, A.R. and Cherry, J.A. (1979). Groundwater. Prentice Hall International, London

Lethbridge, G., Morgan, P., Lewis, S.T. and Jones, D.S. (1993). The influence of a subsurface peat layer on the *in situ* bioremediation of a natural gas production site contaminated with gas condensate. 2nd Int. Conf. on Subsurface Microbiology, Bath, UK.

Salanitro, J.P. (1993). The role of bioattenuation in the management of aromatic hydrocarbon plumes in aquifers. Groundwater Monitoring Review. Fall, pp 150-161.

Towler, P.A., Neaville, C., Lethbridge, G. and Swannell, R.P.J. (2000). Project Siren: Phase 1 Report. Environment Agency R&D Technical Report P358

APPENDICES

APPENDIX B :
4 PAGES A4
16 PAGES A3

APPENDIX C:
1 PAGE A3
5 PAGES A4 (FIGURES BACKED)
18 PAGES A3

APPENDIX E:
10 PAGES A4 (FIGURES BACKED)